



## Application of isotopic and hydrogeochemical techniques to evaluate mixing processes in groundwater systems from a coastal area in Argentina

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### ABSTRACT

Groundwater plays a fundamental role in supporting productive, domestic, and touristic activities in the Lobería District. In this region, two aquifers coexist: a regional aquifer (Pampeano Aquifer) and a local aquifer confined to the coastal dunes, referred to in this study as the Sand-dune Aquifer. To investigate their interaction, an End-Member Mixing Analysis (EMMA) was performed using conservative tracers, including hydrochemical data and stable water isotopes, based on measurements from 32 extraction wells. The results reveal significant groundwater exchange between the Sand-dune and Pampeano Aquifers, with notable contributions in both directions. Well G251 in the Sand-dune Aquifer receives 68% of its contribution from the Sand-dune Aquifer and 32% from the Pampeano Aquifer. Conversely, wells G1027 and G1028 in the Pampeano Aquifer have contributions of 32% and 49% from the Sand-dune Aquifer and 68% and 51% from the Pampeano Aquifer, respectively. However, stable water isotopes were ineffective as tracers for quantifying mixing due to shared recharge conditions and similar isotopic signatures. These findings enhance our understanding of groundwater interactions and provide valuable insights for the integrated management of groundwater resources.

*Keywords: Groundwater; Aquifer; Mixing processes; Hydrogeochemistry; Water isotopes; Management*

## Aplicación de técnicas isotópicas e hidrogeoquímicas para evaluar los procesos de mezcla en sistemas de agua subterránea de una zona costera en Argentina

### RESUMEN

El agua subterránea desempeña un papel fundamental para el desarrollo de actividades productivas, domésticas y turísticas en el Partido de Lobería. En esta región, coexisten dos acuíferos: un acuífero regional (Acuífero Pampeano) y un acuífero local confinado a las dunas costeras, denominado en este estudio como Acuífero Medanosos. Para investigar su interacción, se realizó un Análisis de Mezcla de Componentes Extremos (EMMA, por sus siglas en inglés) utilizando trazadores conservativos, que incluyen datos hidroquímicos e isótopos estables del agua, a partir de mediciones en 31 pozos de extracción. Los resultados revelan un intercambio significativo de agua subterránea entre los acuíferos Medanosos y Pampeano, con contribuciones notables en ambas direcciones. El pozo G251 ubicado en el Acuífero Medanosos recibe un 68% de su aporte del Acuífero Medanosos y un 32% del Acuífero Pampeano. Por el contrario, los pozos G1027 y G1028 ubicados en el Acuífero Pampeano presentan contribuciones del 32% y 49% del Acuífero Medanosos, y del 68% y 51% del Acuífero Pampeano, respectivamente. Los isótopos estables del agua no resultaron efectivos como trazadores para cuantificar la mezcla debido a condiciones de recarga compartidas y firmas isotópicas similares. Estos hallazgos mejoran la comprensión de las interacciones del agua subterránea y proporcionan información valiosa para la gestión integrada de los recursos hídricos subterráneos.

*Palabras clave: Agua subterránea; acuífero; procesos de mezcla; hidrogeoquímica; Isótopos del agua; gestión*

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## 1. Introduction

Approximately 60% of the global population lives less than 60 km from the coast, and this is expected to increase to 75% in the next two decades (Neumann et al. 2015). This demographic trend, coupled with accelerating agricultural, industrial, and touristic development, has significantly impacted coastal groundwater systems (Odeloui et al., 2022). Urbanization-driven transformation of natural ecosystems exacerbates groundwater quality degradation, posing critical challenges to drinking water security in these regions (Liu et al., 2022). Addressing the dual concerns of groundwater quantity and quality is a key challenge of the 21st century, requiring integrated management strategies to mitigate resource depletion and contamination risks while supporting regional development (UNESCO, 2022).

In Argentina, coastal zones represent the most densely populated and infrastructure-intensive areas (Dadon and Matteucci, 2009). The Atlantic coastline of Buenos Aires Province, extending over 600 km, includes more than 30 seaside towns within thirteen municipalities, each exhibiting distinct hydrogeological, demographic, and economic profiles. In this region, the phreatic aquifer serves as the primary source of water for human consumption, particularly in areas where tourism and recreational activities dominate local economies (Dadon and Matteucci, 2009). However, rapid urban expansion and seasonal population surges, driven by tourism, have intensified pressures on coastal groundwater resources, particularly in under-monitored and vulnerable zones (Carretero et al., 2014; Carretero et al., 2024).

The coastal area of the Lobería District, located in the southern part of Buenos Aires Province, exemplifies these challenges. Historically a hub for tourism, the district experiences significant seasonal population increases, with up to 4,000 additional visitors per weekend during summer months. This influx is further compounded by the expansion of tourist complexes and residential developments (gated communities), which, while boosting local economies, also impose substantial demands on groundwater resources. These developments underscore the need for a comprehensive understanding of the region's hydrogeological dynamics to ensure sustainable management of its water resources (Zulaica and Aguilar, 2009).

Groundwater in this region is sourced exclusively from two unconfined aquifers: the regional Pampeano Aquifer and the local Sand-dune Aquifer, that overlaps the first, restricted to the coastal dunes. Their interactions are poorly understood, creating significant challenges for sustainable water resource management. The unconfined nature of these systems renders them particularly susceptible to contamination from anthropogenic activities, including agricultural runoff, wastewater disposal, and saline intrusion. Furthermore, insufficient monitoring of groundwater extraction exacerbates the potential for resource overexploitation and quality degradation.

Interactions between shallow and deeper aquifers have been extensively studied in other coastal settings due to their implications for groundwater quality and sustainability. Shallow aquifers are more vulnerable to contamination, and their interaction with deeper aquifers can facilitate the spread of pollutants, posing significant management challenges (Toth and Katz, 2006; Warner et al., 2016; Zhang et al., 2016; Wali et al., 2019; Jat Baloch et al., 2021). Key processes such as recharge, mixing, mineral dissolution/precipitation, and ion exchange are critical in governing groundwater quality and must be fully characterized to inform management strategies (Tubau et al., 2014; Jean-Baptiste et al., 2020).

To address these challenges, hydrogeochemical and isotopic techniques provide invaluable tools for characterizing recharge sources, salinization mechanisms, and aquifer mixing dynamics (Carretero et al. 2022; Glok Galli et al. 2023; Quiroz Londoño et al. 2008; Zhou et al. 2017), as well as the formulation of water balance terms (Baijiali et al. 1997; Mook and Rozanski 2000). End-Member Mixing Analysis (EMMA) is a widely applied methodology for quantifying mixing proportions in groundwater systems, relying on the identification of potential recharge sources and their hydrochemical and isotopic signatures, as well as the use of conservative tracers to evaluate mixing processes (Tubau et al., 2014; Pelizardi et al., 2017; Lone et al., 2021; Marx et al., 2021; Pall et al., 2023).

The objective of this study is to characterize hydrochemically and isotopically the Pampeano and Sand-dune Aquifers in the coastal region of Lobería to better understand their mixing processes and improve the conceptual hydrogeological model of the region. Specifically, the study evaluates the extent of aquifer mixing in newly developed wells associated with tourism

and scattered housing, utilizing simple water parameters as early warning indicators of potential groundwater degradation. The findings aim to support sustainable groundwater management by providing actionable insights into aquifer dynamics and long-term resource preservation. Additionally, this study contributes to addressing broader challenges of groundwater sustainability in coastal settings worldwide.

## 2. Study Area

The Lobería District is located in the south of the Buenos Aires Province, Argentina (Figure 1), bordering the Tandil District to the north, General Alvarado District to the east, Necochea District to the west, and the Atlantic Ocean to the south. Its coastal area is characterized by the presence of beaches with limited development, situated within the Southern Dune Barrier (Isla et al., 2001), which extends from the town of Miramar to the Coronel Rosales District, reaching maximum widths of up to 3 km. From a climatic perspective, according to the classification by Koeppen and Hendrichs Pérez (1948), temperate climate conditions prevail with a marked influence from the Atlantic Ocean.

Precipitation is predominant throughout the year, ranging between 800 and 900 mm, and the annual average temperature is around 15°C (Vazquez et al., 2017). These conditions are favorable for the development of agricultural activities. Land use in the region can be classified into tourism activities, residential areas, and productive processes. All these sectors obtain their water supply through private wells. The distribution of points of special interest is concentrated in the southwest zone, where the highest accumulation of data from both the deep and shallow aquifers is recorded, which could help define the possible interaction between these two aquifer systems.

Hydrogeologically, the map (Figure 1) shows that the groundwater flow lines (black lines) predominantly follow a north-to-south direction, discharging into the Atlantic Ocean, indicating a consistent hydraulic gradient. The coastal dunes are clearly delineated, acting as significant recharge areas, and the piezometric lines are represented, allowing the identification of groundwater movement from zones of high piezometric head to areas of low piezometric head. This pattern reflects the natural flow dynamics within the coastal hydrogeological system, regulated by geomorphological characteristics and the interaction with local aquifers



Figure 1. Location of the study area and groundwater sampling.

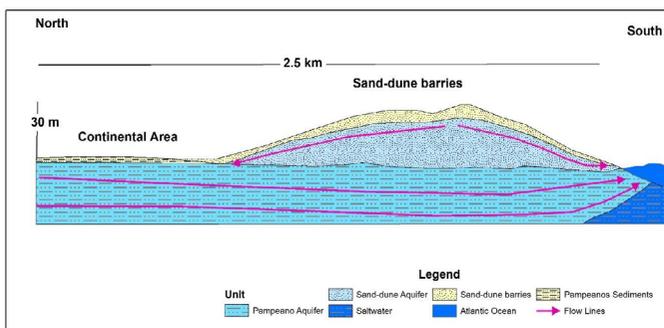
The coastal area of the Lobería District is recognized for the presence of two aquifers. The first, known as the Pampeano Aquifer, is a regional phreatic aquifer that exhibits semi-confined conditions at certain depths (Auge 2004). The hydrogeological basement consists of orthoquartzites from the Balcarce Formation and Precambrian igneous-metamorphic rocks, which outcrop in the hills that border the area to the north. It is estimated that the aquifer thickness in this sector of the inter-hill plain exceeds 100 meters (Quiroz Londoño et al. 2008). Recharge comes exclusively from precipitation, with evapotranspiration being the main form of water output. Various methods estimate an average recharge of 12% of total rainfall, with a value of 130 mm/year over the past

10 years (Giacobone et al. 2023; Quiroz-Londoño et al. 2012). Topography strongly influences the hydrological behavior of the region, with regional flow following a north-south direction with a low hydraulic gradient. Generally, the recharge zone corresponds to the hilly areas, while discharge occurs to the south, directly into the Atlantic Ocean. Average groundwater velocities range from 0.05 m/day (real velocity) to 0.0049 m/day (Darcy velocity), with 93% of the piezometric surface presenting a hydraulic gradient of less than 0.00396. Groundwater age calculations classify the aquifer as modern, with average values between 22.4 and 32.5 years, determined through tritium analysis (Quiroz Londoño et al. 2008).

The second aquifer, defined as the Sand-dune Aquifer, is restricted to the coastal dune area called the Southern Sandy Barrier (Isla et al., 1996; 2024), overlying the Pampeano Aquifer. This local unconfined aquifer has a thickness that does not exceed 20 meters (Quiroz et al., 2010) and presents storage coefficients of 0.2. Its hydraulic properties show permeability (K) values ranging from 2 to 9 m/day (Albouy et al., 2020), while more recent studies report ranges between 21 and 25 m/d, with an average value of 22 m/d (Carretero et al., 2022), highlighting the heterogeneity in its transmissivity.

The sedimentological characterization of the Dune Formation reveals a predominance of fine-grained sand (71.8-84.1%), complemented by smaller fractions of medium-grained sand (4-14%) and very fine sand (5.3-15.9%). Magnetic analyses indicate a distribution of magnetic and non-magnetic minerals in proportions of 15% and 85%, respectively. The petrographic composition includes between 30% and 60% opaque minerals, accompanied by shell fragments, subrounded quartz, plagioclases, and lithic particles, with subordinate presence of potassium feldspar, pyroxenes, olivine, and volcanic glass. The lithic fragments are predominantly of volcanic and sedimentary origin, with a significant presence of plutonic components in the very fine sand fraction (Carretero et al., 2022).

This dune system functions as a “barrier” that alters the regional hydrogeological flow towards the ocean, resulting in water enriched with salts to the northwest. A general schematic of the typical hydrogeological configuration of coastal regions in the province is shown in Figure 2. The natural discharge of water from the aquifer contained within the dunes occurs on both sides of these geoforms, towards the continental plain to the northwest and towards the ocean to the southeast, forming interfaces between freshwater and water with a higher salinity degree (Carretero 2011; Rodrigues Capítulo et al., 2017). This barrier also modifies the natural flow of streams in the area.



**Figure 2.** Typical hydrogeological configuration in the coastal dune sector of southeast Buenos Aires. The Pampeano Aquifer, Sand-dune barriers and the Sand-dune Aquifer are shown along with the groundwater flow lines.

The complex interaction between the two aquifer units poses significant challenges to the sustainable management of groundwater resources. The coexistence of intensive agricultural activities, tourism development, and urban expansion exerts multiple pressures on the hydrogeological system, disrupting its natural balance. Land-use changes, the construction of private infrastructure, and continuous water extraction represent critical factors that may compromise the quality and availability of water resources. These processes, combined with the potential interconnection between aquifers, increase the risk of contamination and water quality degradation, which could have irreversible long-term impacts (Foster et al., 2020; Lamhour et al., 2024).

It is essential to implement integrated management strategies that include the continuous evaluation of hydrogeological dynamics, systematic water

quality monitoring, and policies that promote sustainable resource use. The adoption of approaches based on hydrogeological modeling and risk assessment will enable the anticipation and mitigation of negative impacts, ensuring the long-term preservation of aquifers (Gleeson et al., 2020).

### 3. Materials and Methods

#### 3.1 Sampling procedures

To characterize the groundwater in the study area, monitoring campaigns were conducted during 2022 and 2023. Groundwater samples were collected from 32 wells, including domestic and irrigation wells, for the determination of major ions and stable water isotopes. All monitoring points were georeferenced using a Garmin Etrex Vista GPS. To ensure the representativeness and quality of the samples obtained, water renewal was ensured by continuous pumping, measuring basic variables such as temperature, electrical conductivity (EC), and pH with a HANNA HI 9828 device until stabilization was achieved. The sampling protocol was executed following reproducibility and methodological rigor criteria. High-density polyethylene (HDPE) containers underwent a triple-washing procedure to eliminate potential contaminants, followed by complete filling to minimize contamination during the sampling process.

Sample collection was conducted according to the following specific parameters: For nitrate analysis, samples were collected in pre-washed 250 mL polyethylene bottles. These bottles were hermetically sealed, and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was added to preserve samples at pH below 2. For major ion analysis (cations and anions), samples were collected in pre-washed 1000 mL polyethylene bottles. Cation samples were field-filtered and acidified with nitric acid (HNO<sub>3</sub>) to ensure preservation at pH below 2. Stable water isotopes (δ<sup>18</sup>O and δ<sup>2</sup>H) were sampled in 25 mL polyethylene containers.

Field procedures were executed in accordance with protocols established for Standardized methodologies from APHA (2017), Section 1060B, ensuring the acquisition of representative data with high analytical precision. All water samples were transported under cold-chain conditions to the Laboratory of Hydrogeochemistry and Isotopic Hydrology at the National University of Mar del Plata (UNMdP - CICPBA) for further analysis.

#### 3.2 Hydrochemical analysis

Standardized methodologies from APHA (2017) were used for the quantification of physicochemical parameters. The accuracy and precision of the hydrogeochemical analyses were validated using certified reference materials (CRMs, with errors below 5%) and through the assessment of ionic balance (errors below 10%). The relative discrepancies identified during this evaluation ensured the reliability and consistency of the results throughout the sample quantification process. The contents of calcium (Ca<sup>2+</sup>), potassium (K<sup>+</sup>), and sodium (Na<sup>+</sup>) were determined by flame photometry. Chloride anions (Cl<sup>-</sup>), alkalinity (CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup>), and total hardness were determined by titrimetric techniques; sulfates (SO<sub>4</sub><sup>2-</sup>), and silica (SiO<sub>2</sub>) were determined using turbidimetric and colorimetric techniques, respectively. Measurements were performed using a photometer, following the principles of the Beer-Lambert Law, which establishes the relationship between absorbance and the concentration of the analyzed species (APHA 2017). Nitrates (NO<sub>3</sub><sup>-</sup>) concentrations were measured by using UV-Visible spectrophotometry, while magnesium (Mg<sup>2+</sup>) levels were calculated as the difference between total hardness and calcium hardness, both expressed as mg CaCO<sub>3</sub>/L. The calculation was performed using the following equation.

$$\text{Mg (mg/L)} = [\text{Total Hardness (mg CaCO}_3\text{ / L)} - \text{Calcium Hardness (mg CaCO}_3\text{ / L)}] \times 0.243 \quad (\text{Eq. 1})$$

This approach assumes that the total hardness is primarily due to calcium and magnesium ions, with the conversion factor accounting for the molar mass ratio between magnesium and calcium carbonate.

The spatial location of the sampling wells was performed using QGIS 3.2.0 software (Team 2016). The characterization of hydrogeochemical facies and conventional hydrogeochemical graphs were carried out with AQUACHEM (Calmbach 1997), and statistical analysis with OriginPro software (OriginPro 2016).

### 3.3 Water stable isotope analysis

The determinations of water stable isotopes ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) were carried out using TIWA-45EP laser spectroscopy (Los Gatos Research). The uncertainty values used in these analyses were  $\pm 0.15\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 1.0\text{‰}$  for  $\delta^2\text{H}$ . All isotopic ratio results were reported as  $\delta$  values in permil (‰) relative to the international VSMOW (Vienna Standard Mean Ocean Water; Gonfiantini (1978)). Water samples were plotted in a conventional  $\delta^{18}\text{O}$  vs  $\delta^2\text{H}$  plot, together with the Global Meteoric Water Line (GMWL; Dansgaard 1964) and Local Meteoric Water Line (LMWL; Quiroz Londoño et al., 2015).

### 3.4 End Member Mixing Analysis

For the calculation of mixing ratios, End Member Mixing Analysis (EMMA) was used (Christophersen and Hooper 1992; Penna et al. 2015; Lone et al., 2021). This methodology is based on a series of assumptions framed in the conservation of solutes used as tracers, the linearity of the mixing process as a function of hydrodynamics, and the existence of solutions with extreme concentrations. The following balance equations were used for this methodology (Gibson et al., 2002).

$$Q_w = Q_{PA} + Q_{SdA} \quad (\text{Eq. 2})$$

Where  $Q$  represents the contribution of different water sources, PA the Pampeano Aquifer, and SdA the Sand-dune Aquifer. To express the concentrations of the tracer (EC, Cl<sup>-</sup>, and  $\delta^{18}\text{O}$ ) in source 1 (Pampeano Aquifer; PA) and in source 2 (Sand-dune Aquifer; SdA), we can use the following mathematical expressions.

$$f_{PA} + f_{SdA} = 1 \quad (\text{Eq. 3})$$

$$CE_M = CE_{PA} * f_{PA} + CE_{SdA} * f_{SdA} \quad (\text{Eq. 4})$$

$$Cl_M = Cl_{PA} * f_{PA} + Cl_{SdA} * f_{SdA} \quad (\text{Eq. 5})$$

$$\delta^{18}O_M = \delta^{18}O_{PA} * f_{PA} + \delta^{18}O_{SdA} * f_{SdA} \quad (\text{Eq. 6})$$

Where  $f$  represents the proportion of the water source (PA or SdA) in the mixture (M), EC stands for electrical conductivity, Cl<sup>-</sup> chlorides, and  $\delta$  represents the  $\delta^{18}\text{O}$  composition. These equations were used to estimate the mixing proportions in some wells where the interaction of both aquifers is presumed.

It is important to note that in this study, rainwater is excluded as a potential water source in the formulation of the contribution variables. This document focuses on understanding the mixing processes of aquifers with different hydrochemical and isotopic signatures, the consequences of which could influence the variation in water quality of both hydrological systems.

## 4. Results and Discussion

### 4.1 Hydrochemical characteristics

Chemical information for all 11 wells located over the Sand-dune Aquifer is available for 6, while all wells have data on electrical conductivity and stable water isotopes. In the Pampeano aquifer, 21 wells were identified. Of these, 19 contain isotopic data ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) along with complete chemical information, while the remaining 2 wells have only chemical information.

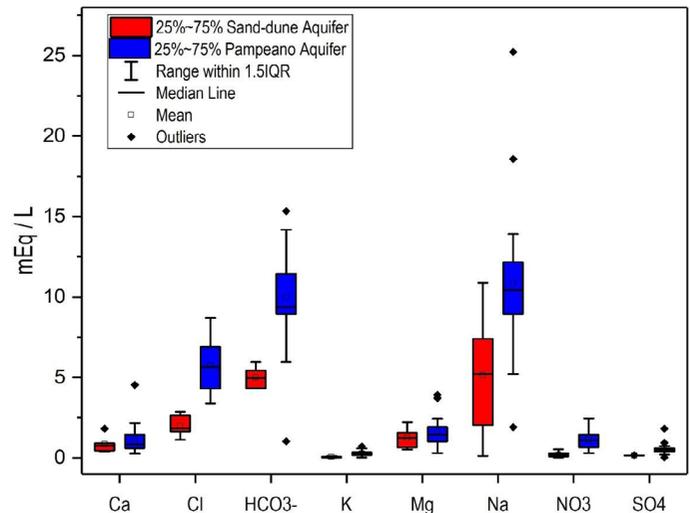
For the *in situ* measured physicochemical variables, the pH values ranged from 7.32 to 7.97, with a mean of 7.59 in the Sand-dune Aquifer, and from 7.23 to 8.01, with a mean of 7.67 in the Pampeano Aquifer. This suggests that the water in both cases is slightly alkaline, consistent with previous research on the Pampeano Aquifer (Lutri et al., 2020). The EC values ranged from 410 to 790  $\mu\text{S}/\text{cm}$ , with a mean value of 531  $\mu\text{S}/\text{cm}$  for wells in the Sand-dune Aquifer, and from 909 to 1845  $\mu\text{S}/\text{cm}$ , with a mean of 1463  $\mu\text{S}/\text{cm}$  for wells in the Pampeano Aquifer. This classifies all samples as freshwaters (Maldonado et al., 2018).

In the Sand-dune Aquifer, the average concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were 34.3 and 30.2 mg/L, respectively, whereas in the Pampeano Aquifer, they were 38.4 and 37.0 mg/L. In both aquifers, the dominant anions were  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ . In the Sand-dune Aquifer, the average concentrations of  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  were 304.9 mg/L and 14.9 mg/L, respectively, while in the Pampeano Aquifer, these values increased to 630.0 mg/L and 51.4 mg/L. The average concentrations of the main ions in the Sand-dune Aquifer are lower than those observed in the Pampeano Aquifer, a phenomenon attributed primarily to the lithological characteristics and the water transit times in each system (Quiroz Londoño et al., 2008).

Total hardness showed mean values of 226.0 mg/L for the Sand-dune Aquifer and 227.7 mg/L for the Pampeano Aquifer, both classified as hard water (Sánchez-Gutiérrez et al., 2020). As for the average Cl<sup>-</sup> concentrations, values of 70.6 mg/L were recorded in the Sand-dune Aquifer and 203.9 mg/L in the Pampeano Aquifer. Regarding  $\text{NO}_3^-$  concentrations, the Sand-dune Aquifer showed an average value of 13.3 mg/L, whereas the Pampeano Aquifer samples recorded an average value of 64.8 mg/L, indicating the impact of anthropogenic activities on groundwater.

The physicochemical results obtained in the study area indicate that its various characteristics affect water quality and consequently limit its uses. To observe differences between the deep and shallow aquifers, changes in ionic compositions as described earlier have been illustrated (Figure 3). The results reveal discrepancies between the two aquifers in terms of chloride and bicarbonate anions, as well as sodium cation, possibly due to varying hydrogeochemical processes.

A critical aspect of this study is the identification of chemical patterns in transition and discharge areas that align with findings from previous studies (Glok Galli et al., 2023). These similarities emphasize the importance of comprehending the intricate hydrogeochemical processes occurring within this aquifer.



**Figure 3.** Ionic composition (mEq/L) of the samples collected from the Sand-dune Aquifer (Red) and the Pampeano Aquifer (Blue).

Tables 1 and 2 present the hydrogeochemical and isotopic characterization of the studied aquifers. These tables compile the major ion concentrations and isotopic signatures, incorporating key statistical parameters (mean and standard deviation). The analyses reveal differences between the Sand-dune and the Pampeano Aquifers regarding salinity, ionic composition, and isotopic signature. The Sand-dune Aquifer is characterized by higher water quality, with lower salinity, a lighter isotopic signature (less enriched  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ), and lower concentrations of contaminants such as nitrates. In contrast, the Pampeano Aquifer exhibits higher mineralization, a more enriched isotopic signature, and greater variability in its chemical composition, attributable to anthropogenic processes and/or mixing phenomena. These defined differences were comprehensively understood through the evaluation of ionic relationships, chemical distribution diagrams, and isotopic signatures within the context of local meteoric water lines.

**Table 1.** Hydrogeochemical and Isotopic data from the Sand-dune Aquifer

Sample	E.C ( $\mu\text{S/cm}$ )	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	pH	$\text{Ca}^{2+}$ (mEq/L)	$\text{Mg}^{2+}$ (mEq/L)	$\text{Na}^+$ (mEq/L)	$\text{K}^+$ (mEq/L)	$\text{HCO}_3^-$ (mEq/L)	$\text{Cl}^-$ (mEq/L)	$\text{SO}_4^{2-}$ (mEq/L)	$\text{NO}_3^-$ (mEq/L)
G1022	484	-5.6	-33.8	7.66	0.85	1.55	0.13	0.02	4.33	1.13	0.16	0.10
G1023	496	-5.6	-34	7.97	0.92	0.65	6.09	0.04	5.97	1.64	0.16	0.54
G1025	458	-5.6	-34.1	7.52	0.68	1.58	2.04	0.03	4.33	1.64	0.15	0.03
G1026	602	-5.3	-33.4	7.76	0.45	2.21	10.87	0.03	5.42	2.03	0.18	0.11
G1032	647	-6.2	-34.3	7.64	1.82	0.52	4.35	0.08	4.56	2.88		0.28
G101	572	-5	-35	7.32	0.41	0.95	7.39	0.14	5.39	2.64	0.14	0.24
G252	500	-5.4	-29.5	--	--	--	--	--	--	--	--	--
G253	470	-4.7	-29.1	--	--	--	--	--	--	--	--	--
G255	410	-5.6	-32.1	--	--	--	--	--	--	--	--	--
G256	410	-5.5	-31.9	--	--	--	--	--	--	--	--	--
G251	790	-5.2	-28.8	--	--	--	--	--	--	--	--	--
Mean	530.82	-5.43	-32.36	7.65	0.86	1.24	5.15	0.05	5.00	1.99	0.16	0.22
Standard Deviation	114.01	0.39	2.27	0.22	0.52	0.65	3.85	0.05	0.69	0.66	0.01	0.18

**Table 2.** Hydrogeochemical and Isotopic data from the Pampean Aquifer

Sample	E.C ( $\mu\text{S/cm}$ )	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	pH	$\text{Ca}^{2+}$ (mEq/L)	$\text{Mg}^{2+}$ (mEq/L)	$\text{Na}^+$ (mEq/L)	$\text{K}^+$ (mEq/L)	$\text{HCO}_3^-$ (mEq/L)	$\text{Cl}^-$ (mEq/L)	$\text{SO}_4^{2-}$ (mEq/L)	$\text{NO}_3^-$ (mEq/L)
G1021	1578	-5.4	-33.3	7.86	0.48	0.79	10.44	0.03	9.11			
G1027	1234	-4.8	-29.8	7.58	1.35	1.19	5.22	0.08	7.05	4.09	0.28	0.79
G1028	1019	-5.2	-27.4	7.73	0.60	2.43	1.91	0.18	5.97	3.38	--	0.49
G1029	1522	-5.6	-30.8	7.52	1.18	1.47	10.00	0.13	9.11	5.13	--	2.46
G1030	1469	-5.3	-30.1	8.01	4.54	0.86	6.52	0.23	1.04	4.29	--	0.98
G1031	1773	-5.3	-28.3	7.75	2.00	3.92	6.96	0.36	8.13	6.32	--	1.57
G1104	1215	-5	-29.5	7.39	0.67	1.28	10.44	0.15	8.77	5.33	0.41	2.03
G114	909	-4.3	-22.5	7.51	0.66	0.91	8.92	0.72	9.46	6.27	0.20	--
G282	1652	-5.5	-31	7.78	0.55	1.93	13.92	0.59	13.91	7.19	0.58	1.17
G517	1780	-5.4	-31.4	7.45	1.62	0.29	25.23	0.31	14.18	8.72	0.94	0.67
G721	1588	-5	-30	7.93	0.70	1.02	12.18	0.28	11.31	4.29	0.52	0.52
G722	1647	-5.2	-31.5	7.6	0.85	1.83	10.87	0.41	8.95	5.90	0.60	1.19
G723	1457	-5.1	-30.5	7.76	0.85	1.26	10.44	0.38	11.14	3.75	0.48	0.65
G162	1200	--	--	7.65	0.28	2.02	13.09	0.28	13.93	6.91	0.68	2.00
G167	1190	--	--	7.73	0.40	1.12	18.57	0.23	15.34	7.78	0.56	1.10
G168	1110	-5.4	-34	7.75	0.26	0.86	12.88	0.25	11.46	5.64	0.50	1.69
G723	1536	-5.3	-30.4	7.68	1.45	1.44	10.87	0.36	13.13	4.32	0.73	1.08
G723	1772	-5.1	-30	7.54	1.62	3.72	8.70	0.28	9.39	7.81	1.82	0.67
G723	1845	-5.2	-31.1	7.23	0.74	2.44	10.44	0.08	10.41	7.16	0.46	0.38
G723	1757	-5.3	-32.4	7.93	2.17	1.69	9.13	0.23	9.21	5.11	0.26	0.30
G722	--	--	--	--	0.85	1.83	10.87	0.41	8.95	5.90	0.60	1.19
Mean	1462.65	-5.19	-30.22	7.67	1.13	1.63	10.84	0.28	10.00	5.76	0.57	1.11
Standard Deviation	282.66	0.29	2.49	0.20	0.95	0.91	4.72	0.17	3.22	1.47	0.39	0.59

#### 4.2 Hydrochemical Facies

A Piper diagram was used to identify hydrochemical facies and infer possible geochemical processes influencing the composition of both aquifers (Figure 4). The diagram reveals a wider dispersion of samples from the Pampeano Aquifer, predominantly classified as sodium-bicarbonate water type, with only two samples showing different facies. On the other hand, the Sand-dune Aquifer primarily exhibits a calcium-magnesium bicarbonate type, with just two samples displaying a different facies (sodium-bicarbonate water type).

The limited availability of accurate data on the depth of the sampled wells constitutes a constraint in this study. User-provided information is often imprecise, typically specifying broad depth ranges rather than precise values during monitoring campaigns. This lack of precision complicates the systematic evaluation of aquifer interactions. Although depth data is unavailable for all wells, the results suggest a potential interaction between aquifers (Figure 4). This is particularly evident in the samples from wells G1027 and G1028, located in the Pampeano Aquifer. The ionic composition of these samples reveals a transitional zone between calcium-magnesium bicarbonate and sodium bicarbonate facies. Specifically, the findings suggest that the Sand-dune Aquifer may be recharging the Pampeano Aquifer in inland areas with lower salinity water characterized by calcium-magnesium bicarbonate facies. This mixing process significantly alters the physicochemical properties of the water.

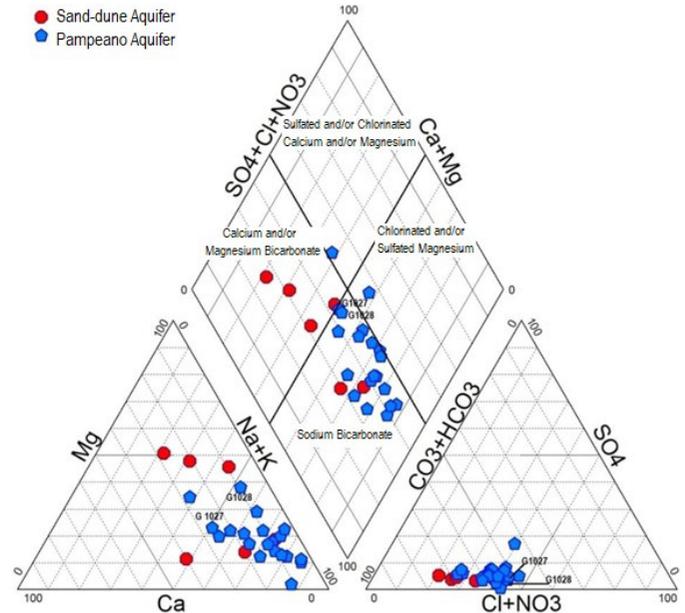
Moreover, this situation reveals an issue framed within regional drilling practices, which frequently prioritize maximum depth and the use of multi-level screens, operating under the erroneous assumption that these designs improve water availability for productive activities. However, such practices often fail to consider the specific hydrogeological boundaries of individual aquifers, potentially exacerbating inter-aquifer exchange and its associated challenges.

Considering the above, wells G1022, G255, G252, and G1023 are representative of the Sand-dune Aquifer. In contrast, wells G1021, G1029, G1030, and G1031 exhibit the chemical composition of the Pampeano Aquifer, despite their spatial proximity to wells G1027 and G1028, which show evidence of mixing between both aquifer systems. This differentiation is based on the geochemical signatures of the wells, particularly those associated with conservative tracers such as water stable isotopes ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ), electrical conductivity (EC), and chloride concentrations ( $\text{Cl}^-$ ). The values of these variables in wells G1027 and G1028 show statistically significant deviations compared to those recorded in the Pampeano Aquifer wells, suggesting a mixing process in the transition zone. However, to confirm the correct assignment of the end members and validate data interpretation, it is deemed necessary to perform a methodological evaluation incorporating an analysis of the spatial distribution of the wells.

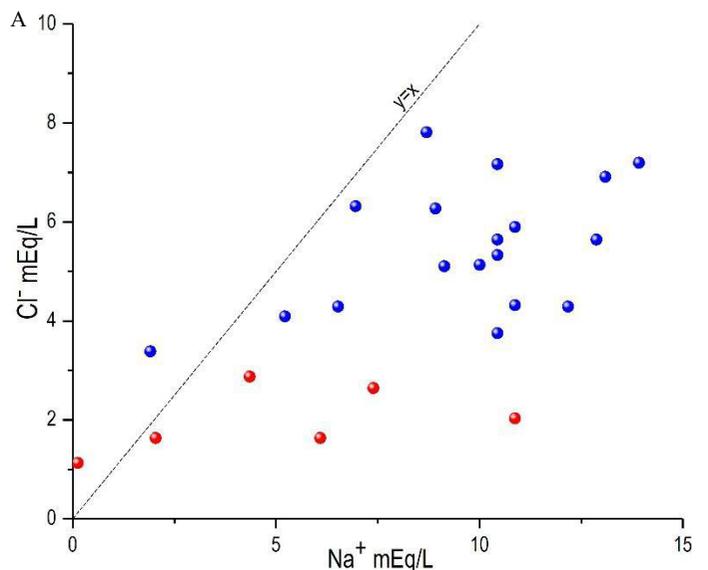
#### 4.3 Geochemical processes

One of the main processes contributing to  $\text{Na}^+$  and  $\text{Cl}^-$  ions in groundwater is halite dissolution, a result of rock interaction. This process can be identified through the distribution of points in a binary diagram relating  $\text{Cl}^-$  and  $\text{Na}^+$  content (Figure 5a). The dispersion of sodium and chloride values indicates that halite dissolution is not the primary process responsible for the presence of these ions in the solution, as halite dissolution would produce equivalent amounts of both ions. Ninety-five percent of the samples fall below the halite dissolution line, suggesting that other factors contribute to changes in the ionic composition of the groundwater (Jat Baloch et al., 2021; Xiao et al., 2023). Elevated sodium values may be associated with ion exchange processes involving calcium and magnesium present in Pampeano sediments. A key aspect of this ionic relationship is the clear differentiation between the two aquifers under study. In the Pampeano Aquifer, chloride values exceed 3 mEq/L, whereas lower values are observed in the Sand-dune Aquifer.

The ionic relationship between  $\text{HCO}_3^- + \text{SO}_4^{2-}$  vs.  $\text{Ca}^{2+} + \text{Mg}^{2+}$  and  $\text{Mg}^{2+}$  vs.  $\text{Ca}^{2+}$  is used to establish the changes in water chemistry due to the weathering of carbonate and silicate rocks (Jat Baloch et al., 2021). However, this process is not dominant in the study area, as the point distribution does not show a linear behavior along the  $y = x$  line, nor do they fall within the range between the  $y = x$  /  $y = 0.5 * x$  lines (Figure 5b and Figure 5c), which identify dolomite and calcite dissolution, respectively. Figure 5b confirms the differentiation process of the aquifers under study. Values greater than 6 mEq/L for  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  species define the Pampeano Aquifer, while lower values characterize the Sand-dune Aquifer.



**Figure 4.** Ionic composition of groundwater from the Pampeano (blue) and Sand-dune (red) Aquifers: A: Calcium and Magnesium Bicarbonate Waters; B: Sodium-Bicarbonate Waters; Samples G1028 and G1027 are potential mixtures originating from both aquifers.



**Figure 5.** Ionic relationships of groundwater in the study area: a)  $\text{Cl}^-$  vs  $\text{Na}^+$ , b)  $\text{Ca}^{2+} + \text{Mg}^{2+}$  vs  $\text{HCO}_3^- + \text{SO}_4^{2-}$ , c)  $\text{Ca}^{2+}$  vs  $\text{Mg}^{2+}$ , d)  $\text{Ca}^{2+}$  vs  $\text{SO}_4^{2-}$ .

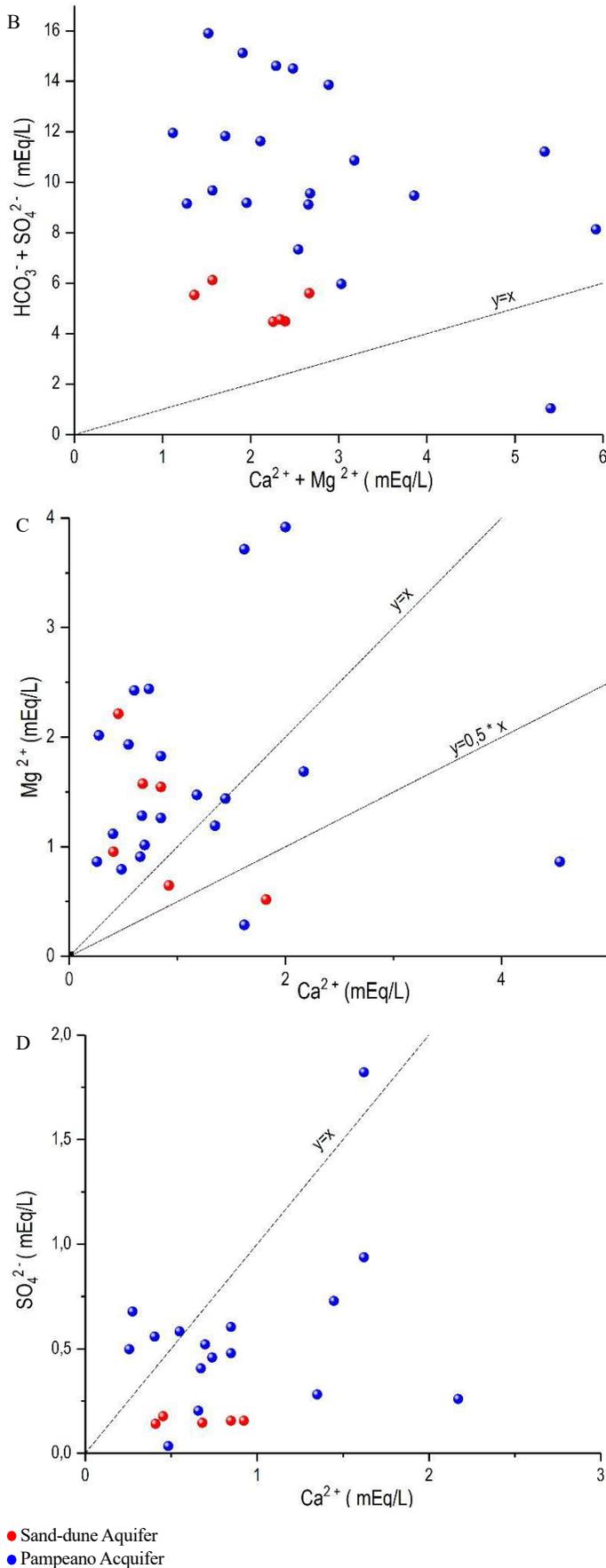


Figure 5d shows the ionic relationship between  $\text{SO}_4^{2-}$  vs  $\text{Ca}^{2+}$  and which establishes the conditions for gypsum dissolution. Most of the points are distributed below the  $y = x$  line, indicating that the source of calcium does not originate from this process. In the various ionic relationships evaluated, the ions do not align with the presented lines, suggesting that cation exchange is the dominant phenomenon driving the chemical changes. This indicates that sediments and geology play a crucial role in the variations of the water's chemical conditions.

To assess whether cation exchange processes modify the chemical properties of groundwater in the study area, the ionic relationship  $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{SO}_4^{2-} + \text{HCO}_3^-)$  vs.  $(\text{Na}^+ - \text{Cl}^-)$  is graphically represented (Figure 6). A linear correlation between these ions is observed ( $R^2 = 0.56$ ) with a slope (-0.82), closely approaching the theoretical value of -1, consistent with findings from other studies in the Pampeano Aquifer (Glok Galli et al., 2023). This correlation suggests the presence of cation exchange processes, where excess sodium in both aquifers likely results from interactions involving the exchange of calcium and magnesium for sodium (Jat Baloch et al., 2021).

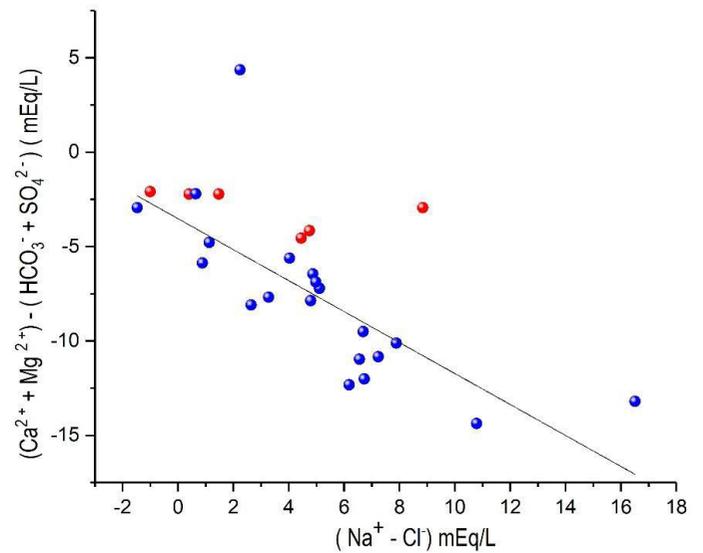


Figure 6. Ionic relationships of groundwater in the study area to identify ion exchange processes.

#### Isotopic characterization

The isotopic composition of the different samples was included in the conventional  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$  plot shown in Figure 7, along with the Global Meteoric Water Line (GMWL) defined by Craig (1961) and the Local Meteoric Water Line (LMWL) defined by Quiroz Londoño et al., (2015). The  $\delta^{18}\text{O}$  values for the Sand-dune Aquifer range from -4.7 to -6.2 ‰, averaging -5.43 ‰, while those for the Pampeano Aquifer vary between -4.30 and -5.60 ‰, averaging -5.19 ‰. In terms of  $\delta^2\text{H}$  values, the Sand-dune Aquifer ranges from -35.0 to -28.8 ‰, averaging -32.36 ‰, whereas the Pampeano Aquifer ranges from -34.0 to -22.5.0 ‰, averaging -30.2 ‰. These findings indicate that the Sand-dune Aquifer generally exhibits a slightly depleted isotopic signature compared to the Pampeano Aquifer.

The isotopic composition of the samples from the studied aquifers could be influenced by mixing and/or evaporation processes during infiltration, as well as by subsequent interactions with the local groundwater. The samples from the Pampeano Aquifer exhibit greater isotopic variation compared to those from the Sand-dune Aquifer. This behavior is primarily attributed to the Pampeano Aquifer's lithological composition, which consists of clayey sediments that limit the infiltration rates and enhance evaporation. These variations are evident in the distribution of the samples along the LMWL and the GMWL.

In contrast, the Sand-dune Aquifer, predominantly composed of sandy sediments, is recharged by rainfall with best infiltration rates. The rapid infiltration minimizes exposure time, thereby reducing the influence of evaporation on the isotopic signature. These differences underscore the distinct

hydrogeological and isotopic dynamics of the two aquifers, emphasizing the critical role of lithology and recharge mechanisms in shaping isotopic variability.

Based on the information provided by hydrochemical analysis and isotopic signatures, variations in electrical conductivity values have been identified, indicating a potential interaction between the two aquifers under study. The EC vs  $\delta^{18}\text{O}$  plot (Figure 8), reveals that in well G251, the salinity levels suggest such an interaction or connection, evidenced by an increase in EC and a slight difference in isotopic content.

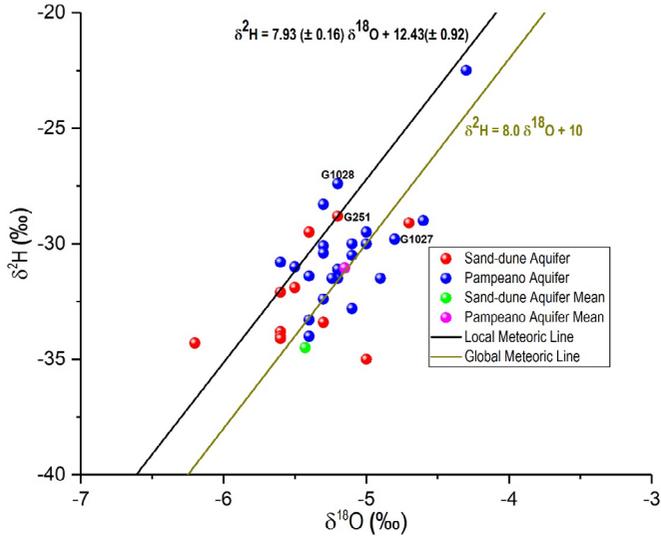


Figure 7. Isotopic content of the Pampeano and Sand-dune aquifers.

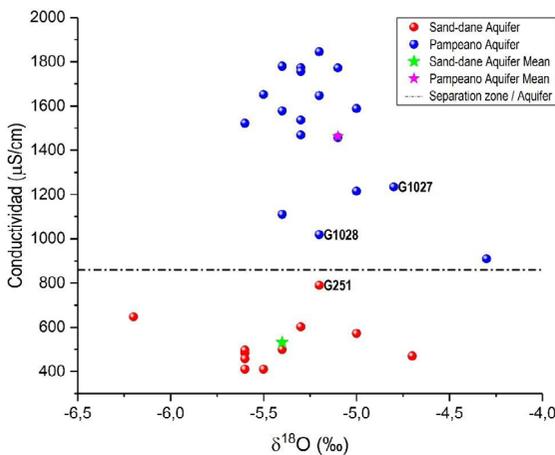


Figure 8.  $\delta^{18}\text{O}$  values and electrical conductivity used in the characterization of aquifers.

4.5 Water quality assessment

To assess the suitability of water from the 32 inventoried wells for human consumption, the concentrations of major ions were compared against the limits specified in the Argentine Food Code (CAA 2021). It was observed

that chloride levels in both aquifers are below the 350 mg/L limit established for potable water. Additionally, sulfate concentrations were found to be below the 400 mg/L limit. The  $\text{NO}_3^-$  present in groundwater can originate from various sources of contamination, such as agricultural activities, human actions, atmospheric deposition, or natural content in the soil, which limits its suitability for direct consumption (Matiatos 2016). The wells exploiting the Sand-dune Aquifer present levels below 45 mg/L, in contrast to the Pampeano Aquifer, where 60% of the wells show values exceeding the limit established by the Argentine Food Code (CAA 2021), thus restricting its use for human consumption.

Total hardness, which reflects the concentrations of calcium and magnesium, is within the established limit of 400 mg/L in the Sand-dune Aquifer, indicating suitable water quality for human consumption. However, in the Pampeano Aquifer, well G1031 shows a total hardness of 597 mg/L, exceeding the potable water limit.

The presence of high levels of hardness and nitrates in the Pampeano Aquifer highlights the non-potability of the water for human consumption. This aspect is relevant because it may pose a risk to the Sand-dune Aquifer due to the presumed mixing, potentially altering or modifying its water quality conditions over time.

5.6 Quantification of mixing contributions

The selected end-members for the mixing proportion analysis and the values of the different conservative tracers used are shown in Table 3.

Table 3. Conservative tracer values for each selected end-member.

Sample	Aquifer	E.C (µS/cm)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Cl(mg/L)
G1022	Sand-dune	484.0	-5.6	-33.8	40
G255	Sand-dune	410.0	-5.6	-32.1	--
G252	Sand-dune	500.0	-5.4	-29.5	--
G1023	Sand-dune	496.0	-5.6	-34.0	58
<b>Mean</b>		<b>472.5</b>	<b>-5.6</b>	<b>-32.4</b>	<b>49.0</b>
G1021	Pampeano	1578	-5.4	-33.3	200
G1029	Pampeano	1522	-5.6	-30.8	182
G1030	Pampeano	1469	-5.3	-30.0	152
G1031	Pampeano	1773	-5.3	-28.3	224
<b>Mean</b>		<b>1585.5</b>	<b>-5.4</b>	<b>-30.6</b>	<b>189.5</b>

The integration of hydrogeochemical and isotopic analyses reveals potential water mixing in wells G251, G1027, and G1028. This interpretation is supported by multiple lines of evidence. Conductivity versus  $\delta^{18}\text{O}$  diagrams (Figure 8) clearly differentiate between the two studied aquifers, with the mixed samples occupying intermediate positions and exhibiting similarities in their tracer variables (EC and  $\delta^{18}\text{O}$ ).

Regarding the isotopic signal, these samples cluster in the upper region of the local meteoric water line (Figure 7), suggesting similar physical processes during infiltration and water-rock interaction. The lithological characteristics of each aquifer significantly influence these processes: the Pampeano Aquifer, dominated by clays, promotes evaporation due to greater water-sediment interaction, while the Sand-dune Aquifer, mainly composed of sands, allows faster infiltration with less interaction. The isotopic similarities of the mentioned samples support the hypothesis of mixing between these units.

The hydrogeochemical patterns (Figure 4) corroborate this interpretation, as the samples with potential mixing exhibit intermediate chemical compositions, distinct from the characteristic extremes of each aquifer. Quantification of these mixing processes indicates varying proportions of contribution from each aquifer, as detailed in Table 4.

Table 4. Results of the calculated mixing proportions.

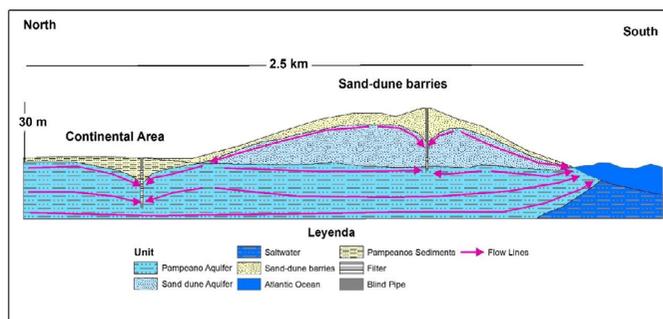
Sample	Aquifer	E.C (µS/cm)	$f_{sda}$	$f_{PA}$	$\delta^{18}\text{O}$ (‰)	$f_{sda}$	$f_{PA}$	Cl (mg/L)	$f_{sda}$	$f_{PA}$
G251	Sand-dune	790.0	0.68	0.32	-5.2	-1.3	2.3	58	--	--
G1027	Pampeano	1234.0	0.32	0.68	-4.8	-4.0	5.0	145	0.32	0.68
G1028	Pampeano	1019.0	0.51	0.49	-5.2	-1.3	2.3	120	0.49	0.51

Considering the calculations performed, we can confirm the interaction between the two aquifers in the coastal sector under study. The elements selected as end-members and the mixing wells have provided key data that align with the conceptual hydrogeological model of the area.

The obtained data reveal that wells near the sand dunes, which are supplied by the Pampeano Aquifer, extract approximately 30% to 50% of water from the Sand-dune Aquifer (Table 4). This process results in a decrease in electrical conductivity, an increase in magnesium and calcium levels, and a reduction in sodium levels. Conversely, wells constructed in the Sand-dune Aquifer can capture up to 30% of their supply from the Pampeano Aquifer, which is reflected in an increase in the electrical conductivity of these wells.

These interaction processes between the waters of both aquifers can have negative consequences for both the quality and quantity of water stored in the Sand-dune Aquifer. Regarding quality, the influx of more saline waters could significantly deteriorate water quality. In terms of quantity, nearby wells would become an additional source of extraction from this aquifer, increasing pressure on the available water resources (Gorelick and Zheng, 2015; Wali et al., 2019).

Figure 9 shows a schematic illustrating the problem of water mixing between the two aquifers as a consequence of anthropogenic activity, indicating how drilling in these aquifers can deteriorate water quality. To prevent the deterioration of the Sand-dune Aquifer, it is proposed to implement actions that promote proper control of wells in this aquifer. These controls should include determining the maximum drilling depth to avoid exceeding the sediment thickness and the appropriate design of corresponding intakes. Periodic conductivity measurements in various intakes can serve as an early warning system for possible aquifer mixing and water quality deterioration. Additionally, it is crucial to control the construction distance of wells in the Pampeano Aquifer, as the results of this study indicate that these intakes are supplied with water from the more superficial aquifer.



**Figure 9.** Hydrogeological configuration in the coastal dune sector with the presence of domestic supply wells in both aquifer units.

The observed interactions between the Pampeano and Sand-dune aquifers have significant implications for coastal aquifer management. The mixing processes identified, such as the influx of more saline water from the Pampeano Aquifer into the Sand-dune Aquifer, lead to changes in water quality, including increased electrical conductivity and elevated magnesium and calcium levels, which may compromise the aquifer's suitability for human consumption and irrigation. Similarly, Carretero et al., (2022) emphasized that mixing processes in coastal aquifers can result in salinization and undesirable ion enrichment, while Manivannan and Elango (2021) highlighted that such interactions exacerbate stress on water resources and reduce aquifer sustainability. These findings underscore the importance of monitoring and managing groundwater use to mitigate negative effects. Proactive measures, such as regulating well depths, controlling the spatial distribution of extractions, and implementing regular monitoring programs using electrical conductivity and isotopic analyses, are essential to detect early signs of salinization or seawater intrusion. Without intervention, continued anthropogenic activity could accelerate aquifer degradation, reducing the availability of potable water and threatening the sustainability of vital groundwater coastal resources.

## 5. Conclusions

The approach of this study broadens our understanding of the geochemical processes that control the groundwater chemistry of waters and provides relevant information for the integrated management of water resources. It helps in understanding the processes by which human activities can risk changes in groundwater quality. The need to continue field data collection to understand the evolution of water chemistry and to provide decision-makers with tools for water resource management becomes evident.

The possible mixture identified in this study underscores a significant challenge within the framework of regional groundwater resource management. The erroneous assumption that deeper drilling guarantees higher water yields has led to inadequate well construction practices by users. The hydrogeochemical and isotopic results presented not only highlight this issue but also provide a basis for initiating detailed hydrogeological studies aimed at enhancing the understanding of aquifer systems in the region. Furthermore, these findings offer a robust foundation for the development and implementation of more effective regulatory policies by governing authorities. This information is essential for improving the management of groundwater resources in the region.

Variations in the concentrations of tracer elements are a tool for identifying mixing processes between aquifers. To deepen the understanding of isotopic and hydrogeochemical processes, it is recommended to implement a systematic water quality monitoring program. This program should focus at a minimum on measurement of electrical conductivity as a key indicator of mixing processes, enabling the early detection of alterations that could impact water quality and, consequently, user health. The information generated will facilitate the timely implementation of protective measures for both aquifers.

The application of the End-Member Mixing Analysis methodology for conservative parameters such as electrical conductivity and chlorides provides evidence of interaction between the studied aquifers. Well G251, located in the Sand-dune Aquifer, has a contribution of 68% from the Sand-dune Aquifer and 32% from the Pampeano Aquifer, while wells G1027 and G1028 have contributions of 32% and 49% from the Sand-dune Aquifer respectively, and 68% and 51% from the Pampeano Aquifer.

The results for the sanitary variables of interest for the Sand-dune Aquifer have complied with the permissible limits of the Argentine Food Code, indicating suitability for human consumption. On the other hand, for the Pampeano Aquifer, 60% of the study wells present adverse conditions due to nitrate levels exceeding the limit of 45 mg/L. This aspect must be controlled to prevent the possible mixing from altering the quality conditions of the Sand-dune Aquifer.

The quantified isotopic values reveal that the Sand-dune Aquifer exhibits a slightly depleted isotopic signature compared to the Pampeano Aquifer. However, these parameters do not allow for a clear differentiation between the two aquifers, primarily because both recharge sources are from precipitation. The slight enrichment present in this sector of the Pampeano Aquifer can be explained by evaporation processes occurring prior to the infiltration and subsequent percolation of water into the aquifer. In this regard, the lithology of both aquifers plays a dominant role, as the sands constituting the Sand-dune Aquifer, having higher permeability, allow for the immediate infiltration of precipitation that recharges it.

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