

Impacts of climate change on fragile alkaline lakes: New hydrogeochemical and hydrogeological insights from Bagno dell'Acqua (Pantelleria Island, Italy)

Marino Domenico Barberio^a, Francesca Gori^{b,*}, Maurizio Barbieri^c, Stan Eugene Beaubien^b, Tiziano Boschetti^d, Francesco Latino Chiocci^b, Valeria Lorenzi^b, Marco Petitta^b

^a Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione Roma1, Italy

^b Department of Earth Sciences, Sapienza University of Rome, Italy

^c Department of Chemical Engineering and Environmental Materials, Sapienza University of Rome, Italy

^d Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Italy

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ABSTRACT

Study region: Alkaline lakes are among the most extreme aquatic environments on Earth, offering insights into unique ecosystems that may be similar to those that gave rise to life on Earth and potentially other planets like Mars. Despite their hydrogeological and geochemical significance, the temporal and spatial evolution of alkaline lakes remains poorly understood due to limited long-term data. To address this, we monitored the volcanic alkaline lake Bagno dell'Acqua (Pantelleria Island, Southern Italy) and nearby springs and wells from May 2021 to June 2023. **Study focus:** Three sampling campaigns were conducted at ten sites. Chemical data confirm a connection between the lake and surrounding thermal springs, with clear evidence of calcium and strontium removal via mineral precipitation. Isotopic analyses ($\delta^{18}\text{O}$, $\delta^2\text{H-H}_2\text{O}$; $\delta^{34}\text{S}$, $\delta^{18}\text{O-SO}_4$; $^{87}\text{Sr}/^{86}\text{Sr}$; $\delta^{11}\text{B}$) and gas compositions further elucidate the system's geochemical dynamics.

New hydrological insights for the region: Over the past two decades, the lake's hydrogeological water budget shows reduced recharge and increased evaporation compared to the 1990s, resulting in a net water loss of 49%. Geochemical markers indicate rising solute concentrations, consistent with reduced freshwater inflow and intensified evaporation. If current trends persist, a progressive increase in salinity and consequently eutrophication may occur, with possible implications for the lake's biogeochemical functioning that warrant further investigation. This study provides a valuable dataset for the conservation and management of closed-basin alkaline lakes and highlights the importance of long-term monitoring under changing climatic conditions.

* Correspondence to: Department of Earth Sciences, Sapienza University of Rome, Piazzale Aldo Moro 5, Rome 00185, Italy.

E-mail address: francesca.gori@uniroma1.it (F. Gori).

1. Introduction

1.1. Alkaline lakes

Alkaline lakes are hydrologically closed systems, typically found in arid or semi-arid climates, where high evaporation rates result in increased solute concentrations and elevated alkalinity. These lakes are characterized by high pH levels (between 9 and 10.5) and are chemically dominated by sodium (Na^+), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}), while maintaining notably low concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) (Raudsepp et al., 2023; Tosca and Tutolo, 2023; Ubertini et al., 2025). High buffering capacity governs their chemical stability and biological productivity (Grant, 2009; Haines et al., 2023). These systems are common in quiescent or recently extinct volcanic regions, where the absence of acidic magmatic gases (e.g., H_2S , HCl , and HF), often filtered by deep hydrothermal systems, allows CO_2 -rich fluids to dominate (D'Alessandro et al., 1994; Pecoraino et al., 2015). The endogenous carbon dioxide, when interacting with silicate rocks, promotes the release of alkalis and the increase of total dissolved inorganic carbon (TDIC) in groundwater. A high TDIC/ $(\text{Ca}^{2+} + \text{Mg}^{2+})$ ratio in inflowing waters is a critical geochemical precondition for the development of alkaline lake waters through progressive evaporative concentration and mineral precipitation (Hardie and Eugster, 1970; Darragi and Tardy, 1987; Mazzoni et al., 2024).

1.2. Alkaline lakes challenges

Alkaline lakes exhibit pronounced sensitivity to climate change. Rising temperatures enhance evaporative losses, thus concentrating solutes and increasing salinity. Simultaneously, reduced inflows due to declining precipitation or groundwater recharge can drastically lower lake volumes, accelerating hydrogeochemical evolution (Stenger-Kovács et al., 2014). The salinization process can promote density stratification, which limits vertical mixing and leads to deep-water anoxia and the release of nutrients. This feedback loop drives eutrophication, reduces biodiversity, and compromises the ecological stability of these systems (Qin et al., 2006; Jeppesen et al., 2015; Lind et al., 2018). However, the thermal stratification and anoxic conditions do not always occur, particularly in shallow lake environments.

1.3. Study case and focus

To deepen our understanding of such extreme environments and to provide new insights for the assessment of the environmental

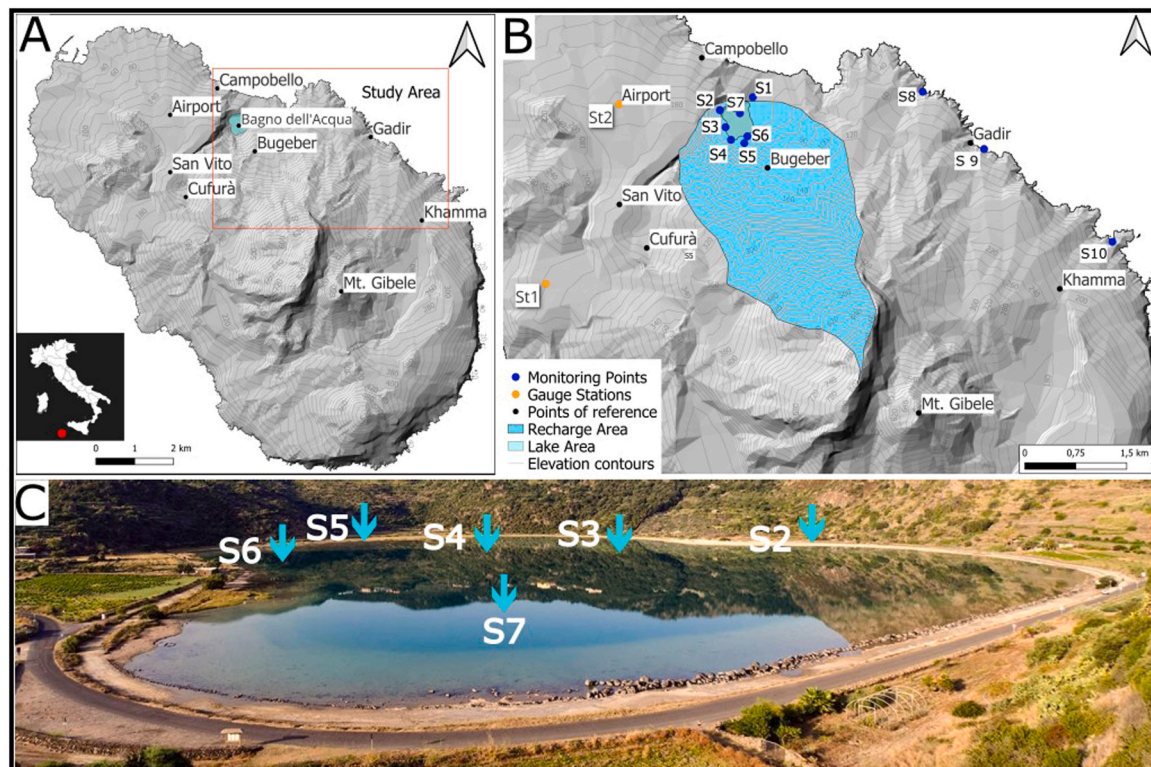


Fig. 1. A) Location of study area; B) location of monitoring points at Bagno dell'Acqua alkaline lake and along the north-eastern coast of the island of Pantelleria; C) Lake area sample points.

impact associated with climate change, we conducted a comprehensive investigation of the volcanic alkaline lake Bagno dell'Acqua, a shallow crater lake located on Pantelleria Island (Italy) that is characterized by high alkalinity and peculiar geochemical conditions. This study, conducted between May 2021 and June 2023, is part of a broader multidisciplinary research project aimed at the conservation of the biodiversity of the Bagno dell'Acqua lake named "Conservazione della Biodiversità del Lago Bagno dell'Acqua (Isola di Pantelleria)" (Antinucci et al., 2023, 2024; Ingrassia et al., 2024; Mazzoni et al., 2024; Pierdomenico et al., 2024). The dynamic balance between groundwater inputs, hydrothermal fluid fluxes, and (bio)geochemical processes makes this lake an ideal natural laboratory for studying the evolution of alkaline lake systems in a volcanic domain. In detail, we performed hydrogeochemical monitoring of ten sites, including lake waters, springs, and wells, using an integrated hydrogeochemical and multi-isotopic approach. Additionally, we updated the hydrogeological water budget of the lake system to evaluate changes over the last 20 years since the calculation of Aiuppa et al., (2007).

2. Geological and hydrogeological settings

Pantelleria Island is the emergent part of a volcano that is located in the Sicily Channel Rift Zone, about 100 km southwest of Sicily and 70 km north of Tunisia (Mattia et al., 2007; Cangemi et al., 2018). The geology of the island mainly consists of products of explosive and effusive volcanic activity, ranging from trachytes to peralkaline rhyolites with subordinate basalts (Civetta et al., 1984; Mahood and Hildreth, 1983). The volcanic system is still active, as the last eruption occurred in 1891, 3 km offshore the Pantelleria northern shore (Conte et al., 2014). Inland, the activity is limited to diffuse hydrothermal activity characterized by low-temperature fumarolic emissions and thermal springs (Parello et al., 2000). Due to the high permeability of the rocks and the low rainfall (approximately 350 mm/year), Pantelleria has no surface waters except for the "Bagno dell'Acqua".

Lake Bagno dell'Acqua is an endorheic alkaline saline lake located inside the "Cinque Denti" caldera depression. It has a sub-circular shape (ca. 450 m long and ca. 350 m wide) (Dongarrà et al., 1983; Bocchi et al., 1988; Madonia et al., 2013) (Fig. 1), a surface area of ~ 0.2 km², and a maximum depth of 12.5 m (Bocchi et al., 1988). It hosts a very specific microbiological assemblage (Piacentini et al., 2026) and, due to its chemistry, it is the site for microbialite formation (Cangemi et al., 2010; Ingrassia et al., 2024; Mazzoni et al., 2024).

Its water balance is strongly controlled by input from net infiltration and a contribution from the thermal aquifer, and water output through evaporation and seepage to groundwater (Aiuppa et al., 2007). All infiltration waters within the basin are assumed to discharge in the sublacustrine zone, identified as the basin's lowest topographic outlet.

The southwestern shore of the lake is characterized by intense hydrothermal activity, including thermal springs with relatively low discharge rates and temperatures around 50 °C, as well as gaseous emissions of volcanic origin (Ubertini et al., 2025). The latter are characterized by CO₂ (98%) and minor amounts of N₂, CH₄, H₂, and He, which derive from the mixing of deep volcanic gases with shallow groundwater and surface gases (D'Alessandro et al., 1994; Parello et al., 2000; Aiuppa et al., 2007). Stable isotope values indicate a mantle-thermometamorphic origin for CO₂ (D'Alessandro et al., 1994) and an abiogenic origin for CH₄ (D'Alessandro et al., 2009). The lake and surrounding area are one of the strongest CO₂ degassing areas on the island (Favara et al., 2001), accounting for an estimated 36% of the island's total emissions (D'Alessandro et al., 2018).

Due to its geographical position, between Sicily and Tunisia, the island of Pantelleria is subject to the typical climatic conditions of southern Sicily and northern Africa. Based on the Thornthwaite climate classification, the climate of Pantelleria is considered semi-arid (Cartabellotta et al., 1998). The average annual maximum temperature is 20.9 °C, while the minimum is 15.3 °C. The island is very windy and has an average annual humidity value of around 85%. During the summer, the humidity value is around 83% while the minimum never drops below 73%.

3. Materials and methods

3.1. Hydrogeochemistry

Three sampling surveys were conducted in May 2021, May 2022, and February 2023 to characterize the hydrogeochemistry of Pantelleria Island's groundwater. Ten monitoring sites were selected within the lake itself, as well as various thermal springs and wells having different hydrogeochemical features (e.g., from low to high mineralization) that are located around the lake and along the northeastern coast of the island (Fig. 1).

Chemical-physical parameters (i.e., pH, electrical conductivity, and temperature) were measured on-site using the multiparametric probe WTW Multi 3420, which has sensor accuracies of ± 0.01 pH units, ± 1 μ S/cm, and ± 0.1 °C, respectively. Samples for major and trace element analyses were filtered in situ through a 0.45 μ m polyethylene filter into 50 ml and 15 ml polyethylene bottles, respectively. Samples for the cation analysis were acidified with HCl. Those collected for trace element determination were acidified to 1% v/v, adding 1 ml of 65% HNO₃ Suprapur® (Supelco), to avoid the precipitation of metals. Samples for the determination of major ions and trace element concentrations were analyzed at the Geochemistry Laboratory of the Department of Earth Sciences at Sapienza University of Rome (Italy) by ion chromatography and inductively coupled plasma mass spectrometry (ICP-MS), respectively. Since the analyzed waters were characterized by very high electrical conductivity values, they were diluted with ultrapure water (18 M Ω cm⁻¹ at 25 °C). Anions (F⁻, Cl⁻, SO₄²⁻, and NO₃⁻) were measured using a Dionex ICS-5000 chromatograph while cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) were analysed using a Dionex ICS-1100 chromatograph. The analytical error associated with these instruments is less than 5%. Alkalinity was measured by titration with 0.05 N HCl on site. The analysis of trace elements was performed using an iCAP-RQ ICP-MS (Thermo Fisher Scientific). Ultrapure water (Millipore, Milli-Q, 16 M Ω cm) was used to prepare blanks, standard solutions, sample

dilutions, and an internal standard, Rh, was used to correct for instrumental drift. The analytical accuracy of this method ranges between 2% and 5%. Samples for analysis of the stable isotope of water ($\delta^{18}\text{O}\text{-H}_2\text{O}$ and $\delta\text{D}\text{-H}_2\text{O}$), $\delta^{34}\text{S}\text{-SO}_4$, $\delta^{18}\text{O}\text{-SO}_4$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{11}\text{B}$ were performed at IT2E Technologies Tracer Isotope Europe Srl in Milan, Italy. Stable isotopes of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) were analyzed using Cavity Ring-Down Spectroscopy (CRDS) with a Picarro L2130-i analyzer (Picarro Inc., California, USA). The results were normalized to the international reference standard Vienna Standard Mean Ocean Water (V-SMOW). The standard deviations of the measurements are approximately $\pm 0.6\text{‰}$ for δD and $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$. Boron isotopes ($\delta^{11}\text{B}$) were determined by Thermal Ionization Mass Spectrometry (TIMS) using a TI-Box instrument (Spectromat, Germany). Measurements were calibrated against NIST SRM 951a standard, with an analytical uncertainty better than $\pm 0.1\text{‰}$. Sulfur and oxygen isotopes in dissolved sulfate ($\delta^{34}\text{S}\text{-SO}_4$ and $\delta^{18}\text{O}\text{-SO}_4$) were analyzed by Elemental Analyzer–Isotope Ratio Mass Spectrometry (EA–IRMS). $^{34}\text{S}/^{32}\text{S}$ ratio of dissolved sulfate was measured with a MAT 253 IRMS (Thermo Scientific, Germany) coupled to a Fisons Elemental Analyzer (UK), and values are reported in permil relative to Vienna Canyon Diablo Troilite (V-CDT), with a precision of $\pm 0.5\text{‰}$. $^{18}\text{O}/^{16}\text{O}$ ratio of dissolved sulfate was measured with a DeltaPlus IRMS (Finnigan MAT, Germany) coupled to a TC/EA unit (Thermo Scientific, Germany), and values are reported in ‰ relative to V-SMOW with a precision of $\pm 0.5\text{‰}$. Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) were measured by TIMS using the TI-Box system (Spectromat, Germany). Values are reported relative to NBS SRM 987, with a precision better than $\pm 5 \times 10^{-5}$ (2 σ).

3.2. Gas geochemistry

Dissolved gas samples were collected in 120 ml borosilicate serum bottles that were filled slowly to minimize turbulent degassing and capped with a butyl rubber septum. Bottles were stored at 4 °C and analyzed within 2–4 weeks using the headspace technique. Gas bubble samples were collected by placing a funnel above a leakage point and allowing the gas to displace water in an inverted 40 ml amber VOA vial. Once filled with the gas sample, the vial was capped using a Teflon-coated silicone septum, and 5 ml of salt-saturated degassed water was added to act as an additional barrier against losses.

Gas analyses were performed in the laboratory using a Carlo Erba 8000 model gas chromatograph with helium carrier gas. Light hydrocarbons (methane, ethylene, ethane, propane) were separated on a 2 m long CBK-BHT100 packed column and analyzed using a Flame Ionization Detector, and carbon dioxide was separated on a 2 m long Porapak-Q packed column and analyzed using a Thermal Conductivity Detector. Analytical reproducibility (1 σ) is about $\pm 5\%$.

3.3. Hydrological budget

The water balance of the endorheic basin of Bagno dell'Acqua Lake was calculated by first dividing it into two sub-basins: the recharge area and the lake itself. For each sub-basin, the balance between inputs and outputs was calculated using the following relationships:

$$B_{RA}: R - ETR$$

$$B_L: R - EI$$

Where B_{RA} and B_L are the water balance of the recharge area and the lake, respectively, R is the rainfall, ETR is the evapotranspiration, and EI is the direct evaporation from the lake surface.

The meteorological data required for the balance calculations were obtained from two weather stations (Buccuram and Aeronautica stations; St. 1 and St. 2, respectively, in Fig. 1b). Specifically, rainfall data were taken from St.1, while all other parameters were sourced from St. 2. This approach was necessary due to the unavailability of rainfall data from St. 2 for the considered period (2019–2023). Fig. 1b shows the extent of the basin and the delineated sub-basins.

Evapotranspiration (ETR) for the recharge basin was estimated on an annual basis using the Turc method, as modified by Santoro (1970) for the Sicilian area (Aiuppa et al., 2007). This involves applying the following equation:

$$ETR = \frac{P}{\sqrt{0.9 + \left(\frac{P}{L}\right)^2}}$$

Where ETR = annual average real evapotranspiration in mm, P = annual average precipitation in mm, T = annual average temperature (°C), $L = 300 + 25 \times T + 0.05 \times T^3$.

Based on an analysis of 192 Sicilian basins, Santoro (1970) proposed a modified expression for L for temperature ranges between 10 °C and 18 °C:

$$L = 586 - 10 \times T + 0.05 \times T^3$$

It should be noted that surface runoff was neglected in the water balance, as it is expected to occur only during rare, intense rainfall events (Madonia et al., 2013).

For the calculation of direct evaporation from the lake surface, the following Mayer formula was used, as presented in Aiuppa et al., (2007):

$$EI = 11 \times [e_s - (e_s \times R_h / 100)] \times (1 + 0.0622 \times W_s)$$

Where e_s is the saturated water vapour at the monthly average air temperature, R_h is the monthly average relative air humidity, and W_s is the monthly average wind speed.

4. Results and discussion

In this section, we present and discuss the results of the hydrogeochemical, and gas-geochemical surveys carried out on the lake and its adjacent springs, which provide an updated and improved understanding of the geochemical and isotopic framework characterizing the lake ecosystem (see [Supplementary Table S1 and S2](#)). Additionally, we report data from the hydrogeological budget for the period 2019–2023. These results are then compared with those published by [Aiuppa et al. \(2007\)](#), which refer to the period 1990–1994.

4.1. Hydrogeochemical characterization

All samples plotted on a Langelier-Ludwig diagram ([Fig. 2](#)) fall within the upper left quadrant, corresponding to the chloride-alkaline facies. The main data trend implies mixing between lake waters and the Liuzza well waters (from [Paz et al., 2016](#)), which belong to the bicarbonate-alkaline facies typical of volcanic aquifers. This trend passes through the domain of geothermal brines and results in a pronounced alkaline equilibrium characterized by high concentrations of chloride and sodium ions.

The stable isotopes of water (δD and $\delta^{18}O$; [Fig. 3](#)) show a good alignment with the Southern Italy Meteoric Water Line ([Longinelli and Selmo, 2003](#)), indicating that meteoric recharge represents the primary source of groundwater in the system. However, most samples are slightly shifted toward higher (less negative) isotopic values, suggesting the influence of secondary processes like mixing with marine-derived waters and evaporation. In particular, the trend of some samples toward values closer to zero supports the contribution of a seawater component within the volcanic aquifer. This interpretation is consistent with the position of samples S3 and S5, which are characterized by higher temperatures and likely reflect deeper circulation pathways where interaction with marine-derived fluids may be enhanced.

In contrast, the lake sample (S7) shows a clear deviation from the meteoric line toward more positive $\delta^{18}O$ and δD values, plotting within the lagoonal field. This isotopic shift is typical of evaporation-driven fractionation in closed or semi-closed basins, where preferential loss of lighter isotopes leads to enrichment in the heavier isotopes.

Overall, the isotopic dataset highlights the coexistence of two main processes controlling the system: (i) meteoric recharge partially modified by mixing with marine-derived waters in the aquifer, and (ii) strong evaporative enrichment affecting the lake water. These processes are consistent with the hydrogeological setting of a coastal volcanic system characterized by both deep fluid inputs and intense surface evaporation.

[Fig. 4](#) shows the different fields useful for discriminating the origin of sulfate in solution ([Clark and Fritz, 2013](#)). The $\delta^{18}O$ and $\delta^{34}S$ values of sulfate from all analyzed samples plot within or very close to the evaporite field ([Fig. 4a](#)), clearly excluding significant contributions from atmospheric deposition or from the oxidation of reduced sulfur compounds. Moreover, the relatively narrow range of $\delta^{18}O$ values, coupled with the variability in $\delta^{34}S$, supports a dominant control by sulfate derived from marine evaporites rather than in situ oxidation processes. The position of the samples in proximity to the modern marine sulfate composition further suggests that seawater represents the ultimate source of sulfur. However, the systematic deviation of the samples from the modern marine sulfate

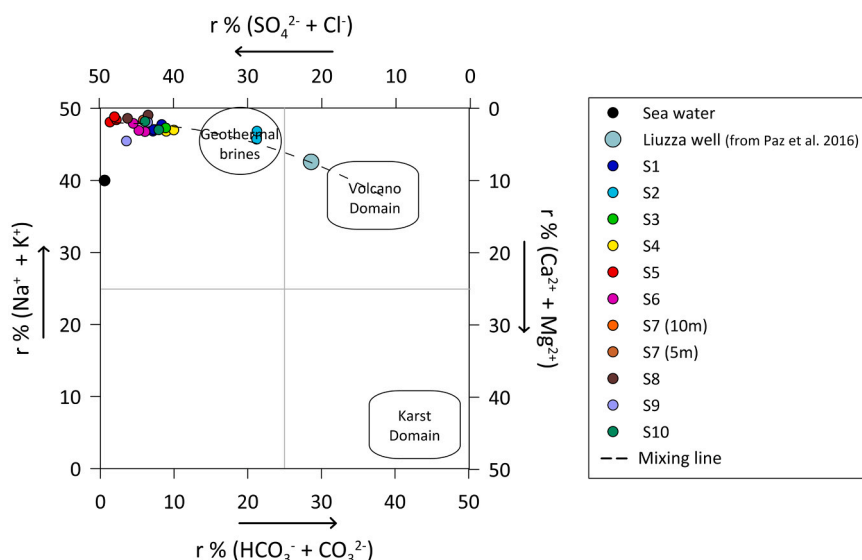


Fig. 2. Langelier-Ludwig hydrogeochemical characterization diagram of the sampled waters. The figure also highlights the domains of various water types (carbonate–volcanic–geothermal–marine). In addition, it plots data from the “Liuzza well ([Paz et al., 2016](#)), a volcanic aquifer sample in the bicarbonate-alkaline facies that represents the least mineralized end-member of the study area.

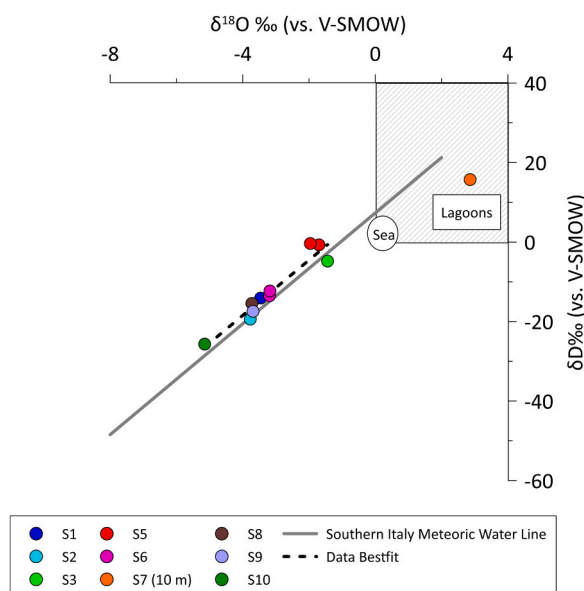


Fig. 3. Stable isotopes of water (δD and $\delta^{18}\text{O}$) from the sampling points. The field representing seawater is displayed with a white circle, while the lagoon water field, corresponding to positive isotope values, is shown as a hatched rectangle.

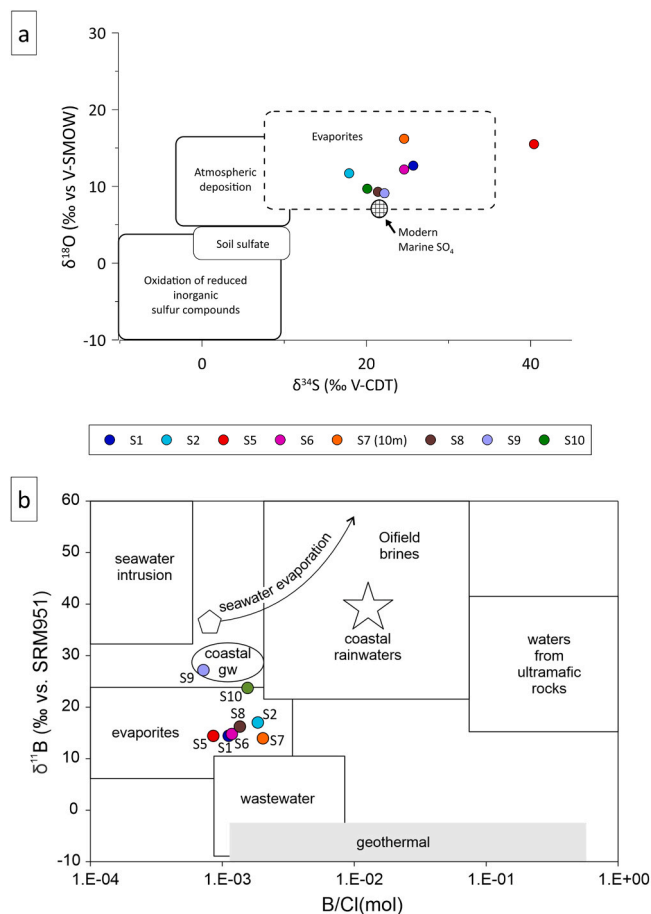


Fig. 4. a) Stable isotopes of the sulfate in the investigated waters together with fields used to discriminate their origin (Clark and Fritz, 2013); b) $\delta^{11}\text{B}$ versus B/Cl; fields redrawn from Vengosh (2014), Boschetti et al. (2013), Boschetti et al. (2015).

field indicates that the original isotopic signal has been affected by secondary fractionation processes, such as water–rock interaction and mixing with meteoric waters. Although all samples fall within the evaporitic domain (Fig. 4a), two distinct isotopic trends can be recognized. Samples S8, S9, and S10, located on the coast, show compositions closer to present-day marine sulfate, suggesting limited post-depositional modification and pointing to the dissolution of gypsum or anhydrite formed under relatively low hydrothermal temperatures ($T \leq 250^\circ\text{C}$) (Awaleh et al., 2022). In these cases, the isotopic signature of the parent evaporite is largely preserved.

Conversely, samples S1, S5, S6, and S7 are characterized by higher $\delta^3\text{S}(\text{SO}_4)$, and slightly higher $\delta^1\text{O}(\text{SO}_4)$, values compared to modern seawater. This enrichment is consistent with isotopic fractionation induced by bacterial sulfate reduction (BSR), a process that preferentially removes lighter isotopes (^{32}S), leaving the residual sulfate enriched in ^{34}S (Boschetti et al., 2011). The isotopic shift observed in these samples therefore suggests that microbial activity has played a significant role in modifying the original evaporitic sulfate signature. Overall, the distribution of the data in Fig. 4a highlights a system dominated by evaporite dissolution, with the superimposed effects of mixing and biologically mediated fractionation processes controlling the final isotopic composition of dissolved sulfate. In general, the variation in $\delta^3\text{S}$ – $\delta^1\text{O}$ slopes among the samples reflects differences in BSR kinetics, with steeper slopes indicating lower kinetic effects and shallower slopes indicating stronger kinetic control (Boschetti et al., 2011). The samples with the highest $\delta^1\text{O}(\text{SO}_4)$ values (S5 and S7) also show the highest $\delta^1\text{O}(\text{H}_2\text{O})$ values (Fig. 4a). Despite the differences in slope, the relatively high $\delta^1\text{O}(\text{SO}_4)$ value of these samples are consistent with oxygen isotope exchange between sulfate and water, likely catalyzed by bacterial sulfate reduction (Boschetti et al., 2011; Clark and Fritz, 2013). Notably, the most evaporated sample (S7) still reaches high $\delta^1\text{O}(\text{SO}_4)$ values despite the apparently slower BSR kinetics, likely due to its higher $\delta^1\text{O}(\text{H}_2\text{O})$. For this sample, the fractionation factor, $1000 \ln \alpha^{18}\text{O}(\text{SO}_4\text{--H}_2\text{O}) = 13.2\text{‰}$, corresponds to an equilibrium temperature of $85 \pm 1^\circ\text{C}$ (Boschetti, 2013), which is inconsistent with the measured temperature ($19 \pm 7^\circ\text{C}$), indicating sluggish kinetics. In contrast, for sample S5, the calculated fractionation factor, $1000 \ln \alpha^{18}\text{O}(\text{SO}_4\text{--H}_2\text{O}) = 17.3\text{‰}$, corresponds to an equilibrium temperature of $53 \pm 2^\circ\text{C}$, in agreement with the measured temperature ($53 \pm 1^\circ\text{C}$), thus supporting isotopic equilibrium between sulfate and water.

Boron isotopic values indicate that most samples exhibit a pronounced evaporative signature (Fig. 4b), in agreement with previous evidence from sulfate isotopes and supporting the dominant role of evaporation in controlling the lake's geochemical evolution. However, samples S9 and S10 display values closer to those typically observed in coastal environments, suggesting a possible external contribution.

The strontium isotopic ratio ($^{87}\text{Sr}/^{86}\text{Sr}$), which is not affected by isotopic fractionation, represents a robust tracer of source contributions and water–rock interaction processes. Most of the sampled waters show isotopic ratios consistent with those of the volcanic rocks of Pantelleria Island (Civetta et al., 1984), indicating that water–rock interaction within the volcanic substrate is the primary control on dissolved strontium.

In contrast, samples S8, S9, and S10 along the coast exhibit slightly higher $^{87}\text{Sr}/^{86}\text{Sr}$ values, trending toward the seawater signature (Fig. 5). This shift suggests a mixing process between volcanogenic fluids and a marine-derived component, likely related to seawater intrusion or the contribution of marine aerosols. The deviation observed in these samples is consistent with their spatial location and supports the hypothesis of localized external inputs superimposed on the dominant volcanic signature.

Overall, the combined boron and strontium isotopic evidence highlights the coexistence of two main processes: (i) strong evaporative concentration within the closed lake system, and (ii) localized mixing with marine-derived fluids, which becomes more evident in specific sampling sites.

In summary, the hydrogeochemistry of Lake Bagno dell'Acqua and nearby springs outlines a complex system resulting from the mixing of meteoric, marine-derived, and geothermal volcanic fluids, further influenced by evaporation and prolonged water–rock interaction. In agreement with previous studies (Azzaro et al., 1983; Dongarrà et al., 1983; Parello et al., 2000; Aiuppa et al., 2007; Cangemi et al., 2010; Pecoraino et al., 2015; Ingrassia et al., 2024), the dominance of Na^+ and Cl^- defines the typical geochemical signature of Pantelleria's groundwater. The low Ca^{2+} /alkalinity ratio promotes high pH (up to 9.3) through CaCO_3 precipitation and, combined with silicate weathering, drives progressive alkalization under evaporative stress. Isotopic data (δD , $\delta^{18}\text{O}\text{--H}_2\text{O}$, $\delta^{34}\text{S}$, $\delta^{18}\text{O}\text{--SO}_4$, $^{87}\text{Sr}/^{86}\text{Sr}$) confirm evaporative enrichment and mixing of volcanic, marine, and meteoric components, defining a ground-water–thermal evolutionary system.

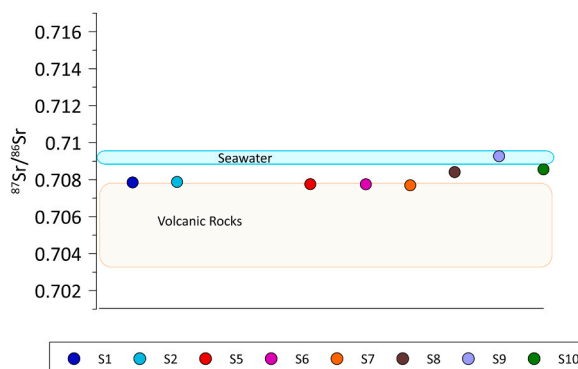


Fig. 5. $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio of the samples.

4.2. Gas-geochemical composition

Dissolved gas samples have highly variable concentrations (Fig. 6a), with CO_2 ranging from 0.1 to 14.7 mmol/L and CH_4 from 10 to 710 nmol/L. Regarding the former, there is a strong correlation, as expected, with pH ($r^2=0.68$) and a moderate one with temperature ($r^2=0.55$). The two highest values are associated with samples S2 and S5 near the lake, in areas that have deep-origin CO_2 leakage on the surface. Of the two coastal sites measured, the S9 value is moderately high (implying deep CO_2 input) while that for sample S10 is very low. The CH_4 values of these groundwater samples are all relatively low, with slightly higher concentrations in the springs near the lake.

The surface water sample from the lake (S7, 10 m depth) is clearly different due to exchange with the atmosphere and sediments as well as biogeochemical processes that regulate in situ production and mineral precipitation reactions. The concentration of CO_2 is 0.05 mmol/L, with pCO_2 values measured here and in shallow waters throughout the lake ranging from 1700 to 1900 μatm . Given the high pH values in the lake, $\text{CO}_2(\text{aq})$ (2.2 mg/L) is a minor dissolved inorganic carbon (DIC) species compared to HCO_3^- and CO_3^{2-} (2556 and 384 mg/L, respectively; Cangemi et al., 2010). The highest CH_4 concentration is observed in the lake sample, possibly linked to microbial activity in the oxic alkaline waters, diffusive flux from the anoxic sediments, and/or bubble dissolution.

Gas bubble samples were collected exclusively in the lake, both close to the shore in water < 0.6 m deep and by scuba divers in waters 1–2 m deep (see Figure S1 for locations). All sites, except B34, are natural bubbling points that consist primarily of CO_2 (64–98%) plus lesser amounts of CH_4 (0.005–14%) and N_2 (0.03–31%) (Fig. 6b). Instead, sample B34 was collected by puncturing a shallow confining clay layer to release trapped gas that is primarily CH_4 (91%) with minor CO_2 (5%) and N_2 (2.2%) and trace C_2H_6 (53 ppm).

The amount of bubbling gas that dissolves into the lake waters is a function of gas solubility, initial bubble size and release depth. Simulations, using the Bubble Dissolution Model (Kassa, 2025), indicate that 7 mm diameter bubbles released in 0.6 m deep water transfer about 40% and 2% of their original CO_2 and CH_4 content, respectively, to the lake water, while bubbles released in 2 m deep water transfer about 90% and < 10%, respectively. Smaller bubbles result in greater dissolution.

Alkaline lakes are dynamic environments for carbon cycling (Pecoraino et al., 2015), with CH_4 and CO_2 playing important roles in various chemical and biochemical processes. For example, high primary productivity in Bagno dell'Acqua Lake (Piacentini et al., 2026) yields organic-enriched laminations (Calò et al., 2013) or accumulations (Aiuppa et al., 2007) that can lead to methanogenesis in the sediments, like that observed at site B34 (Figure S1), while the potential for aerobic methanogenesis in the water column has been highlighted in other alkaline lakes (cf. Fazi et al., 2021). Regarding CO_2 , dissolved concentrations are enhanced because DIC saturation increases exponentially with pH (Fukushi and Matsumiya, 2018), with saline lakes that have pH values > 9 acting as weak CO_2 sinks (Duarte et al., 2008). Because of this, the constant and significant addition of CO_2 via both dissolving bubbles and spring waters can be incorporated into the system, with concentrations being kept relatively stable due to biologically mediated aragonite and dolomite precipitation both in the water column and in microbialites (Ingrassia et al., 2024).

It is possible that environmental changes linked to a diminished hydrologic cycle could impact this carbon cycling in the lake. For example, increased salinity could affect microbial community viability and mineral solubility, reduced lake surface area could decrease the input of bubbling CO_2 along the shallow shoreline, and/or decreased inflow could change nutrient balances, amongst others. The complex interaction of these processes is difficult to predict, and long-term studies of other saline / alkaline lakes have yielded conflicting results (Verschuren et al., 1999) that highlight the uniqueness of each lake. The fact that Bagno dell'Acqua Lake is already subject to seasonal variations that cause significant changes in salinity and lake surface area (Aiuppa et al., 2007), however, does imply that the biogeochemical system may be able to withstand changes within a limited range.

4.3. Hydrogeological budget

To verify how the hydrogeological budget has changed over 20 years since the calculations of Aiuppa et al. (2007), we follow the same investigative methodology. Meteorological data from stations St. 1 and St. 2 were used to calculate the hydrological balance of

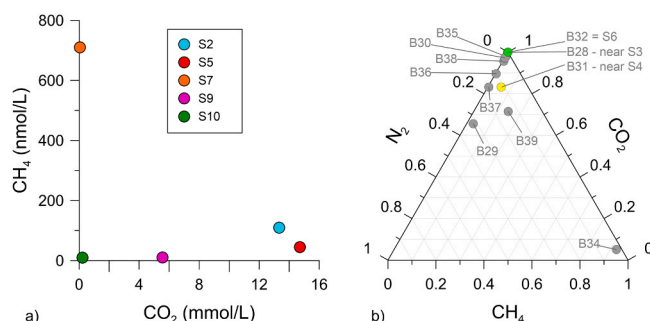


Fig. 6. a) Relationship between dissolved CH_4 and CO_2 ; note the much higher CH_4 value in the lake sample (S7) compared to the groundwater samples.; b) Ternary plot of CO_2 - CH_4 - N_2 concentrations in gas bubble samples collected in the lake; points corresponding to water sample locations are labelled (S3, S4, S6), while the locations of the gas bubble samples are reported in Fig. S1.

the two identified sub-basins for the period 2019–2023 (see Fig. 1b). Table 1 shows average annual values throughout the considered period. The lake's surface area has remained stable, thus the areal extents from Aiuppa et al., (2007), were used for the budget calculation. Similarly, for the calculation of evapotranspiration, we adopted the Turc formula as modified for Sicilian basins (Santoro, 1970), in line with the approach used by Aiuppa et al. (2007). The calculated annual averages are shown in Table 1 (under “Recharge area”). Direct evaporation from the lake surface was calculated using the Mayer formula, again as applied in Aiuppa (2007). The results of this analysis are also presented in Table 1 (under “Lake”). Figs. 7a and 7b show a synthesis of annual budget results for both the lake and the recharge area.

It is worth noting that the present-day recharge from the hydrogeological basin has decreased compared with the 1990–1994 period (Aiuppa et al., 2007), corresponding to a reduction of about 194,000 m³. Considering the data reported in Table 1, this decrease is attributable to a lower value of net infiltration, basically due to the rainfall decline. At the same time, direct evaporation from the lake surface has increased by about 83,000 m³ compared to the estimates of Aiuppa et al. (2007) for the time interval 1990–1994. Considering the formula reported in the Methods section for estimating evaporation from the lake surface, the values obtained for the period 2019–2023 are higher than those for 1990–1994 due to the combined effects of multiple factors, including air temperature, humidity, wind speed, and saturated water vapour pressure (see Table 1 for details). This results in a total water budget loss for the basin–lake system of 49%, corresponding to approximately 277,000 m³ (see Table 2; Figs. 7c, 7d). The adopted approach (from Aiuppa et al., 2007), together with the use of meteorological data from multiple stations, introduces an inherent level of approximation. Uncertainties associated with the applied methods were not quantitatively assessed. The water balance relies on a set of assumptions, explicitly detailed in the Methods section, which are intentionally kept consistent with those of Aiuppa et al. (2007) to ensure a robust and meaningful comparison.

Despite this substantial water budget deficit, the water surplus in the basin—defined as a net positive contribution from subsurface inputs that offsets evaporative losses, as hypothesized by Aiuppa et al. (2007)—appears to be preserved (see Table 2).

However, these results highlight a potential role of climate change in affecting sensitive and unique ecosystems such as those of alkaline lakes. Indeed, the scenario described carries implications for possible future trends. In particular, if the identified trend continues over the next 20 years, a critical phase for the lake's hydrological regime is expected to be reached, as further reductions in recharge relative to evaporation could lead to significant increases in salinity and associated changes in the lake's biogeochemical functioning.

To corroborate these observations derived from the hydrogeological water balance of the basin–lake system, we collected historical geochemical data for the lake waters (D'Alessandro et al., 1994; Duchi et al., 1994; Aiuppa et al., 2007; Pecoraino et al., 2015), searching for potential evidence of increased mineralization processes.

Fig. 8 displays the Na vs. Cl ratio for both the water samples collected in this study and historical samples from the same sampling points (springs, wells, and lake). It can be observed that, while the concentrations of Na and Cl in the spring waters sampled in this work are consistent with historical data, the lake waters show a higher Na/Cl ratio (i.e., S7).

To better visualize the historical trend, we included the concentrations of Cl, SO₄, and Na from 1966 to the present regarding the chemical composition of the lake waters (D'Alessandro et al., 1994; Duchi et al., 1994; Aiuppa et al., 2007; Pecoraino et al., 2015). As shown in Fig. 9, there is a marked increase in the concentrations of Cl, Na, and SO₄ of about 7970 ppm, 5660 ppm, and 770 ppm, respectively. This increase can be explained by a decrease in the lake's water renewal rates, as testified by the calculated hydrogeological balance.

The observed reduction in lake recharge, together with the associated increase in salinity and modifications in gas dynamics, may have significant implications for the lake's biogeochemical functioning. In particular, shifts in water balance can alter stratification patterns and residence times, thereby influencing redox conditions and the distribution of dissolved gases such as methane and carbon dioxide. These changes may affect microbial metabolic pathways, including methanogenesis and methane oxidation, which play a central role in carbon cycling within the system. Increased salinity may further constrain microbial community composition, potentially favoring extremophile taxa while limiting overall metabolic diversity and activity. In addition, variations in hydrological inputs and evaporation-driven concentration processes can modify nutrient availability and recycling, with possible consequences for primary productivity and trophic interactions. Although these interpretations remain speculative and are not directly tested in this study, they highlight plausible mechanisms through which ongoing hydrogeochemical changes could impact ecosystem functioning and the resilience of the lake's unique biota.

5. Conclusions

The multi-year hydrogeological and hydrogeochemical monitoring of the alkaline lake Bagno dell'Acqua and its surrounding hydrothermal system provides a detailed reconstruction of the recent evolution of a closed and climatically sensitive ecosystem. The integrated approach, combining chemical, isotopic, and hydrological analyses, highlights the coupling between climatic variability and geological controls governing the lake's stability. The main findings can be summarized as follows:

- The hydrogeochemistry of lake and spring waters reveals a mixing between meteoric, marine-derived, and geothermal volcanic fluids.
- The stable isotope data of water indicate variable mixing and evaporation, with the lake showing clear evaporative enrichment. Boron, sulfate, and strontium isotopes further constrain the origin of the fluids, suggesting a dual-source isotopic signature intermediate between marine and water–rock interaction processes.

Table 1

Hydrological parameters for the recharge area and the lake. In detail, L is the evaporating power of the atmosphere, ETR TURC is the annual average real evapotranspiration (mm), IE is net infiltration, RH is the monthly average relative air humidity, Ws is the monthly average wind speed, Es is the saturated water vapour at the monthly average air temperature, and El is the direct evaporation from the lake surface.

Recharge area							Lake					
Year	Annual average Temperature °C	Annual cumulative Rainfall mm/yr	L	ETR TURC	IE mm/yr	Annual IE Recharge area m ³	RH %	Ws m/s	Es	El	Rainfall-El mm/yr	Annual Lake Budget m ³
2019	18.92	413	735.31	374.34	38.26	278837	73.71	6.30	17.60	922.77	-510	-99993
2020	19.05	501	741.06	430.07	70.93	516944	72.69	5.12	17.35	889.83	-389	-76210
2021	19.56	528	764.70	449.77	77.83	567209	67.71	5.57	18.22	1169.34	-642	-125782
2022	20.02	386	787.01	361.58	24.62	179416	68.10	4.67	18.80	1099.94	-714	-139893
2023	19.54	518	763.62	444.16	73.84	538171	68.43	4.78	18.11	1072.45	-554	-108672
2019–2023	19.42	469	757.88	414.11	54.97	400592	70.13	5.29	18.02	1030.87	-562	-110110
1990–1994	18.3	510	709.42	428.62	81.68	595251	78.83	6.42	16.70	648.00	-138	-26989

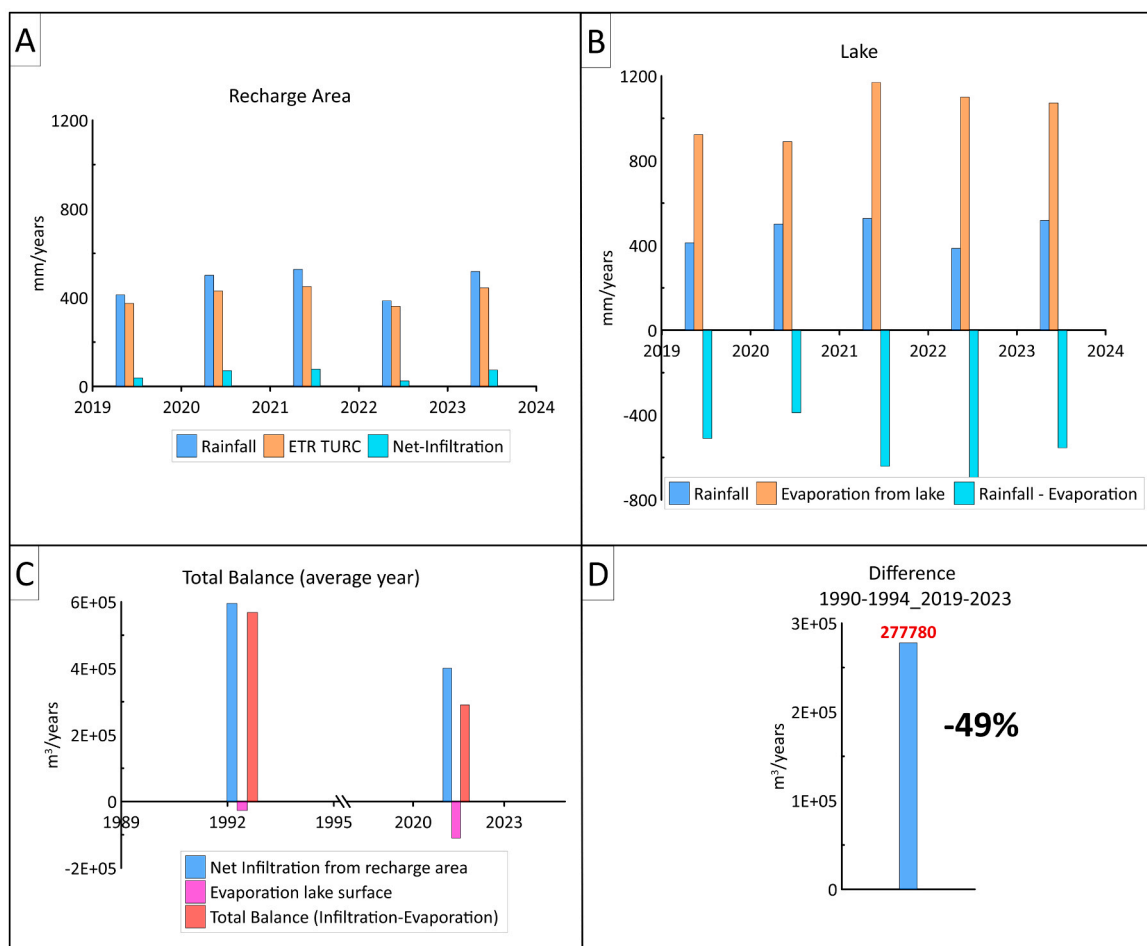


Fig. 7. A) and B) budget for the recharge area and the lake, respectively; C) total balance comparison between the investigated periods; D) difference between the periods resulting in a net water loss of 49% (277,780 m³/years).

Table 2

Hydrogeological balance for the periods 1990–1994 and 2019–2023, and comparison.

	1990–1994 m³	2019–2023 m³	Comparison m³
Net infiltration from Recharge area	595251	400592	194659
Lake Budget	-26989	-110110	83121
Total Balance	568261	290482	277780

- The hydrological balance reveals a marked shift over the past two decades, with recharge decreasing and evaporation increasing compared with the 1990–1994 period. The combined effect has resulted in a net annual water loss of roughly 49%.
- Geochemical indicators, including Na^+ vs. Cl^- , point to continuous solute enrichment in the last century, possibly consistent with decreased inflow and intensified evaporation.
- CO_2 and CH_4 data highlight the complexity of carbon cycling in the lake and the difficulty of predicting how environmental changes may affect the equilibrium amongst the various biogeochemical processes.
- The study reveals an increasing vulnerability of the system, suggesting that continued climatic stress could push the lake toward a critical state within the next two decades, potentially enhancing salinity and affecting the lake's biogeochemical processes encompassing the formation of microbialites of extreme ecological interest. For these reasons, we highlight the importance of continuous hydrological measurements (e.g., water level and evaporation rates), repeated geochemical and isotopic analyses, and the monitoring of dissolved gases and key biogeochemical parameters.

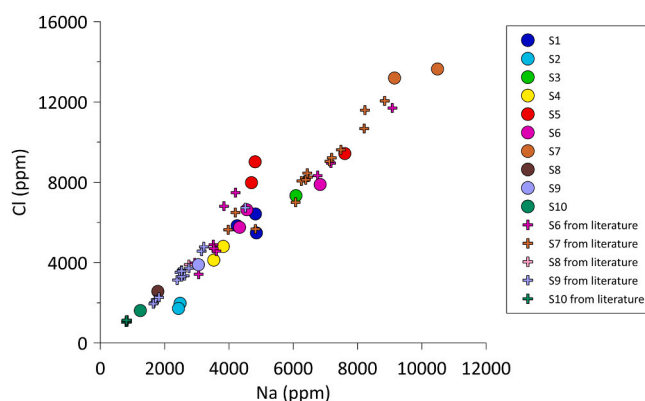


Fig. 8. Binary plot of Na vs. Cl ratio of the investigated sites and lake water sample (S7). Historical data and data from this study are represented by plus symbols and circles, respectively.

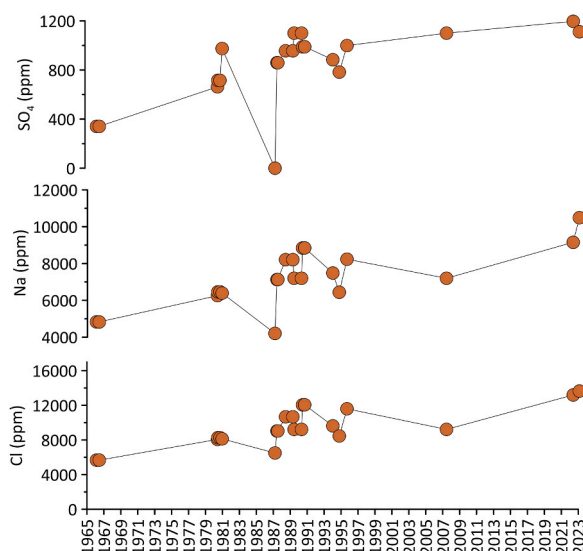


Fig. 9. Time series of major ions (Cl, Na, SO₄) in Lake Bagno dell'Acqua, integrating historical data with results from the present study (2021–2023).

CRediT authorship contribution statement

Tiziano Boschetti: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Stan Eugene Beaubien:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Maurizio Barbieri:** Writing – review & editing, Supervision, Resources. **Francesca Gori:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marino Domenico Barberio:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marco Petitta:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition. **Valeria Lorenzi:** Writing – review & editing, Writing – original draft, Visualization, Data curation. **Francesco Latino Chiocci:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Francesco Latino Chiocci reports financial support was provided by Ente Parco Nazionale di Pantelleria. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ejrh.2026.103530](https://doi.org/10.1016/j.ejrh.2026.103530).

Data availability

Data will be made available on request.

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