



Chemical variation of surface water and groundwater in relation to water balance in the watershed of El Pescado Creek (Central-Eastern Argentina)

María Isabel Delgado^{1,2} · Eleonora Carol³ · María Elicia Mac Donagh⁴ · María Adela Casco²

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Abstract

The watershed of El Pescado Creek has been established as a protected landscape; however, it is currently exposed to an intense land use and coverage change process, based on the conversion of grassland areas into greenhouse horticulture and urbanized areas. The aim of this work was to analyze hydrochemical modifications in this changing scenario, to identify parameter variations associated to water balance. The monitory network included surface water and groundwater samplings during winter, spring and summer of 2017. Daily water balance was estimated throughout the annual cycle. Electrical conductivity and pH were determined together with major ions (Na^+ , K^+ , Mg^{2+} , Ca_2^+ , CO_3^{2-} , HCO_3^- , Cl^- , SO_4^{2-} and NO_3^-). The analysis of water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) was performed for one sampling date. Water-balance variations during short-term periods affected surface water chemistry, although no relevant influence on deep groundwater was registered. Major ions variation in the surface water of the upper watershed might be related to runoff alteration caused by recently established impervious cover and by the dynamic of groundwater inputs. Isotopic analysis of surface water shows deviation from local meteoric line, with an isotopic enrichment following a tendency associated to evaporation processes. Deep groundwater samples express a recharge process by rainfall infiltration, with little or no previous evaporation (deuterium amounts were similar to those corresponding to local rainfall). Incipient evaporation processes are registered for shallow groundwater, possibly occurring before infiltration in the non-saturated zone, or right from the phreatic, when it is near the surface.

Keywords Major ions · Water stable isotopes · Flatland watershed · Water balance · Seasonal variation

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✉ María Isabel Delgado
isabeldelgado@agro.unlp.edu.ar

Eleonora Carol
eleocarol@fcnym.unlp.edu.ar

María Elicia Mac Donagh
mmacdonagh@fcnym.unlp.edu.ar

María Adela Casco
casco@fcnym.unlp.edu.ar

³ Facultad de Ciencias Naturales y Museo, Centro de Investigaciones Geológicas (CIG), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET-UNLP), Universidad Nacional de La Plata, Diagonal 113, N° 275, B1904DPK La Plata, Argentina

⁴ División Ficología, Museo de La Plata, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Paseo del Bosque S/N, B1900FWA La Plata, Argentina

¹ Facultad de Ciencias Agrarias y Forestales, Universidad Nacional de La Plata, La Plata, Argentina

² División Ficología, Museo de La Plata, Facultad de Ciencias Naturales y Museo, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de La Plata, Paseo del Bosque S/N, B1900FWA La Plata, Argentina

Introduction

The geochemical study of surface water and groundwater is essential to understand river ecology and the sources of chemical species (Bhatt et al. 2014). Physical and chemical characteristics of water under natural conditions are influenced by many factors, such as topography, geology, and inputs through rainwater, water/rock interaction and climate, and also by anthropogenic factors (Melaku et al. 2007). For instance, anthropic impervious covers, such as urbanizations, tend to increase runoff and peak flows, with the consequent increase in flood frequency and pollutant transport (Hibbs and Sharp 2012). Also, fertilizers might cause pollution problems in water resources; particularly the concentration of NO_2^- and NO_3^- carried by runoff has been directly related to the amount of water used for irrigation and the land-use practices (Ghaly and Ramakrishnan 2015; Shin et al. 2017).

The study of major ion chemistry might lead to identification of geochemical processes that control groundwater quality (Subba Rao and Surya Rao 2010). Together with dissolution and alteration of minerals, ion exchange represents one of the main processes conditioning the hydrochemistry of groundwater flow (Carol et al. 2012), and also surface water (Atkinson 2018). On the other hand, water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) are ideal natural tracers for understanding water cycle and related water modification processes, such as mixing between different water bodies and determining salinity sources, among others (Kattan 2015).

At a watershed scale, the use of these environmental tracers represents a useful approach, especially in areas with scarce basic knowledge on water quality and the interaction between surface water and groundwater (Oyarzún et al. 2015). At the same time, regarding watershed management, the requirement to integrate information has gained increasing weight, recognizing the need to link the drainage area and aquifer to the near coastal zone and to develop an understanding of associated natural flows of water, energy, biota and chemicals (McDonnell 2015). In this way, considering that land-use and land-cover change is a critical driver for the study of watershed hydrological changes (Wei et al. 2013), the aim of this work was to analyze the chemical variation of surface water and groundwater in the watershed of El Pescado Creek (Central-East Argentina), to identify parameter variations associated to water balance and land use. The area belongs to the Argentine Pampas, which represents the heart of agricultural production (D'Andrea et al. 2019), where hydrological monitoring networks are virtually nonexistent (Cesanelli and Guarracino 2011).

Materials and methods

Study area

The flatland watershed of El Pescado Creek (349 km²) is located in the northeast of the Buenos Aires Province (Argentina), draining its water into the Río de la Plata. Topographic elevation is between 30 and 2.5 m asl (above sea level), with regional groundwater flow following north-eastward direction. Phreatic level is 15 m bgs (below ground surface) near the water divide in the upper watershed of El Pescado Creek and less than 1 m bgs in the lower watershed. Hydraulic gradients vary from 1.8 to 0.5 m/km (Carol et al. 2012). Watercourses in the high plains tend to be well defined, expressing downstream a floodplain that might extend up to 500 m wide, finally turning rambléd in the coastal plain (Auge 2000). The watercourse is fed with both surface water excess and groundwater discharge from phreatic aquifer, which is recharged with water infiltrated from rainfall (Carol et al. 2012). Climate is characterized as humid-temperate, with mean annual temperature of 16 °C and mean annual precipitation of 1025.7 mm (period 1970–2016). Precipitation expressed predominance over evapotranspiration in the annual water balance, with water excess between April and October and water deficit between November and March (Delgado et al. 2018).

The watershed represents a great extension of grassland, but in recent years, it is going through a progressive change in land use and land cover, tending to intensive agriculture activities and urbanizations (Delgado et al. 2018) that have led to modifications in the infiltration—runoff patterns (Delgado et al. 2020). A sector of the upper watershed currently belongs to the Horticultural Belt of La Plata (HBLP) “Cinturón Hortícola Platense”, which is the main productive region of fresh vegetables in Argentina. By 2010, the HBLP already registered 1047 farms, being 75% of them dedicated to horticulture (Gargoloff et al. 2010), representing less than 3000 ha under greenhouse horticulture (Staviski 2013).

Sampling and analysis

A monitoring network was designed along the entire watershed, including sampling sites for surface water and shallow (approximately 3 m depth) and deep (between 15 and 40 m depth) groundwater. Results shown on this work correspond to sampling campaigns performed in July, October and December of 2017. Sample collection, preservation, and chemical analysis of water samples were carried out in accordance with the standard methods proposed

by the American Public Health Association (APHA 1998). Chemical analyses were determined in the Laboratory of Geochemistry of the Centro de Investigaciones Geológicas (CONICET-UNLP), at the National University of La Plata. Sodium (Na^+) and potassium (K^+) were determined by flame photometry. Magnesium (Mg^{2+}), calcium (Ca^{2+}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and chloride (Cl^-) were determined by volumetric methods. Sulphate (SO_4^{2-}) and nitrates (NO_3^-) were measured by visible-UV spectrophotometry. Three repetitions were done, being the average value expressed as final result. The analytical error in 90% of the samples was below 10%. Electrical conductivity (EC) and pH were measured with a Horiba U 10 multimeter. Stiff graphics were built with Diagrammes software (Simler 2009) aiming to obtain a better representation of ionic concentration to compare relationship between surface water and groundwater under different hydrological scenarios. Diagrammes is a free distributed software, created by the Laboratoire d'Hydrogéologie d'Avignon (France), which allows to generate many different graphical representations and also some statistical analysis based on water chemical characteristics.

Stable isotopes of the water molecule ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were measured for the December's sampling using a continuous flow mass spectrometer (Thermo Finnigan MAT Delta Plus XL) at the Stable Isotopes laboratory of the National University of San Luis. Isotopic results are expressed as δ , defined as $\delta = 1000(\text{R}_s - \text{R}_r) / \text{R}_r \text{‰}$, where δ is the isotopic deviation in ‰ relative to Vienna Standard Mean Ocean Water (V-SMOW) (Gonfiantini 1978); s: sample; r: International reference; R: isotopic ratio ($^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$). The analytical accuracy is $\pm 0.05\text{‰}$ and $\pm 0.5\text{‰}$, for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively, and the isotopic values were compared with the local meteoric line $\delta^2\text{H} = 8 * \delta^{18}\text{O} + 14$ (Dapeña and Panarello 2004).

In order to estimate evaporative isotopic enrichment, the analytical model proposed by Gonfiantini (1986)—based on the approach by Craig and Gordon (1965)—was used. Gonfiantini states that the isotopic composition of water, δ , varies with the decrease in the residual or remaining water volume fraction, $f = V/V_0$. The relationship between these two variables can be expressed as:

$$\frac{d\delta}{d \ln f} = \frac{h(\delta - \delta_\alpha) - (\delta + 1)\left(\Delta \epsilon + \frac{\epsilon}{\alpha}\right)}{1 - h + \Delta \epsilon}, \quad (1)$$

where h is the relative humidity of the air; δ_α the isotopic composition of atmospheric water steam; α the equilibrium fractionation factor, being $\epsilon = \alpha - 1$. After adequate integration, with δ_0 defined as the initial isotopic composition of water at $f=1$, Gonfiantini's expression for $\delta(f)$ becomes:

$$\delta = \left(\delta_0 - \frac{A}{B}\right)f^B + \frac{A}{B}, \quad (2)$$

with A and B given by:

$$A = \frac{h\delta_\alpha + \Delta \epsilon + \epsilon / \alpha}{1 - h + \Delta \epsilon}, \quad (3)$$

$$B = \frac{h - \Delta \epsilon - \epsilon / \alpha}{1 - h + \Delta \epsilon}. \quad (4)$$

Solute concentration can be expressed as a function of the evaporated water fraction. Therefore, the enriched concentration C' can be estimated as follows:

$$C' = \frac{C_0}{(1-x)}, \quad (5)$$

where C_0 is the initial concentration, x is the evaporated water fraction; i.e., $x = V/V_0$ ($0 < x < 1$), with V being the present volume and V_0 the initial volume. Evaporation percentages at 5% increments were calculated considering C_0 coming from groundwater with the least isotopic enrichment, and the relative humidity being the average (0.80) based on the mean value for the area.

Daily water balances (Thorntwaite and Mather 1957) were done to analyze the relationship between chemical results and the hydrological characteristics. Meteorological data (rainfall and temperature) were obtained from the Agrometeorological Section of the Hirschhorn Experimental Station from the School of Agricultural and Forest Sciences of the National University of La Plata, located next to the upper watershed of El Pescado Creek.

Results and discussion

Major ions' content in surface water shows that saline concentration increases from the upper watershed to the sink, in the three sampling campaigns. Groundwater tends to be more saline than surface water (mean EC: 0.44, 2.89 and 0.82 mS/cm, for surface water, shallow and deep groundwater, respectively). The highest spatial and temporal chemical variability is registered in shallow groundwater, while deep groundwater pumped from the phreatic aquifer (between 15 and 40 m) expressed scarce variability. Regarding chemical facies, the dominant ones are sodium bicarbonate, with only sodium chloride facies in the sampling site next to the Río de la Plata (Fig. 1). Previous studies in the watershed indicated groundwater discharge towards the watercourse (Carol et al. 2012); however, in this research, ion concentrations in surface water were in all cases lower than in groundwater, reflecting that the input provided by groundwater discharge

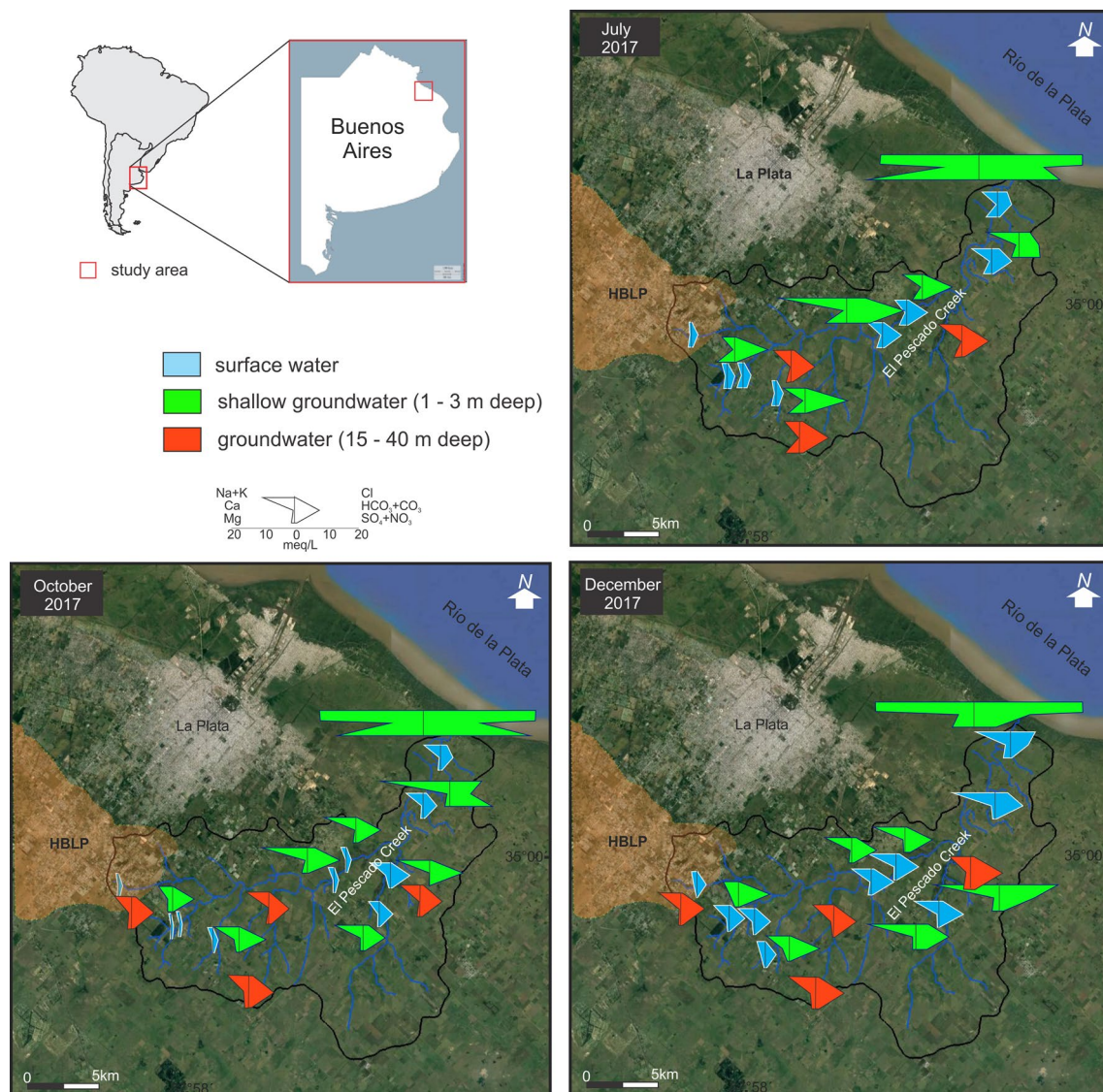


Fig. 1 Location of the study area. Stiff graphics expressing water chemistry (meq/L) for the three sampling campaigns (2017) in the watershed of El Pescado Creek. The Horticultural Belt of La Plata (HBLP) is indicated in orange

is not relevant compared with the one provided by surface runoff.

The pH values of surface water and shallow groundwater varied between 6.6 and 8.6; meanwhile, in deep groundwater, pH was more alkaline, with values between 7.7 and 8.7 (Fig. 2a). Values of 8.5 or above are normally associated with leaching of CaCO₃ in soil and with sodium carbonate and bicarbonate (Mahanta et al. 2020). Differences in pH values found in the watershed of El Pescado Creek are related to the reactions that occur in the non-saturated zone and soil where rainfall and soil minerals interact and those that occur between the aquifer matrix and the groundwater flux in the saturated zone. In the unsaturated zone, rainwater reacts with the CO_{2(g)} in the atmosphere

and in the sediment pores, generating HCO₃⁻ and H⁺. The latter imparts acidity to water, which attacks the minerals, especially the carbonate and silicates that dominate in soil minerals. The dissolution of these minerals decreases acidity, which in the unsaturated zone is recovered by the dissolution of more CO_{2(g)}, mainly generated by the roots and the decomposition of organic matter in the soil, and secondarily by the atmosphere. These reactions occurring in the unsaturated zone and more superficial sectors of the aquifer create a buffer system that maintains the pH values. When water reaches the water table and it mixes with the groundwater flow as the dissolution of minerals consumes H⁺ and CO_{2(g)}, it loses acidity as it is unable to incorporate CO_{2(g)} to the system, decreasing its capacity to dissolve

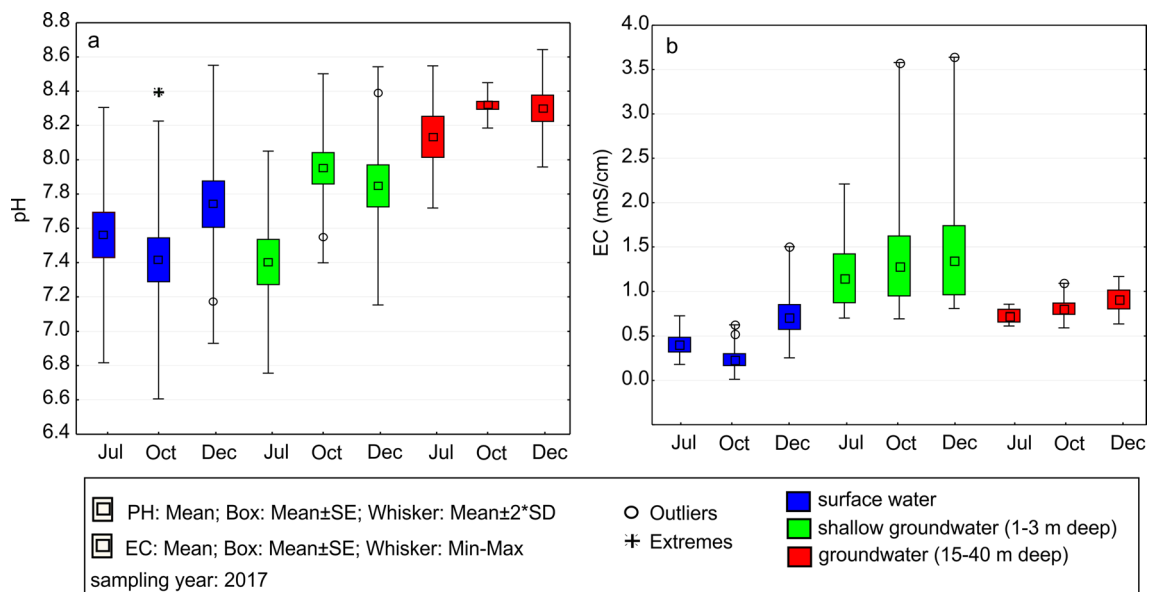


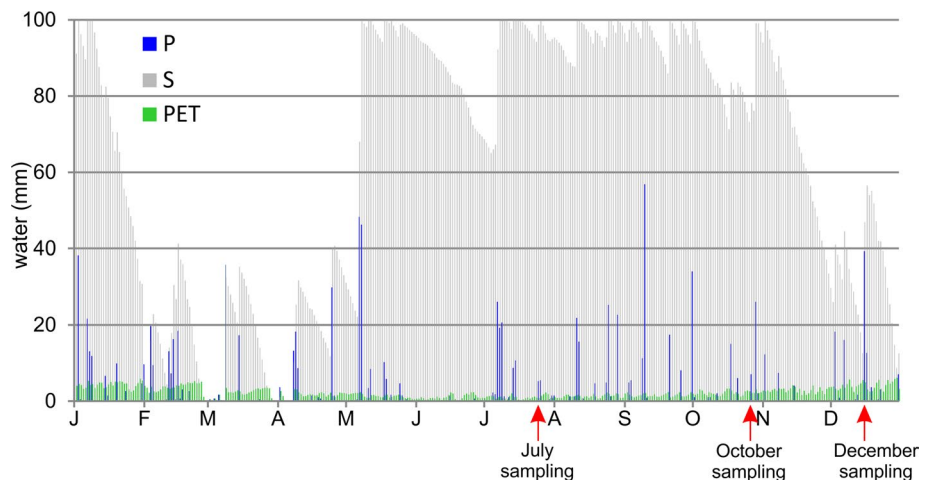
Fig. 2 Variability of pH and electrical conductivity (mS/cm) values in the three sampling dates in surface water and groundwater

and alter minerals (Hem 1985; Appelo and Postma 2005). With the groundwater flow, the pH in the water tends to increase, which explains the most alkaline and least variable values in the deepest groundwater.

The EC values in surface water are lower than those of groundwater, probably due to the main input which is from runoff and to a lesser extent from shallow groundwater discharge. Shallow groundwater presents the highest variability and the highest conductivity values (Fig. 2b). This can be explained because some samples correspond to the coastal plain, which is characterized by high salinity, mainly in the lower basin area of the studied stream (Logan et al. 1999). In contrast, the deepest groundwater samples correspond only to sampling points in the loessic plain environment, where the EC is at a regional scale generally less than 1.5 mS/cm (Logan et al. 1999).

Although July sampling corresponds to the water excess period (winter), it shows a particular characteristic that do not agree with the expected water surplus situation. In May, water reserve increased, with two precipitation events above 40 mm, but this water was consumed during June and July, when rainfalls were scarce (Fig. 3). Consequently, although July sampling is expected to represent a period of water excess, it actually shows the effect of a water deficit period due to limited previous precipitations. The increase in ionic concentration is more evident in the case of surface water, which directly responds to water balance, instead, for groundwater, where variations tend to be in a longer term, and this was not observed. Electrical conductivity of surface water triplicates its value from the upper watershed to the sink (going from 0.18 up to 0.72 mS/cm). Instead, EC value for shallow groundwater varied from 0.70 mS/cm in the

Fig. 3 Water balance for year 2017 in the watershed of El Pescado Creek. *P* precipitation, *S* water storage in soil, *PET* potential evapotranspiration. The three sampling campaigns are indicated with red arrows: winter (July), spring (October) and summer (December)



upper watershed, to 2.21 mS/cm in the middle watershed and 13.36 mS/cm near the sink. Deep groundwater EC varied between 0.85 mS/cm in the upper watershed and 0.72 mS/cm in the middle watershed. Regarding the acidity of surface water for this sampling, values of pH were between 7.20 in the upper watershed, gradually increasing up to 7.95 near the sink. For shallow groundwater, pH values varied between 7.06 and 7.85, meanwhile, deep groundwater varied between 7.91 and 8.32 (Fig. 2).

The October sampling (coincident with spring) took place after 5 months of maximum water storage in the soil, with dominance of surface runoff and prevalence of precipitation over evapotranspiration. This runoff increment, together with an evapotranspiration decrease explains the lower saline contents found in surface water of the upper watershed (EC 0.08 mS/cm) in comparison with July (EC 0.18 mS/cm). Tributary streams from the southwest contained less salinity than those from the southeast, suggesting that the increase of surface runoff in these areas might be a result of the impervious cover installed for greenhouse horticulture (Delgado et al. 2018). Shallow groundwater EC values increased from 0.69 mS/cm in the upper watershed, up to 14.29 mS/cm near the sink. Deep groundwater EC varied between 0.97 mS/cm in the upper watershed and 1.09 mS/cm in the middle watershed. The pH of surface water samples showed the lowest values (6.97) of all sampling campaigns in the upper watershed, whereas near the sink values reaching 8.40 were measured. Groundwater values of pH showed scarce variations within the watershed (minimum 7.55; maximum 8.39).

In December sampling (summer), due to a minor water storage in the soil and a consequently minor surface runoff, evapotranspiration turns to be more relevant in this season. This performance is more evident in surface water than in groundwater, where chemical characteristics are less variable. Electrical conductivity of surface water varied from values around 0.25 mS/cm in the upper watershed, to 1.50 mS/cm near the sink. In shallow groundwater, EC values increased from 0.83 mS/cm in the upper watershed, up to 13.39 mS/cm near the sink. Deep groundwater EC varied between 0.70 mS/cm in the upper watershed and 1.17 mS/cm in the middle watershed. The pH values for surface water increased from 7.17 in the upper watershed up to 8.20 in the middle watershed, with a pH value of 7.60 near the sink. The groundwater pH varied between 7.46 and 8.52.

Table 1 NO_3^- concentration in the watershed of El Pescado Creek, expressed in meq/L

	July	October	December
Surface water	0.36 ± 0.11	0.18 ± 0.05	0.11 ± 0.05
Shallow groundwater	0.12 ± 0.08	0.15 ± 0.26	0.65 ± 1.15
Deep groundwater	0.36 ± 0.23	0.34 ± 0.19	0.38 ± 0.31

The values of NO_3^- found for each sampling date are shown in Table 1, expressed in meq/L. In July sampling, the highest content of NO_3^- (0.53 meq/L) corresponded to a deep groundwater well placed in the upper watershed, which is used for human consumption. However, this value is equivalent to 33 mg/L, below the limit of 45 mg/L established by the Argentinean Alimentary Code (CAA 2012) for drinking water and international legislations (EC 1998; WHO 2004). In October sampling, the maximum value of NO_3^- was found in a shallow groundwater well from the low-basin (0.82 meq/L), not used for human consumption. This value, equivalent to 51 mg/L, exceeds the established limits. In December sampling, there are two shallow groundwater wells exceeding the mentioned limit, but they are not used as drinking source either. Present results show similar or scarcely lower values in groundwater than those established as chemical background at a regional scale (Zabala et al. 2016; Borzi et al. 2019) and even than those figures found twenty years ago in the El Pescado watershed (Laurencena et al. 2001). These last authors found increments in the concentration of NO_3^- between 1987 and 2000, coincident in time with the expansion of agriculture and livestock raising.

In regard to surface water, studies performed in this creek previously to the expansion of the intensive agriculture (Mercado 2003) found concentrations ten times lower than those found in this research. Meanwhile, more recent studies, close to the arrival of greenhouses (Cortezzi et al. 2013) show similar figures to those recorded by the present study in October and December samplings. The watershed is going through a relevant land-use change process related to the expansion of intensive agriculture (Delgado et al. 2018), which could be acting as an additional source of nitrates incorporated as fertilizers, at least for surface water.

Aiming to study the recharge processes by precipitation and evaporation, isotopic values were analyzed together with hydrochemical data for December sampling. Isotopic content of groundwater varies from -5.70 to -4.45 for $\delta^{18}\text{O}$ and from -31.0 to -25.0 for $\delta^2\text{H}$, with the minor enrichments in the deepest samples. In the case of surface water, $\delta^{18}\text{O}$ values vary from -3.80 to 0.50 and $\delta^2\text{H}$ values vary from -23.5 to -4.0 (Fig. 4). Graphical representation of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (Fig. 4a) shows groundwater samples around the local meteoric line (Dapeña and Panarello 2004), expressing recharge processes by rainfall infiltration. Groundwater recharge caused by rainfall infiltration, with little or none previous evaporation is also evident in excess values of deuterium (Fig. 4b), which are similar to the ones of local rainfall (value of 14, according to Dapeña and Panarello 2004). Deepest groundwater samples show the smallest deviation from this value, which could be interpreted as the recharge associated to periods of water excess and low evaporation taking place in winter, as reported for nearby watersheds

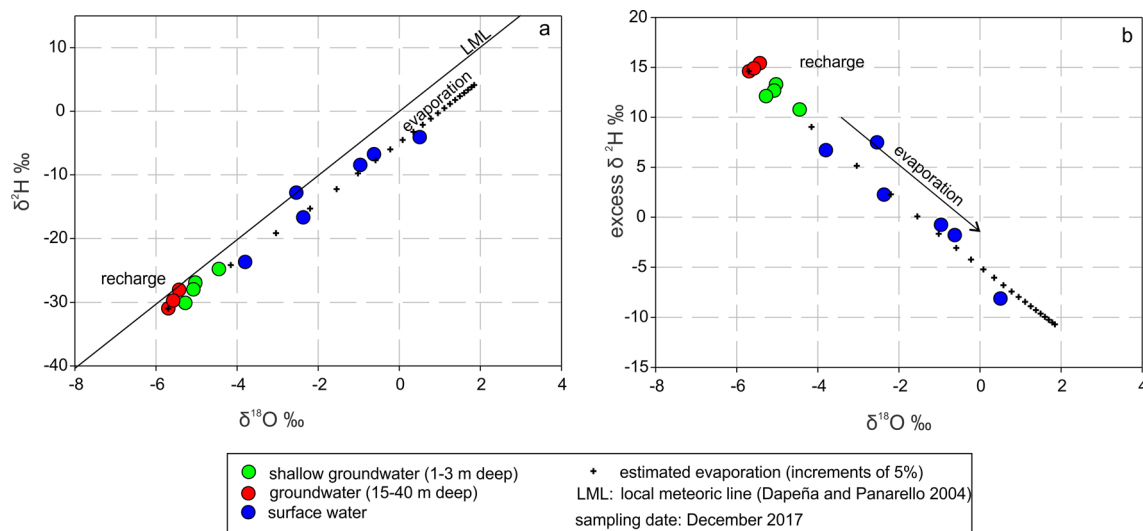


Fig. 4 Water stable isotopes for the watershed of El Pescado Creek (December sampling, 2017). LML is the local meteoric line $\delta^2\text{H} = 8 * \delta^{18}\text{O} + 14$ (Dapeña and Panarello 2004)

(Borzi et al. 2019). In shallow groundwater samples, incipient evaporation processes are registered with values between 2 and 4%, these might be occurring before infiltration in non-saturated zone, or right from the phreatic, when it is located near the surface.

On the other hand, surface water samples deviate from the local meteoric line (Fig. 4a) with an isotopic enrichment following a tendency associated to evaporation processes, accounting with estimated evaporation percentages between 5 and 45%. This trend, which is also shown in the graphic of deuterium excess as a function of $\delta^{18}\text{O}$ (Fig. 4b), where surface water follows a tendency related to negative deuterium excesses, typically associated to evaporation processes.

The relation of $\delta^{18}\text{O}$ as a function of major ions shows that ionic variations are mainly caused by evaporation processes (Fig. 5). Only one shallow groundwater sample, placed in the low watershed (associated to the coastal plain environment), expresses an increment of ionic content with isotopic variation, characteristic of processes of mineral and salt sediment dissolution (Clark 2015). In this sample, the mentioned tendency is appreciated in the relations $\delta^{18}\text{O}$ as a function of Cl^- and Na^+ (Fig. 5a, b) suggesting halite dissolution, usually mentioned as salt crusts in this area (Cellone et al. 2019), being responsible for the high electrical conductivity in this area of the watershed and for the presence of sodium chloride facies. Dissolution of gypsum and dolomite–calcite could be also providing ions to water (Fig. 5c–f), although increments for SO_4^{2-} , Ca^{2+} , Mg^{2+} and HCO_3^- observed in these samples are quite less than the ones related to Cl^- and Na^+ (Logan et al. 1999).

On the other groundwater samples, only slight increases are observed in $\text{CO}_3^{2-} + \text{HCO}_3^-$ and Ca^{2+} which occur

without isotopic variation. This could be associated to dissolution of carbonates from aquifer's loessic sediments (Teruggi 1957) during rainfall infiltration. In this context, groundwater should be expressing as dominantly calcium bicarbonate facies, instead, dominant cation is Na^+ . Previous studies in El Pescado Creek and other nearby watersheds have shown that Na/Ca exchange that occurs as a result of the interaction with clay minerals from the aquifer matrix is responsible for predominance of sodium bicarbonate facies (Carol et al. 2012; Zabala et al. 2016; Borzi et al. 2019). On the other hand, and in relation to $\text{CO}_3^{2-} + \text{HCO}_3^-$ ions, the observed decrease in these ions in surface water concentrations in respect to the one given by evaporation might be indicating $\text{CO}_{2(\text{g})}$ volatilization, associated to the same evaporation process.

Conclusion

This study shows that water-balance variations caused chemical changes mainly in surface water and shallow groundwater. On the contrary, deep groundwater tends to express scarce variability. Chemical facies of surface water and groundwater are dominantly sodium bicarbonate. Although there is groundwater discharge into the watercourse, this input is not relevant when compared with the one provided by surface runoff. This behavior is reflected in the lower salinity values and the concentration of major ions registered in the surface water, together with an isotopic signal related to rainfall evaporation. Chemical variations of groundwater could be associated to the recharge from rainfall infiltration, together with the interaction with sediments of the aquifer

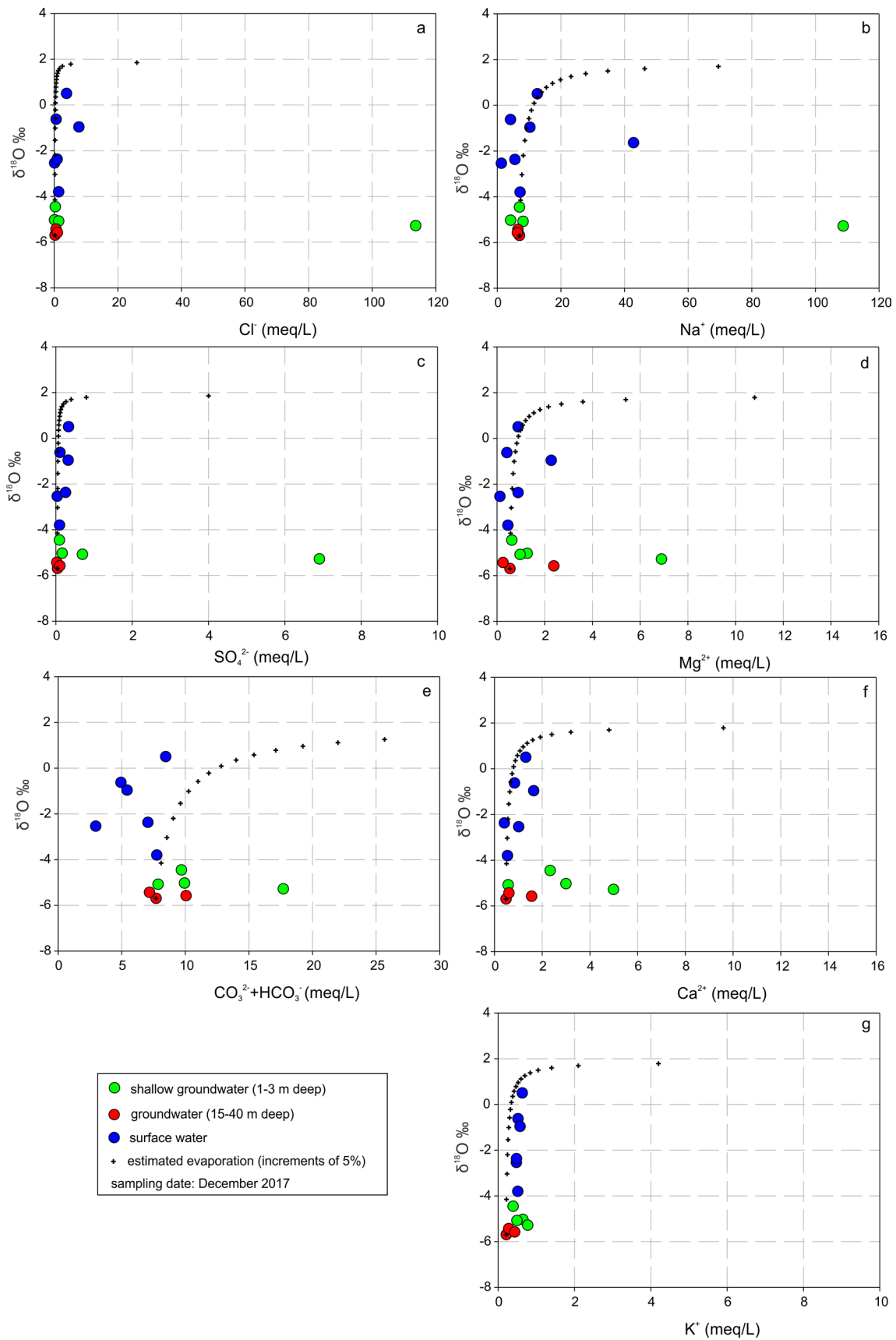


Fig. 5 $\delta^{18}\text{O}$ as a function of major ions for the watershed of El Pescado Creek (December sampling, 2017)

matrix. Dissolution processes of $\text{CO}_{2(g)}$ and carbonates were identified, expressing cationic exchange as another conditional process of water chemistry. On the other hand, nitrate concentrations in groundwater were similar or slightly lower than those of regional figures, showing no chemical disturbance. However, potentially expected effects associated to fertilizers used in intensive agriculture were observed in surface water, where nitrates reached higher concentration than those reported previously to the establishment of greenhouses.

The relevant process of territorial transformation that is taking place (mainly associated to the expansion of the intensive agriculture and the non-planned urbanization), represents a complex source of changes towards the watershed management. These land-use changes might not only be represented by drinking water and crop irrigation resource consumption, but also by the increase in surface runoff as a result of greenhouse establishment. In this regard, results suggest potential modifications in the water chemical characteristics considering short- and long-term periods.

This research might help understand water dynamics in the watershed of El Pescado Creek, being potentially useful to local authorities involved in water management for the area. Considering that similar territorial changes regarding land use are taking place in others watersheds of the region, these results might be also helpful for the study of nearby watersheds with similar patterns of land-use change.

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