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# Hydrogeochemical and isotopic characterisation of groundwater in a sand-dune phreatic aquifer on the northeastern coast of the province of Buenos Aires, Argentina

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This contribution presents the hydrochemical and isotopic characterisation of the phreatic aquifer located in the Partido de la Costa, province of Buenos Aires, Argentina. In the sand-dune barrier geomorphological environment, groundwater is mainly a low-salinity Ca-$HCO_3$ and Na-$HCO_3$-type, being in general suitable for drinking, whereas in the continental plain (silty clay sediments), groundwater is a Na-Cl type with high salinity and unsuitable for human consumption. The general isotopic composition of the area ranges from $-6.8$ to $-4.3‰$ for $\delta^{18}O$ and from $-39$ to $-21‰$ for $\delta^{2}H$, showing that rainwater rapidly infiltrates into the sandy substrate and reaches the water table almost without significant modification in its isotopic composition. These analyses, combined with other chemical parameters, made it possible to corroborate that in the eastern area of the phreatic aquifer, there is no contamination from marine salt water.

**Keywords:** Argentina; coastal aquifer; groundwater; hydrogen-2; hydrogeochemistry; oxygen-18; sand-dune deposits; water cycle

## 1. Introduction

On the northeastern coast of the province of Buenos Aires, Argentina, the only drinking water source for a permanent population greater than 10,000 inhabitants is the low-salinity groundwater restricted to a strip of coastal dunes. Tourism is the main economic activity, and in summer the region experiences a high tourist season in which the population increases fivefold. A proper knowledge of the drinking water available will play a decisive role in ensuring the well-being of both local residents and tourists.

As regards the water supply to the population, there is a pumping field located outside the urbanised area. Only a small percentage of the houses (approximately 25 %) are supplied with water from the pumping field, which is treated before its distribution. The remaining 75 % cover their needs using residential water wells and the water is untreated. As for the provision of sewers, a large percentage of the residences in the town are connected (80 %) [1]. Given this situation, a chemical characterisation is necessary in order to assess the quality of the water consumed by the population.

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Saltwater intrusion is an environmental problem that affects several coastal aquifers worldwide [2–7], and there are some areas on the coast of Buenos Aires where this phenomenon has been identified as affecting the drinking water quality [8,9]. Chemical characterisation combined with the use of stable isotopes is a useful methodology to detect saltwater intrusion [10–14], mixing processes and hydrogeological processes that might affect the groundwater chemical composition.

The aim of this contribution is to carry out the hydrochemical and isotopic characterisation of the phreatic aquifer located in the coastal sand-dune barrier in the Partido de la Costa, province of Buenos Aires, Argentina, also taking into consideration the possible effects of seasonality of recharge on the hydrochemical composition of a shallow groundwater. This characterisation focuses on the phreatic aquifer in order to define areas where the chemical quality of groundwater is suitable for water supply to the population.

## 2. Study area

The study area is the town of San Clemente del Tuyú, Partido de la Costa, Buenos Aires, Argentina (36° 22′ Lat S, 56° 44′ Long W) (Figure 1). The study area comprises two geomorphological environments: the sand-dune barrier and the continental plain. The sand-dune barrier, whose width varies between 2 and 4 km, consists of a beach and dune system. The beach area, which slopes towards the east, is rectilinear – with a width ranging from 50 to 150 m – accretionary, and there is no escarpment. Low-elevation dunes fixed by sparse vegetation are located to the west of the beach. Both the beach and the dunes are characterised by fine-grained sand, and the grain size generally decreases from south to north [15]. The mineralogy of the sand includes quartz, plagioclase, potassium feldspar, hornblende, augite, and a fraction of opaque minerals such as magnetite, hematite and ilmenite [16,17]. The continental plain – related to a former tidal environment – is composed of silty clay sediments. It is located to the west of the coastal dune and is marked by generally low elevations (less than 5 m above sea level) surrounding the Samborombón Bay with a regional slope of $10^{-5}$ m m$^{-1}$ towards the north.

The tides are mixed, predominantly semidiurnal, with tidal ranges of less than 2 m [18]. Due to the morphology of the sand-dune barrier and the fact that the coast is microtidal, the effect of the tides can only be observed in the foreshore.

The continental plain is connected to the Samborombón Bay through tidal channels where the tidal influence can be observed and salt marshes are formed. The water in the Samborombón Bay is a mixture of fresh water of the Río de la Plata and salt water of the Atlantic Ocean, which results in a total dissolved solids (TDS) content of around 20,000 mg l$^{-1}$. The continental plain is the discharge zone of the regional groundwater flow system, which could explain the high salinity in the area [19–21]. This plain has been widely studied by Carol et al. [22–24], who ascribe the source of groundwater salinity to the fact that rainfall recharge in conjunction with an almost zero regional hydraulic gradient result in a long residence time of water in the shallow aquifer of the continental plain. Dissolution of gypsum and halite, as well as other chlorides, within the sedimentary formations and soil water is thus responsible for groundwater salinity [25].

The pumping field previously mentioned is located outside the urbanised area to the south and is composed of seven horizontal Ranney-type wells (rate 1.94 $10^{-3}$ m$^3$ s$^{-1}$). The structure comprises a central concrete caisson, 4 m in diameter, excavated to a depth of 8 m, at which point a series of four gravel-packed horizontal laterals extend from within the caisson in a radial pattern located at 4 m depth. The laterals are 4 and 6 m long and both are about 0.05 m in diameter. There are also 21 well point systems, each one connected to 10 wells (rate 3.6 $10^{-3}$ m$^3$ s$^{-1}$). The extraction depth varies between 4 and 6 m. This type of conventional water well is small in diameter, consisting of a battery of shallow-depth boreholes connected to a central water pump.

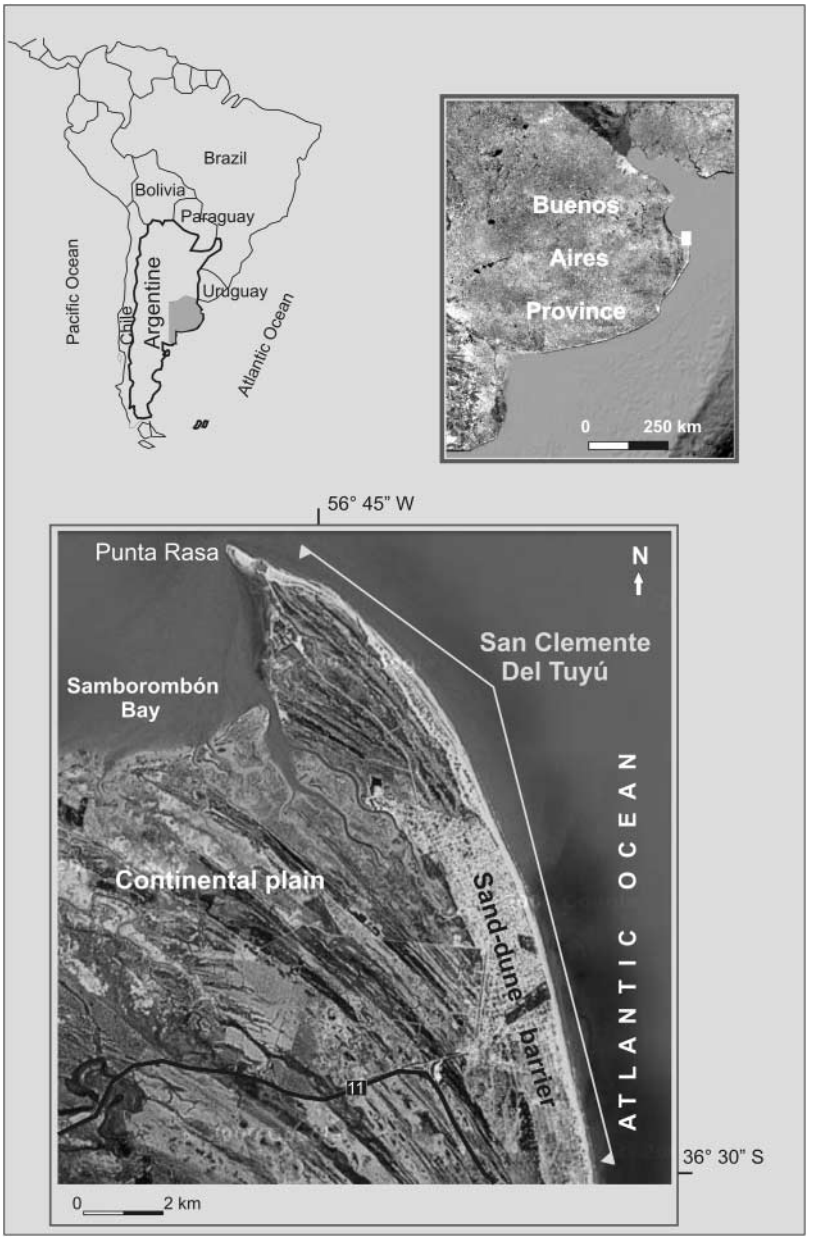


Figure 1. Location map.

All the wells are concentrated in an area of about 0.23 $km^2$. The annual extraction rate is about 200,000 $m^3$ with a progressively increasing trend [1]. There are no significant losses from the water distribution network that contribute to the recharge, since the network is less than 20 years old and in good condition. The same applies for the sewage system, which is under 10 years old. Low concentrations of nitrates in the groundwater would support this assumption [26].

Regarding the residential water wells, in general they are 4 m deep with 3 m casing pipes of 2 inches (5.1 cm) in diameter and a 1 m filter. These low-flow-rate water wells are located in the houses in order to supply the families' demands.

## 3. Methodology

Hydrogeological surveys and the interpretation of the geological and geomorphological aspects of the area were carried out in order to establish its general characteristics. In October 2006 and July 2008, water samples were collected using a water sample bailer from 39 wells drilled to a depth of between 3 and 5 m; pH and electrical conductivity (EC) were measured *in situ*. The chemical analyses were performed by the Laboratorio de Ingeniería Sanitaria (LIS, Laboratory of Sanitary Engineering) of the Universidad Nacional de La Plata (UNLP, National University of La Plata), applying standard methods (Table 1).

Piper diagrams were used to analyse the results. Isoconcentration maps of different parameters were drawn using a GIS tool, and a hydrochemical study was conducted according to the different seasons and geomorphological environments.

Average, maximum and minimum values of chemical components were calculated and compared for each survey for the sand-dune barrier and the continental plain.

For the analysis of oxygen-18 ($\delta^{18}O$) and deuterium ($\delta^{2}H$), 14 shallow wells were sampled in July 2009. EC and chloride were also determined in those samples.

The isotopic analyses were carried out by the Instituto de Geocronología y Geología Isotópica (INGEIS, Geochronology and Isotope Geology Institute) of the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, National Scientific and Technical Research Council) and the Universidad de Buenos Aires (UBA, University of Buenos Aires), Argentina. Samples were treated following conventional techniques and measured using high-precision laser spectroscopy, i.e. off-axis integrated cavity output spectroscopy. Results are expressed in the usual way as $\delta$ notation, defined in the equation:

$$\delta = \frac{1000(R\mathrm{s} - R\mathrm{p})}{R\mathrm{p}}[‰],$$

where $\delta$ is the isotope deviation in ‰, s the sample, p the international reference, $R$ the isotope ratios ($^{2}H/^{1}H$, $^{18}O/^{16}O$). Values are relative to the Vienna Standard Mean Ocean Water (V-SMOW) [27]. Uncertainties are $\pm 0.3$ ‰ for $\delta^{18}O$ and $\pm 1.0$ ‰ for $\delta^{2}H$, respectively.

The isotopic composition of rainwater was compared with the rain collection station at Ciudad Universitaria (City of Buenos Aires), period 1979–2003, and the station at Azul (province

Table 1. Methods applied for the chemical analysis.

| Determination | Technique | Method |
|---|---|---|
| pH | Potentiometric | SM-4500-H+ |
| Chloride | Mohr | SM-4500-Cl |
| Total hardness | EDTA titrimetric | SM-2340 C |
| EC | Conductimeter | SM-2510 B |
| Sulphate | Nephelometric | SM-4500-SO4-E |
| Fluorine | Ion-selective electrode | SM-4500 F C |
| Ammonium | Ion-selective electrode | SM-4500-NH3-D |
| Nitrate | Ion-selective electrode | SM-4500-NO3-D |
| Nitrite | Ilosva von Ilosva | SM-4500 NO2-adaptation |
| TDS | Gravimetric | SM-2540 B |
| Iron | Colorimetric | SM-3500-Fe B |
| Calcium | EDTA titrimetric | SM-3500-Ca B |
| Magnesium | Calculation | SM-3500-Mg B |
| Manganese | Persulphate | SM-3500 M and B |
| Sodium | Flame emission photometry | SM-3500-Na B |
| Potassium | Flame emission photometry | SM-3500-K B |
| Carbonate | Titrimetric | SM-2320 B |
| Bicarbonate | Titrimetric | SM-2320 B |

of Buenos Aires), period 1998–2007, and the local meteoric water line as defined by Dapeña [28] and Dapeña et al. [29], i.e. $\delta^2H = 8\delta^{18}O + (13 \pm 1)$ for these stations. These rain collectors are part of the Red Nacional de Colectores (National Rain Collection Network) set up by the Instituto de Geocronología y Geología Isotópica (Geochronology and Isotope Geology Institute, INGEIS, CONICET-UBA) within the framework of the Global Network for Isotopes in Precipitation (GNIP), created by the International Atomic Energy Agency and the World Meteorological Organization [10,30–32]. These measurements were supplemented by meteorological information, such as the mean surface air temperature and the amount of precipitation.

Additionally, in order to characterise the isotopic composition of the local rain ('input function'), a station to collect monthly composite samples of precipitation was set up in the town of San Clemente del Tuyú in April 2011, where an intensive observation was carried out from April to August 2011. Cases with precipitation below 2 mm were not taken into consideration, since isotope composition in extremely small samples is modified by evaporation during precipitation [33]. The statistical treatment was performed following standard procedures proposed by the International Atomic Energy Agency [34].

The groundwater samples were classified according to their location on the dune. The data were represented in a conventional $\delta^2H$ versus $\delta^{18}O$ diagram with the local meteoric water line. Also a $\delta^2H$ versus chloride graph was plotted to evaluate the presence of saline intrusion.

The monthly rainfall in the town of San Clemente del Tuyú was analysed; the water surplus was determined by means of a water budget following Thornthwaite and Mather [35] and the mean monthly $ET_0$ (reference crop evapotranspiration) values following the Penman–Monteith method [36] using the AGROAGUA v.5.0 software [37].

Manual groundwater level measurements were carried out, using a monitoring network, in October 2006, November 2007 and then monthly since February 2008. The data were entered into a geographic information system (GIS), and groundwater flow maps were made for the sampling dates.

## 4. Results

### 4.1. *Hydrogeological characterisation*

The area is located in the Región Costera (Coastal Region) [38], where the hydrodynamic behaviour is controlled by the geomorphology.

The freshwater phreatic aquifer occurs in the sand-dune barrier with a thickness ranging from 4 to 10 m, increasing from north to south, and decreasing to the east (towards the seawater interface) and to the west (towards the continental brackish water). From a geological viewpoint, this system coincides with Holocene sand and shelly sand [39], overlying a clayey aquiclude (30 m thick) with sand lens intercalations containing high-salinity water. The conceptual model in Figure 2 was developed based on information from the literature [40], geological borehole logs and vertical electric sounding [41]. The hydrological basement, according to a well drilled by the Consejo Federal de Inversiones (Federal Council of Investments) [40], can only be defined as a low permeability system.

In general, the phreatic aquifer has a transmissivity of the order of $100\,m^2\,d^{-1}$ [41], a specific yield of 0.10 and an average hydraulic conductivity of $20\,m\,d^{-1}$ [42]. On the basis of groundwater maps, the average hydraulic gradient was estimated as being 0.0023 towards the east and 0.0032 towards the west, with an estimated average effective velocity of $0.046\,m\,d^{-1}$ towards the east and $0.064\,m\,d^{-1}$ towards the west [43].

Freshwater reserves are limited and restricted to the groundwater of the coastal sand-dune barrier, whose regime strongly depends on the weather conditions. The only natural source of

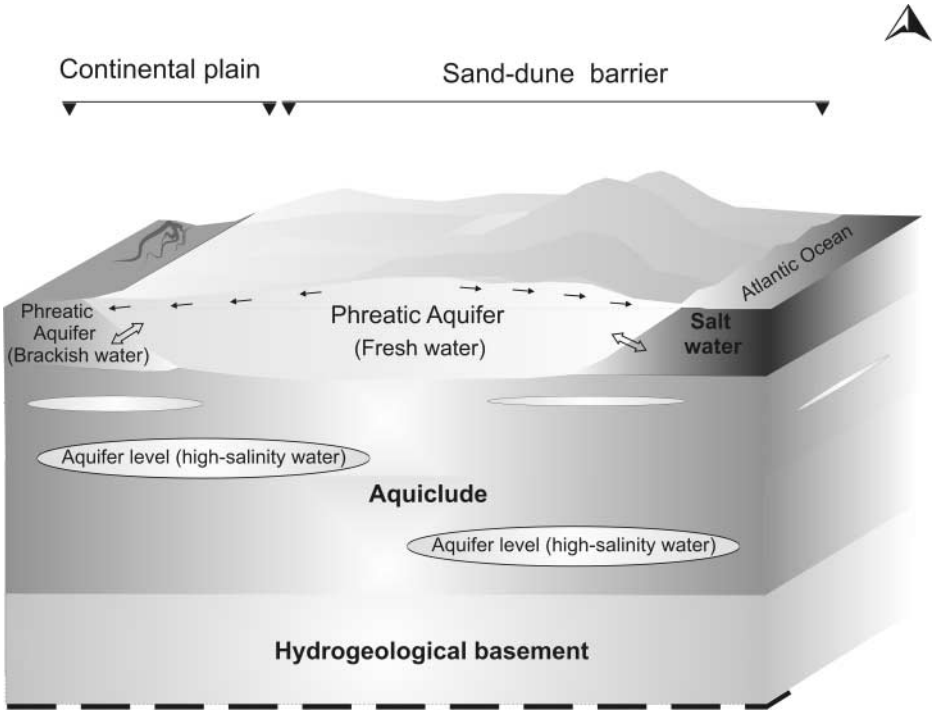


Figure 2. Schematic of the hydrogeological system of the study site.

recharge is the infiltration of water surplus from precipitation. The climate is humid temperate, regionally homogeneous, with an average annual rainfall of the order of 900 mm and an average temperature of 14.6°C. The rainfall pattern shows that 65 % of the annual rainfall occurs in the rainy season (October–March), whereas 35 % occurs in the dry season (April–September). The highest temperatures occur in the rainy season, with an average maximum of 22.2°C in January; the average maximum potential evapotranspiration (PET) occurs from December to March and it is about 67 mm. The dry season is the coldest, with an average minimum temperature of 7.6°C in July and an average minimum PET of 36 mm in June and July [43].

In general, different contributions on the recharge estimation report a strong correlation with precipitation [44,45], establishing that the greater the precipitation, the greater the recharge to the aquifer. However, in the study area, the climatic conditions indicate a rainy season (warm) and a dry season (cold), with the dry period being more significant regarding the increase in the water table and the consequent response in the recharge. In the rainy period, evapotranspiration from groundwater occurs, given the shallow depth of the water table; the effects of this evapotranspiration also cause a decrease in the water surplus that might infiltrate (Figure 3(a) and 3(b)).

Groundwater mainly recharges in the centre of the sand dune and discharges in two opposing directions: to the east, towards the sea, and to the west, towards the continental plain [41–46] (Figure 4). Geomorphological features have a direct influence on groundwater dynamics and chemistry. The area with the highest water-table position coincides with the maximum heights in the sand dunes. The sand-dune barrier shows no development of a soil profile: it is sandy, excessively drained and unstable. Due to the characteristics of the soil and the sediment, surface runoff is not considered in the area. Following a rainfall event, the response of the water table, which lies at a shallow depth (less than 2 m), is nearly immediate (within a day) [41].

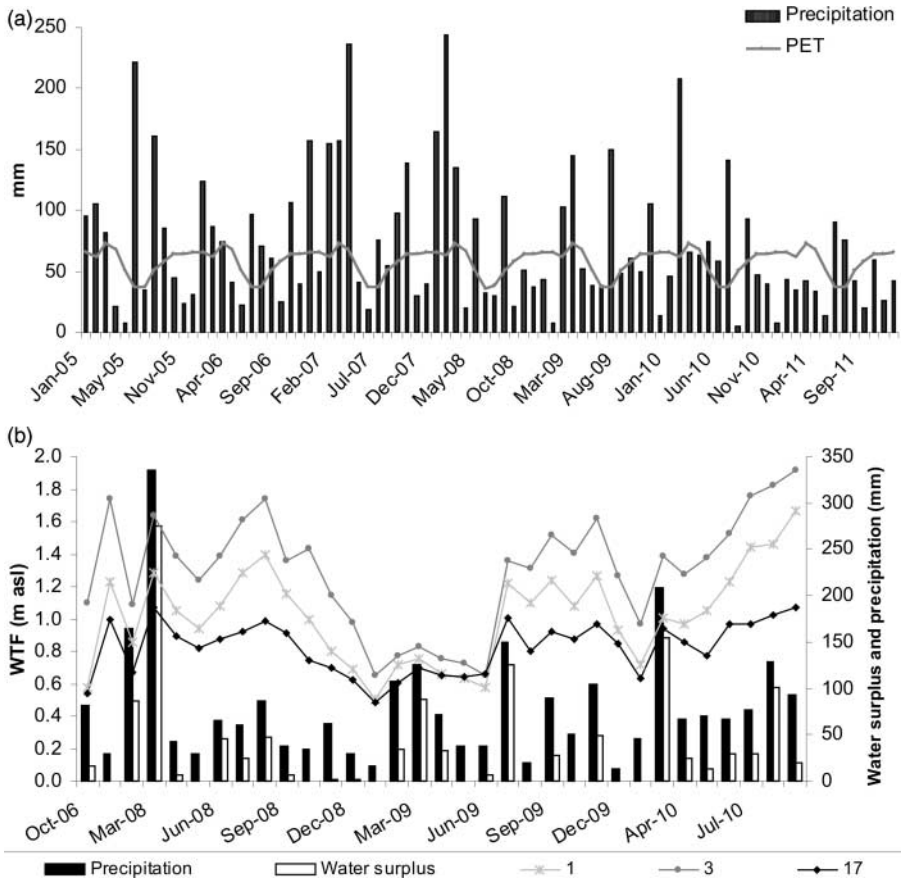


Figure 3. (a) Precipitation and PET for the period 5 January/11 December. (b) Water-table fluctuation for three typical wells, precipitation and calculated water surplus for the analysed period.

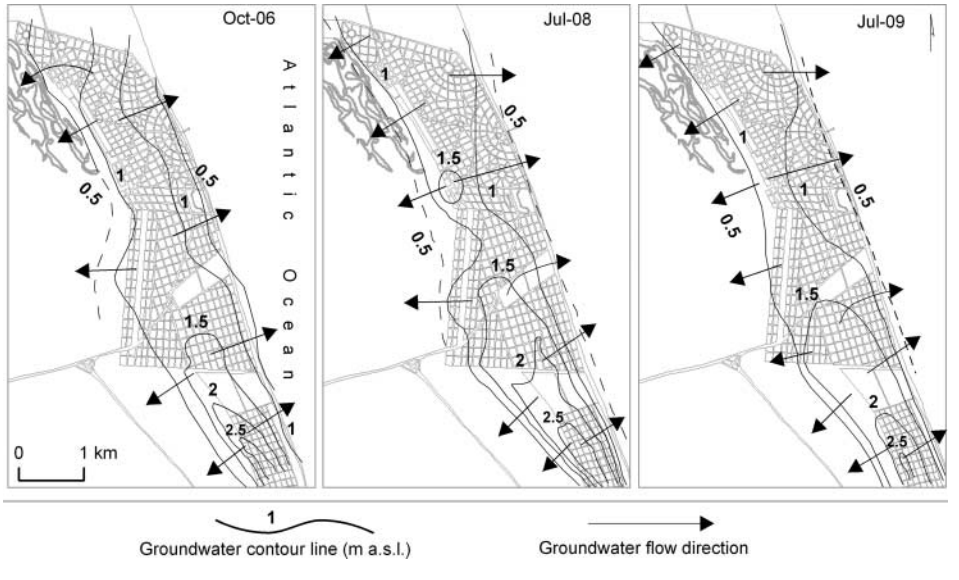


Figure 4. Isophreatic maps for the sampling dates.

Table 2. Precipitation, calculated PET and water surplus from the water budget for the dates of sampling and the previous month.

| | Precipitation (mm) | PET (mm) | Water surplus (mm) |
|---|---|---|---|
| September 2006 | 25 | 58 | 0 |
| October 2006 | 81 | 69 | 16 |
| June 2008 | 65 | 38 | 45 |
| July 2008 | 60 | 37 | 25 |
| June 2009 | 38 | 43 | 6 |
| July 2009 | 150 | 38 | 126 |

The groundwater flow maps (Figure 4) reflect the water table situation at the time of sampling. In October 2006 (rainy season), the groundwater levels were deeper than in July 2008 and July 2009 (dry season), which can be verified by the water surplus values of the water budget (Table 2). Regarding the months of the dry season, in July 2008 the water tables were higher than in July 2009, despite the fact that in the latter the precipitation was higher and, in consequence, the water surplus values were also higher. In this case, it is necessary to analyse the situation in the previous month, since in June 2008, the water surplus was 45 mm, while in June 2009 it was only 6 mm. The precipitation that fell in July 2009 enabled the system to recover from a situation where the water tables were much lower (Figure 3(b)).

### 4.2. *Hydrochemistry*

Data from the samplings performed in 2006 and 2008 allowed the formulation of a general chemical characterisation. The complete list of analytes is recorded in Table 3. From these data, it is possible to distinguish chemical differences between the sand-dune barrier and the continental plain environments, as shown in Figure 5. In the sand-dune barrier, groundwater is mainly low-salinity Ca-$HCO_3$ and Na-$HCO_3$-type waters, whereas in the continental plain, groundwater is the Na-Cl type with high saline content. In the Piper diagrams (Figure 5), small variations in the distribution of the results of both samples are observed. In general, the presence of Ca-$HCO_3$ and Na-$HCO_3$-type waters, identified in the sand dune, is related to recently infiltrated water or to the groundwater flux of limited significance. On the other hand, Na-Cl-type water from the continental plain must be associated with a regional groundwater flow and to evaporation effects.

It is also possible to make a general description of the groundwater chemistry according to each survey and its season of sampling. From the samples taken in October 2006 in the sand-dune barrier, the TDS are not higher than 1710 mg $l^{-1}$ (Figure 6). Chloride concentrations are lower than 400 mg $l^{-1}$; average bicarbonate content is about 540 mg $l^{-1}$; and sulphate is lower than 84 mg $l^{-1}$. Calcium concentrations vary between 20 and 264 mg $l^{-1}$; average sodium concentrations are 121 mg $l^{-1}$ and potassium contents are lower than 43 mg $l^{-1}$. Magnesium concentrations show a more heterogeneous distribution, with values below 50 mg $l^{-1}$ in most of the areas, only ranging from 50 to 112 mg $l^{-1}$ in some limited sectors.

In the survey performed in July 2008, the samples taken from the sand-dune have a TDS content that varies between 149 and 1597 mg $l^{-1}$. Chloride concentrations are lower than 160 mg $l^{-1}$. Average bicarbonate content is about 500 mg $l^{-1}$, and sulphate is lower than 45 mg $l^{-1}$. Calcium concentrations vary between 12 and 65 mg $l^{-1}$; average sodium content is 83 mg $l^{-1}$ and potassium contents are lower than 28 mg $l^{-1}$. Magnesium concentrations are lower than 53 mg $l^{-1}$.

Nitrate, nitrite and ammonium concentrations are mostly the same for both surveys. Although nitrate content is between 3 and 33 mg $l^{-1}$, there was one case in particular, in the urbanised area in the 2006 survey, where nitrate concentrations higher than 50 mg $l^{-1}$ were detected, with a maximum of 180 mg $l^{-1}$ (Figure 6). The source of such a high nitrate concentration is anthropogenic,

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Table 3. Chemical composition for the groundwater samples.

| | | October 2006 | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Well n° | pH | EC ($\mu S\,cm^{-1}$) | TDS ($mg\,l^{-1}$) | Alkalinity ($mg\,l^{-1}$) | $HCO_3^-$ ($mg\,l^{-1}$) | Total hardness ($mg\,l^{-1}$) | $SO_4^{2-}$ ($mg\,l^{-1}$) | $Ca^{2+}$ ($mg\,l^{-1}$) | $Mg^{2+}$ ($mg\,l^{-1}$) | $Na^+$ ($mg\,l^{-1}$) | $K^+$ ($mg\,l^{-1}$) | $F^-$ ($mg\,l^{-1}$) | $Cl^-$ ($mg\,l^{-1}$) | $NO_3^-$ ($mg\,l^{-1}$) | $NO_2^-$ ($mg\,l^{-1}$) | $NH_4^+$ ($mg\,l^{-1}$) | $Fe^{2+}$ ($mg\,l^{-1}$) | $Mn^{2+}$ ($mg\,l^{-1}$) |
| 172 | 7.2 | 917 | 500 | 400 | 488 | 330 | 41 | 120 | 7 | 61 | 12 | 0.8 | 28 | 4 | <0.01 | <0.03 | 0.03 | 0.14 |
| 103 | 7.3 | 1601 | 905 | 480 | 586 | 260 | 56 | 68 | 22 | 218 | 43 | 0.4 | 170 | 33 | 0.01 | <0.03 | 0.03 | 0.04 |
| 58-1 | 7.7 | 2140 | 1240 | 540 | 659 | 390 | 30 | 116 | 24 | 281 | 28 | 0.5 | 362 | 12 | <0.01 | <0.03 | <0.03 | <0.03 |
| 58 | 7.5 | 672 | 310 | 250 | 305 | 200 | 16 | 72 | 5 | 44 | 11 | 0.3 | 28 | 4 | <0.01 | <0.03 | 0.03 | <0.03 |
| 53 | 7.4 | 1158 | 595 | 400 | 488 | 350 | 6 | 80 | 36 | 81 | 20 | 0.5 | 106 | 4 | 0.08 | <0.03 | 0.07 | 0.28 |
| KK | 7.2 | 1500 | 770 | 510 | 622 | 260 | 10 | 96 | 5 | 188 | 25 | 0.4 | 149 | 4 | <0.01 | 0.05 | 0.06 | <0.03 |
| JJ | 7.1 | 3360 | 2030 | 680 | 830 | 670 | 9 | 172 | 58 | 477 | 38 | 0.5 | 760 | 7 | <0.01 | <0.03 | 0.1 | <0.03 |
| II | 7.2 | 1263 | 650 | 410 | 500 | 290 | 24 | 116 | <2 | 145 | 18 | 0.4 | 149 | 4 | 0.15 | <0.03 | 0.03 | 0.28 |
| HH | 7.3 | 2540 | 1565 | 490 | 599 | 520 | 10 | 156 | 32 | 316 | 37 | 0.4 | 547 | 4 | 0.25 | 0.03 | 0.18 | 0.72 |
| GG | 7.3 | 5410 | 3220 | 950 | 1159 | 420 | 9 | 88 | 49 | 998 | 36 | 1.4 | 1264 | 18 | 0.2 | 0.03 | 0.23 | <0.03 |
| DD | 7.4 | 887 | 490 | 390 | 476 | 350 | 23 | 64 | 46 | 66 | 11 | 0.3 | 71 | 5 | <0.01 | <0.03 | <0.03 | 0.74 |
| CC | 7.4 | 1205 | 1575 | 450 | 549 | 370 | 11 | 104 | 27 | 80 | 23 | 0.5 | 64 | 3 | 0.2 | <0.03 | 0.75 | 1.2 |
| BB | 7.2 | 7000 | 4190 | 1380 | 1684 | 900 | 9 | 156 | 124 | 1220 | 47 | 0.8 | 1597 | 26 | 0.3 | 0.03 | 0.14 | <0.03 |
| AA | 6.7 | 2200 | 1710 | 680 | 830 | 860 | 33 | 264 | 49 | 132 | 19 | 0.8 | 362 | 5 | <0.01 | 0.03 | 3.5 | 0.37 |
| Z | 7.9 | 962 | 515 | 280 | 342 | 240 | 31 | 60 | 22 | 94 | 18 | 0.4 | 106 | 10 | <0.01 | 0.03 | <0.03 | <0.03 |
| Y | 7.4 | 1777 | 865 | 440 | 537 | 380 | 6 | 84 | 41 | 212 | 42 | 0.5 | 256 | 9 | <0.01 | 0.03 | 0.3 | 0.17 |
| X | 7.3 | 6350 | 3410 | 870 | 1061 | 750 | 49 | 148 | 92 | 1033 | 46 | 0.8 | 1505 | 28 | <0.01 | <0.03 | 0.11 | <0.03 |
| W | 7.1 | 6190 | 3320 | 620 | 756 | 890 | 62 | 236 | 73 | 890 | 38 | 0.4 | 1633 | 31 | <0.01 | 0.03 | 0.6 | <0.03 |
| U | 7.2 | 1641 | 920 | 570 | 695 | 510 | 23 | 160 | 27 | 145 | 22 | 0.4 | 192 | 4 | <0.01 | <0.03 | 0.32 | 0.18 |
| T | 7.2 | 1180 | 680 | 390 | 476 | 380 | 42 | 20 | 83 | 94 | 17 | 0.4 | 149 | 5 | <0.01 | <0.03 | 0.35 | 0.06 |
| S | 7.0 | 832 | 580 | 410 | 500 | 150 | 23 | 40 | 13 | 125 | 11 | 0.2 | 28 | 8 | <0.01 | <0.03 | 0.18 | 0.21 |
| R | 7.4 | 1350 | 760 | 460 | 561 | 300 | 26 | 100 | 13 | 142 | 31 | 0.4 | 128 | 5 | 0.09 | <0.03 | 0.09 | 0.04 |
| Q | 7.4 | 1468 | 830 | 370 | 451 | 280 | 59 | 100 | 7 | 198 | 20 | 0.2 | 213 | 51 | 0.09 | 0.03 | <0.03 | 0.53 |
| P | 7.4 | 1125 | 610 | 490 | 598 | 320 | 20 | 52 | 48 | 142 | 16 | 0.4 | 114 | 13 | 0.12 | <0.03 | 0.03 | 0.08 |
| O | 7.0 | 1155 | 720 | 630 | 769 | 480 | 6 | 64 | 80 | 81 | 32 | 0.3 | 57 | 4 | 0.03 | 1 | 0.92 | 0.23 |
| N | 7.5 | 671 | 420 | 350 | 427 | 250 | 29 | 84 | 10 | 68 | 9.8 | 0.3 | 28 | 5 | <0.01 | <0.03 | 0.5 | 0.21 |
| M | 7.4 | 1407 | 790 | 340 | 415 | 230 | 60 | 88 | 3 | 197 | 20 | 0.3 | 121 | 180 | 0.15 | <0.03 | 0.03 | 0.06 |
| L | 7.2 | 1743 | 1120 | 400 | 488 | 400 | 34 | 128 | 20 | 68 | 26 | 0.2 | 334 | 5 | 0.2 | <0.03 | 0.35 | <0.03 |
| K | 7.6 | 808 | 460 | 330 | 403 | 280 | 12 | 68 | 27 | 68 | 16 | 0.2 | 60 | 12 | <0.01 | <0.03 | 0.04 | 0.04 |
| J | 7.3 | 1459 | 1090 | 250 | 305 | 295 | 97 | 100 | 11 | 188 | 37 | 0.2 | 195 | 180 | 0.03 | <0.03 | 0.05 | 0.4 |
| I | 7.7 | 1578 | 950 | 520 | 634 | 410 | 23 | 112 | 32 | 185 | 37 | 0.3 | 245 | 5 | <0.01 | <0.03 | 0.16 | 0.04 |
| H | 7.4 | 644 | 340 | 280 | 342 | 260 | 11 | 76 | 17 | 39 | 13 | 0.3 | 35 | 10 | <0.01 | <0.03 | 0.04 | <0.03 |
| G | 7.0 | 1528 | 940 | 540 | 659 | 600 | 11 | 136 | 63 | 97 | 26 | 0.6 | 213 | 4 | <0.01 | 0.04 | 0.22 | <0.03 |

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Table 3. Continued

| Well n° | pH | EC ($\mu S\,cm^{-1}$) | TDS ($mg\,l^{-1}$) | Alkalinity ($mg\,l^{-1}$) | $HCO_3^-$ ($mg\,l^{-1}$) | Total hardness ($mg\,l^{-1}$) | $SO_4^{2-}$ ($mg\,l^{-1}$) | $Ca^{2+}$ ($mg\,l^{-1}$) | $Mg^{2+}$ ($mg\,l^{-1}$) | $Na^+$ ($mg\,l^{-1}$) | $K^+$ ($mg\,l^{-1}$) | $F^-$ ($mg\,l^{-1}$) | $Cl^-$ ($mg\,l^{-1}$) | $NO_3^-$ ($mg\,l^{-1}$) | $NO_2^-$ ($mg\,l^{-1}$) | $NH_4^+$ ($mg\,l^{-1}$) | $Fe^{2+}$ ($mg\,l^{-1}$) | $Mn^{2+}$ ($mg\,l^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| October 2006 | | | | | | | | | | | | | | | | | | |
| F | 7.3 | 1919 | 1180 | 780 | 952 | 750 | 84 | 116 | 112 | 152 | 31 | 0.7 | 192 | 4 | 0.04 | 0.03 | 0.56 | 0.07 |
| E | 7.2 | 772 | 470 | 320 | 390 | 370 | 19 | 104 | 27 | 47 | 13 | 0.5 | 71 | 4 | 0.05 | <0.03 | 0.5 | <0.03 |
| D | 7.0 | 2560 | 1600 | 460 | 561 | 640 | 148 | 156 | 61 | 312 | 37 | 0.4 | 554 | 4 | <0.01 | 1.5 | 0.15 | 0.15 |
| C | 7.1 | 4120 | 2420 | 610 | 744 | 750 | 70 | 152 | 90 | 548 | 36 | 0.4 | 994 | 10 | 0.2 | 0.09 | 0.6 | <0.03 |
| B | 7.1 | 3380 | 1980 | 555 | 677 | 640 | 139 | 184 | 44 | 451 | 26 | 0.4 | 639 | 97 | 0.25 | <0.03 | 0.1 | 0.05 |
| A | 7.1 | 985 | 640 | 390 | 476 | 450 | 28 | 128 | 32 | 58 | 14 | 0.2 | 85 | 7 | 0.01 | <0.03 | 0.56 | 0.04 |
| July 2008 | | | | | | | | | | | | | | | | | | |
| 1 | 7.1 | 11,120 | 7418 | 644 | 1400 | 785 | 593 | 220 | 206 | 1535 | 40 | 0.6 | 3182 | 54 | <0.01 | <0.03 | | |
| 2 | 7.7 | 990 | 663 | 292 | 154 | 356 | 33 | 44 | 11 | 78 | 9.8 | 0.4 | 98 | 31 | <0.01 | <0.03 | | |
| 3 | 7.6 | 757 | 505 | 361 | 172 | 440 | 15 | 24 | 27 | 74 | 17 | 0.4 | 30 | 4 | <0.01 | <0.03 | | |
| 4 | 7.7 | 744 | 499 | 322 | 160 | 392 | 19 | 38 | 16 | 68 | 11 | 0.3 | 45 | 4 | <0.01 | <0.03 | | |
| 5 | 7.3 | 1187 | 790 | 559 | 122 | 682 | 16 | 24 | 15 | 103 | 10 | 0.2 | 65 | 4 | <0.01 | <0.03 | | |
| 6 | 7.4 | 2620 | 1745 | 431 | 380 | 526 | 115 | 92 | 36 | 242 | 25 | 0.4 | 536 | 4 | <0.01 | <0.03 | | |
| 7 | 7.4 | 1135 | 760 | 416 | 90 | 508 | 4 | 26 | 6 | 145 | 11 | 0.4 | 110 | 4 | <0.01 | <0.03 | | |
| 8 | 7.6 | 571 | 380 | 198 | 168 | 242 | 11 | 44 | 14 | 15 | 8.1 | 0.2 | 32 | 24 | <0.01 | <0.03 | | |
| 9 | 8.4 | 218 | 149 | 99 | 42 | 121 | 4 | 12 | 3 | 30 | 5.1 | 0.2 | 12 | 5 | <0.01 | <0.03 | | |
| 10 | 8.1 | 899 | 601 | 317 | 100 | 387 | 25 | 13 | 16 | 102 | 18 | 0.2 | 81 | 4 | <0.01 | <0.03 | | |
| 11 | 7.3 | 1481 | 986 | 651 | 308 | 794 | 9 | 36 | 53 | 96 | 22 | 0.4 | 110 | 7 | <0.01 | <0.03 | | |
| 12 | 7.5 | 8650 | 5770 | 1292 | 612 | 1576 | 48 | 28 | 132 | 1475 | 59 | 0.5 | 2091 | 30 | 0.01 | <0.03 | | |
| 13 | 7.8 | 2560 | 1710 | 851 | 374 | 1038 | 333 | 48 | 62 | 304 | 41 | 0.6 | 180 | 3 | <0.01 | <0.03 | | |
| 14 | 7.6 | 1085 | 725 | 376 | 150 | 459 | 45 | 48 | 7 | 92 | 20 | 0.4 | 94 | 3 | <0.01 | <0.03 | | |
| 15 | 7.5 | 587 | 395 | 332 | 320 | 405 | 1 | 43 | 52 | 13 | 4.5 | 0.3 | 12 | 3 | <0.01 | <0.03 | | |
| 16 | 8.1 | 1193 | 796 | 394 | 72 | 481 | 39 | 14 | 9 | 210 | 17 | 0.5 | 125 | 4 | <0.01 | <0.03 | | |
| 17 | 7.8 | 774 | 519 | 302 | 340 | 368 | 22 | 48 | 53 | 55 | 10 | 0.3 | 68 | 4 | <0.01 | <0.03 | | |
| 18 | 7.3 | 1159 | 774 | 480 | 242 | 586 | 1 | 65 | 19 | 121 | 19 | 0.3 | 115 | 4 | 0.05 | <0.03 | | |
| 19 | 7.8 | 1112 | 744 | 540 | 166 | 659 | 1 | 42 | 15 | 174 | 21 | 1.1 | 58 | 4 | <0.01 | <0.03 | | |
| 20 | 7.4 | 11,390 | 7599 | 1403 | 536 | 1712 | 158 | 71 | 87 | 1995 | 65 | 0.9 | 2864 | 51 | <0.01 | <0.03 | | |
| 21 | 7.6 | 3770 | 2518 | 589 | 250 | 719 | 67 | 33 | 41 | 625 | 35 | 0.7 | 836 | 7 | <0.01 | <0.03 | | |
| 22 | 7.8 | 563 | 375 | 228 | 84 | 278 | 10 | 28 | 3 | 27 | 4.4 | 0.3 | 41 | 3 | <0.01 | <0.03 | | |
| 23 | 8.0 | 2390 | 1597 | 1109 | 113 | 1353 | 1 | 21 | 15 | 399 | 28 | 1.7 | 160 | 3 | <0.01 | <0.03 | | |
| 24 | 7.4 | 720 | 482 | 386 | 152 | 471 | <1 | 32 | 17 | 32 | 7.1 | 0.2 | 23 | 3 | <0.01 | <0.03 | | |
| 25 | 8.1 | 686 | 458 | 267 | 155 | 326 | 16 | 21 | 25 | 55 | 19 | 0.2 | 62 | 3 | <0.01 | <0.03 | | |

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| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 26 | 8 | 857 | 573 | 238 | 157 | 290 | 23 | 21 | 25 | 57 | 22 | 0.2 | 104 | 28 | <0.01 | <0.03 |
| 28 | 7.1 | 855 | 572 | 421 | 170 | 514 | <1 | 37 | 19 | 23 | 16 | 0.4 | 45 | 4 | <0.01 | <0.03 |
| 29 | 7.3 | 1599 | 1069 | 644 | 227 | 786 | <1 | 32 | 36 | 138 | 16 | 0.6 | 147 | 14 | <0.01 | <0.03 |
| 30 | 7.8 | 619 | 414 | 327 | 180 | 399 | 1 | 43 | 18 | 41 | 12 | 0.6 | 23 | 4 | <0.01 | <0.03 |
| 31 | 7.5 | 571 | 382 | 287 | 98 | 350 | 6 | 21 | 11 | 26 | 5.1 | 0.3 | 22 | 4 | <0.01 | <0.03 |
| 32 | 7.1 | 809 | 542 | 406 | 146 | 495 | <1 | 34 | 15 | 35 | 8.6 | 0.4 | 39 | 4 | <0.01 | <0.03 |
| 33 | 7.5 | 687 | 460 | 312 | 168 | 381 | 12 | 29 | 23 | 40 | 10 | 0.3 | 40 | 4 | <0.01 | <0.03 |
| 34 | 6.9 | 1374 | 919 | 589 | 214 | 719 | <1 | 27 | 36 | 82 | 9.5 | 0.2 | 115 | 3 | <0.01 | <0.03 |
| 35 | 6.9 | 1215 | 811 | 540 | 196 | 659 | <1 | 26 | 32 | 75 | 13 | 0.8 | 89 | 4 | <0.01 | <0.03 |
| 36 | 7.1 | 1081 | 722 | 480 | 164 | 586 | <1 | 33 | 20 | 57 | 8.1 | 0.3 | 69 | 5 | <0.01 | <0.03 |
| 37 | 6.9 | 1155 | 771 | 540 | 182 | 659 | <1 | 32 | 25 | 60 | 17 | 0.4 | 66 | 4 | <0.01 | <0.03 |
| 38 | 6.9 | 1130 | 757 | 520 | 196 | 634 | <1 | 34 | 27 | 85 | 12 | 0.3 | 67 | 4 | <0.01 | <0.03 |
| 39 | 7.4 | 730 | 490 | 339 | 127 | 414 | <1 | 36 | 9 | 56 | 9.2 | 0.2 | 37 | 4 | <0.01 | <0.03 |
| 42 | 7.7 | 780 | 522 | 317 | 211 | 387 | 25 | 57 | 17 | 87 | 17 | 0.3 | 55 | 8 | <0.01 | <0.03 |

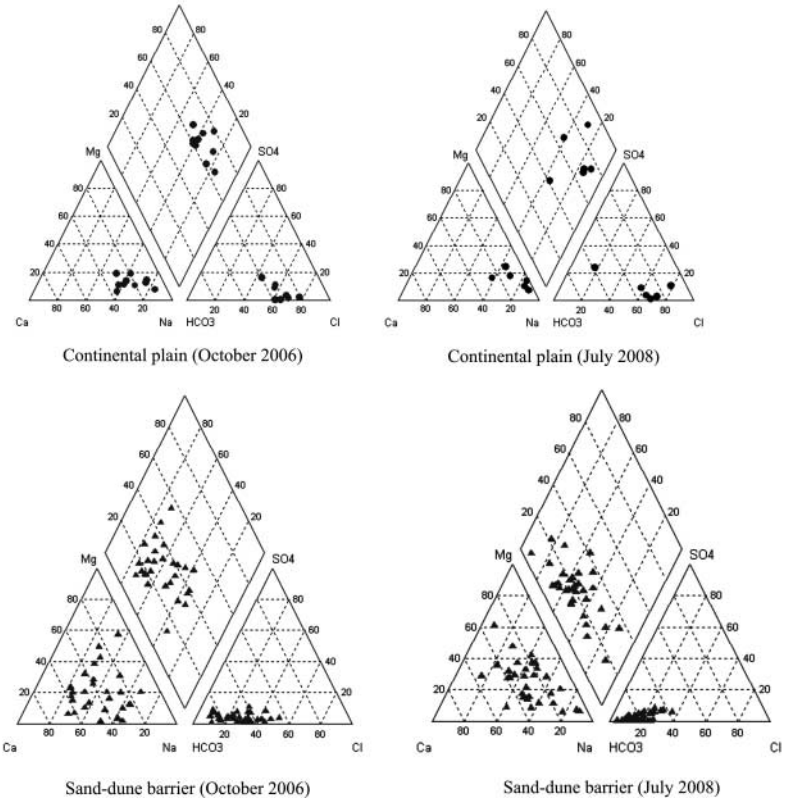


Figure 5. Piper diagrams for the groundwater samples according to the geomorphological environment.

with the samples having been taken near houses that are not connected to the sewer system and that have cesspit tanks. Nitrite content ranges from 0.01 to 0.2 mg $l^{-1}$. Ammonium also has low concentrations, in general lower than 0.03 mg $l^{-1}$.

According to these results, it can be observed that, in general, the lower concentrations occur in the samples taken in July 2008 (Table 4). In the sand-dune environment, which is the main area of recharge, in June 2008 the water surplus was 45 mm and in July 2008 it was 25 mm, while in September 2006 it was 0 mm and in October 2006 it was 16 mm. Higher surpluses in July 2008 might promote the dilution of the chemical components. Higher concentrations occur in the October 2006 samples, which could be due to the fact that in this month PET (69 mm) is higher than in July 2008 (37 mm), and that evaporation processes in the water table are favoured due to the shallowness of the groundwater (Table 2).

The continental plain, according to the samples collected in October 2006, is characterised by an average TDS higher than 2400 mg $l^{-1}$ with extreme values of 4190 mg $l^{-1}$ (Figure 6). Chloride contents vary between 200 and 1633 mg $l^{-1}$. As for the bicarbonate, it ranges from 300 to 1684 mg $l^{-1}$ and sulphate contents are lower than 150 mg $l^{-1}$. Sodium concentrations are between 188 and 1220 mg $l^{-1}$, and potassium contents are between 26 and 47 mg $l^{-1}$. Magnesium contents vary between 11 and 124 mg $l^{-1}$ and calcium concentrations range from 88 to 236 mg $l^{-1}$.

The samples taken in the July 2008 survey show an average TDS higher than 4000 mg $l^{-1}$, with extreme values of 7599 mg $l^{-1}$ (Figure 6). Chloride contents vary between 180 and 3182 mg $l^{-1}$. As for the bicarbonate, it ranges from 526 to 1712 mg $l^{-1}$. Sulphate contents range from 48 to 593 mg $l^{-1}$, sodium concentrations are between 242 and 1995 mg $l^{-1}$, and potassium contents are

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Table 4. Average, maximum and minimum concentrations calculated for each survey for the sand-dune barrier and the continental plain.

| | Sand dune | | | | | | Continental plain | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | October 2006 Avg[a] | October 2006 Max[b] | October 2006 Min[c] | July 2008 Avg[a] | July 2008 Max[b] | July 2008 Min[c] | October 2006 Avg[a] | October 2006 Max[b] | October 2006 Min[c] | July 2008 Avg[a] | July 2008 Max[b] | July 2008 Min[c] |
| pH | 7.3 | 7.9 | 6.7 | 7.5 | 8.4 | 6.9 | 7.2 | 7.3 | 7.0 | 7.5 | 7.8 | 7.1 |
| E.C ($\mu S\,cm^{-1}$) | 1279 | 2200 | 644 | 961 | 2390 | 218 | 4237 | 7000 | 1459 | 6685 | 11,390 | 2560 |
| TDS ($mg\,l^{-1}$) | 777 | 1710 | 310 | 642 | 1597 | 149 | 2483 | 4190 | 1090 | 4460 | 7599 | 1710 |
| Alkalinity ($mg\,l^{-1}$) | 441 | 780 | 250 | 412 | 1109 | 99 | 687 | 1380 | 250 | 868 | 1403 | 431 |
| Total hardness ($mg\,l^{-1}$) | 369 | 860 | 150 | 168 | 340 | 42 | 648 | 900 | 295 | 592 | 1400 | 250 |
| $Ca^{2+}$ ($mg\,l^{-1}$) | 97 | 264 | 20 | 33 | 65 | 12 | 155 | 236 | 88 | 82 | 220 | 28 |
| $Mg^{2+}$ ($mg\,l^{-1}$) | 32 | 112 | 3 | 21 | 53 | 3 | 63 | 124 | 11 | 94 | 206 | 36 |
| $Na^{+}$ ($mg\,l^{-1}$) | 121 | 281 | 39 | 83 | 399 | 13 | 643 | 1220 | 188 | 1029 | 1995 | 242 |
| $K^{+}$ ($mg\,l^{-1}$) | 22 | 43 | 9.8 | 13 | 28 | 4.4 | 38 | 47 | 26 | 44 | 65 | 25 |
| $Fe^{2+}$ ($mg\,l^{-1}$) | 0.39 | 3.5 | 0.03 | | | | 0.2 | 0.6 | 0.05 | | | |
| $Mn^{2+}$ ($mg\,l^{-1}$) | 0.24 | 1.2 | 0.04 | | | | 0.3 | 0.4 | 0.05 | | | |
| $HCO_3^{-}$ ($mg\,l^{-1}$) | 539 | 952 | 305 | 502 | 1353 | 121 | 838 | 1684 | 305 | 1059 | 1712 | 526 |
| $SO_4^{2-}$ ($mg\,l^{-1}$) | 27 | 84 | 6 | 15 | 45 | 1 | 60 | 148 | 9 | 219 | 593 | 48 |
| $NH_4^{+}$ ($mg\,l^{-1}$) | 0.16 | 1 | 0.03 | < 0.03 | < 0.03 | < 0.03 | 0.3 | 1.5 | 0.03 | < 0.03 | < 0.03 | < 0.03 |
| $F^{-}$ ($mg\,l^{-1}$) | 0.40 | 0.8 | 0.2 | 0.4 | 1.7 | 0.2 | 0.6 | 1.4 | 0.2 | 0.6 | 0.9 | 0.4 |
| $Cl^{-}$ ($mg\,l^{-1}$) | 142 | 362 | 28 | 68 | 160 | 12 | 969 | 1633 | 195 | 1615 | 3182 | 180 |
| $NO_3^{-}$ ($mg\,l^{-1}$) | 15 | 180 | 3 | 6.5 | 31 | 3 | 41 | 180 | 4 | 25 | 54 | 3 |
| $NO_2^{-}$ ($mg\,l^{-1}$) | 0.09 | 0.2 | 0.01 | 0.05 | 0.05 | 0.05 | 0.2 | 0.3 | 0.03 | 0.01 | 0.01 | 0.01 |

[a]Average.
[b]Maximum.
[c]Minimum.

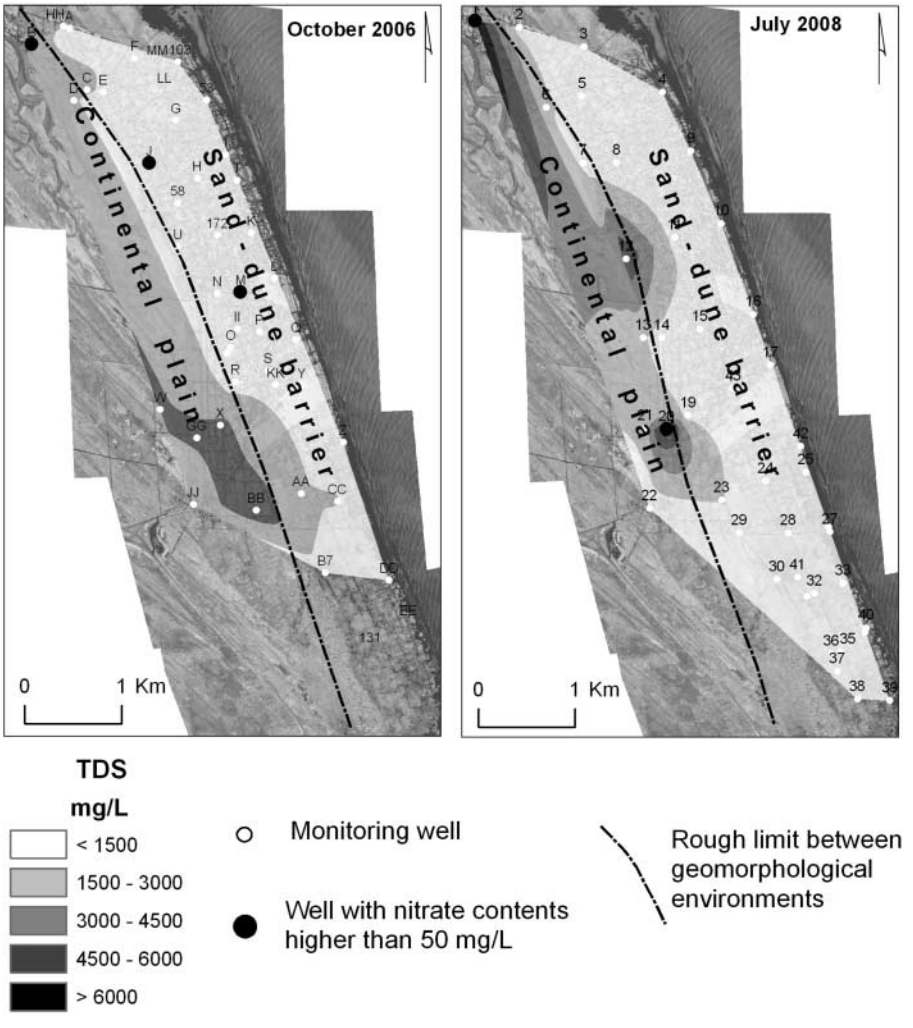


Figure 6. Distribution of TDS for the study area and wells with high nitrate contents.

between 25 and 65 mg $l^{-1}$. Magnesium contents vary between 36 and 206 mg $l^{-1}$ and calcium concentrations range from 28 to 220 mg $l^{-1}$.

Just as for the sand-dune barrier, nitrate, nitrite and ammonium contents are mostly the same for both surveys. As for nitrates, concentration values are between 3 and 31 mg $l^{-1}$, but there are also some particular cases with higher concentrations: between 97 and 180 mg $l^{-1}$ in 2006, and 51 and 54 mg $l^{-1}$ in 2008 (Figure 6). The source of nitrates is also anthropogenic. Nitrite concentrations range from 0.01 to 0.3 mg $l^{-1}$ and ammonium also has low concentrations, in general, around 0.03 mg $l^{-1}$.

In the continental plain, the higher concentrations are observed in the samples taken in July 2008 (Table 4). The connection of the continental plain with the Samborombón Bay through tidal channels and the tidal influence are factors that could modify the chemical composition, concealing any seasonal effects. In addition, the area is affected by storm surges locally known as *sudestadas* (southeasters) [47], which are strong winds from the east–southeast sector that cause an additional mean water level rise and the advance of the brackish water from the bay towards the

continental plain, modifying the concentration of the chemical components and, consequently, the groundwater.

A relationship between the geomorphological environments and the majority of the chemical components was expected to be corroborated; however, this was not possible in the case of iron and manganese. The sand from the sand dune contains a significant fraction of magnetic minerals coming from uncoloured, brown and black volcanic glass with magnetite inclusions and hematitisation phenomena, and individual crystals of magnetite showing replacement by hematite [48]. The phreatic aquifer is considered to be homogeneous and, for this reason, it was expected that a homogeneous distribution of iron and manganese would be found in this environment. In the continental plain, with silty clay sediments, lower concentrations were expected. Iron and manganese were only analysed for the 2006 survey. Iron concentrations range from 0.03 to 3.5 mg $l^{-1}$, and manganese concentrations range from 0.04 to 1.2 mg $l^{-1}$. The maximum values for both are located in the southern sector of the sand dune. For manganese, there are high values in the central area of the sand dune, and they decrease, in general, in the flow direction toward the east and the west. There is no particular pattern for iron distribution.

### 4.3. *Isotopic composition*

As indicated above, in order to interpret the isotopic composition of the hydrological system, the long records from the GNIP stations of Buenos Aires and Azul were used [28,29,32]. These stations are close to San Clemente del Tuyú and they are representative of the hydrological Pampean systems. The long-term regional isotopic composition records show a wide range of variation mainly due to the source of the vapour mass and also to a seasonal effect, as well as to other processes that modified the climate of the region, such as the ENSO phenomena, ITCZ zone and the low-level jet [28,29,40,49,50]. The precipitation samples collected in Buenos Aires and Azul show a good correlation between temperature and mean monthly isotope composition from January to April. Nevertheless, an inversion of the slope can be observed during the colder months (May–August) [28,29,51]. In addition, in certain years, the most depleted values are recorded

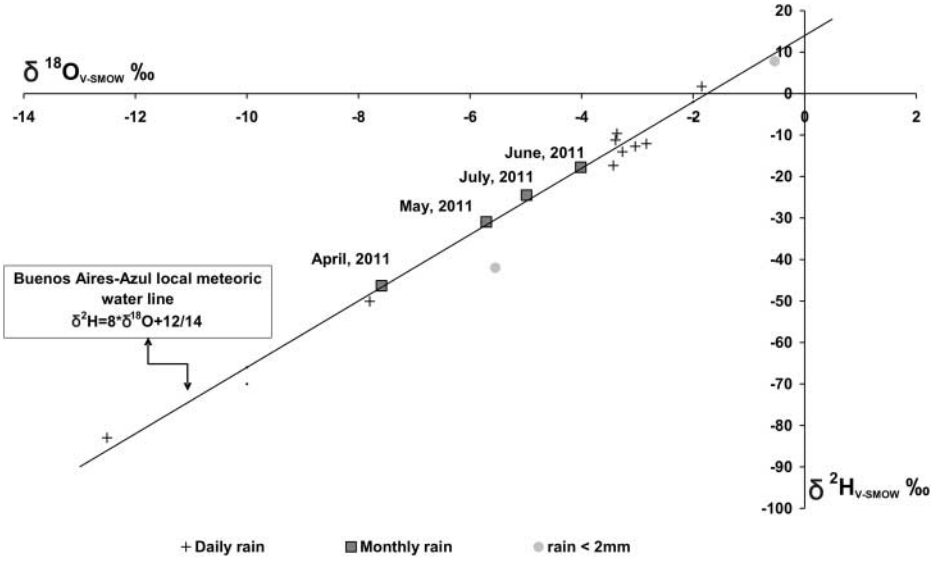


Figure 7. $\delta^2H$ versus $\delta^{18}O$ diagram of daily and monthly rain samples showing the Buenos Aires – Azul local meteoric line.

Table 5. $\delta^{18}O$ and $\delta^{2}H$ values, TDS, chloride (Cl) and EC for the 2009 samples.

| Well # | Location in the sand dune | $\delta^{18}O$ ‰ V-SMOW | $\delta^{2}H$ ‰ V-SMOW | TDS (mg $l^{-1}$) | Cl (mg $l^{-1}$) | EC ($\mu$S $cm^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | Western area | −4.5 | −27 | 7580 | 3061 | 10,770 |
| 6 | | −5.7 | −35 | 1850 | 482 | 2550 |
| 12 | | −4.8 | −30 | 9251 | 3422 | 12,530 |
| 3 | Central area | −5.0 | −29 | 543 | 38 | 770 |
| 5 | | −5.3 | −30 | 776 | 123 | 1113 |
| 43 | | −5.2 | −30 | 817 | 90 | 130 |
| 23 | | −5.9 | −36 | 1088 | 94 | 1515 |
| 24 | | −5.7 | −32 | 494 | 22 | 714 |
| 38 | | −4.6 | −25 | 1167 | 160 | 1623 |
| 41 | | −5.3 | −30 | 1230 | 270 | 1777 |
| 4 | Eastern area | −4.3 | −21 | 424 | 29 | 605 |
| 25 | | −5.3 | −30 | 469 | 67 | 680 |
| 33 | | −5.4 | −31 | 451 | 41 | 652 |
| 39 | | −6.8 | −39 | 415 | 27 | 589 |

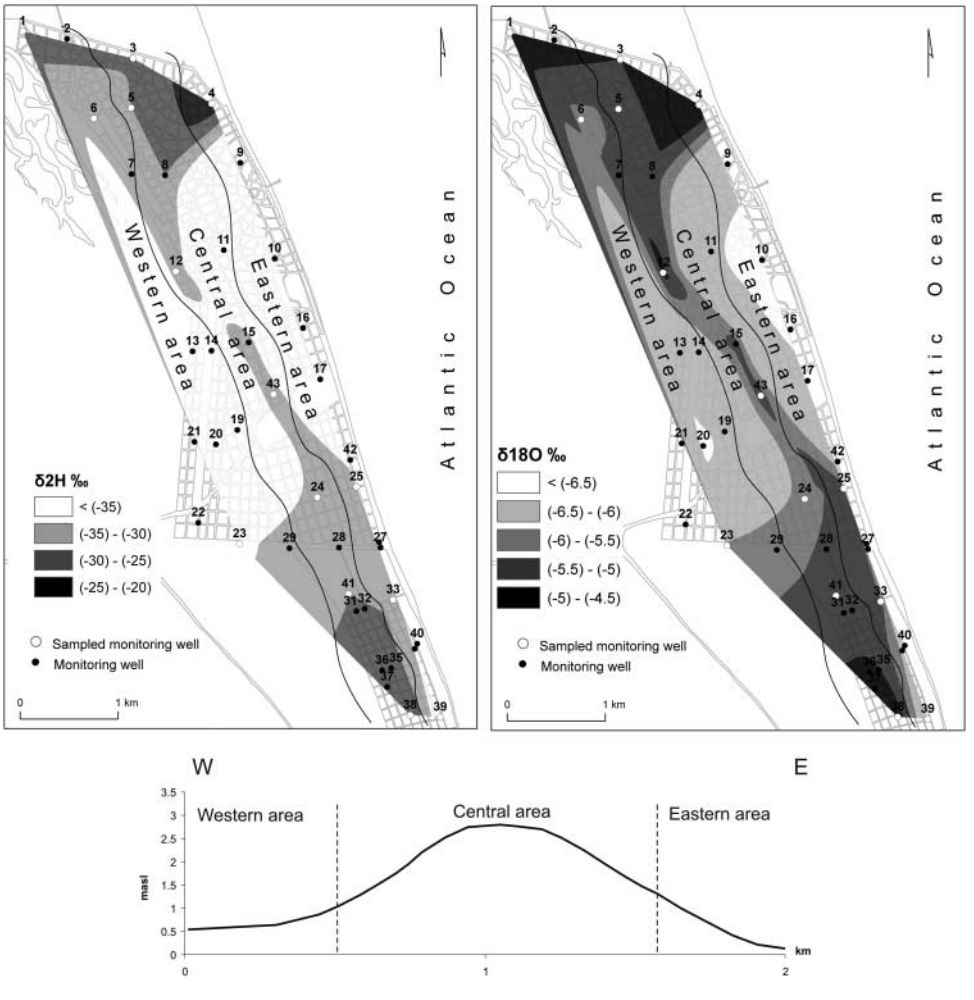


Figure 8. Distribution maps of $\delta^{18}O$ and $\delta^{2}H$ with a schematic of a topographic W–E section.

during the February–March period (Southern Hemisphere summer). This pattern is marked by more depleted contents, with $\delta^{18}O$ values lower than −10 ‰, certainly linked to the air mass source. Despite the fact that the San Clemente del Tuyú isotope record station is not sufficient to estimate the local meteoric line, the monthly weighted average could be calculated for April, May, June and July 2011. The distribution of the daily and monthly local rain water composition along the Buenos Aires – Azul local meteoric line are shown in Figure 7 in order to illustrate the previously mentioned rain variability.

The general groundwater isotopic composition of the area ranges from −6.8 to −4.3 ‰ for $\delta^{18}O$ and from −39 to −21 ‰ for $\delta^{2}H$ (Table 5). Although there is some expected overlap of the isotope content according to the dune morphology, the wells located in the western area of the sand dune are represented by $\delta^{18}O$ values from −5.7 to −4.5 ‰ and by $\delta^{2}H$ values from −35 to −27 ‰. The groundwater in the central area of the dune varies in $\delta^{18}O$ between −5.9 and −4.6 ‰ and from −36 to −29 ‰ for $\delta^{2}H$. The eastern area is characterised by $\delta^{18}O$ values from −6.8 to −4.3 ‰, while $\delta^{2}H$ is between −39 and −21 ‰ (Figure 8). The relatively more enriched values observed in the central area in an E–W profile in the sampled period are explained by the fact that the recharge is greater in the centre of the dune in the dry season and also by the fact that the average isotope composition of precipitation, the only source of recharge, during the dry season is comparatively more enriched.

Some of the variations in the groundwater isotopic contents observed in each area could be due to the action of several combined local processes, such as rain variability, selective infiltration, evaporation prior to infiltration or evaporation from the phreatic zone, and percolation through preferential channels – all of which do not alter the isotopic composition of the original rain associated with the permeability of the sediments – as well as water mixing – e.g. with water from the continental plain, seawater, etc. Panarello et al. [51] also explained the variations in groundwater isotopic compositions using the same phenomena in an earlier research project carried out in the coastal area of the province of Buenos Aires.

Figure 9 shows the conventional $\delta^{2}H$ versus $\delta^{18}O$ plot, where the groundwater samples collected in San Clemente del Tuyú are located along the Buenos Aires – Azul meteoric water line, indicating

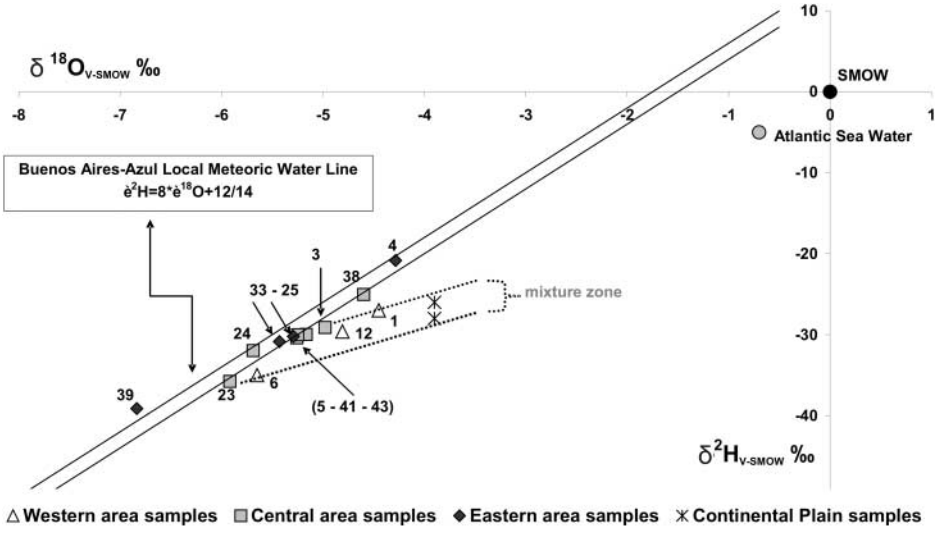


Figure 9. $\delta^{2}H$ versus $\delta^{18}O$ diagram of all samples with continental plain samples from Carol et al. [25], the Buenos Aires – Azul local meteoric line, SMOW (standard mean ocean water).

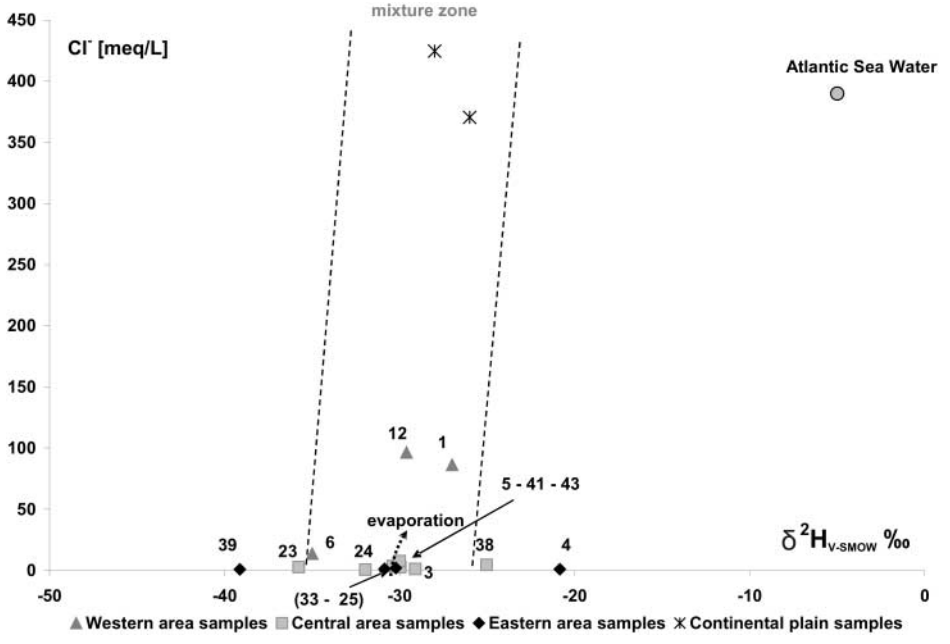


Figure 10. $\delta^2$H versus chloride diagram. Samples from the continental plain [25] represent the brackish end member.

the meteoric origin of groundwater. It can be observed that the groundwater samples from the central area of the dune show some evaporation following an evaporation line.

The groundwater samples from the western area depart from the meteoric local line. This phenomenon could be produced by evaporation or by the mixing of fresh water and salt or brackish water [52,53]. In this case, it could be due to both processes, in which the mixture results from the adjacent brackish water of the continental plain. In the $\delta^2$H versus chloride scatter plot (Figure 10), it is possible to infer this mixing zone, which is also consistent with chemical parameters such as EC and TDS. It was also corroborated by plotting two samples, representing the end member ($\delta^2\mathrm{H} \cong -27$ ‰, $\mathrm{Cl} \cong 390\ \mathrm{mEq\,l^{-1}}$), taken by Carol et al. [25] from areas in the proximity of the continental plain. Also, the isotopic composition of a sea-water sample taken from the Atlantic Ocean near the study area was plotted in the diagram in order to support or reject the existence of a groundwater mixing process.

On the eastern side of the sand dune, where the fresh water–marine salt water interface is located, saltwater intrusion might be possible. Upon comparing groundwater samples with the Atlantic Ocean salt water, no mixing process was observed (Figures 9 and 10) indicating the absence of the saltwater intrusion phenomenon in this area.

## 5. Conclusions

The chemical data made it possible to recognise that the groundwater chemistry in the geomorphological environments described is influenced by different hydrological processes.

Low-salinity Ca-$HCO_3$ and Na-$HCO_3$-type water from the sand-dune barrier respond to the rapid infiltration of precipitation through sandy sediments.

In the continental plain, high-salinity Na-Cl-type water might be produced by the larger contact time between the water and the silty clay soils, which favours the dissolution of chemical

components. Besides, this is an area which is connected to tidal channels and is frequently flooded by them, thus contributing brackish water to the phreatic aquifer.

A seasonal variability has been recognised and shows that in the sand dune the lowest concentrations occur in the samples taken in July 2008, associated to a higher recharge and lower evaporation. In the continental plain, the highest concentrations were observed in the July 2008 samples. The connection of the continental plain with the Samborombón Bay through tidal channels and the tidal influence might modify the chemical composition, masking any seasonal effect.

The analysis through the use of the stable isotopes oxygen-18 and deuterium allows us to verify that rainwater infiltrates quickly in the sandy substrate, reaching the water table almost without modification in its isotopic composition. Also, this methodology combined with other chemical parameters made it possible to corroborate that, for the time being, in the eastern area of the phreatic aquifer, there is no contamination by marine salt water. In addition, in the western area, the mixture with brackish water from the continental plain has been verified. The groundwater samples from the central area of the dune show some evaporation following an evaporation line. The aquifer is a dynamic system where the groundwater reflects the importance of recharge in the dunes and the variability in the regional precipitation.

The groundwater from the continental plain is unfit for human consumption due to the high salinity and high contents of most of the chemical components. On the other hand, groundwater in the sand dunes is suitable for drinking except in the areas with high concentration of iron and manganese and some specific locations with high nitrate contents. Even though saltwater intrusion was not detected, in order to maintain this situation, groundwater should be pumped using only low-flow water wells, drilled to a shallow depth and with a system similar to the one in the pumping field. The same precaution should be taken in order to avoid brackish water intrusion from the continental plain.

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