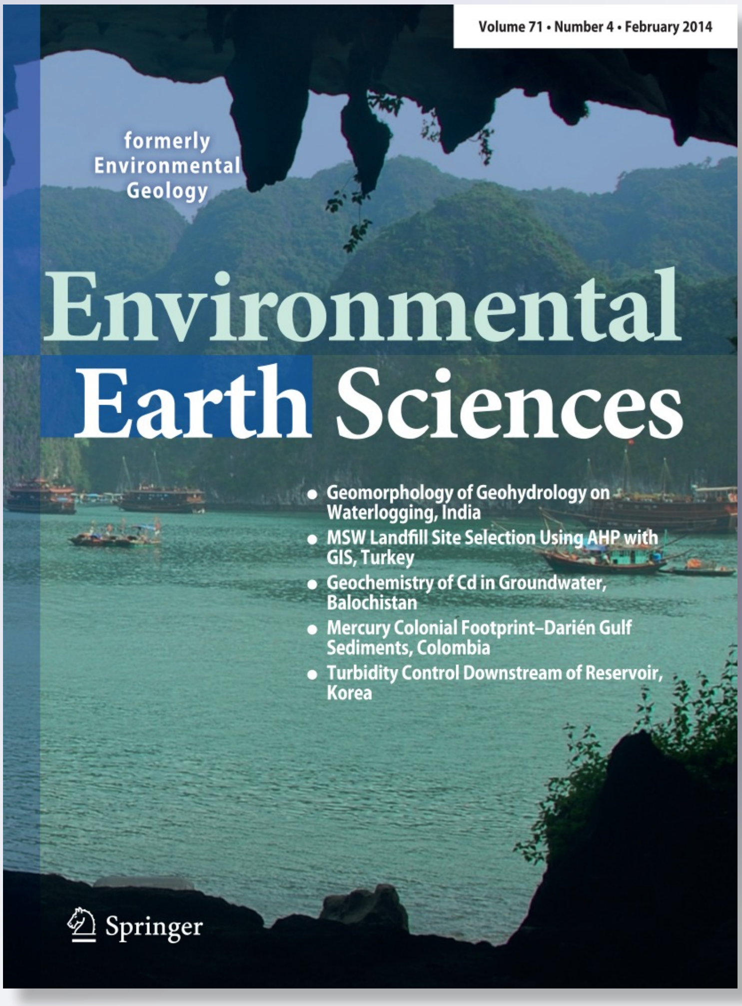
Hydrogeochemistry and isotope techniques to determine water interactions in groundwater-dependent shallow lakes, Wet Pampa Plain, Argentina

Asunción Romanelli, Orlando Mauricio Quiroz Londoño, Daniel Emilio Martínez, Héctor Enrique Massone & Alicia Haydée Escalante

Environmental Earth Sciences

ISSN 1866-6280
Volume 71
Number 4

Environ Earth Sci (2014) 71:1953-1966
DOI 10.1007/s12665-013-2601-y



Springer

Environ Earth Sci (2014) 71:1953–1966
DOI 10.1007/s12665-013-2601-y

ORIGINAL ARTICLE

Hydrogeochemistry and isotope techniques to determine water interactions in groundwater-dependent shallow lakes, Wet Pampa Plain, Argentina

Asunción Romanelli · Orlando Mauricio Quiroz Londoño ·
Daniel Emilio Martínez · Héctor Enrique Massone ·
Alicia Haydée Escalante

Received: 11 July 2012 / Accepted: 5 June 2013 / Published online: 20 June 2013

Abstract This paper gives an account of the implementation of hydrochemical and isotopic techniques to identify and explain the processes that govern solute exchange in two groundwater-dependent shallow lakes in the Southeastern Pampa Plain of Argentina. Water samples (lakes, streams, spring water and groundwater) for hydrochemical and stable isotopic determination were collected and the main physical–chemical parameters were measured. The combination of stable isotope data with hydrogeochemical techniques was used for the identification of sources and preferential recharge areas to these aquatic ecosystems which allowed the explanation of the lake water origin. The hydrochemical processes which explain Los Padres Lake water chemistry are evaporation from groundwater, CO_2 input, calcite dissolution, Na^+ release by Ca^{2+} and Mg^{2+} exchange, and sulfate reduction. The model that best aligns with La Brava Lake hydrochemical constraints includes: mixing, CO_2 and calcite dissolution, cationic exchange with Na^+ release and Mg^{2+} adsorption, and to a lesser extent, Ca/Na exchange. This model suggests that the fractured aquifer contribution to this water body is greater than 50 %. An isotopic-specific fingerprint for each lake was identified, finding a higher evaporation rate for La Brava Lake compared to Los Padres Lake. Isotopic data demonstrate the importance of these shallow lakes as recharge areas to the regional aquifer, becoming areas of high groundwater vulnerability. The Tandilia Range System, considered in many hydrogeological studies as the impermeable bedrock of the Pampean aquifer, acts as a fissured aquifer in this area, contributing to low salinity waters and with a fingerprint similar to groundwater isotopic composition.

Keywords Environmental isotopes · Hydrogeochemistry · Groundwater/surface water interactions · Pampean aquifer · Solute exchange

Introduction

Groundwater and surface water are not isolated components of the hydrologic system, but instead, interact in a variety of physiographic and climatic landscapes. Therefore, an understanding of the basic principles of interactions between groundwater and surface water (GW–SW) is needed for an effective management of water resources (Sophocleus 2002). Furthermore, the interaction between these two components of the hydrologic system has

---

A. Romanelli (✉) · O. M. Quiroz Londoño ·
D. E. Martínez · A. H. Escalante
Consejo Nacional de Investigaciones Científicas y Técnicas
(CONICET), Instituto de Investigaciones Marinas y Costeras
(IIMyC), Mar del Plata, Argentina
e-mail: aromanel@mdp.edu.ar;
asuncionromanelli@hotmail.com

O. M. Quiroz Londoño
e-mail: qlondono@mdp.edu.ar

D. E. Martínez
e-mail: demarti@mdp.edu.ar

A. H. Escalante
e-mail: aescalan@mdp.edu.ar

A. Romanelli · O. M. Quiroz Londoño ·
D. E. Martínez · H. E. Massone
Instituto de Geología de Costas y del Cuaternario, Universidad
Nacional de Mar del Plata, FCEyN, Funes 3350, Nivel 1,
7600 Mar del Plata, Argentina
e-mail: hmassone@mdp.edu.ar

A. H. Escalante
Laboratorio de Limnología, FCEyN, Universidad Nacional de
Mar del Plata, Funes 3250, Nivel 2, 7600 Mar del Plata,
Argentina

important implications for the successful protection and management of high environmental values usually attached to lake and wetland habitats. Recognition that the protection of such systems extends beyond the immediate recognizable boundaries of the surface water bodies implies that it is necessary to understand the pattern of groundwater flow in relation to them (Turner and Townley 2006). In this sense, in order to understand these interactions in relation to climate, landform, geology, and other biotic factors, a sound hydrogeological framework is required (Sophocleus 2002).

Lakes are integrated into the global water cycle and are, therefore, influenced by precipitation, evaporation and water fluxes by groundwater and/or surface water (Mook 2002; Burkert et al. 2004; Froehlich et al. 2005). In addition to biotic and abiotic activities within the lakes, organic material, nutrients, and elements from the surroundings will be transferred via the water flow into the system (Burkert et al. 2004). Moreover, the chemical composition of water in lakes is the outcome of lithological, climatic, biological and human factors and of geochemical processes interacting in the aquifers and across the catchment (Fernández Aláez et al. 2006).

Although it is generally assumed that topographically high areas are groundwater recharge areas and topographically low areas are groundwater discharge areas, this is true primarily for regional flow systems. The superposition of local flow systems associated with surface water bodies on this regional framework results in complex interactions between groundwater and surface water in all landscapes, regardless of regional topographic position. Fluxes of water and chemicals from and to groundwater reflect the positions of the surface water bodies with respect to different-scale groundwater flow systems. Moreover, local geological controls on seepage distribution through their beds could modify the potential groundwater inflow or draw water from the surface water body (Winter 1999).

Significant thought and effort has been devoted to the development of new and improved methods to assess GW–SW interactions, such as the use of natural tracers like heat, electrical conductivity, Cl^- and SO_4^{2-} content, ^{18}O, ^{2}H, among others (Fette et al. 2005; Fleckenstein et al. 2010; Vogt et al. 2010). The strengths of using isotopes as tracers allow them to reach their maximum by a combination of stable isotope data (δ^2H and $\delta^{18}O$) with hydrogeochemical data. The most important factor in the use of stable isotopes is their unequivocal ability to distinguish former lake water on the downgradient side of a particular lake from upgradient groundwater (Turner and Townley 2006). Moreover, they are important tools in the validity and adjustment of conceptual hydrogeological models (Fontes 1980; Clark and Fritz 1997; Mazor 1991; Quiroz Londoño et al. 2008). Stable isotope data taken from the components of the hydrologic cycle can provide useful information on the relationship between rainwater and groundwater and among surface waters (Goni 2006). Another useful tool for the analysis of hydrological systems is the hydrogeochemical interpretation of representative water-sample analysis which permits the characterization of different water sources, identification and verification of flow lines, identification of mixing processes and quantification of the interaction between different water sources (Martínez et al. 2000; Wang et al. 2006).

The Pampa Plain is one of the most extended plain regions of the world. Climate, as well as its geomorphology, has resulted in the development of wetland systems and very shallow lakes (Iriondo 1989), which play an important role in the overall hydrological cycle of Buenos Aires Province (Southern Pampa) (Fernández Cirelli and Miretzky 2004). They contribute to the equilibrium of physical and biological systems among several ecosystem services (i.e. nutrient cycling, water and climate regulation, habitat provision, recreation). Intensive human activities in these ecosystems lead to an equilibrium disruption, making them highly vulnerable systems. Previous work has showed that groundwater is an important water source in these lakes (Drago and Quirós 1996; Miretzky et al. 2000, 2001; Fernández Cirelli and Miretzky 2004; Romanelli et al. 2010) however; the complex intrinsic relationships between the local geology and water chemistry in lake-groundwater interactions are yet to be elucidated. The processes that govern solute exchange in groundwater dependent lakes in the Wet Pampa Plain can be assessed using natural tracers such as electrical conductivity, Cl^- content, ^{18}O and ^{2}H. The aim of the present study is to identify and explain the hydrogeochemical processes involved in aquifer–shallow lake interaction in the South-eastern Pampa Plain using hydrochemical and isotopic techniques. It is expected that the knowledge of such water interactions would improve water management in the region, avoiding threats to groundwater and surface resource availability and quality which could generate an increase in the dissatisfaction of water users and a consequent change in land and water use behavior of people in the area.

Study area

The Pampa plain in Argentina is characterized by a geomorphological environment which corresponds mostly to that of gently sloped plains (slope values 0.5 %) crossed by two block mountain systems ("Tandilia and Ventania ranges"). Over the past 20 years, annual precipitation values have ranged from 587 to 1,442 mm/year, with an average of 979 mm/year. The highest precipitation values are recorded between December and March. The evapotranspiration potential values estimated for the same period by the Thornthwaite method, ranged from 696 to 766 mm/

year, with an average of 732 mm/year. Climate conditions are highly variable, but a more restricted area, called Wet Pampa is characterized by a humid climate, very good soils and a resulting high agricultural productivity (soya beans, wheat, sunflowers, corn, potatoes), which is the main sustenance of the country's economy.

Flat-land landscapes in humid to sub-humid climates, like the Pampa Plain, have a rather negligible surface relief; the basin boundaries are diffuse or undetermined, with shallow water courses which do not make up for a well-defined surface drainage system, with groundwater levels close to the surface, and soils consisting of fine-grained sediments. Such characteristics make the hydrological cycle components different from those of typical hydrological scenarios. The infiltration proceeds at a very slow rate and the water may remain for a long time stagnant on the surface putting agricultural lands at a greater risk of flooding and/or salinization (Usunoff et al. 1999).

Two shallow permanent lakes located in the southeastern Wet Pampa Plain were selected for this study: La Brava (4.00 km^2) and Los Padres (2.16 km^2) (Romanelli et al. 2010) (Fig. 1). The first one has a structural origin (Ringuelet 1962), while the second one was originated from wind deflation and accumulation processes (Martínez 2000). Each water body has only one inflow stream which is born in the Tandilia Ranges (a block mountain system with a maximum elevation of 300 m asl) and flows through agricultural lands before discharging to the shallow lake, and an outflow one. The effluent–influent behavior of these lakes in relation to groundwater is well known in the area (Cionchi et al. 1982; Kruse 1987); however, the processes, sources and preferential recharge areas to these aquatic ecosystems were not yet identified.

Geologically, the Tandilia Range System in the area consists of two large units: a Precambrian crystalline bedrock (Marchese and Di Paola 1975), and a set of sedimentary rocks of Precambrian-Lower Paleozoic origin (Dalla Salda and Iñiguez 1979). They are both considered as hydrogeological bedrock. An inter-range fringe surrounds the blocks; it is formed by hills which quickly give way to the plain areas that reach the sea. Hills and plains are formed by Cenozoic loess-like sediments mainly of the Pleistocene–Holocene age.

The upper Pleistocene–Holocene cover of the area is a sequence of silt, silt-clayed and fine sand sediments of aeolian and fluvial origin that constitute to an aquifer system known as Pampean Aquifer (Sala 1975). The Pampeano Aquifer in the area is an unconfined multi-layered phreatic aquifer, with a maximum thickness ranging from 70 to 100 m, and a hydraulic conductivity of 10 m/day (Bocanegra et al. 1993). Typical values of unsaturated zone thickness are in the range from 2 to 10 m. Recharge is due to an infiltration of precipitation excess, and discharge occurs towards surface streams, river and water bodies, and directly to the Atlantic Ocean. Recharge in the Pampeano aquifer has been calculated from different approaches, giving results of nearly 15 % of total rainfall (135 mm/year) (Quiroz Londoño et al. 2012).

La Brava Range represents the western limit of La Brava Lake. Mauriño et al. (1981) defined the structural features of this range, establishing a hierarchy of high-angle faults with a southeastern fault inclination and two joint groups which give an important secondary porosity (Fig. 1). Intermittent spring presence in this range suggests water movement through the fissure system by the quartzite outcropping on it (Tapia 1937; Kruse 1987).

Materials and methods

A regular sample grid was designed for each lake to collect water samples for hydrochemical and stable isotopic determination (^{18}O and ^{2}H) and to measure the main physical–chemical parameters at different depths. Electrical conductivity (EC), pH and temperature were in situ measured at 0.5 m, 1 m, 2 m and maximum depth using a multi-parameter probe HANNA HI 9828. A total of 35 and 33 samples were obtained from La Brava and Los Padres lakes, respectively. Moreover, several points were selected to obtain surface and depth samples for their chemical analysis and isotopic determination. The main streams, spring water and groundwater were also sampled and recorded using a global positioning system (GPS). The collection, preservation and chemical analysis for major ions of water samples were carried out following the standard methods given by the American Public Health Association (APHA American Public Health Association 1998). Chemical analysis was performed applying standard methods: chloride following Mhor method, sulfate by turbidimetry, calcium and magnesium by complexometric titrations with EDTA, sodium and potassium by flame spectrometry, and carbonate-bicarbonate by potentiometric titrations. Water temperature, pH and electrical conductivity were measured in situ.

Stable isotopes (^{18}O and ^{2}H) were measured in shallow lakes, streams, springs and groundwater. A total of 61 samples were analyzed using a laser spectroscopy DLT-100 Liquid–Water Isotope Analyzer, Automated Injection designed by Los Gatos Research at the Hydrochemical and Isotopic Hydrology Laboratory (National University of Mar del Plata). The results were expressed like δ (‰), defined as:

$$\delta = \left(\frac{Rs - Rp}{Rp}\right) \times 1{,}000\,‰ \quad (1)$$

where δ is the isotopic deviation in ‰, s is the sample, p, the international reference, and R is the isotopic ratio (^{2}H/^{1}H, ^{18}O/^{16}O). All δ values of water samples were

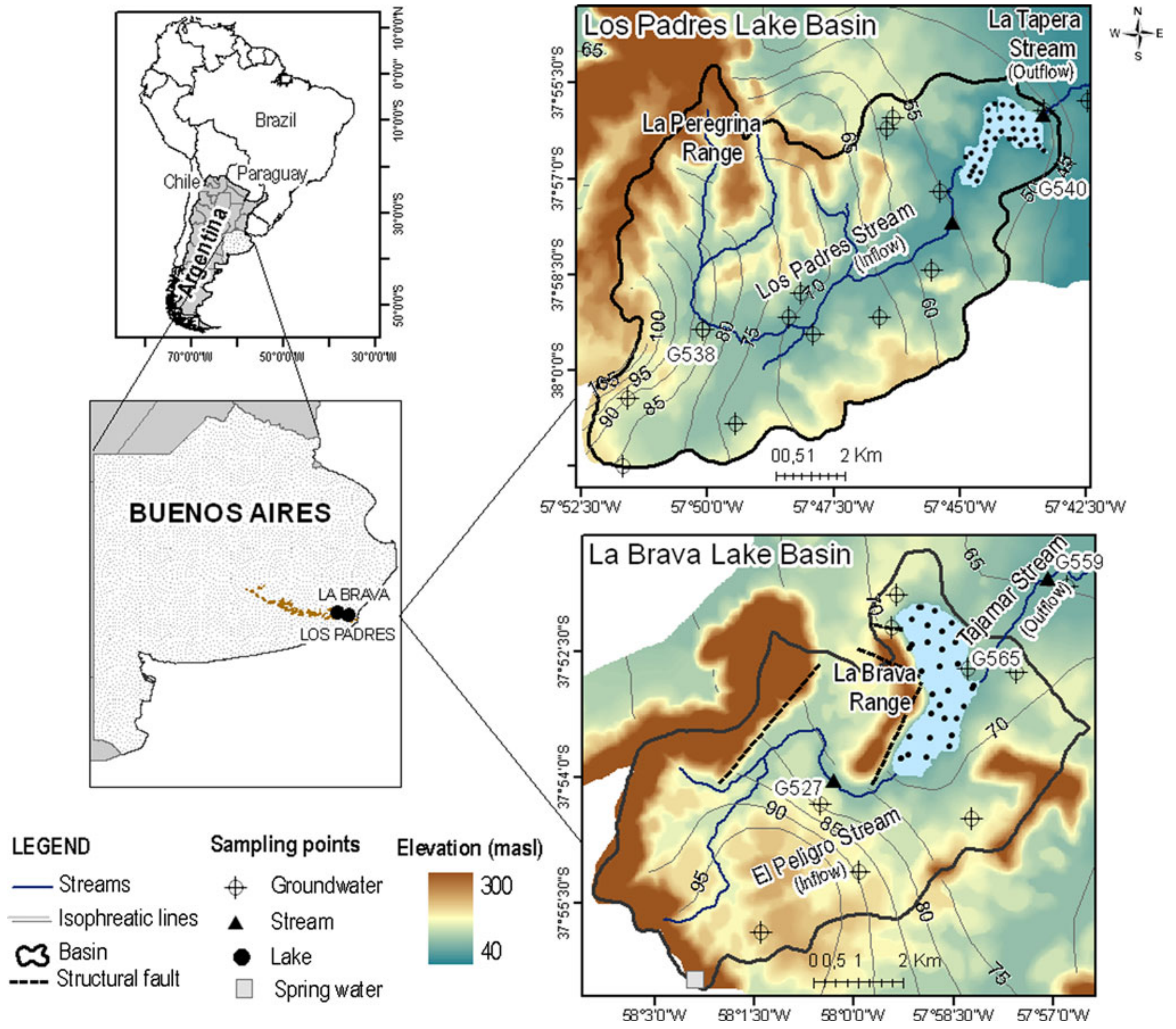


Fig. 1 Location map and sampling sites

conventionally reported relative to the international standard Vienna Standard Mean Ocean Water (VSMOW) (Gonfiantini 1978). The analytical uncertainties were ±0.3 and ±2.0 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively.

The hydrochemical information was analyzed following a general statistical characterization and conventional diagrams by Piper and Schoeller (Hem 1992). Isovalue contour maps of different parameters were drawn to identify different sectors. Hydrogeochemical inverse mass balance models were numerically tested using NETPATH software (Plummer et al. 1991). Field activities were conducted during November 2008 and November 2009. Lake sampling was carried out during a single day in November (spring), between 9:00 a.m. and 18:00 p.m. Stream and groundwater samples were also collected that same day. Moreover, hydrochemical data from different dates within the same year were included in this study. Rainwater composition values from a weather station located 50 km east from the area were included in the isotopic analysis (Quiroz Londoño et al. 2008).

Results and discussion

Hydrogeochemistry

Tables 1 and 2 show the statistical parameters of the water ionic content in groundwater, streams and lakes. The ionic content in La Brava and Los Padres lakes at different depths is shown in Tables 3 and 4. Major water ionic

Table 1 Water ionic composition in La Brava Lake Basin

Parameter (mg/l)	Groundwater ($N = 13$)			Inflow (SEP; $N = 4$)			Outflow (STJ; $N = 6$)			Lake ($N = 35$)		
	Min	Max	Media	Min	Max	Media	Min	Max	Media	Min	Max	Media
Ca^{2+}	5.2	34.3	15.9	28.8	52.2	40.1	13.5	39.0	21.4	19.6	55.7	31.8
Mg^{2+}	7.2	64.4	35.5	21.4	43.7	30.3	20.0	37.8	27.4	9.0	63.1	29.5
Na^{+}	105.0	398.0	249.6	126.4	266.4	183.6	111.0	306.0	170.0	106.5	271.0	194.5
K^{+}	2.2	11.0	4.9	3.2	4.9	4.1	7.7	9.7	8.9	2.9	10.9	6.6
Cl^{-}	48.1	173.0	99.1	62.8	250.0	141.0	56.5	173.0	89.3	56.5	128.8	89.2
HCO_3^{-}	240.0	894.2	484.2	282.2	388.7	334.3	320.0	1041.2	559.0	223.6	857.5	418.4
CO_3^{2-}	0.0	53.3	32.8	0.0	0.0	0.0	0.0	63.9	10.7	42.6	171.5	84.3
SO_4^{2-}	1.0	48.3	17.4	17.8	66.4	31.9	4.9	76.8	27.9	2.2	77.6	26.9
Hardness	58.6	303.1	187.9	161.2	283.8	239.6	117.0	232.0	167.7	118.6	322.5	185.9

Min minimum, *Max* maximum, *N* sample number

Table 2 Water ionic composition in Los Padres Lake Basin

Parameters (mg/l)	Groundwater ($N = 19$)			Inflow (SLP; $N = 4$)			Outflow (SLT; $N = 3$)			Lake ($N = 33$)		
	Min	Max	Media	Min	Max	Media	Min	Max	Media	Min	Max	Media
Ca^{2+}	9.2	96.0	40.8	20.6	49.5	34.9	20.0	23.7	21.8	18.9	50.4	27.9
Mg^{2+}	3.8	167.0	73.6	21.6	67.3	43.3	28.3	42.3	34.3	19.0	47.4	32.6
Na^{+}	46.8	357.6	138.9	98.6	162.4	136.4	112.0	273.0	178.3	203.6	400.0	277.0
K^{+}	3.1	14.8	6.9	5.2	9.6	7.3	5.7	8.9	7.6	3.5	9.8	7.6
Cl^{-}	57.7	185.9	99.6	89.7	122.0	107.6	47.1	153.9	93.7	48.1	128.2	88.0
HCO_3^{-}	330.0	833.0	513.9	308.6	596.4	403.5	314.1	372.7	335.6	396.0	841.4	555.3
CO_3^{2-}	0.0	53.2	5.6	0.0	64.0	24.0	53.3	85.2	67.5	0.0	364.0	112.6
SO_4^{2-}	3.2	65.0	23.3	12.1	25.0	16.5	10.9	54.0	25.4	13.0	41.0	24.3
Hardness	37.0	825.0	391.2	214.1	332.0	267.6	178.0	226.3	197.8	148.3	260.3	205.3

Min minimum, *Max* maximum, *N* sample number

composition in La Brava and Los Padres lake basins and physicochemical spatial distribution in each lake is shown in Figs. 2 and 3, respectively.

Groundwater

Regionally, sodium and magnesium were the dominant cations in the chemical composition of groundwater, whose values vary between 46.8–398.0 mg/l, and between 3.8–167.0 mg/l, respectively (Tables 1, 2). As for the anions, bicarbonate (ranging from 240.0 to 894.2 mg/l) and chloride (between 48.1 and 185.9 mg/l) predominate. Less abundant cations in the groundwater are calcium (5.2–96.0 mg/l) and potassium (2.2–14.8 mg/l). Related to the anions, sulfate and carbonate are less frequent with a variation range of 1.00–65.0 and 0.00–53.3 mg/l, respectively.

Sodium bicarbonate groundwater type dominates in La Brava Lake Basin (Fig. 2a). It presents a great homogeneity in its cationic composition. Its anionic composition is generally bicarbonate although some chloride-enriched water (140.0–173.0 mg/l) was detected in the northern basin. Los Padres Lake Basin has chemically evolved groundwaters due to a longer time of groundwater circulation through the aquifer, allowing the occurrence of a modifying process that alters the ionic content of water from a calcium magnesium bicarbonate type to sodium bicarbonate waters (Fig. 2b).

Regarding groundwater origin and sources of ions in the area, Na^{+} and Mg^{2+} are attributed to feldspar and volcanic glass hydrolysis in loessic sediments, respectively (Logan et al. 1999). Bicarbonate concentration is controlled by calcite dissolution in the sediments that constitute the aquifer and in a stratiform disseminated form. In the case of chlorides, several studies performed on the Pampean aquifer showed that its concentration is the result of evaporation and incorporation into groundwater through rainwater infiltration (Bonorino et al. 2001; Mariño and Bonorino 2005). The hydrolysis of calcium carbonate (crude or disseminated) is the main source of calcium in groundwater. Because potassium is almost irreversibly fixed in clay materials and it participates in the formation of secondary minerals it is presented in low concentrations

Table 3 Water ionic content at different depths in La Brava Lake

Depth (m):	1			2			3		
Parameter (mg/l)	Min	Max	Media	Min	Max	Media	Min	Max	Media
Ca^{2+}	19.60	52.60	30.69	30.00	55.70	40.78	25.80	36.10	30.97
Mg^{2+}	9.00	63.10	30.11	15.10	29.40	20.58	27.80	46.70	38.84
$Na^+ + K^+$	109.33	281.86	208.91	147.45	273.40	207.06	116.01	139.09	130.03
Cl^-	56.50	119.30	87.26	84.80	107.00	97.40	75.40	128.80	101.57
HCO_3^-	223.60	857.50	423.03	292.80	563.50	379.35	341.00	551.20	468.90
CO_3^{2-}	42.60	171.05	82.19	42.60	171.50	80.15	63.90	171.50	119.30
SO_4^{2-}	9.82	77.60	27.46	2.22	51.00	25.11	18.00	29.10	23.77

Min minimum, *Max* maximum

Table 4 Water ionic content at different depths in Los Padres Lake

Depth (m):	0.5			1		
Parameter (mg/l)	Min	Max	Media	Min	Max	Media
Ca^{2+}	18.90	50.40	28.30	25.20	28.50	26.30
Mg^{2+}	19.00	47.40	32.54	26.90	35.10	30.83
$Na^+ + K^+$	203.63	399.95	276.58	250.70	336.29	291.84
Cl^-	48.08	128.20	88.07	83.30	89.70	86.50
HCO_3^-	396.00	841.40	558.99	477.50	576.40	535.77
CO_3^{2-}	0.00	364.00	111.43	75.80	151.60	126.33
SO_4^{2-}	13.00	38.00	23.66	20.00	41.00	32.33

Min minimum, *Max* maximum

(Matthess 1982). Gypsum dissolution from surface soil horizons, in addition to evaporation and concentration of meteoric water surplus in the area, is the main sulfate source of groundwater in the Pampean aquifer (Rossi 1996; Logan et al. 1999).

Groundwater electrical conductivity in La Brava Lake Basin reached 1,110.0 μS/cm with a mean value of 829.6 μS/cm. The pH ranged between 7.29 and 8.77 with a mean value of 7.87. The recorded temperature ranged from 14.5 to 19.8 °C with an average of 16.6 °C. The waters are slightly alkaline and with low salinity. Groundwater in Los Padres Lake Basin is slightly alkaline, with pH values ranging from 7.04 to 8.25, with an average value of 7.48. The EC ranged from 460.0 to 1,440.0 μS/cm with a mean value of 785.9 μS/cm. The temperature variation ranged from 14.4 to 18.2 °C, with an average of 16.0 °C.

Streams

The main streams in the area were sampled: El Peligro (SEP) and Los Padres (SLP), both inflow water courses, and the outlets Tajamar (STJ) and La Tapera (SLT) from La Brava and Los Padres lakes, respectively (Fig. 1). In general, streams present a sodium bicarbonate water type. Inflow water courses have higher calcium and magnesium concentrations in comparison to the effluents, probably due to groundwater contribution. The mean EC value is higher in SLP (808 μS/cm) than in SEP (658 μS/cm) as it flows over a longer distance (17.60 km) before discharging to the lake allowing higher interaction with elements from the surroundings and from evaporation processes. Regarding the outflow streams, a higher mean EC value of 704 (STJ) and 822 μS/cm (SLT) was detected in the outflow streams. Moreover, the magnesium and chloride contents in SLT are higher than in STJ. These facts could be explained by the existence of a gate in the headwater of SLT, causing a marked reduction of water flow velocity and enhancing water salinity.

Shallow lakes

Water ionic composition is homogenous in La Brava Lake, sodium bicarbonate being the predominant water type (Fig. 2a). The pH values range between 8.50 and 9.39, with an average of 9.17. A slight decrease in depth (from 9.27 to 8.58 at 0.5 and 4 m, respectively) is detected probably due to a lower photosynthetic activity in that zone. Electrical conductivity varies from 565 to 658 μS/cm with a mean value of 651 μS/cm.

The ionic spatial distribution in La Brava Lake is shown in Fig. 2b. Regarding its anionic composition, the lowest Cl^- values (<80 mg/l) are located close to the western limit of La Brava Range, spatially coinciding with the regional fault system described by Mauriño et al. (1981). Lowest sulfate concentration (<30 mg/l) is located in the N and W sectors of the lake. The erratic distribution of bicarbonate and carbonate can be attributed to the fact that they are fundamentally dependent on several physico-chemical parameters such as pH and CO_2 pressure, which can be affected by aquatic metabolism. Photosynthesis tends to reduce CO_2 content and to increase pH, while the

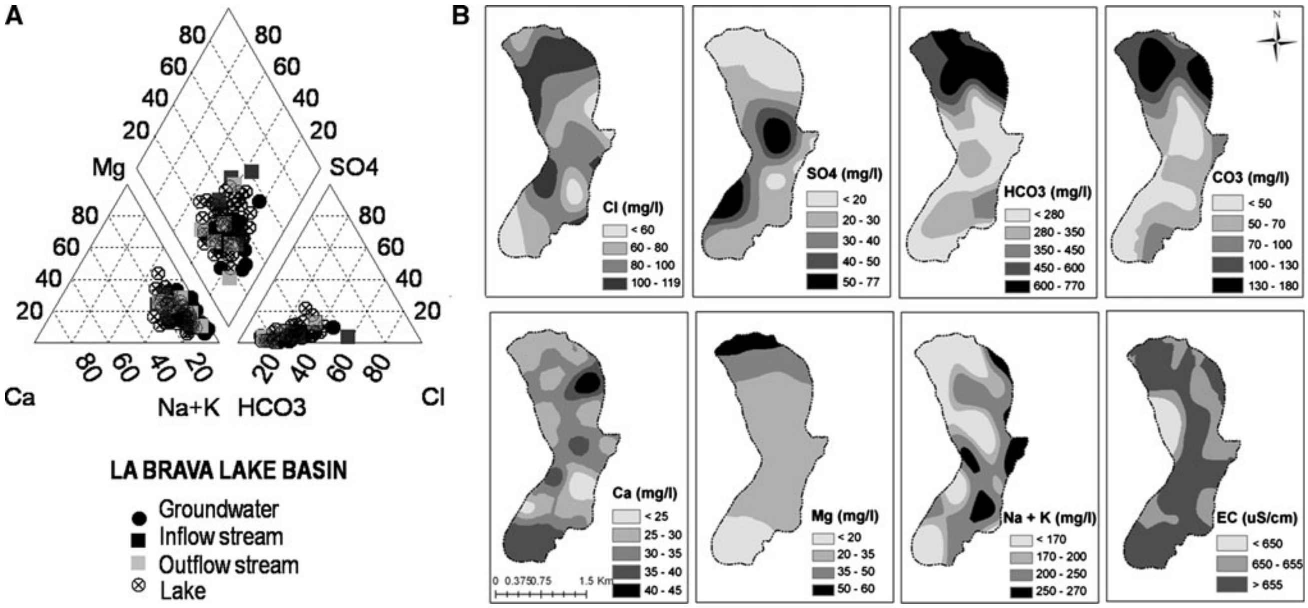


Fig. 2 **a** Major water ionic composition and **b** spatial distribution of ion concentration and EC in La Brava Lake

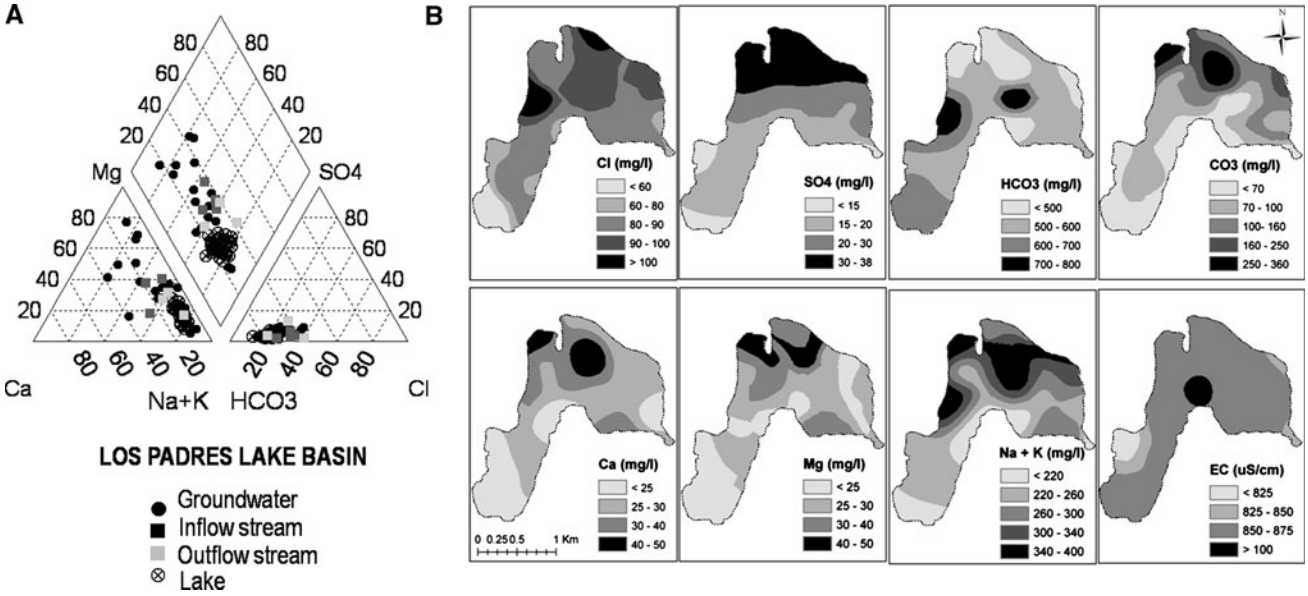


Fig. 3 **a** Major water ionic composition and **b** Spatial distribution of ion concentration and EC in Los Padres Lake

respiration process causes the opposite effects (Wetzel 2001). Related to its cationic content, magnesium values lower than 20 mg/l are found in the south sector of the water body, while the maximum values (>35 mg/l) are located on its north shore. Potassium has the lowest spatial variability. The lowest sodium concentration is located in its north and west margins. This cation has the highest spatial variability in the water body under study.

The EC distribution in La Brava Lake shows the predominance of values higher than 655.0 μS/cm and a lower EC zone (569.0 μS/cm) located in the western sector of the aquatic system in contact with La Brava Range front (Fig. 2b). This fact, together with Cl^- and SO_4^{2-} distribution patterns, suggests a recharge zone to the water body from the fissure system in the quartzite rocks that constitutes the range, i.e. a dilution of lake water by mixing water with lower sulfate and chloride is evident.

Los Padres Lake presents a homogenous ionic composition with sodium and bicarbonate predominance (Fig. 3a). The water is slightly alkaline with pH values ranging between 8.00 and 9.02 with an average of 8.66, while two samples obtained at 2 m of depth have a pH average of 7.73 probably due to the same reason mentioned for La Brava Lake. The mean EC value is 854 µS/cm, with a variation from 805.0 to 895.0 µS/cm. The spatial distribution of the ion concentration of each chemical element analyzed in Los Padres Lake is shown in Fig. 3b. The lowest chloride values (<80 mg/l) are located in the SW sector, coinciding with the inflow stream discharge. This variation suggests a recharge area to the waterbody. A decrease in sulfate content is also present in the SW extreme of the aquatic system, indicating a water dilution due to the mixing with rainwater or with water depleted in sulfate from its inflow stream. Carbonate together with bicarbonate has the highest spatial variation, probably as a consequence of the same facts mentioned for La Brava Lake. Calcium concentrations above 30 mg/l are observed in the N sector of the water body. Its concentration is attributed to calcite dissolution from the sediments of the gully area. The K^+ content in this ecosystem is low. Sodium values are higher than 300 mg/l in the N and W sectors. The spatial analysis of EC in this shallow lake shows predominant values in the range 850–875 µS/cm, with lower values near Los Padres Stream delta also coinciding with the Cl^- and SO_4^{-2} distribution patterns, suggesting a recharge zone to the water body.

The high pH values found in the lake waters, which in all cases exceed those measured in the aquifer, can be linked to the decreased partial pressure of CO_2 during groundwater discharge into the water bodies and to evaporation. This causes the increase in pH and precipitation of $CaCO_3$. The latter process is observed along coast lines, especially in those areas with lower EC in the shallow lakes. A similar process is evident in the inflow streams confirming their gaining behavior.

Isotopic composition

The isotopic composition of 25 groundwater, 4 stream water, 1 spring and 30 lake samples (18 and 12 samples in La Brava and Los Padres, respectively) was analyzed. Isotopic data together with the global meteoric water line (GMWL) were plotted in a conventional diagram δ^2H vs. $\delta^{18}O$ (Fig. 4). Most groundwater samples appeared grouped around a mean value ($\delta^{18}O = -5.44$ ‰ and $\delta^2H = -29.37$ ‰), showing a relatively constant isotopic composition. The isotopic composition of groundwater is near to the average isotope composition of rainfall in the area, indicating that it is a well-mixed system only recharged by rainfall.

Isotopic composition of the inflow stream waters of both lakes (SEP and SLP) is similar to groundwater (mean values of $\delta^{18}O = -5.52$ ‰ and $\delta^2H = -28.87$ ‰), showing its contribution to stream flow. On the other hand, outflow streams of La Brava and Los Padres lakes (SLT and STJ) with higher isotopic content acquire their own isotopic fingerprint (mean values of $\delta^{18}O = 0.28$ ‰ and $\delta^2H = 3.72$ ‰ for STJ and $\delta^{18}O = -1.30$ ‰ and $\delta^2H = -5.85$ ‰ for SLT). Both outflow streams show similar isotopic values in comparison to the water lake which they originated from.

Lake samples show a more enriched isotopic composition than their recharge sources (groundwater, inflow streams and to a lesser extent, rainwater); with δ^2H and $\delta^{18}O$ ‰ mean value of 2.641 and −0.456 in La Brava Lake and of −10.544 ‰ and −1.402 in Los Padres Lake, respectively. Evaporation lines for each shallow lake, considering groundwater in each basin as a starting point, were calculated and defined by the following equations: $\delta^2H = 6.04\ \delta^{18}O + 2.92$ and $\delta^2H = 4.56\ \delta^{18}O - 4.15$ for La Brava and Los Padres lakes, respectively.

There is a significant difference between the isotopic content of lakes, showing La Brava Lake to have a greater isotopic enrichment. By plotting Cl^- vs. $\delta\ ^{18}O$ (Fig. 5), evaporation processes from groundwater can be deduced in Los Padres Lake. Meanwhile, the chloride concentration in La Brava Lake is lower than the groundwater mean value of its basin. The average Cl^- content is 90.37 mg/l in this water body and 112.28 mg/l in groundwater. This fact indicates that a source with lower salinity and similar isotopic content is recharging the lake, explaining the Cl^- decrease and its isotopic fingerprint.

Isotopic homogeneity in depth can be recognized in these two lakes, suggesting mixed systems. According to $\delta\ ^{18}O$ spatial distribution, more depleted values were found on the western shore of La Brava Lake in coincidence with the fault system described by Mauriño et al. (1981) (Fig. 6a). This would indicate a preferential discharge zone from the fissure system of La Brava Range, which is further corroborated by low EC and low Cl^- content. In Los Padres Lake, higher $\delta^{18}O$ values were detected on the southeastern shore, corresponding to a more shallow water column (>0.5 m), and showing a greater water evaporation process (Fig. 6b).

Four groundwater samples appeared with more enriched isotopic composition (Fig. 4). Well G565, located near to La Brava Lake, presents an isotopic fingerprint similar to this water body indicating a strong influence of this shallow lake on groundwater recharge. Likewise, well G575 shows an isotopic content similar to Los Padres Lake. Following the flow path of these two lakes, isotopic composition indicates water mixing of these lakes and the aquifer (wells G559 and G540) (Fig. 6a, b). In this way, the effluent–influent behavior of La Brava and Los Padres lakes is confirmed.

Hydrogeochemical modeling

Water interactions in both groundwater-dependent lake systems could be seen as a mixing process. According to

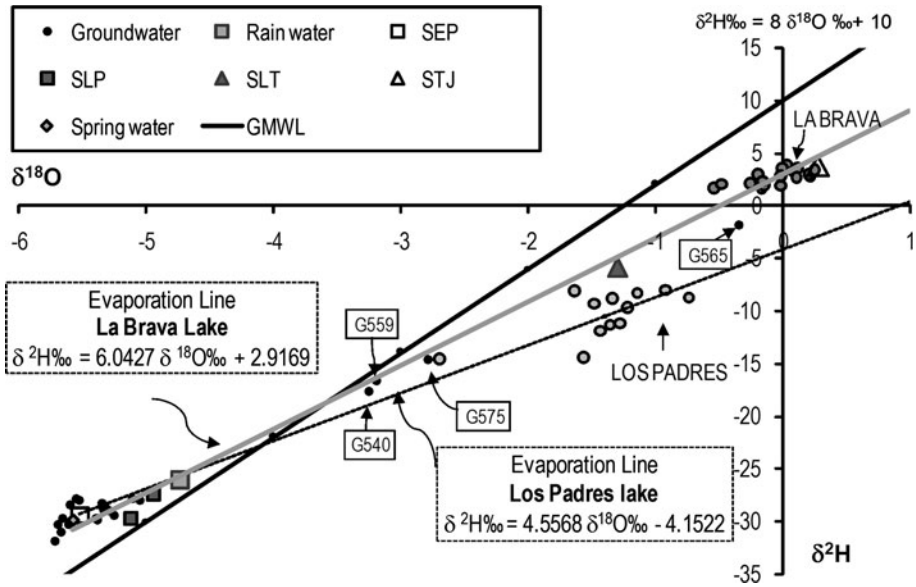


Fig. 4 Isotopic composition (δ^{18}O and δ^{2}H) in groundwater, shallow lakes, rainwater, springwater and stream water. *SEP* El Peligro Stream, *SLP* Los Padres Stream, *STJ* Tajamar Stream, *SLT* La Tapera Stream, *G565* well closed to La Brava Lake, *G575* well closed to Los Padres Lake, *G559* well located downstream La Brava Lake, *G540* well located downstream Los Padres Lake

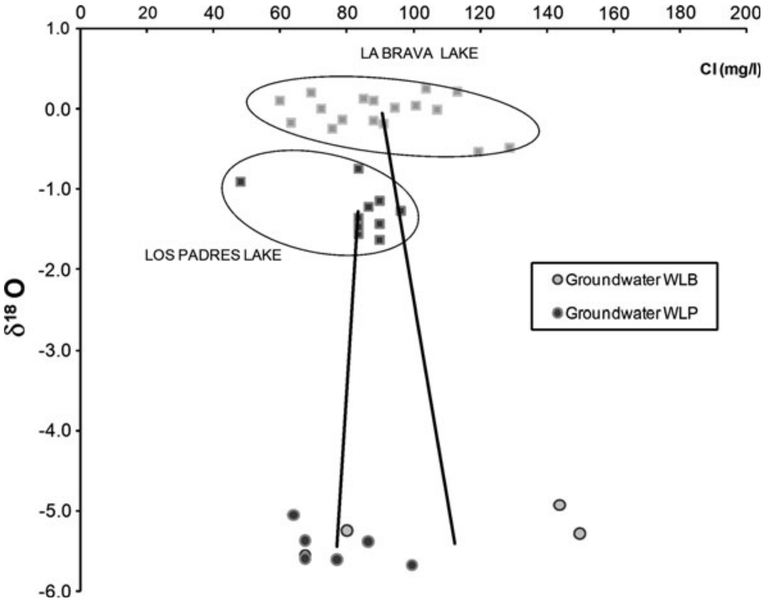


Fig. 5 ^{18}O vs Cl^{-} content in groundwater and shallow lakes. *WLB* La Brava Lake Basin, *WLP* Los Padres Lake Basin

Appelo and Postma (1993), a mixing of different water types can induce reactions which lead to a water composition that is different from the conservative mixture. To achieve a better conceptual model of the processes that determine lake chemical composition and taking into account the obtained hydrogeochemical and isotopic information, hydrogeochemical modeling was performed. One set of samples from each lake basin was represented in Schoeller diagrams (Fig. 7). These samples were the input data in the hydrochemical models.

Two water samples, representative of the recharge sources of La Brava Lake, were selected. The first one was a groundwater sample obtained from the aquifer general recharge area, assuming that groundwater is the major contributing source to the lake. As indicated by chemical and isotopic data, water flow from the fracture system or springs in the fringe range can be a second lake recharge source. For this reason, a spring water sample taken from the contact area of the aquifer and the quartzite rocks that make up the ranges of the basin was included in the analysis.

The analysis in La Brava Lake Basin yields a water type variation from Na–Mg–HCO_3 (Well G527) and Mg–Ca–HCO_3 (spring water) to Na–HCO_3 (shallow lake). Differences in Ca^{2+} concentrations between the water recharge sources were detected (Fig. 7a). In general, bicarbonate concentration in groundwater is quite constant, as expected in phreatic aquifers and/or in areas where calcite

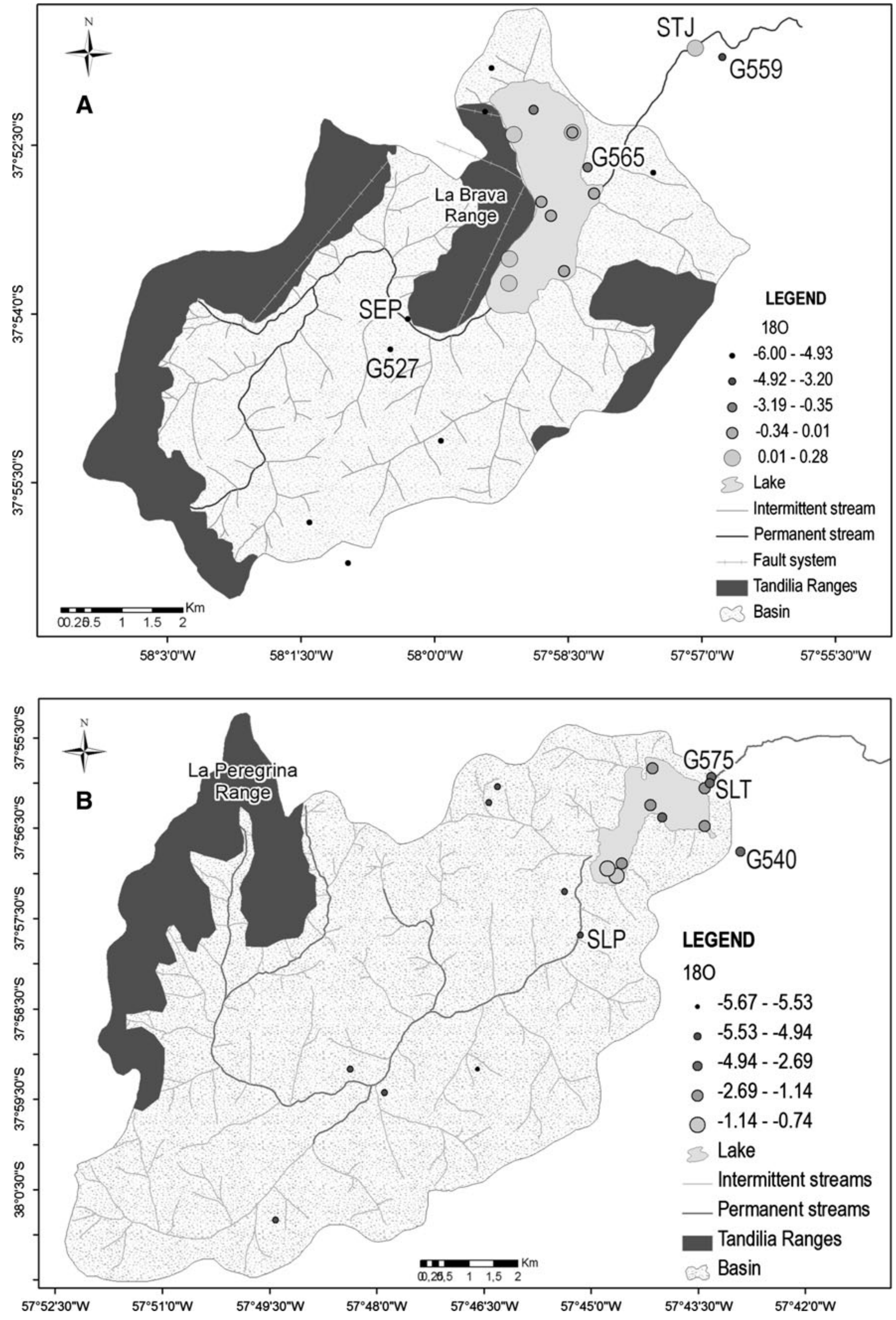


Fig. 6 δ^{18}O values in **a** La Brava and **b** Los Padres lake basins

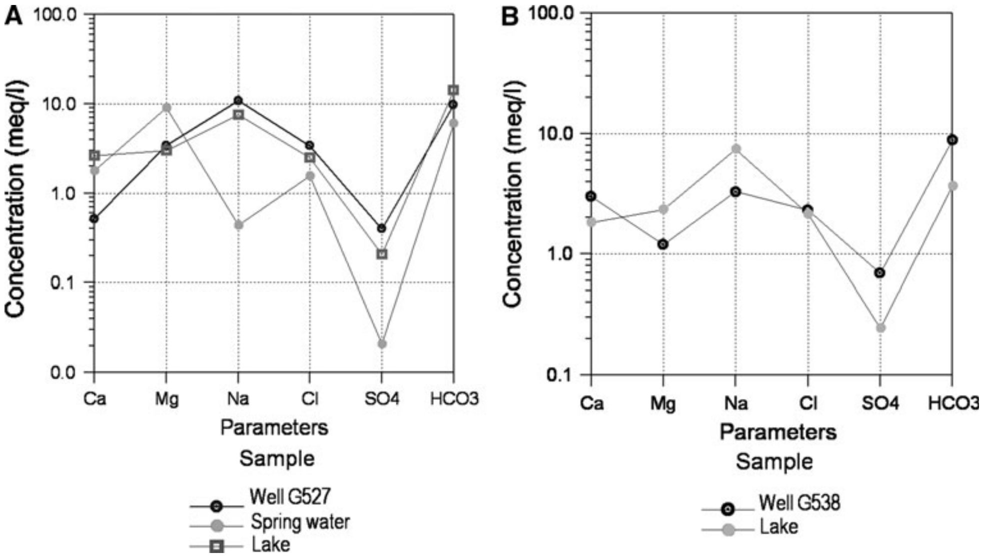


Fig. 7 Schoeller diagrams showing the ionic composition of samples from **a** La Brava and **b** Los Padres lake basins

equilibrium prevails. Chloride content decreases in the lake, validating the dilution process due to water inflow with a lower salinity. Alternative explanations for sodium and sulfate decreasing trends can be suggested. In the first case, probably as a consequence of cationic exchange processes; while in the second one, possibly due to reduction processes or gypsum precipitation. Magnesium increase is explained by Na/Mg exchange.

The analysis in Los Padres Lake Basin includes a groundwater sample from the recharge area and a lake sample. A common evolutionary trend (Chevotarev 1955) is noticeable, water types evolve from a Na–Ca–HCO_3 type in the recharge area (Well 538) to a Na–HCO_3 type towards the lake. The calcium and magnesium presence can be explained by carbonate dissolution and silicate weathering (amphibole, pyroxene and plagioclase) from the loess (Martínez and Bocanegra 2002). Sodium content in water is a result of cation exchange, with Ca^{2+} and/or Mg^{2+} adsorption and Na^+ release (Fig. 7b).

Based on the interpretation of hydrochemical and isotopic data, the main conceptual models related to the water sources and residence time in each one of the considered shallow lakes can be achieved. The existing conceptual models partially developed from piezometric contours and previous references (Cionchi et al. 1982; Kruse 1987; Romanelli et al. 2010) indicate an influent-effluent behavior of groundwater with respect to both lakes. The new evidence presented above using hydrochemical and isotopic data supports these conceptual models for Los Padres Lake, but a new hydrogeological conceptual model, adding the contribution of water from the fractured aquifer, has been mentioned for La Brava Lake.

The use of hydrogeochemical inverse models is a useful tool to test numerically conceptual hydrodynamic models (Martínez et al. 2000). The main conceptual models have been formulated under the mass balance concept and implemented in a NETPATH code environment. Hydrochemical and isotopic data suggest that groundwater is the main water contributor to both lakes, assuming that the contribution from their inflow streams is mainly base flow.

In the first model run, the sample from G538 (recharge area) was taken as the initial solution, while the sample taken in representation of Los Padres Lake (WLP033) was the final one. The obtained hydrochemical processes from this model include evaporation, CO_2 input, calcite dissolution, Na^+ release by Ca^{2+} and Mg^{2+} exchange, and sulfate reduction, resulting in sodium-magnesium bicarbonate waters (Table 5). Model including gypsum as a phase was performed to explain sulfate depletion. However, it was rejected since gypsum precipitation is thermodynamically impossible due to its SI (<0). Consequently, sulfate reduction (Fe–S) was included in the model. Fieldwork during summer months showed that lake sediments especially those located in coastal areas may have an anaerobic condition. These optimal conditions allow sulfate reduction, forming sulfhydric acid.

Secondly, hydrogeochemical modeling was used between spring water and a representative sample of the recharge area (G527) in La Brava Basin, while the final solution was a lake sample (WLB018). The model that best adjusts to the lake hydrochemical constraints includes: mixing, CO_2 and calcite dissolution, cationic exchange with Na^+ release and Mg^{2+} adsorption and, to a lesser extent, Ca/Na exchange, resulting in sodium bicarbonate waters (Table 5). Four hydrogeochemical models were obtained for La Brava Lake, yielding that the fissured aquifer contribution to the water body is greater than 50 %. This value, in fact, should be higher since the lake isotopic content shows evaporation from a recharge source with lower Cl^- content, i.e. water from the fissure system. The

Table 5 Numeric results of the hydrogeochemical models

Initial solution	Final solution	Mixing factor	Evaporation factor	CO_2 (gas)	Calcite	Exchange		Gypsum	Fe–S	NaCl
						Ca/Na	Mg/Na			
Springwater	WLB011	0.509	–	3.319	0.108	−0.627	1.632	–	–	0.033
G527		0.490								
G538	WLP033		1.424	0.574	−0.949	0.156	−0.336	–	−0.237	–

Mass transfer values in millimol per kilogram of water

Transference parameters included for each phase: CO_2 (gas)—C 1,0000; Calcite—Ca 1,0000, C 1,0000; Gypsum—Ca 1,0000, S 1,0000; Ca/Na exchange—Ca 1,0000, Na 2,0000; Mg/Na exchange—Na 2,0000, Mg 1,0000; NaCl—Na 1,0000, Cl 1,0000; Fe–S—Fe 1,0000, S 1,0000

evaporation component can be obtained from the lake water balance equation, based on mass conservation:

$$dV_L/dt = I_S + I_G + P - O_S - O_G - E, \qquad (2)$$

where V_L is lake volume, I_S, I_G, O_S and O_G represent surface and groundwater input and output to the system, respectively, P is precipitation and E is lake evaporation (Mook 2002). However, the evaporation parameter is still unknown.

Conclusions

The combination of stable isotopic data with hydrogeochemical techniques shows a clear common water origin in both shallow lake systems. The isotopic composition of all the components of the water cycle corresponds to rainfall or some fraction of it. Most groundwater and stream water samples upstream from the lakes are near to the monthly weighted average of rainfall stable composition. Regarding the hydrochemical composition, groundwater and inflow streams are similar confirming that these are gaining courses, and making it almost impossible to differentiate between both water sources. Moreover, rainwater is the main source of groundwater recharge. To sum up, groundwater is directly or indirectly the main water contribution to the lakes, from the aquifer or channeled through the inflow stream respectively.

Different hydrogeochemical and isotopic processes that explain aquifer–shallow lake interaction in the southeastern Pampa Plain are recognized; however, some differences between these water bodies have been identified and can be related to lake origin. Evaporation is a common process in both freshwater systems, which is indicated by the evaporation lines observed in the isotopic composition, despite the evaporation line slope in the case of La Brava indicating lesser evaporation than in Los Padres Lake. Hydrogeochemical processes responsible for solute exchange in the studied groundwater dependent lakes were identified. In Los Padres Lake, the obtained hydrochemical reactions after the hydrogeochemical model include: evaporation (1.424 factor, i.e. 1.424 l of groundwater are required to obtain 1 l of lake water), CO_2 input, calcite dissolution, Na^+ release by Ca^{2+} and Mg^{2+} exchange, and sulfate reduction. The model that best adjusts to La Brava Lake hydrochemical constraints includes: mixing, CO_2 and calcite dissolution, cationic exchange with Na^+ release and Mg^{2+} adsorption, and, to a lesser extent, Ca/Na exchange. As Cl^- concentrations are lower in La Brava Lake in comparison to groundwater and stream water input, inverse models cannot include evaporation as a process despite the stable isotopes clearly indicating evaporation; an isotopic enriched water source input but with lower chloride content than the detritic aquifer is needed. Fractured aquifer contribution is suggested and through inverse modeling using quartzite spring water composition, an input of about 50 % to La Brava Lake water budget is obtained.

La Brava and Los Padres lakes both present effluent-influent behavior, operating as a discharge and recharge area of both surface water and groundwater. Upstream, these lakes are gaining water bodies receiving groundwater and stream water inputs, acting as reactors where evaporation, equilibrium and exchange processes take place. Downstream, lake discharge occurs through their outflow streams and by infiltration to the aquifer.

According to the obtained data in this work, lake origin could be an influence in their chemical features; therefore, lakes with structural origin (close to ranges) could be receiving a significant contribution from the fissure system resulting in isotopic enriched water but with low salinity in comparison to the aquifer. The Tandilia Range System, considered in many hydrogeological studies as the impermeable bedrock of the Pampean aquifer, acts as a fissured aquifer in this area, contributing to low salinity waters and with a fingerprint similar to groundwater.

Acknowledgments The authors would like to thank the financial support of the National University of Mar del Plata through ARQ 168/07 and EXA 388/08 the International Atomic Energy Agency (IAEA). The authors are also grateful to Mr. A. Ferrante for technical assistance and Mr. G. Bernava for chemical analysis. One of the authors (AR) wishes to thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for fellowship support.

References

APHA American Public Health Association (1998) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC

Appelo CAJ, Postma D (1993) Geochemistry, groundwater and pollution. A.A. Balkema, Rotterdam

Bocanegra EM, Martínez DE, Massone HE, Cionchi J (1993) Exploitation effect and salt water intrusion in the Mar del Plata aquifer, Argentina. In Custodio E, Galofre A (eds) Study and modeling of salt water intrusion into aquifer, CIMNE-UPC Publishing, Barcelona, pp 177–191

Bonorino G, Albouny R, Rossi S (2001) La influencia del sistema carbonatado sobre el quimismo del agua subterránea Cuenca Superior del Arroyo Chasicó. Geoacta, N° 26, pp 1–11

Burkert U, Ginzel G, Babenzien HD, Koschel R (2004) The hydrogeology of a catchment area and an artificially divided dystrophic lake—consequences for the limnology of Lake Fuchskuhle. Biogeochemistry 71:225–246

Chevotarev II (1955) Metamorphism of natural water in the crust of weathering. Geochim Cosmochim Acta 8:22–48

Cionchi JL, Schnack EJ, Álvarez JR, Bocanegra EM, Bogliano JE, Del Río JL (1982) Caracterización hidrogeológica y físico-ambiental de la Laguna de Los Padres, Partido de Gral. Pueyrredón, Provincia de Bs. As. Convenio Municipalidad de Gral. Pueyrredón-CGCyC, UNMdP

Clark I, Fritz P (1997) Environmental isotopes in hydrogeology. Lewis Publisher, New York, ISBN: 1566702496

Dalla Salda L, Iñiguez RM (1979) "La Tinta", Precambrico y Paleozoico de Buenos Aires. VII Congr Geol Arg I, Neuquén, Argentina, pp 539–550

Drago E, Quirós R (1996) The hydrochemistry of the inland waters of Argentina: a review. Int J Salt Lake Res 4:315–325

Fernández Aláez C, Fernández Aláez M, Trigal Domínguez C, Santos BL (2006) Hydrochemistry of northwest Spain ponds and its relationships to groundwaters. Limnetica 251–2:433–452

Fernández Cirelli A, Miretzky P (2004) Ionic relations: a tool for studying hydrogeochemical processes in Pampean shallow lakes Buenos Aires, Argentina. Quat Int 114:113–121

Fette M, Kipfer R, Schubert CJ, Hoehn E, Wehrli B (2005) Assessing river-groundwater exchange in the regulated Rhone River Switzerland using stable isotopes and geochemical tracers. Appl Geochem 20(4):701–712

Fleckenstein JH, Krause S, Hannah DM, Boano F (2010) Groundwater-surface water interactions: new methods and models to improve understanding of processes and dynamics. Adv Water Resour 33:1291–1295

Fontes J Ch (1980) Environmental isotopes in groundwater hydrology. In: Fritz P, Fontes J Ch (eds) The terrestrial environmental handbook of environmental isotopes geochemistry, vol I. Elsevier, Amsterdam, pp 75–140

Froehlich KFO, Gonfiantini R, Rozanski K (2005) Isotopes in lake studies: a historical perspective. In: Aggarwal PK, Gat JR Froehlich KFO (eds) Isotopes in the water cycle. Past, present and future of a developing science, 1st edn. Springer, The Netherlands, pp 139–150

Gonfiantini R (1978) Standards for stable isotope measurements in natural compounds. Nature 271:534

Goni IB (2006) Tracing stable isotope values from meteoric water to groundwater in the southwestern part of the Chad basin. Hydrogeol J 14:742–775

Hem JD (1992) Study and interpretation of the chemical characteristics of natural waters. U.S.G.S. Water-Supply Paper 2254, fourth printing

Iriondo M (1989) The quaternary lakes of Argentina. Paleogr Paleoclimatol Paleoecol 70:81–88

Kruse E (1987) El agua subterránea en el régimen hidrológico de Laguna la Brava [Groundwater in the hydrological regime of La Brava Lake]. Informe 40, Comisión de Investigaciones Científicas de la Provincia de Buenos Aires

Logan WS, Auge M, Panarello HO (1999) Bicarbonate, sulphate and chloride water in a shallow, clastic-dominated coastal flow system, Argentina. Groundwater 37(2):287–295

Marchese H, Di Paola E (1975) Reinterpretación estratigráfica de la perforación Punta Mogotes N°1, Provincia de Buenos Aires. Rev Asoc Geol Arg 301:17–44

Mariño E, Bonorino G (2005) Evolución hidroquímica de un acuífero loéssico. Caso General Pico-Dorila, Provincia de La Pampa, Argentina. Geoacta 30:1–12

Martínez G (2000) Geomorfología y geología del Cenozoico superior de las cuencas de drenaje de los arroyos Los Cueros y Seco, Sierras Septentrionales de la provincia de Buenos Aires. Tesis Doctoral. Universidad Nacional del Sur. Inédito

Martínez DE, Bocanegra EM (2002) Hydrochemistry and cationic exchange processes in the coastal aquifer of Mar del Plata, Argentina. Hydrogeol J 10(3):393–408

Martínez DE, Bocanegra EM, Manzano M (2000) La modelación hidrogeoquímica como herramienta en estudios hidrogeológicos. Boletín Geológico y Minero 111–4:83–98

Matthess G (1982) The properties of groundwater. Wiley, USA, p 406

Mauriño V, Varde O, Scanavino R (1981) Investigaciones geológicas y geotécnicas realizadas para el proyecto de una central hidroeléctrica de acumulación por bombeo. VIII Congreso Geológico Argentino, Actas II, San Luis, pp 45–66

Mazor E (1991) Chemical and isotopic groundwater hydrology. Marcel Dekker, New York, p 413

Miretzky P, Conzonno V, Fernandez Cirelli A (2000) Hydrochemistry of Pampean ponds in the lower stream bed of Salado river drainage basin Argentina. Environ Geol 39:951–956

Miretzky P, Conzonno V, Fernandez Cirelli A (2001) Geochemical mechanism controlling Pampean ponds hydrochemistry. Salado river drainage basin. Argentina. Revista Brasileira de Recursos Hidricos 6 4, 29–39

Mook WG (2002) Isótopos Ambientales en el Ciclo Hidrológico. Principios y Aplicaciones. Publicaciones del Instituto Geológico y Minero de España. Serie: Guias y Manuales N°1. 2002. IGME, Madrid

Plummer LN, Prestemon EC, Parkhurst DL (1991) An interactive code NETPATH for modelling NET geochemical reactions along a flow PATH. US Geol Surv Water Resour Invest 4078:227

Quiroz Londoño OM, Martínez DE, Dapeña C, Massone H (2008) Hydrogeochemistry and isotope analyses used to determine groundwater recharge and flow in low-gradient catchments of the province of Buenos Aires, Argentina. Hydrogeol J 16:1113–1127

Quiroz Londoño OM, Martinez DE, Massone HE (2012) Estimación de recarga de acuíferos en ambientes de llanura con base en variaciones de nivel freático. Revista Tecnología y Ciencias del Agua. México 2:123–130

Ringuelet RA (1962) Rasgos principales de las lagunas pampeanas con criterio bioecológico. Anales de la Comisión de Investigación Científica CIC, vol III. La Plata, Argentina

Romanelli A, Quiroz Londoño OM, Massone HE, Martínez DE, Bocanegra E (2010) El agua subterránea en el funcionamiento hidrológico de los humedales del Sudeste Bonaerense, Provincia de Buenos Aires, Argentina. Boletín Geológico y Minero. 121 4:373–386. ISSN: 0366-0176

Rossi P (1996) Evolución hidrogeoquímica del agua subterránea en la Cuenca Superior del Arroyo Chasicó, provincia de Buenos. Tesis doctoral en Ciencias Geológicas. Universidad Nacional del Sur, Bahía Blanca, Argentina

Sala JM (1975) Recursos Hídricos especial mención de las aguas. Relatorio Geología de la Provincia de Buenos Aires, IV Congreso Geológico Argentino, Buenos Aires, September 1975

Sophocleus M (2002) Interaction between groundwater and surface water: the state of the science. Hydrogeol J 10(1):52–67

Tapia A (1937) Una investigación geológica en la Brava. Revista Geográfica Americana, pp 167–176

Turner JV, Townley LR (2006) Determination of groundwater flow-through regimes of shallow lakes and wetlands from numerical analysis of stable isotope and chloride tracer distribution patterns. J Hydrol 320:451–483

Usunoff E, Varni M, Weinzettel P, Rivas R (1999) Hidrogeología de Grandes Llanuras: la Pampa Húmeda. Boletín Geológico y Minero 110(4):47–62

Vogt T, Hoehn E, Schneider P, Freund A, Schirmer M, Cirpka OA (2010) Fluctuations of electrical conductivity as a natural tracer for bank filtration in a losing stream. Adv Water Resour 33:1296–1308

Wang Y, Guo Q, Su C, Ma T (2006) Strontium isotope characterization and major ion geochemistry of karst water flow, Shentou, northern China. J Hydrol 328:592–603

Wetzel RG (2001) Limnology. Lake and river ecosystems, 3rd edn. Academic Press, San Diego, p 1006

Winter TC (1999) Relation of streams, lakes, and wetlands to groundwater flow systems. Hydrogeol J 7:28–45