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THEMATIC ISSUE

# Relationship between electrical conductivity, $^{18}O$ of water and $NO_3$ content in different streamflow stages

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## Abstract

The Ballenera Creek has 160 $km^2$ being a small catchment in the Pampa Plain in Argentina. This area has been deeply modified by human action through agricultural activities. From 2013 to 2017, electrical conductivity, stable isotopes of water and nitrate concentration monitoring program were conducted. The sampling included weekly and bimonthly samples in two sites along the stream, several groundwater wells and monthly precipitation. Chemical and isotopic tracers are used to discriminate the streamflow components and to evaluate their incidence in the nitrate concentration. The easiest conceptual model for gaining streams contemplates two main elements: direct runoff and groundwater (baseflow and pre-event water). The direct runoff has the lowest electrical conductivity and $^{18}O_w$ variable content. The baseflow component is characterized by the highest electrical conductivity and isotope composition quite constant. Finally, pre-event water has an intermediate electrical conductivity and isotopic content close to the rainfall-weighted average composition. The nitrate concentration obtained was in general related to the different stream stages and was a useful indicator to evaluate the fertilization in agricultural zones.

**Keywords** Baseflow · Pre-event water · Hydrochemistry · Isotopes · Small catchment

## Introduction

In gaining rivers, streamwater is formed by two main components, a superficial flow fast coming from rains and an underground slow flow, which is called baseflow and supports the streamflow during dry periods (Winter 1999; Martinez et al. 2010, 2017). Baseflow is usually supplied by shallow unconfined aquifers, having waters younger than 50 years at depths ranging between 10 and 100 m (Seiler and Lindner 1995). The differences between the isotopic composition of rainwater and groundwater are also the basis for a baseflow quantification methodology (Maloszewski et al. 1996; Kendall and McDonnell 1998; Vitvar et al. 2002; Klaus and McDonnell 2013).

The contribution of groundwater to streamwater constitutes the baseflow, and researchers gave diverse denominations, i.e., old flow, old water (Hewlett and Hibbert 1965; Kendall and McDonnell 1998; Chapman 1999; Kirchner 2003). Moreover, Kirchner (2003) analyzed the answer of streams to great rainfalls and defined the concept of pre-event water as the rapid mobilization of old water.

The old water or pre-event water would correspond to water that existed in the basin before it began to rain. In this way, it is common to associate the new water with the one coming from the rapid flow and the old water with water which forms the baseflow. The application of classical concepts in hydrochemical evolution of natural waters makes it possible to associate old water with that which has acquired in its transit greater salinity and evolution toward sodium sulfate and sodium chloride water types (Chebotarev 1955; Martinez et al. 2006).

Kirchner (2003), in his first paradox, questions how the water that has been stored in the basin for weeks or months is mobilized and released as quickly as a response to certain precipitations. While in the second paradox he mentions the

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chemical variability of old water, thinking of the unsaturated zone as different compartments where different volumes of pre-event water are stored and released quickly during storm events. The paradox of this behavior according to Kirchner (2003) is that concentrations of chemical reactive species, such as calcium, silicon, aluminum or hydrogen, are highly sensitive to discharge. Although baseflow and pre-event water flow in unsaturated areas behave as old water, they often leave a distinguishable signature. In other words, not all old water is the same. One possible explanation could be attributed to different old water storage ponds, each with different chemical characteristics and mobilized in high and low flows.

In agricultural areas where the nitrate inputs can be related to the application periods in crops, additional information can be taken from this seasonality and it can be interesting to explore how this information can add to the understanding of a system. An oxidizing environment is needed for the analyses.

The goal of this contribution is to identify the relationships between electrical conductivity, $^{18}$O of water in different streamflow stages and to evaluate the incidence of the streamflow composition in nitrate concentration.

A small catchment in the Argentine Pampa Plain was selected considering its geological, morphological and hydrogeological features, especially the hydrogeological characterization of the unconfined aquifer and its relationship with streamwater. The Pampa Plain is an extended geographical region (about $1.5 \times 10^6$ km$^2$) with humid temperate climate characterized by very small slopes and a wide cover of Quaternary sediments. The studied catchment is La Ballenera covering a small area of this Pampa Plain in southeast of Buenos Aires Province.

Mineral fertilizers of chemical synthesis are used to cover the crops macronutrient required that soil cannot provide: mainly nitrogen and phosphorus. In this catchment, the most widespread sources of these supplies are urea and diammonium phosphate. Applications usually vary between 46 and 115 kg of N/ha (100 and 250 kg of urea) for corn, wheat and potato crops. Another fertilizer with some diffusion is the UAN, but being liquid, it is lesser used than urea. The common values of phosphate fertilizers are around 70 and 100 kg of diammonium phosphate during seedtime of grain crops.

## Physiographic and geological setting

The study area is located in the region called Interserrana Pampa Plain, which is a flat area extended between Tandilia and Ventania mountain ranges in the Buenos Aires Province (Argentina) and is part of the Wet Pampa Plain region. La Ballenera catchment is a small basin having a total area of 160.13 km$^2$ with orientation N–S and perpendicular to the coastline (Fig. 1). The main towns in the basin are Miramar and Comandante Nicanor Otamendi with 30,000 and 7000 inhabitants, respectively. The region has been deeply modified by human action through agricultural activities. Nowadays, the intensive agriculture is the main economic activity, principally wheat crops, barley, maize, sunflower, soybean and potato cultivation (Huarte and Capezio 2013).

The area has a "moderate-humid" climate (Köppen's classification) or "subhumid–humid, mesothermal, without water deficiency" type (Thornthwaite's method) (Thornthwaite 1948). In the last 44 years (1971–2013), the annual rainfall average in the catchment is 900 mm, and the monthly rainfall average is 74 mm (Calvi et al. 2014). The mean annual temperature is 13.5 °C (CHEM, 2013). According to the water balance calculated for the basin, 77.2% is evaporated and 22.8% is the recharge of the aquifer (Calvi 2017). During the studied period 2013–2017, the water balance shows water excess and there are not temporary variations in each annual balance (Calvi 2017).

The regional geological and hydrogeological features in the study area have been described by Sala (1975), Sala et al. (1983), Kruse (1986) and Gonzalez (2005). The "Complejo Buenos Aires" and the "Balcarce" Formations are part of the hydrogeological hard rock basement. The multilayered unconfined–semiconfined aquifer sequence called "Pampean sediments" is composed by loess-like silt and silty sand with frequently including precipitated $CaCO_3$ layers. Quaternary deposits have a thickness between 30 and 100 m, hydraulic conductivity 10 m/d (Sala 1975), porosity of 20% or 30% (Martínez and Bocanegra 2002) and transmissivity around 800–1000 m$^2$/d.

The catchment was classified in two geomorphologic areas named Hilly and Plains areas (Fig. 1) (Calvi et al. 2016a). The first one system has slopes in the order of 1.71–15.8%, and vadose zone has a thickness around 5 m. The second one has slopes less than 1.7% with a vadose zone of 1 m and occupies more than 90% of the basin. This characteristic leads to dominant vertical hydrologic processes, i.e., infiltration and evaporation (Calvi et al. 2016b). As a consequence, the intense agricultural activity with spring fertilizing season leads to strong leaching of fertilizer products. Moreover, in this small catchment is observed a rapid response of stream discharge to rainfall. The calculated baseflow in the studied period for La Ballenera Creek is close to 0.03–0.04 m$^3$/s (Calvi 2017).

## Methodology

Water samples were taken in two points on the stream, SLBA placed at upper-middle basin on the bridge over Route 77 and SLBB sited at low basin on the bridge over Route 11 (Fig. 1). A larger sequence of weekly samples, i.e., 198 samples, has been taken at SLBA during June 2013–May 2017. At SLBB, 52 samples have been taken in the period

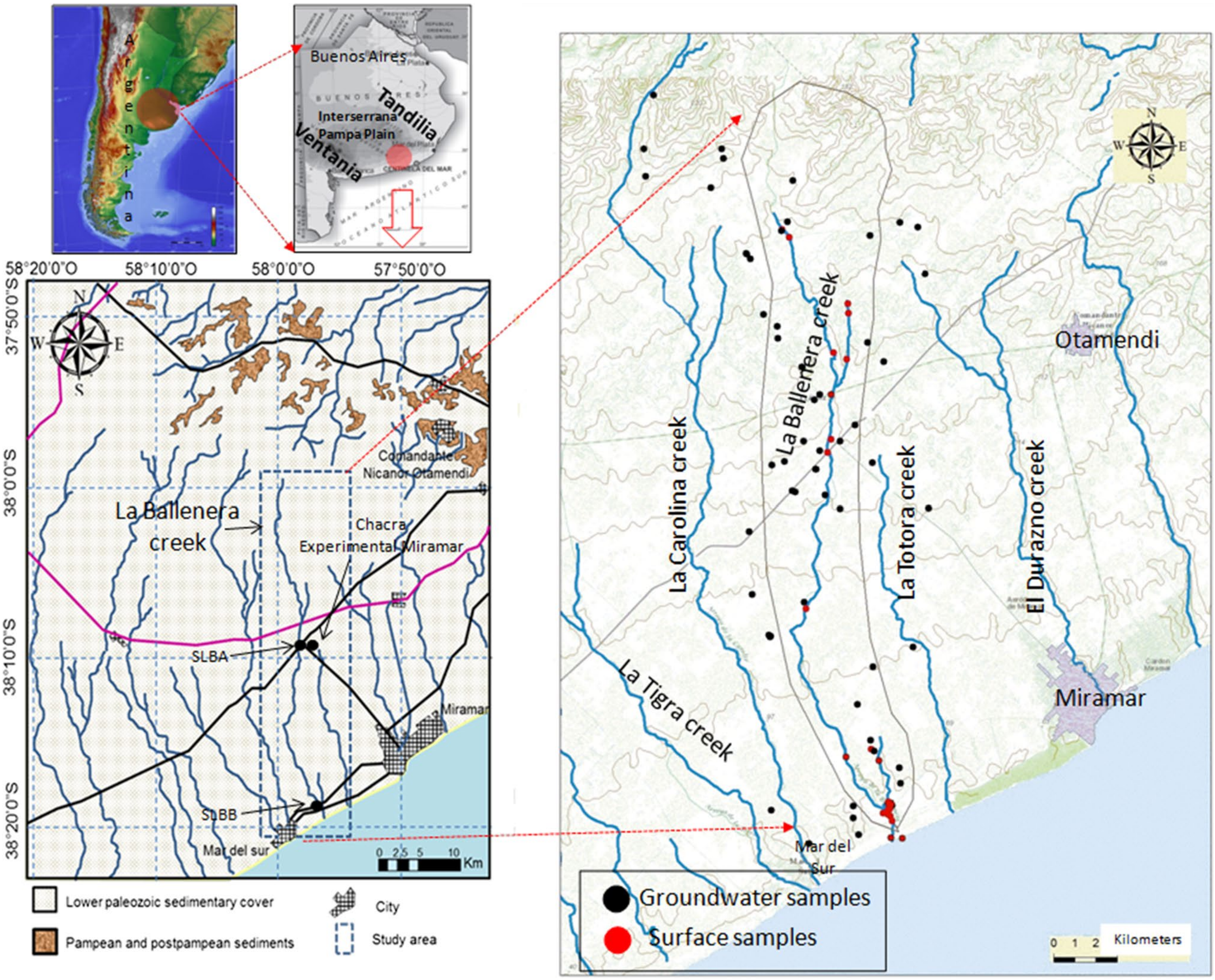


**Fig. 1** Location and geological characteristics

June 2013–October 2015, mostly taken with a bimonthly frequency. Groundwater samples were taken in October 2013 and July 2014 on about 73 sampling wells. In addition, the weekly rain record was studied, and monthly rain samples were taken at LMI station located in the Chacra Experimental Miramar.

Major ions have been analyzed on the streamwater and groundwater samples using standard methods (APHA-AWWA-WPCF 1989): calcium and magnesium by titration with EDTA, chloride by the Mohr method, sodium and potassium by flame photometric measurements, sulfate by turbimetric method and alkalinity by potentiometric titration. In this contribution, the nitrate concentration was measured by brucine method with limit 0.1 mg/L and the mean error was 1%. Electrical conductivity (EC) was measured in all samples of groundwater and in water samples taken in SLBB. In SLBA, EC was only analyzed in the period between June 2013 and October 2015. All samples were analyzed at the Laboratory of the Institute of Coastal and Quaternary Geology of the National University of Mar del Plata. No dissolved oxygen or another redox condition indicator was measured. Oxidizing conditions were assumed from previous studies in the area, where almost zero concentration of reduced nitrogen species, ammonium and nitrite was observed (Martínez et al. 2014).

Isotopic analysis ($^{18}O$ and $^{2}H$) was made on streamwater, groundwater and precipitation samples by Laser Spectroscopy (OA-ICOS: Off-Axis Integrated Cavity Output Spectroscopy) (Lis et al. 2008) at the Institute of Geochronology and Isotope Geology (INGEIS) and at the Institute of Coastal and Quaternary Geology of the National University of Mar del Plata. The results are expressed as (‰) versus V-SMOW (Gonfiantini 1978). Uncertainties are ± 0.3‰ for $\delta^{18}O$ and ± 1.0‰ for $\delta^{2}H$, respectively.

The discharge was measured at SLBA during October 2013–May 2017. This stream does not have gauge station, so it was necessary to use an alternative method. Therefore, during the mentioned period the height of water in the stream was weekly measured. After that, measuring the discharge using a current meter and the height of water at the same time, it was possible to obtain one function to translate the heights of water on discharges (Calvi 2017). Then, during the cited period the height of water in the stream was measured during each sampling date (weekly). Later a set of 15 discharge measurements were performed by using a flowmeter in different flow stages, and the regression among water height and discharge was obtained with an $R^2 = 0.91$. Using the obtained regression equation, all the height measurements were transformed in discharge (Calvi 2017).

## Results

### Hydrochemical characterization

The statistical parameters that characterize the contents of the major components for streamwater at SLBA and SLBB stations and groundwater are shown in Tables 1, 2 and 3. From the hydrochemical point of view, all the samples are classified as sodium bicarbonate type. Groundwater is lightly alkaline (Table 1). Streamwater at SLBA and SLBB station is mainly alkaline, with pH values between 7.6 and 8.8 and 7.3 and 8.9, respectively (Table 1). The chemical composition in both stations is sodium bicarbonate type.

Groundwater EC varies in the sense of the flow from the Hilly zone (543 µS/cm) to Plain area with ponds (2260 µS/cm). Streamwater EC is highly depending on rain periods and the site of the stream network measured. At SLBA, minimum and maximum values are 418 and 1458 µS/cm, respectively, with an average of 1237 µS/cm. With respect to SLBB, these values are 386 and 1699 µS/cm with an average of 1443 µS/cm. The variability is mostly due to the time elapsed between precipitation events and sampling.

The groundwater nitrate concentration is usually very high, and 48% of samples exceed the value of 50 mg/L fixed by World Health Organization for drinking water (WHO 2004). In the case of streamwater stations, nitrate concentration is always elevated. The maximum value is in the order of 120 mg/L at SLBA and 115 mg/L at SLBB.

Nitrate concentration is plotted with EC values measured in both stations (Figs. 2, 3). Nitrate in surface water at SLBA was measured between June 2013 and May 2017,

**Table 1** Statistical parameters of chemical composition of groundwater

| Parameters | Unit | Min. | Max. | Mean | SD | *n* |
|---|---|---|---|---|---|---|
| Temp | °C | 11.8 | 21.6 | 15.4 | 1.3 | 73 |
| pH | | 6.8 | 8.5 | 7.6 | 0.4 | 73 |
| CE | µS/cm | 543.0 | 2260.0 | 1301.0 | 324.6 | |
| $Na^+$ | mg/L | 50.0 | 400.0 | 227.8 | 74.5 | 73 |
| $K^+$ | mg/L | 3.0 | 30.0 | 11.9 | 5.8 | 73 |
| $Mg^{+2}$ | mg/L | 8.8 | 92.4 | 38.5 | 15.6 | 73 |
| $Ca^{+2}$ | mg/L | 11.0 | 88.0 | 38.3 | 13.7 | 73 |
| $Cl^-$ | mg/L | 44.7 | 294.0 | 126.3 | 51.6 | 73 |
| $So_4^{-2}$ | mg/L | 13.0 | 94.0 | 42.3 | 17.7 | 73 |
| $HCO_3$- | mg/L | 284.0 | 1031.0 | 600.3 | 126.8 | 73 |
| $NO_3$- | mg/L | 4.0 | 250.0 | 62.3 | 61.0 | 73 |

**Table 2** Statistical parameters of chemical composition of streamwater in SLBA station

| Parameters | Unit | Min. | Max. | Mean | SD | *n* |
|---|---|---|---|---|---|---|
| pH | | 7.6 | 8.8 | 8.3 | 0.2 | 186 |
| CE | µS/cm | 418.0 | 1458.0 | 1237.4 | 215.3 | 93 |
| $Na^+$ | mg/L | 60.0 | 400.0 | 266.5 | 49.0 | 198 |
| $K^+$ | mg/L | 3.0 | 52.5 | 14.5 | 7.6 | 198 |
| $Mg^{+2}$ | mg/L | 2.0 | 116.0 | 25.9 | 12.6 | 198 |
| $Ca^{+2}$ | mg/L | 8.0 | 46.0 | 27.9 | 10.3 | 198 |
| $Cl^-$ | mg/L | 44.7 | 187.0 | 115.8 | 25.8 | 198 |
| $So_4^{-2}$ | mg/L | 8.0 | 60.0 | 39.9 | 11.0 | 198 |
| $HCO_3$- | mg/L | 190.0 | 1028.0 | 653.4 | 131.4 | 198 |
| $CO_3^{-2}$ | mg/L | 0.0 | 114.0 | 41.1 | 23.7 | 83 |
| $NO_3$- | mg/L | 2.0 | 120.0 | 28.8 | 20.6 | 198 |

**Table 3** Statistical parameters of chemical composition of streamwater in SLBB station

| Parameters | Unit | Min. | Max. | Mean | SD | *n* |
|---|---|---|---|---|---|---|
| pH | | 7.3 | 8.9 | 8.2 | 0.3 | 52 |
| CE | µS/cm | 386.0 | 1699.0 | 1443.6 | 258.6 | 52 |
| $Na^+$ | mg/L | 140.0 | 370.0 | 287.5 | 50.9 | 52 |
| $K^+$ | mg/L | 6.0 | 29.0 | 14.0 | 5.0 | 52 |
| $Mg^{+2}$ | mg/L | 6.3 | 79.2 | 24.4 | 13.1 | 52 |
| $Ca^{+2}$ | mg/L | 10.0 | 50.0 | 30.2 | 10.5 | 52 |
| $Cl^-$ | mg/L | 86.0 | 206.0 | 153.1 | 28.7 | 52 |
| $So_4^{-2}$ | mg/L | 29.0 | 170.0 | 66.3 | 30.9 | 52 |
| $HCO_3$- | mg/L | 280.0 | 863.0 | 655.4 | 111.7 | 52 |
| $CO_3^{-2}$ | mg/L | 15.5 | 96.7 | 51.5 | 21.0 | 52 |
| $NO_3$- | mg/L | 0.5 | 115.0 | 22.7 | 25.6 | 52 |

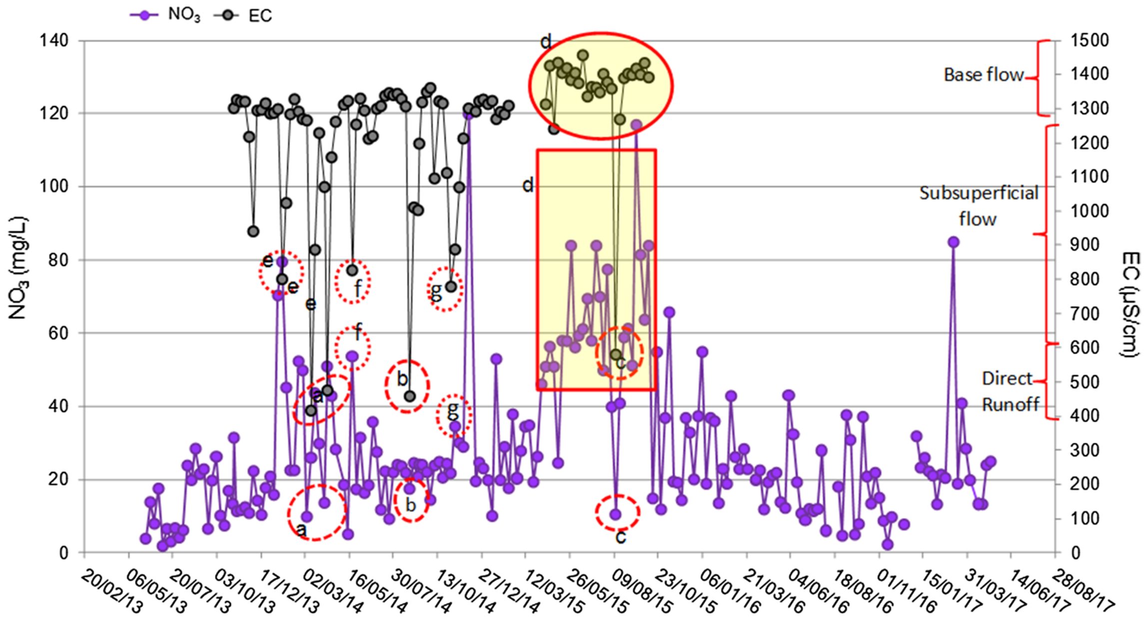


**Fig. 2** Nitrate and EC at SLBA station during sampling period

but it was only possible to analyze the period between June 2013 and October 2015 because of the incomplete EC record (Fig. 2). Moreover, SLBB was only sampled in the period June 2013–October 2015. Furthermore, the relation among nitrate concentration and the weekly accumulated precipitation was analyzed for the period June 2013–May 2017. EC values decrease around 400 µS/cm after rainy periods as expected. For example, this is remarked in Figs. 2 (point a, b, c) and 4 (point a, b, c), where nitrate concentration also drops. Samples with EC between 1300 and 600 µS/cm show intermediate and variable nitrate concentration, and this is related to rains (Figs. 2, 4: points e, f and g). The maximum conductivity, around 1450 µS/cm, shows high nitrate values which correspond to low precipitation (Figs. 2, 4: interval d).

SLBB sampling station is located downstream of SLBA, and it always has higher EC values. SLBB shows a similar behavior that SLBA with the maximum conductivity around 1700 µS/cm and high nitrate values when precipitation is low or absent (Figs. 2, 3: interval d). The EC range from 1300 to 600 µS/cm has a similar behavior as SLBA for the same interval, i.e., intermediate and variable nitrate concentration during rainy periods (Fig. 3: points 1, 2 and 3; Figs. 2 and 4: points e, f and g).

## Isotopic characterization

The data collected at Chacra Miramar station (LMI) during Sept 2013–Nov 2016 are not enough to build a Local Meteoric Water Line (LMWL). Nevertheless, La Ballenera catchment is located between GNIP stations Azul and stations of Quequén Grande basin and both stations have similar behavior. The LMWL defined in Azul is $\delta^2H = 8.16$

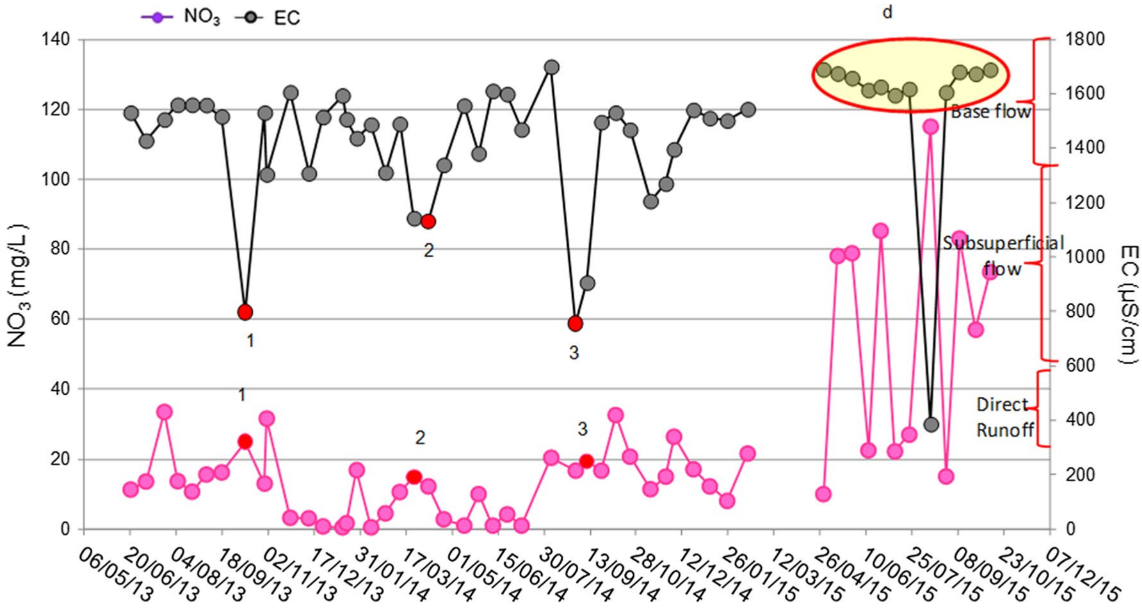


**Fig. 3** Nitrate and EC at SLBB station during sampling period

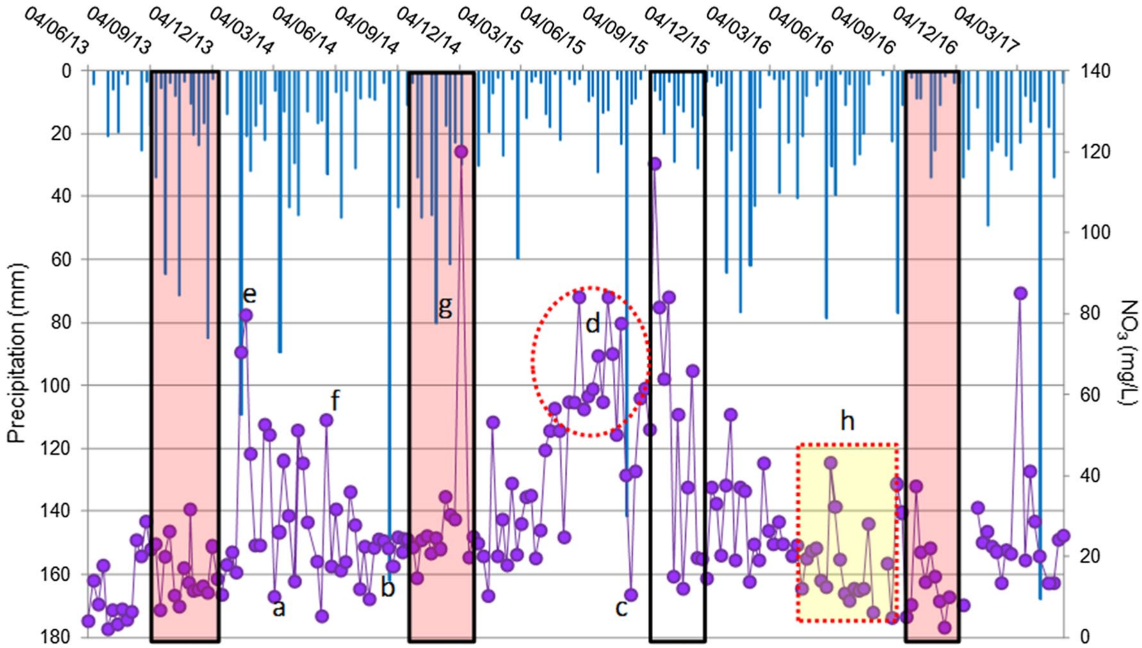


**Fig. 4** $NO_3$ and weekly accumulation of precipitation at SLBA during sampling period

$\delta^{18}O + 13$ (Dapeña et al. 2010). The arithmetic isotopic mean of precipitation in Chacra Miramar is $\delta\,^{18}O = -5.2‰$, $\delta^2H = -28‰$ and deuterium excess $d = 13$ ($n = 16$). Single precipitations show a wide distribution with values varying between −8.7 and −2.5‰ for $\delta^{18}O$ and between −58 and −3‰ for $\delta^2H$. These variations are associated mainly with temperature, continental and amount effects, and certainly they are linked to the air masses source (Dapeña et al. 2010; Martínez et al. 2011, 2017). It is noticed that this region was affected with huge precipitations due to a very strong ENSO phenomenon during 2015–2016.

Figure 5 shows the distribution of $\delta^{18}O$ in groundwater. Isotopic mean value in the Hilly area is −5.4‰ $\delta^{18}O$ and −31‰ $\delta^2H$, meanwhile in the Plain area with ponds is −4.5‰ $\delta^{18}O$ and −25‰ $\delta^2H$. The difference in the groundwater isotopic composition of both zones is due to

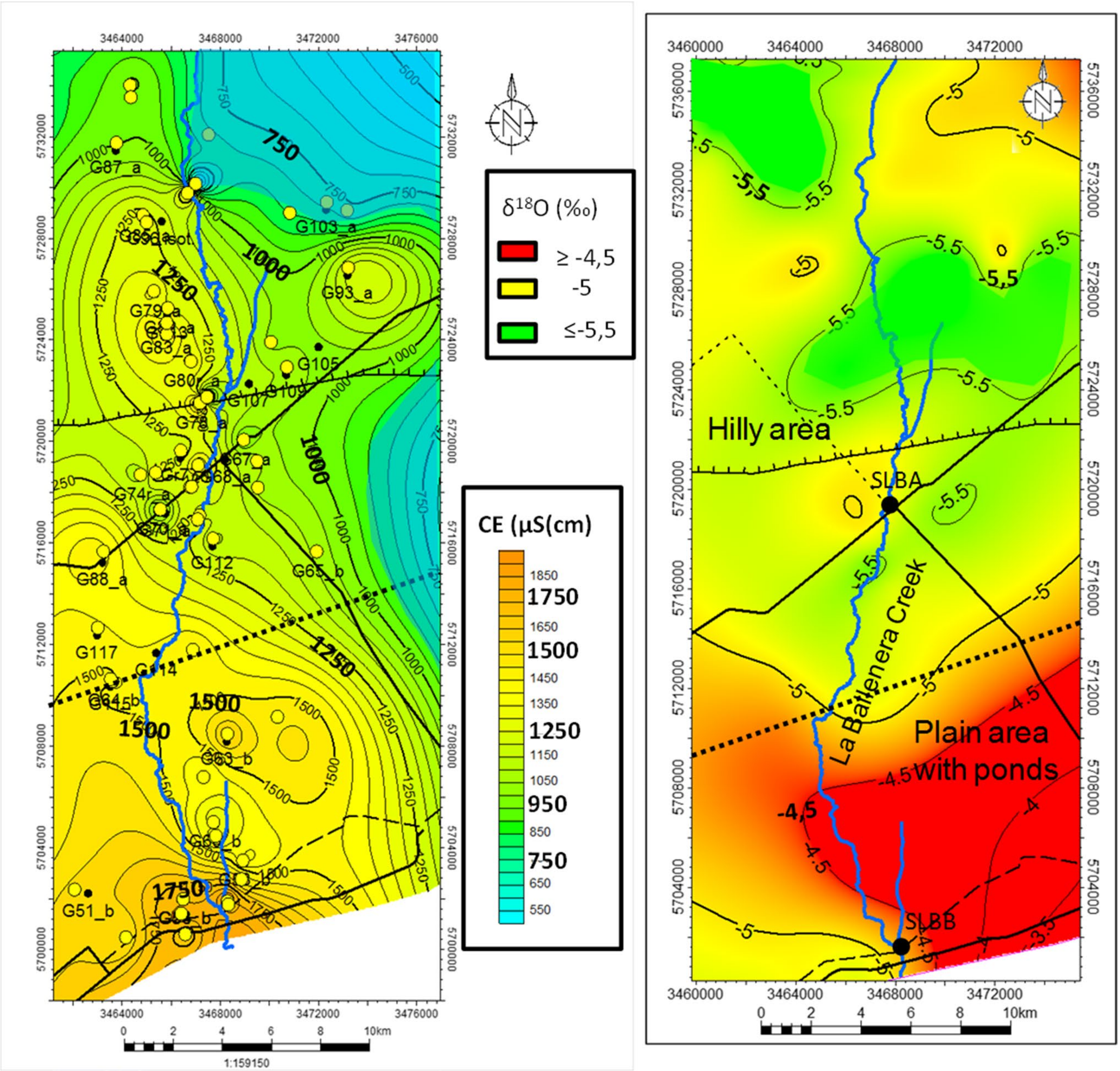


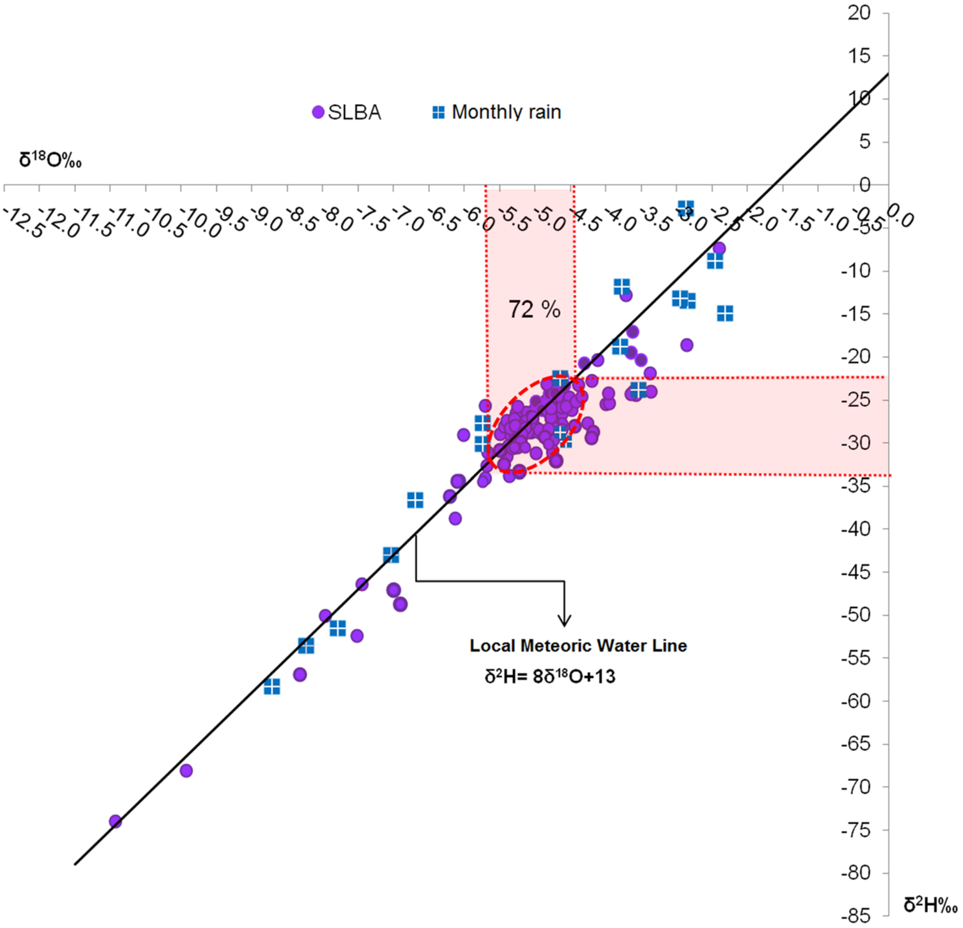
**Fig. 5** Groundwater **a** electrical conductivity (μS/cm), **b** $\delta^{18}O$ (‰)

geomorphological characteristics (Figs. 1, 5b), i.e., the different thickness of the unsaturated zone determines the possibility of some evaporation in the unsaturated zone and, in addition, in the Plain area with ponds some samples show local processes of evaporation prior to infiltration.

The isotopic composition of streamwater in SLBA and SLBB station is represented in a conventional scatter plot $\delta^2H$ *vs.* $\delta^{18}O$ jointly with the LMWL (Figs. 6, 7). SLBA streamwater isotopic content varies between − 10.9 and − 2.4‰ for $\delta^{18}O$, and − 74 and − 7‰ for $\delta^2H$, where 72% of samples ($n = 147$) are between − 5.7 and − 4.5‰ for $\delta^{18}O$ and − 34 and − 22‰ for $\delta^2H$ (Fig. 6). SLBB isotopic values are in the range − 7.8 to − 2.7‰ for $\delta^{18}O$ and − 51 to − 16‰ for $\delta^2H$, and 72% of samples ($n = 54$) are between − 4.9 and − 3.3‰ for $\delta^{18}O$, and − 29 and − 16‰ for $\delta^2H$ (Fig. 7). Samples with values more depleted and enriched reflect the direct rainfall on the stream. Other samples are aligned on an evaporation line (Fig. 7).

The mean $\delta^{18}O$ content of the stream at both stations is close to groundwater isotopic composition of each geomorphological zone, i.e., SLBA located in Hilly zone -5.4‰ and SLBB site in Plain area with ponds − 4.5‰ (Figs. 5b, 6, 7). The major part of the year La Ballenera is a gaining stream. This is consequence of homogenous distribution of annual

**Fig. 6** δ$^{2}$H versus δ$^{18}$O at SLBA station



rain, small variation of the phreatic level and the distribution of isophreatic lines.

## Relationship between nitrate concentration and δ$^{18}$O

The time series of nitrate concentration and discharge values for the period June 2013–May 2017 was drawn in order to analyze the relationship among those variables (Fig. 8). For the analysis, the fertilization periods have been indicated. Moreover, it must be taken into account that complementary irrigation is applied in the periods January–February and October–November.

Some dates show low nitrate concentrations with high discharge (Fig. 8: points a, b and c). The same dates exhibit low conductivities associated with high accumulated weekly precipitations (Figs. 2, 4). In the same way, high discharge and low nitrate values are observed during the rainy winter 2016 (Fig. 8; 2, 4: point h). However, some moments show an opposite behavior, i.e., with increase in discharge the nitrate values also increase (Fig. 8: points e, f, g) with an intermediate value of EC (Fig. 2: points e, f, g). This contradicting behavior can be related to changes in the land use, making the use of nitrates to define streamflow a risky issue, if all the conditions are not adequately taken into account.

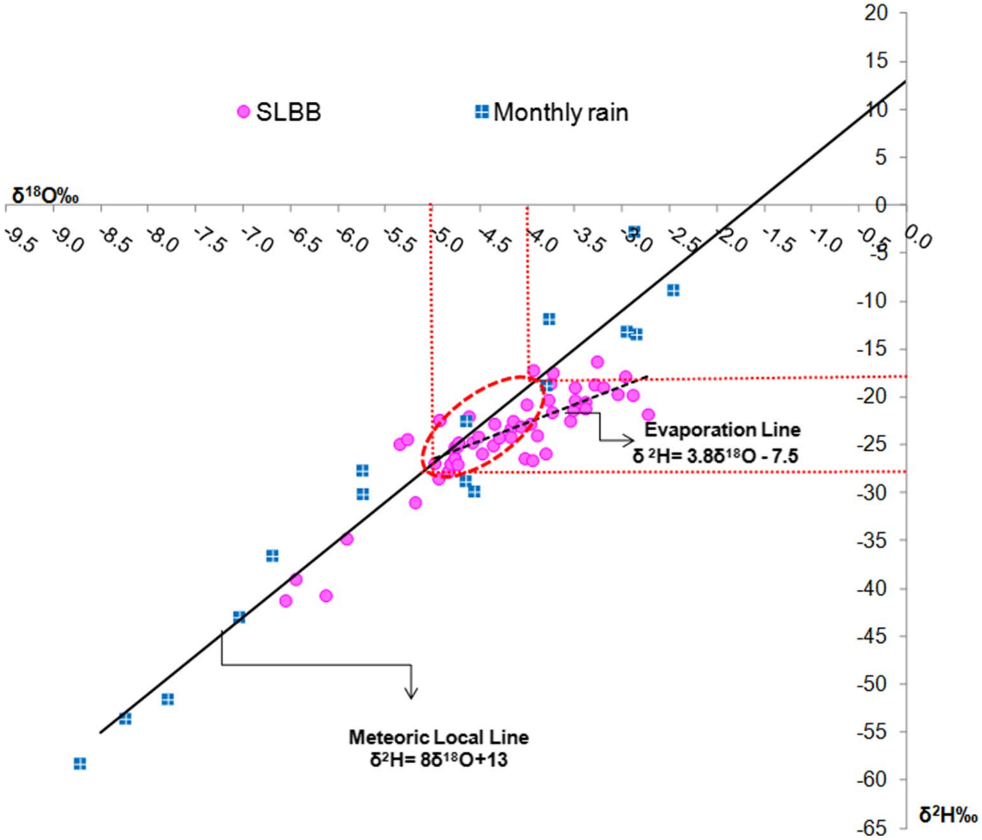
The autumn–winter 2015 seasons were low rainfall stage and the discharge was low (0.04 m$^{3}$/s). During this period, crops were neither fertilized nor irrigated but streamwater showed very high nitrate levels and EC was also elevated around 1500 µS/cm (Figs. 8, 2, 4: interval d).

Figures 9 and 10 show the relationship between nitrate concentration and δ$^{18}$O content in SLBA during June 2013 to May 2017 and a detail in the sampling common period June 2013–October 2015 of SLBA and SLBB. The mean groundwater δ$^{18}$O of each geomorphological zone is highlighted in Fig. 10.

At SLBA and SLBB, during autumn–winter 2015, when the discharge is in the lowest levels (baseflow), δ$^{18}$O of streamwater and groundwater are similar. At this time, it is noticeable that the highest concentration of nitrate was measured (Figs. 9, 10: interval d).

As mention before, in some dates, streamwater shows depleted and enriched isotopic composition associated to

**Fig. 7** $\delta^2$H versus $\delta^{18}$O at SLBB station



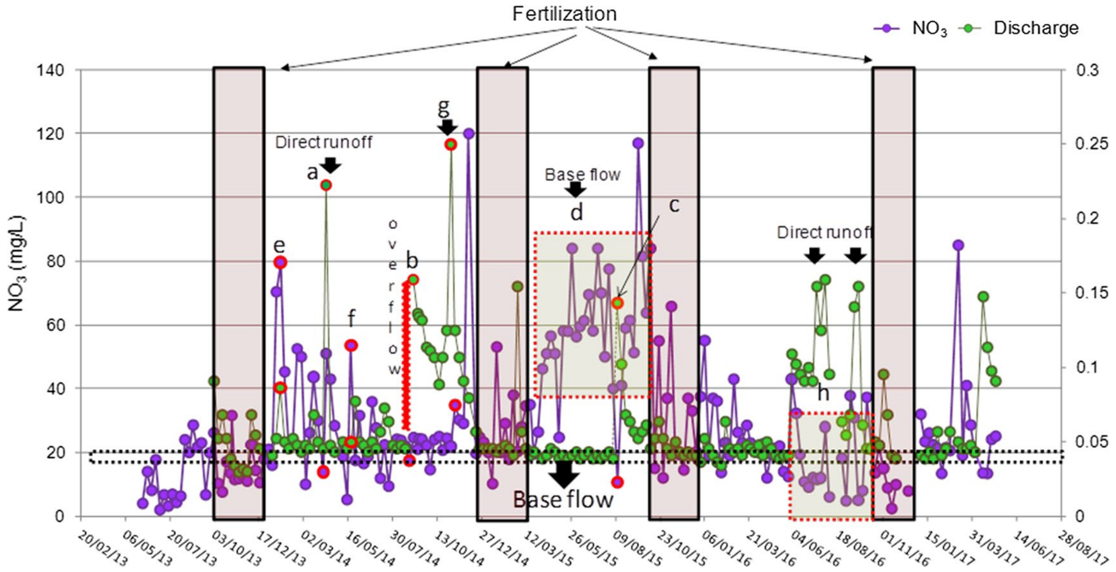


**Fig. 8** Nitrate and discharge at SLBA during sampling period

precipitation events (Figs. 6, 7). In addition, also related to meteorological events, in some cases the nitrate content is low (Fig. 9: points a, b, c, h) and in another it is high (Fig. 9: points d, e, f).

## Discussion

The identification of direct runoff and baseflow in streams, based on chemistry and environmental isotopic tracers,

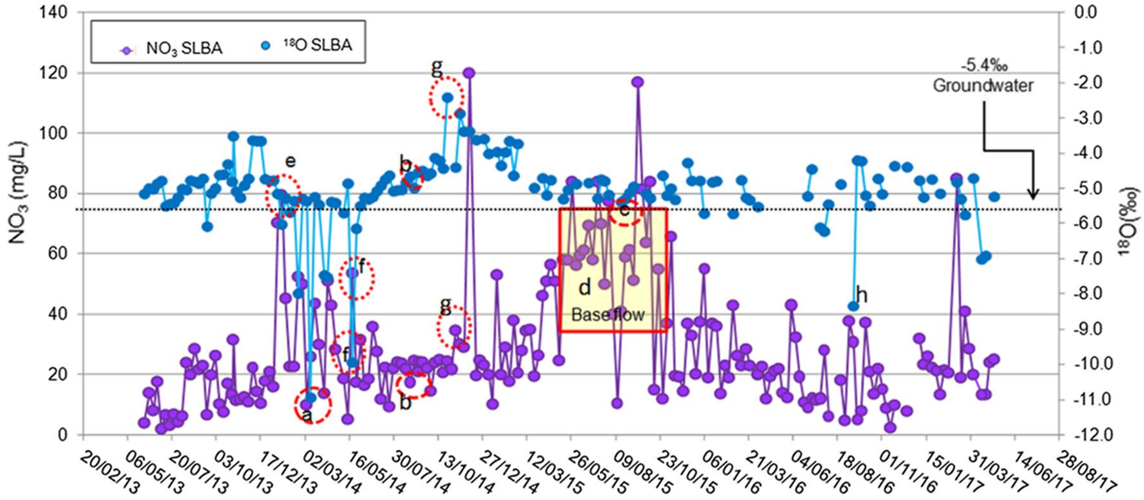


**Fig. 9** Nitrate and $^{18}$O during 2013–2017 at SLBA

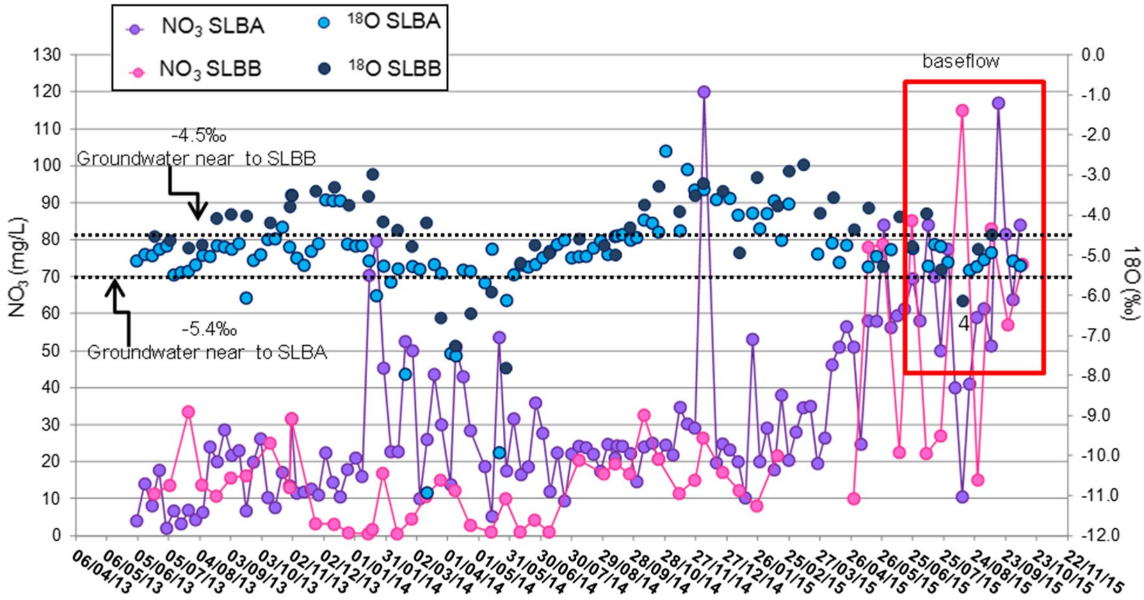


**Fig. 10** Nitrate and δ$^{18}$O (‰) during 2013–2015 at SLBA and SLBB

has commonly been done in small catchments (Hewlett and Hibbert 1965; Stauffer 1985). La Ballenera basin has a thick unconfined sedimentary aquifer, low slopes and a gaining stream. As mentioned before, during the studied period water balance and baseflow do not show variations. The use of fertilizers is regulated by the Agricultural Ministry and the agricultural crew of Miramar. They establish the volumes to be applied according to the type of crop.

The main features of the hydrogeological environment allow us to believe that it is also possible to use chemical and isotopic tracers for separation of streamflow components.

The chemical composition of the southeast Buenos Aires Province precipitation is highly variable due to differences in rainfall origin. They are bicarbonate type with variable cationic compositions and low EC around 100 µS/cm (Martinez et al. 2017). This low salinity makes it possible to use EC as a representative parameter for the identification of direct runoff. In addition, the isotopic composition of precipitation is highly variable, associated mainly with temperature, continental and amount effects and certainly they are linked to the air masses source. High depleted values as − 8.7‰ $\delta^{18}$O are linked to the amount effect, and the most enriched values as − 2.5‰ $\delta^{18}$O are related to precipitation originated in marine sources (Dapeña et al. 2010; Martínez et al. 2011, 2017).

EC of groundwater varies between 543 and 2260 µS/cm, in the Hilly area is around 1300 µS/cm and in the Plain area with ponds is close to 1800 µS/cm (Fig. 5b).

Nitrate concentrations are commonly very high with values up to 250 mg/L, and the main source of nitrate is due to fertilization. As mentioned before, water isotopic composition is characteristic for each geomorphological area with values around − 5.4‰ $\delta^{18}$O for the first one and − 4.5‰ $\delta^{18}$O for the last one.

Streamwater EC is highly depending on rainy periods. At SLBA, the values vary between 418 and 1458 µS/cm, and at SLBB these values are from 386 to 1699 µS/cm. Nitrate concentration is always high in both stations. The maximum values are about 120 mg/L at SLBA and 115 mg/L at SLBB. The isotopic composition of most samples at SLBA is around − 5.7 to − 4.5‰ for $\delta^{18}$O, but some extreme values between − 10.9 and − 2.4‰ for $\delta^{18}$O were measured. SLBB isotopic values of most samples are in the range − 4.9 and − 3.3‰ for $\delta^{18}$O with a great interval from − 7.8 to − 2.7‰ for $\delta^{18}$O. Some of the more depleted and enriched values indicate the direct rainfall on the stream. After heavy rain events, the streamflow isotopic composition is related to the composition of precipitation, due to both direct runoff and channel interception. Samples below the Local Meteoric Water Line show evaporation process related to summer season (Figs. 6, 7).

Considering EC and $\delta^{18}O_w$ of the two main components, direct runoff and groundwater are possible to identify their contribution to streamflow composition. The groundwater component is composed by the baseflow and pre-event water flow in unsaturated areas (Kirchner 2003). The baseflow corresponds to the lowest discharge (0.04 $m^3$/s). It is characterized by EC from 1500 to 1300 µs/cm at SLBA and 1700 to 1300 µs/cm at SLBB (Figs. 2, 3), $\delta^{18}O_w$ content around − 5.4‰ at SLBA and − 4,5‰ at SLBB (Figs. 9, 10) and elevated nitrate concentration above 60 mg/L (Figs. 2, 3, 4). In autumn–winter (July–August 2015), the baseflow is easy to observe and even measure at field in both sites. For the analyzed stream stage, the $NO_3$ is around 60–90 mg/L which can be related to groundwater contribution.

The pre-event water or subsuperficial flow composition is here proposed from a deductive analysis indicating that intermediate EC values and ion concentrations among groundwater and surface runoff can be expected. The pre-event water or subsuperficial flow has intermediate values of EC (1300–600 µs/cm), nitrate (20–40 mg/L) and $\delta^{18}O_w$ close to isotopic composition of precipitation (Figs. 2, 3, 9, 10). This water is released to the stream with some delay respect to the other components of direct runoff. The pre-event water is easy to recognize because is related to preceding rainy days or irrigation moments that shoot this previous "old water" to the stream in the sense of Kirchner (2003). This intermediate nitrate values could be related to the concentration that this old water had.

The final component is direct runoff composed of channel interception and overland flow with low EC (600–300 µs/cm) and $\delta^{18}O_w$ variable depending on meteorological events. The low nitrate concentration < 20 mg/L is due to dilution process generated by discharge increase (Figs. 2, 3, 9, 10). For example, it is well detected during extraordinary rains as August 2014 (Figs. 2, 3).

## Conclusions

In most sedimentary basins in humid and subhumid climate and plain environments, like the Argentine Pampa, the easiest conceptual model for gaining streams contemplates two main components, direct runoff and groundwater (baseflow and pre-event water). These components are possible to discriminat using EC and $^{18}O_w$. The direct runoff has the lowest EC and $^{18}O_w$ variable content. The baseflow component is characterized by the highest EC and isotope composition quite constant. Finally, pre-event water has an intermediate EC and isotopic content close to the rainfall-weighted average composition.

According to the obtained results, nitrate concentration was in general related to the different stream stages and was a useful indicator to evaluate the fertilization in agricultural zones.

Relationship between electrical conductivity and $^{18}$O of water as a tracer together with precipitation and discharge is a practical and easy methodology to analyze streamflow components in small catchments.

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