

HYDROGEOCHEMISTRY, ISOTOPIC COMPOSITION AND WATER AGE IN THE HYDROLOGIC SYSTEM OF A LARGE CATCHMENT WITHIN A PLAIN HUMID ENVIRONMENT (ARGENTINE PAMPAS): QUEQUÉN GRANDE RIVER, ARGENTINA

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ABSTRACT

The Quequén Grande River (QGR) is a large catchment (10 000 km²) in the Pampa Plain in Argentina. From November 2004 to April 2013, a hydrochemical and stable isotopes monitoring program was conducted, which included three sampling stations of monthly composite precipitation, weekly samples in two sites along the river and several groundwater samples.

A standard data interpretation was initially performed applying standard statistics, Piper diagrams and $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ diagrams. The time evolution of the values of $\delta^{18}\text{O}$ in precipitation and streamwater were also determined.

The integration of hydrogeochemistry and stable isotopes data indicates the existence of three main components of streamflow: (i) baseflow characterized by electrical conductivity (EC) from 1200 to 1800 $\mu\text{S}/\text{cm}$ and an isotope composition quite constant around $\delta^{18}\text{O} -5.3\text{‰}$ and $\delta^2\text{H} -33.8\text{‰}$. Water age for groundwater contribution is typically around 30 to 40 years using chlorofluorocarbons; (ii) direct runoff composed of channel interception and overland flow, which is of low EC in the order of 50 to 100 $\mu\text{S}/\text{cm}$, and a highly variable isotopic composition; and (iii) transitory flow (pre-event water that is stored within the subsoil) with an intermediate EC and isotopic composition close to that of the weighted average composition of precipitation.

The hydrochemical and stable isotopic data allow the differentiation between baseflow and direct runoff. In addition to this, chlorofluorocarbon dating is a useful tool in assessing the dominance of baseflow in a stream. The data lead to a conceptual model in which an intermediate flow system, with mean residence time (MRT) of around 35 years, discharges into the drainage network. A regional flow system (MRT > 50 years) discharges to the ocean. It is concluded that in this large plain catchment streamflow separation, only two components can be applied in: (i) short storm precipitation events having a high sampling frequency and (ii) during long dry periods when pre-event soil water is not released. Copyright © 2016 John Wiley & Sons, Ltd.

KEY WORDS: Pampa Plain Argentina; isotope hydrology; mean residence time; CFCs; noble gases; streamflow separation

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INTRODUCTION

The surface and groundwater contributions to rivers have been described in various manners: direct runoff and baseflow (Hewlett and Hibbert, 1965), new flow and old flow (Chapman, 1999), young water and old water (Kirchner, 2003). Nevertheless, the response of streams to precipitation events is complex, due partly to the phenomenon that was described by Kirchner (2003) as the fast mobilization of old water, one of his paradoxes that has been observed in small catchments. Recent evidence indicates that pre-existent water is quickly released during storm phenomena (McDonnell, 2003).

Most of the techniques used to separate streamflow components are based on discharge records and some graphic or mathematical differentiation of the hydrograph (Chapman, 1999; Wittemberg, 1999); however, these techniques do not recognize many important features in the water flow components, which can be studied using hydrogeochemical and isotopic techniques. The basic concepts of the chemical evolution of natural waters allow us to associate old water with that corresponding to longer groundwater flow paths, with an evolution towards chloride or sulfate water types. Total dissolved solids in groundwater should be useful to differentiate its participation in the streamwater composition from that coming from rainwater, which is a low salinity water. Furthermore, the differences between the isotopic composition of rainwater and groundwater are also the basis for a methodology for baseflow quantification (Maloszewski

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et al., 1992; Dewalle *et al.*, 1997; Kendall and McDonnell, 1998; Klaus and McDonnell, 2013). Nevertheless, these works dealt with a small catchment where detailed data at event scale are available.

Many applications of the method can be found in small and meso-scale catchments, but very few applications upon large catchments have been done (Tekleab *et al.*, 2013), such as the studies from Taylor *et al.* (1989), Liu *et al.* (2008) and Soulsby *et al.* (2015). The aim of this contribution is to evaluate the usefulness of hydrogeochemical, stable isotopes and water age dating techniques for separating components of the hydrological system in large catchments. A large catchment in the Argentine Pampas Plain was selected, taking into account its geological, morphological and hydrogeological features.

HYDROLOGY AND HYDROGEOLOGY

The Pampas Plain is an extended geographical region (about $1.5 \cdot 10^6 \text{ km}^2$) characterized by slopes usually ranging

between 0.001% and 0.05% and a wide cover of Neogene and Quaternary sediments. The Quequén Grande River (QGR) catchment is situated within this geographical region, covering an area of close to $10\,000 \text{ km}^2$. It is located in a sedimentary basin between two mountain ranges; the Tandilia range formed by Precambrian metamorphic rocks and Lower Paleozoic sedimentary rocks, and the Ventania range formed by a sequence of Paleozoic sedimentary rocks. QGR headwaters are located at the Tandilia range. The origin of the present valley is considered to be a case of fluvial capture (Cortizo and Isla, 2000), intercepting other courses that previously discharged directly into the Atlantic Ocean (Figure 1). These courses constitute the tributaries discharging into the left margin of the river. The QGR length is 180 km, and the total drainage network is 1162 km.

The average annual temperature is 14°C , July being the coldest month with a mean value of 7.3°C , and January the warmest with a mean value of 21°C . Average precipitation for the period 1961–1990 was 855 mm/y (Campo de Ferreras and Piccolo, 1997). Evapotranspiration was calculated applying the Thornthwaite (1948) method, which is

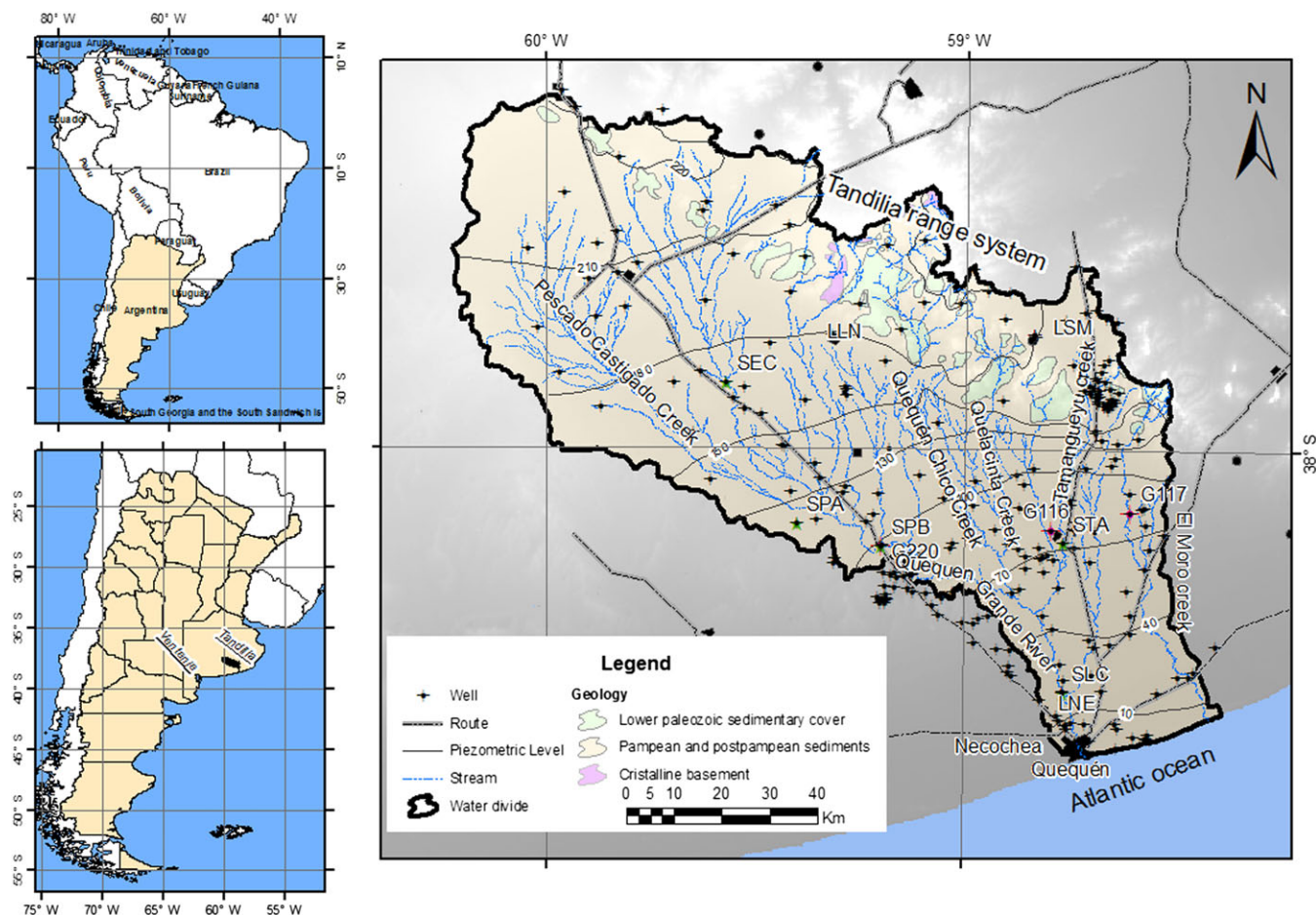


Figure 1. Location map and sampling sites. [Colour figure can be viewed at wileyonlinelibrary.com]

740 mm/y, resulting in a water excess of 115 mm/y (Kruse *et al.*, 1997). QGR average flow was 11 m³/s for the period 1960–1980 (Kruse *et al.*, 1997) and 17 m³/s for the period 1980–1990 (Varela and Teruggi, 2001). One gauge station exists in the catchment, and it is located 15 km upstream from the outlet to the sea. Records dating back from 1960 are discontinuous showing many gaps. Using the two most complete series of daily flow records, 1986–1990 and 1994–2000, a proportion of baseflow oscillating between 60% and 90% was obtained (Martínez *et al.*, 2007) by using HYSEP (Sloto and Crouse, 1996), and around 70% by using BFLOW (Arnold and Allen, 1999). Peak values were reached during extraordinary floods, like 567.9 and 758.5 m³/s in November 1985, 426.1 m³/s in October 1998, and 908 m³/s in August 2002.

The sedimentary sequence covering the basement rocks initiates with red sandstones and clays of continental origin and Miocene age, overlapped by green and blue clays of marine origin, also of Miocene age. The Miocene series is followed by a thick sequence of loess-like silt and silty-sand sediments, frequently including precipitated CaCO₃ layers, called *Pampeano* sediments (Fidalgo *et al.*, 1975). Finally, the Holocene is locally represented by sand deposits forming dunes corresponding to the *Post-pampeano* sediments. The set formed by *Pampeano* and *Post-pampeano* deposits constitute a hydrogeological unit known as Pampeano Aquifer.

Groundwater flow path is generally aligned with surface water flow direction. Most of the drainage network shows a gaining behaviour in the major proportion of the stream courses. Recharge to the aquifer is by precipitation and was calculated by using different methods (Quiroz Londoño *et al.*, 2008): the annual balance at edaphic level with the Thornthwaite method, for a 10-year period (1995–2005), obtaining a recharge value of 13% of total precipitation, and the calculated recharge value reached a high of 17% if calculations were made using individual annual values for the same decade applying the chloride balance method. Discharge is mainly through the streams and as underground flow directly to the sea (Bocanegra *et al.*, 2005).

METHODS

Groundwater samples were taken seasonally between 2005 and 2013 from about 173 sampling wells (Figure 1), by pumping until pH, temperature and electrical conductivity (EC) stabilization. These parameters were recorded in the field, where also alkalinity was determined by H₂SO₄ titration. Surface water was sampled weekly at five different points along the stream network (Figure 1) during the period 2005–2008. From November 2004 to April 2013, a larger sequence of weekly samples were gathered from the sites SPB and SLC, located on the main trunk of the Quequén

Grande River. The other three sites were placed in the tributaries: two at the headwaters (SPA and SEC) and the last one at the lower part of the catchment (STA). Finally, three sampling stations of monthly composite precipitation for isotopic determinations have been in operation since November 2004, using collectors designed by the International Atomic Energy Agency (IAEA, 2002). Two of the rain gauge locations are in the upper catchment area, at San Manuel Village (LSM) at 180 m. a.s.l. and La Negra site (LLN) at 240 m. a.s.l., and the remaining gauge is close to the coast at LNE at 28 m. a.s.l.

Major ions have been analyzed on the samples taken during the shortest period (2005–2008), after filtering (45 µm pore membrane), using standard methods (APHA, 1992).

Stable isotope determinations were performed with High-Precision Laser Spectroscopy Off-axis integrated cavity output spectroscopy for liquid water (Lis *et al.*, 2008) manufactured by Los Gatos Research DLT-100 at the laboratory of the Institute of Coastal and Quaternary Geology of the National University of Mar del Plata. Six injections per sample were carried out, discarding the first two in order to minimize the memory effect (Penna *et al.*, 2012). Results are expressed as isotopic deviations δ in per mil (‰). Values are referred to Vienna Standard Mean Ocean Water (V-SMOW) and normalized to the V-SMOW-SLAP scale (Gonfiantini, 1978; Coplen, 1988). Analytical uncertainties are for δ¹⁸O: ±0.3‰ for laser spectroscopy, and for δ²H: ±1‰.

One litre of water samples were enriched by electrolysis and measured by liquid scintillation counting for tritium analysis, at the National Institute of Geochronology and Isotope Geology. The ³H concentrations are expressed as tritium units. The average uncertainties are ±0.5 TU (tritium units, where one TU is defined as one tritium atom per 10¹⁸ hydrogen atoms (Gröening and Rozanski, 2003).

Dating groundwater by using chlorofluorocarbon (CFC) gases CFC-11, CFC-12 and CFC-113 (Cook and Solomon, 1997) is based on the solubility of gases in water and in the increasing concentration of CFCs in the atmosphere since the 1950s. The solubility is determined by Henry's law

$$C_i = K_H p_i \quad (1)$$

Where C_i is the dissolved gas concentration, p_i is the gas partial pressure and K_H is Henry's constant. As K_H is dependent on recharge temperature and water salinity, and p_i dependent on total atmospheric pressure, which is related to recharge elevation, it is necessary to estimate these variables and to relate the measured CFCs concentrations to the partial pressure existing within a specific year.

Samples for CFCs were collected in 250 ml dark glass bottles in two sampling campaigns, one during May 2008, which included three groundwater and three surface water

samples, and the other during September 2009 that included three streamwater samples and one groundwater sample (Figure 1). Some points were sampled in both campaigns. CFCs measurements were performed by gas chromatography with electron capture detector at the Dissolved Gas Lab of the University of Utah.

RESULTS AND DISCUSSION

A total of 255 rain water samples, 343 groundwater samples and 928 streamwater samples were taken, giving a total of 1526 samples. EC and stable isotopes were determined for each sample, while major ion chemical analyses were performed on a smaller number, which is explained in the succeeding sections for each water type: precipitation, streamwater and groundwater.

Hydrochemical and isotopic characterization of rain water

The most complete rain water data series of composite monthly samples of rainwater were for stable isotopes determination and occasional chemical analyses (depending on the collected volume) from the gauges installed in the towns of La Negra (LLN), Necochea (LNE) and San Manuel (LSM). Statistical parameters of the major ion composition of rainwater are shown in Table I.

The chemical composition of precipitation can be highly variable. This is not only because of rainfall origin from different air masses but also because analytical procedures and uncertainties can cause up to 20% in variability. Bicarbonate is the dominant ion as a result of atmospheric CO₂ dissolution. Terrigenous components of calcium-magnesium can be

associated with atmospheric dust, while chloride, sulfate and sodium can be related to sea sprays.

Isotopic contents range between $-10.6‰$ and $-0.3‰$ for $\delta^{18}\text{O}$ and between $-74‰$ and $-0.5‰$ for $\delta^2\text{H}$. Average values for stable isotopes in precipitation in the catchment, integrating the three stations ($n=255$) are $\delta^{18}\text{O} = -5.1‰$ and $\delta^2\text{H} = -29.2‰$. Weighted mean values calculated for the collectors are LSM $\delta^{18}\text{O} = -5.0‰$ and $\delta^2\text{H} = -30.5‰$, LLN $\delta^{18}\text{O} = -5.2‰$ and $\delta^2\text{H} = -31.4‰$ and LNE $\delta^{18}\text{O} = -4.8‰$ and $\delta^2\text{H} = -31.2‰$. Sample distribution with reference to the Global Meteoric Water Line (Figure 2) shows a wide variability due mainly to temperature effects, a superimposed amount effect and also the origin of mass air (González *et al.*, 2009). More depleted samples, also for $\delta^{18}\text{O}$ or $\delta^2\text{H}$, correspond usually to winter. Another cause for isotopic variations is the continental effect. Precipitation from the collector closer to the coast (LNE) presents most enriched values. The local meteoric water lines (LMWL) were calculated using orthogonal regression (IAEA, 1992) (Figure 2). It is very close to the global meteoric water line (Craig, 1961), indicating that the local precipitation have an isotopic composition controlled by equilibrium fractionation with the vapor phase.

The records of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation for the period from November 2004 to July 2013 at the LSM station show a behaviour approximately sinusoidal in accordance with seasonality and the temperature effect. Nevertheless, this behaviour is modified by the amount effect, which produces the most depleted values.

Tritium measurements were carried out on a small group of samples ($n=14$) taken during the first stages of the study. The amount of analyzed samples remained restricted to this number mainly due to the laboratory availability. The values

Table I. Rain water: statistical parameters of chemical and isotopic composition

Total number of Samples: 255						
Parameter	Unit	Min	Max	Average	Standard deviation	Sample number
pH		6.67	9.00	7.13	7.14	27.00
Cond	$\mu\text{S}/\text{cm}$	2.60	96.60	57.50	28.03	25.00
Ca	mg/l	1.30	13.50	6.59	3.46	25.00
Mg	mg/l	0.20	13.10	3.80	3.76	25.00
Na	mg/l	0.00	34.00	13.69	8.87	23.00
K	mg/l	0.00	7.27	1.88	1.96	22.00
Cl	mg/l	5.17	70.50	23.77	20.33	29.00
HCO ₃	mg/l	16.40	86.40	45.65	20.56	25.00
SO ₄	mg/l	0.00	42.90	9.14	10.38	21.00
NO ₃	mg/l	0.00	6.70	0.86	1.86	13.00
F	mg/l	0.00	1.05	0.37	0.41	13.00
Si	mg/l	0.00	13.00	2.82	3.15	15.00
$\delta^{18}\text{O}$	‰	-10.6	-0.35	-5.14	2.55	250.00
$\delta^2\text{H}$	‰	-74.00	-0.42	-29.2	20.27	250.00
^3H	T.U.	3.90	10.50	7.61	1.69	14.00

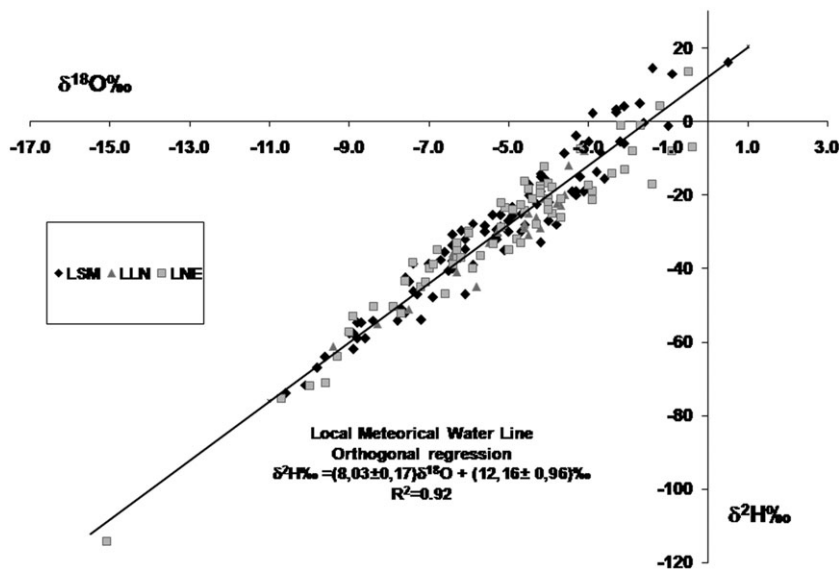


Figure 2. $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ diagram for rain water samples, local meteoric water line and Global Meteoric Water Line.

vary between 3.9 and 10.50 TU with a weighted average value of 7.75 TU. These ^3H values are quite high for the southern hemisphere and can be a consequence of the existence of nuclear power plant 400 km to the north of the study area, which has been operational since 1974. This Atucha nuclear power plant releases tritium into the atmosphere with a concentration measured in the air of about 1 to 6 Bq/m³ (Bruno *et al.*, 1981).

Hydrochemical and isotopic characterization of groundwater

Groundwater has been characterized by using 343 samples obtained from 173 wells. Statistics of the ionic content and

isotopic composition are shown in Table II. Sodium is the dominant cation followed by magnesium and calcium. Bicarbonate is the dominant anion in most of the samples, followed by chloride and sulfate at lower proportions. Chloride and sulfate type waters are located in the area around SPB.

Along a flow line, groundwater increases in salinity and moves from bicarbonate calcium-magnesium to bicarbonate sodium type. Rain water infiltrates and dissolves mainly calcium carbonate and reacts with the less stable minerals in the pampean loess, magnesium silicates, becoming calcium-magnesium bicarbonate in the recharge zone. During its evolution, calcite equilibrium is achieved

Table II. Groundwater: statistical parameters of chemical and isotopic composition

Total number of samples: 343

Parameter	Unit	Min	Max	Average	Standard deviation	Sample number
pH		6.89	8.96	7.53	7.61	276
Cond	$\mu\text{s}/\text{cm}$	410.00	7580.00	1178.92	914.79	278
Ca	mg/l	4.03	363.80	29.12	31.20	260
Mg	mg/l	1.44	490.50	45.90	62.06	260
Na	mg/l	22.62	1337.10	222.61	170.89	222
K	mg/l	1.70	28.00	8.47	3.06	221
Cl	mg/l	21.00	2877.20	170.94	320.60	260
HCO ₃	mg/l	1.61	1357.50	667.82	192.44	260
SO ₄	mg/l	5.53	855.00	71.10	104.67	258
F	mg/l	0.00	6.00	1.78	1.13	178
NO ₃	mg/l	1.00	263.30	57.83	47.27	306
Si	mg/l	3.03	115.00	46.07	20.64	248
$\delta^{18}\text{O}$	‰	-6.10	-4.20	-5.31	0.40	80
$\delta^2\text{H}$	‰	-39.00	-22.46	-33.76	2.86	80
Tritium	T.U.	0.50	3.50	2.11	0.73	11

at short distances along the flow path. Martinez *et al.* (2012) showed a calcite saturation index (SI_{CaCO_3}) map of the catchment where only few points close to the mountain range are undersaturated. Being the main anion, bicarbonate, controlled by calcite equilibrium, the cationic composition evolves according to exchange processes uptaking mostly calcium and releasing sodium. Gypsum equilibrium included in the mass balance models showed mass transferences in the order of 10^{-2} mmol/L. Some chloride waters can be observed, belonging to a deep borehole close to SPB site. The higher salinity in this zone has been explained by the upward discharge of regional deeper flow lines due to the existence of an impermeable rock block outcropping to the west (Martinez *et al.*, 2012; Quiroz Londoño *et al.*, 2015).

Groundwater isotopic composition jointly with the LMWL were plotted on a δ^2H vs. $\delta^{18}O$ diagram (Figure 3), the samples showing a narrow range of variation indicating a relatively homogeneous composition. $\delta^{18}O$ values were between -6.1‰ and -4.2‰ , and δ^2H between -39‰ and -22‰ . Average values were -5.3‰ for $\delta^{18}O$ and -34‰ for δ^2H . Groundwater flow results in a well mixed system (Gat and Tzur, 1967) and its isotopic composition can be used as a tracer.

Hydrochemical and isotopic characterization of Quequén River and its tributaries

Weekly samples have been taken from two points (SPB and SLC) of the QGR over an 8-year period, and additional samples were gathered at three different tributaries (SEC, SPA and STA) (Figure 1). EC and stable isotope being measured

in all samples, while major ion analyses were carried out on the samples taken between 2005 and 2008.

Streamwater is mainly alkaline, with pH values between 6.58 and 9.72 with an average value of 8.04. Extreme low and high values correspond, respectively, to samples taken after heavy rains or at some stagnant point where evaporation is important, but 80% of the measurements ranged from 7.6 to 8.6. Furthermore, EC is very variable depending on rain periods and on the stream network site that is being measured. Minimum value of EC was $158.3 \mu\text{s/cm}$ and maximum of $3270 \mu\text{s/cm}$, with an average value of $1454.8 \mu\text{s/cm}$. The reasons for this variability were mostly the time elapsed between precipitation events and sampling, and geological aspects having influence over the main chemistry.

EC values measured “in situ” at the sites SPB and SLC between November 2004 and December 2011 were quite stable, decreasing after rainy periods as expected. EC records for the SPB site, presented higher values than those observed in SLC for the same dates. It is noticeable that, being the sampling point SPB located upstream of SLC, it constantly held higher EC values.

Streamwater is mostly sodium-bicarbonate type. The statistical parameters of main physicochemical, chemical and isotopic measurements are shown in Table III. Some samples correspond to sodium-sulfate and sodium-chloride facies, mainly those taken at the SPB site. This is due to the existence of thick layers of gypsum in the confluence where the QGR is formed (Del Blanco *et al.*, 2005), adding an important amount of sulfate and calcium to the solution. The calcium added during the dissolution of gypsum is likely to be removed by calcite precipitation. The saturation index for calcite in streamwater samples is slightly supersaturated.

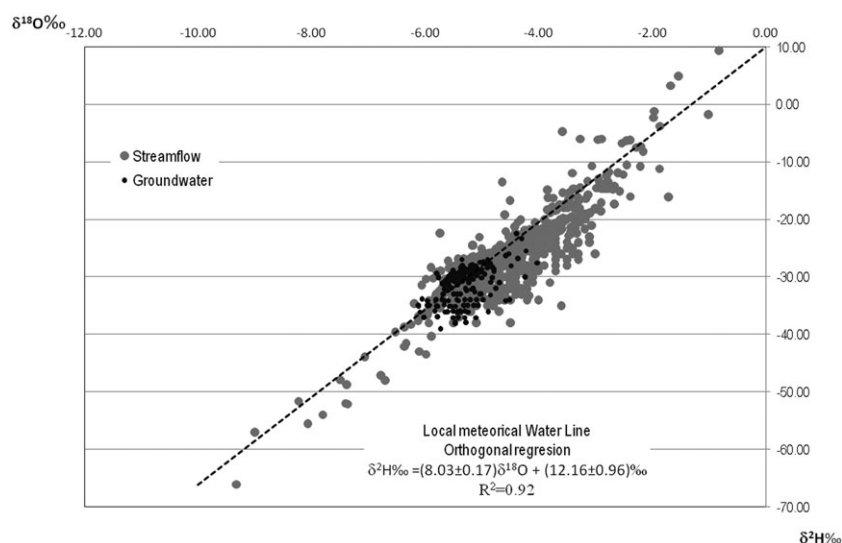


Figure 3. Isotopic composition of streamflow and groundwater.

Table III. Streamwater: statistical parameters of chemical and isotopic composition

Number of Samples: 928						
Parameter	Unit	Min	Max	Average	Standard deviation	Sample number
pH		6.58	9.23	8.01	7.70	330
Cond	µs/cm	158.30	3270.00	1454.8	438.3	486
Ca	mg/l	5.18	236.00	30.06	23.38	328
Mg	mg/l	2.00	68.00	28.70	12.74	328
Na	mg/l	24.10	786.00	314.26	107.36	324
K	mg/l	2.70	29.40	9.20	2.98	325
Cl	mg/l	15.30	780.00	189.78	103.93	328
HCO ₃	mg/l	4.47	1171.60	650.50	197.05	328
SO ₄	mg/l	1.35	550.00	108.17	78.24	324
F	mg/l	0.00	6.50	2.12	1.12	327
NO ₃	mg/l	0.00	251.00	14.76	20.29	301
Si	mg/l	0.05	161.00	31.04	16.30	320
δ ¹⁸ O	‰	-9.33	2.20	-4.50	0.93	793
δ ² H	‰	-66.09	11.00	-28.81	7.12	790
Tritium	T.U.	0.80	7.10	2.77	1.67	21

Dissolved solids are higher at the SPB point because of the dissolution of gypsum layers upstream. The discharge downstream SPB of the tributary Quelacinta Creek, whose sources lie within the sandstone hills, introduces a diluted and isotope depleted water, decreasing the salinity and the isotope content towards SLC.

The isotopic composition of rivers is represented in a conventional scatter plot δ²H vs. δ¹⁸O jointly with the LMWL (Figure 3). Stream water values are disposed along the water line but most samples plot around -40‰ and -18‰ for δ²H and -6.0‰ and -3.0‰ for δ¹⁸O. More depleted values are usually associated to strong rain dates. Extremely enriched values are linked to enriched precipitations.

Variation in δ¹⁸O at the two sites with the amount of precipitation at the LSM gauge is shown in Figure 4. A sinusoidal δ¹⁸O variation was observed because of the temperature effect and seasonal storm patterns. In exceptional cases, enriched precipitations directly affect the streamflow composition, as was observed in October 2007.

Strong rainy periods result in very light waters (δ¹⁸O about -10‰), which can be observed particularly during the extreme rains that occurred in March 2007 and April 2008, which were more than 120 mm and 80 mm in a single day, respectively. In general, δ¹⁸O were lower for SLC than SPB on any considered date.

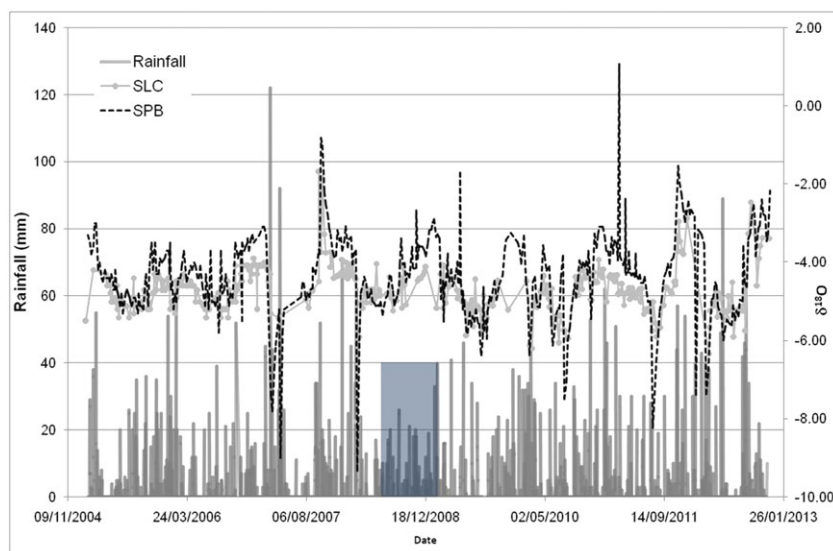


Figure 4. Variation of δ¹⁸O in streamflow and its relation with the rainfall. [Colour figure can be viewed at wileyonlinelibrary.com]

The composition of streamwater discharge can be divided into two main end members according to its isotopic composition, corresponding to direct runoff (rain) and baseflow (groundwater) using the equations (Genereux and Hooper, 1998):

$$f_r = \frac{\delta^{18}O_{gw} - \delta^{18}O_s}{\delta^{18}O_{gw} - \delta^{18}O_r} \quad (2)$$

$$f_{gw} = \frac{\delta^{18}O_s - \delta^{18}O_r}{\delta^{18}O_{gw} - \delta^{18}O_r} \quad (3)$$

where f_r is the fraction of rain water in streamflow composition, f_{gw} is the fraction of groundwater in streamflow composition, $\delta^{18}O_r$ is the concentration of the tracer in rain water, $\delta^{18}O_{gw}$ is the concentration of the tracer in groundwater and $\delta^{18}O_s$ is the concentration of the tracer

The procedure was as follows: to assume that the weighted monthly value of isotopes in precipitation can be used for each week in the month. Secondly, step the propagation of the uncertainty in the measurements to the calculated fractions from Equations 2 and 3 was analyzed. In the case of a function $y = G(x_1, x_2, \dots, x_n)$ when the error W_x are independent, the propagation of the error to the calculated variable W_y can be estimated from:

$$W_y = \left[\sum_{i=1}^n \left(\frac{\partial y}{\partial x_i} W_{x_i} \right)^2 \right]^{1/2} \quad (6)$$

which when applied to Equations 2 and 3 results into the following:

$$W_f = \left\{ \left[\frac{C_{gw} - C_r}{(C_{gw} - C_r)^2} W_{C_r} \right]^2 + \left[\frac{C_s - C_r}{(C_{gw} - C_r)^2} W_{C_{gw}} \right]^2 + \left[\frac{-1}{(C_{gw} - C_r)} W_{C_s} \right]^2 \right\}^{1/2} \quad (7)$$

in streamflow. Nevertheless, in this case, the different sampling periods for rain (monthly composite) and streamwater (weekly single sample), and the similarity between groundwater values and average rain values, makes it impossible to apply Equations 2 and 3 to calculate baseflow proportion in streamflow.

When many instant samples for precipitation over a short period are available, separation using stable isotopes can be carried out. Heavy precipitations occurred during April 2007 and sequences of four water samples were collected at SPB over a period of 17 days. Calculation results indicate that streamflow was almost 100% groundwater in 13 April 2007, lowering to a 20.6% in April 20 after a rain storm of 90 mm in a day, and returning to 87.5% just a week later.

Despite of the previously mentioned difficulties, it has been possible to select a period in which most of the records accomplished the relationship $C_r \geq C_s \geq C_{gw}$, making it possible to apply Equations 2 and 3, and therefore defining the notation

$$C_{gw} = \delta^{18}O_{gw}; \quad C_r = \delta^{18}O_r; \quad C_s = \delta^{18}O_s$$

$$f_r = \frac{C_{gw} - C_s}{C_{gw} - C_r} \quad (4)$$

$$f_{gw} = \frac{C_s - C_r}{C_{gw} - C_r} \quad (5)$$

Taking into account Equations 2 and 3, and that $W_{\delta^{18}O_r} = W_{\delta^{18}O_{gw}} = W_{\delta^{18}O_s} = 0.3 \%$, Equation 5 can be reduced to

$$W_f = \frac{0.3}{|C_{gw} - C_r|} \left(f_r^2 + f_{gw}^2 + 1 \right)^{1/2} \quad (8)$$

Except for some outlier points where one of the fractions is greater than 1, it is fulfilled: $f_r + f_{gw} = 1 \Rightarrow (f_r^2 + f_{gw}^2 + 1)^{1/2} \leq \sqrt{2}$, and for most of the cases in a selected period $|C_{gw} - C_r| \geq 1.5$, because C_r takes values between 0 and -2.8 , while $C_{gw} = -5.0$. This explains why the calculated error is below the analytical error of the measured variables.

The fractions of streamflow f_r , assigned to event water, and f_{gw} , assigned to prevent water, for the referred period, plus the calculated error, have been plotted in Figure 5. The amount of precipitation is also shown in Figure 5, and the Pearson correlation coefficient between f_r and precipitation have been obtained, being of 0.40, with a p -value = 0.024.

From the former paragraphs, it can be concluded that a two end members flow separation cannot be applied to this large catchment except during short periods. The period for which the Genereux equations were successfully applied corresponds to July 2008 to February 2009, which was a relatively dry period, in correspondence to a strong La Niña

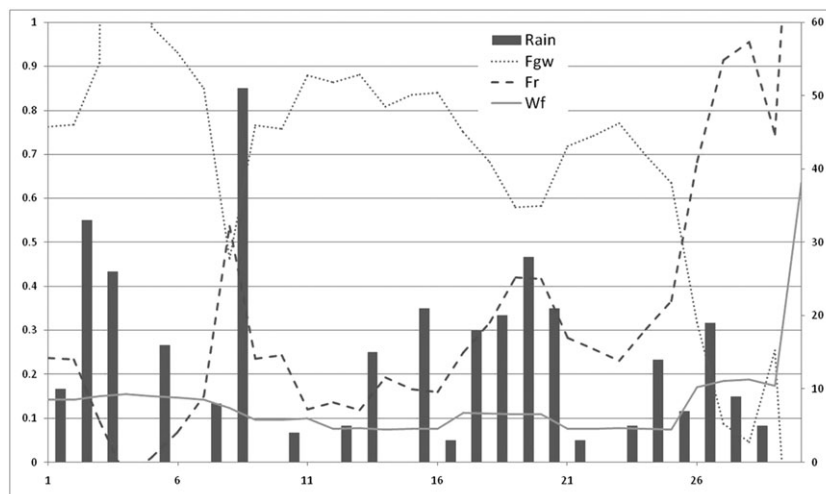


Figure 5. Fraction of pre-event water (fgw) and event water (fr) and uncertainty of the components calculated for the period July 2008 to February 2009.

phase of the ENSO phenomena. It is difficult to demonstrate the origin of this behaviour, but a hypothesis could be formulated: the streamflow separation as two components cannot be performed for most of the record because, as it is said, the condition $C_r \geq C_s \geq C_{gw}$ is not fulfilled. Probably soil water, as pre-event water, is forming a significant proportion of the streamflow, and as it has not been characterized because of the complexity of such a large catchment, the separation has not arrived to reliable results. In the period where the separation could be done, little precipitation, falling below of 20 mm/month (Figure 4), didn't lead to soil water release, streamflow being formed by just two components. In other words, in this large catchment, the quick

release of pre-existent during storm phenomena (McDonnell, 2003) does not take place during dry periods.

Apparent water age

Chlorofluorocarbon-based apparent ages of groundwater are within the order of 35 years for a shallow well (G116 is 25 m deep) and 60 years or older for deeper wells (G117 is 100 m deep and G220 is 80 m deep). Stream water (during baseflow) has been dated in the order of 30 to 40 years in almost all of the sites (Table IV).

Tritium measurements can be used as a relative dating tool considering that its presence indicates some proportion

Table IV. Mean residence time obtained from CFCs measurements

Sample	Type of sample	Sampling date	CFC-11 (pmol/kg)	CFC-12 (pmol/kg)	CFC-113 (pmol/ kg)	Age CFC11	Age CFC12	Age CFC113
STC	Stream	May 8	3.64	1.64	0.37	1985	1983	1989.5
G117	Deep well	May 8	0.03	0.00	0.00	1952	—	1943
G220	Deep well	May 8	0.02	0.00	0.00	1952	—	1943
G156	Shallow well	May 8	16.70	0.75	0.18	—	1975	1982
WLS030	Pond	May 8	3.88	1.65	0.42	1989	1985.5	—
SSB	Stream	May 9	3.22	1.35	0.32	1978	1976	1986
SPT1	Stream	Sep 9	1.66	1.07	0.11	1973	1974.5	1978.5
SPT2	Stream	Sep 9	1.56	1.04	0.13	1973	1974.5	1980
SPT3	Stream	Sep 9	1.51	1.12	0.12	1972	1975	1979.5
STC1	Stream	Sep 9	1.58	2.62	0.27	1973	Cont	1986
STC2	Stream	Sep 9	1.71	2.93	0.28	1973	Cont	1986
MTB1	Spring	Sep 9	0.84	1.03	0.10	1968	1974	1978
MTB2	Spring	Sep 9	0.74	0.99	0.10	1968	1974	1978
MTB3	Spring	Sep 9	0.71	0.97	0.10	1967	1973.5	1978
G156_1	Shallow well	Sep 9	0.46	0.94	0.06	1965	1973.5	1974.5
G156_2	Shallow well	Sep 9	0.66	1.07	0.08	1967	1974.5	1976.5
G156_3	Shallow well	Sep 9	0.48	1.01	0.05	1965	1974	1973

of water recharged after the 1960s. Rain water is characterized by high ^3H contents between 3.9 and 10.5 TU, with a mean value of 7.61 TU. On the other hand, groundwater ranges from 0.5 to 3.5 TU with an average value of 2.1 TU, and streamwater have values from 0.8 to 7.1 TU, being 2.8 TU the average value.

Keeping in mind a qualitative dating approach based on these measurements (Clark and Fritz, 1997), precipitation water corresponds to modern water (<5 years), groundwater to submodern water (recharged prior 1952) or to a mix between submodern and modern water, and streamwater ranges from the previous mix to modern. The similarity of the ^3H mean value for streamwater to the mean value for groundwater indicates the dominance of baseflow in streamwater composition, while the variation expresses the proportion of surface runoff (high ^3H values) or baseflow (low ^3H values).

CONCLUSIONS

The chemical characterization of rainwater showed a great variability seemed to depend on the origin of the storms, but in general, its low salinity makes it possible to use EC as a representative parameter for this final member. On the other hand, rainwater is highly variable in its isotopic composition, mainly because of the temperature effect, being more enriched during summer months and rather depleted during winter, and, as mentioned, the storms origins. A slight continental effect was also observed. Mean values plus or minus one standard deviation are -7.1‰ and -2.7‰ for $\delta^{18}\text{O}$ and -47‰ and -13.6‰ for $\delta^2\text{H}$. Very depleted values ($\delta^{18}\text{O} -10.6\text{‰}$ and $\delta^2\text{H} -74\text{‰}$) are related to the amount effect, and more enriched values are linked to precipitation originated in marine sources.

Groundwater in the recharge area is mainly sodium-bicarbonate and with values of EC below $1000\ \mu\text{s}/\text{cm}$. The variability of the chemical composition of groundwater along the flowpath made it difficult to use ions in solution as good tracers for the origin of surface waters. In contrast, isotopic composition was almost homogeneous along all flowpaths, as it is defined during recharge and then no modified in the underground. This means that groundwater flow resulted in a well mixed system and that its isotopic composition can be used as a tracer.

The different apparent ages provided by the various methods used for dating can be understood taking into consideration the different components of streamflow and the scale dependent flow systems in a basin. For example, groundwater ages obtained using CFC concentrations varied between 30 and 50 years. This variation was related to sampling depth within shallow wells having younger apparent ages. On the other hand, the apparent age of streamflow is

in the order of the younger ground waters (30 years) from CFCs determinations. Groundwater with ages about 30 to 40 years constituted the upper part of the aquifer, an intermediate flow system, discharging through the QGR network and becoming baseflow in streams. Older groundwater corresponded to the regional flow system discharging mostly into the sea.

Taking into account the observed tracer values, streamwater composition appears to be the result of mixing three main components:

- (1) Baseflow: characterized by EC from 1200 to $1800\ \mu\text{s}/\text{cm}$ and an isotope composition quite constant of around $\delta^{18}\text{O} -5.3\text{‰}$ and $\delta^2\text{H} -34\text{‰}$. Tritium mean value was around 2 TU, and the water age for groundwater contribution was typically around 30 to 40 years using CFCs.
- (2) Direct runoff is composed of channel interception and overland flow, which was of low EC in the order of 50 to $100\ \mu\text{s}/\text{cm}$, and a highly variable isotopic composition affected by different storm sources and isotopic effects. Tritium values were higher than 4 TU.
- (3) Translatory flow with an intermediate EC and isotopic composition close to that of the weighted average composition of precipitation. This water is pre-event water, and it is released to the stream with some delay relative to the other components of direct runoff.

The combination of the mentioned components results in a poor correlation between $\delta^{18}\text{O}$ and EC, mainly because of the existence of two types of water having the same stable isotopic composition and a different EC and the fact that precipitation is always low salinity (e.g. low EC) but highly variable in isotopic composition. The existence of pre-event soil water component was deduced from the failed attempt to separate the streamflow into two components.

It is concluded that in this large plain catchment streamflow, the separation of just two components can only being applied in the following: (i) short storm precipitation events having a high sampling frequency, and (ii) during long dry periods when pre-event soil water is not released, such as those related to La Niña phase of the ENSO.

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