The Origin and Water Quality of Spring Systems in Monchique, Portugal: A Focus on Long-Term Sustainability and Elevated Sodium Levels

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Abstract

Spring water systems in Monchique, SW Portugal, not only serve diverse local utilities–from thermal baths to bottled water–but also represent a microcosm of a global concern: elevated sodium levels in spring-sourced bottled waters. This research employs hydrogeochemical and isotopic analyses to investigate the origin, hierarchy and quality of the springs offering a new focus on elevated sodium concentrations, a known global cardiometabolic risk factor. The springs arise from a complex hydrogeological system formed by extensive faulting between argillaceous country-rocks and intruded Cretaceous syenites. Here we show that thermal springs with temperatures of 23-31°C, have a groundwater age of 5000 years, indicative of extended water-rock interactions and recharge at elevations of 450 to 650 m revealing a hitherto unreported resilience in regional groundwater hydraulics. Conversely, cold springs recharging from 200 m to the area’s peak at 900 m follow shorter paths within the regolith influenced by shallow geological features. The study detects nitrate contamination from surface sources in the cold springs and relatively high sodium levels in the geothermal springs that approach or surpass guideline values. Elevated sodium is attributed, for the first time, to long-term interactions and cation exchange with Na-rich syenites, possibly intensified by heat-induced dissolution at depth. This study informs current perspectives on the long-term sustainability and public health implications of spring water systems. The ion chemistry and isotopic evidence suggest that thermal springs, due to their longer circulation times, are less vulnerable to climatic shifts compared to the more susceptible cold springs. While offering specific
insights into the Monchique springs, the research has broad implications to similar high-sodium thermal springs across the Iberian Peninsula and potentially worldwide.

Keywords
Water Quality; Springs; Monchique; Portugal; Sodium; Isotope; rock–water interactions.

Highlights:
• Thermal springs in Monchique exhibit a 5000-year water-rock interactions.
• High-altitude meteoric water sustains geothermal and cold springs in Monchique.
• Local recharge and land use linked to nitrate contamination in cold springs.
• Syenite host rock and ion-exchange processes drive elevated sodium in geothermal springs.

1 Introduction
Spring systems worldwide, such as the famous thermal springs of Iceland and New Zealand and the karst springs of the Dinaric Alps, have long attracted hydrogeological interest (Guo and Wang, 2012; Jukić and Denić-Jukić, 2015; Soto et al., 2019; White, 1957). These systems demonstrate important interactions between geology, climate and water resources offering a rich area of study (Asnin et al., 2022; Negri et al., 2018; Reyes et al., 2010). In this context, the Monchique Springs in Southern Portugal are an exemplar within a global framework.

Southern Portugal is characterised by the Serra (i.e., mountains), Barrocal (i.e., mountain footslopes) and Littoral (i.e., coastal) landscapes. The Serra, a line of hills and small mountains, encompasses more than half of the entire area of southern Portugal delineating the northern border between the relatively water-rich provinces of the Algarve and the comparatively arid Alentejo. The geology of the mountainous areas is distinct marked by a regionally extensive syenite laccolith (González-Castillo et al., 2014) of Cretaceous age with 72 Ma (Miranda et al., 2009) overlain by a thick layer of argillaceous country rocks, which limit the potential for groundwater storage. In some parts of this area (i.e., Monchique and its surroundings), the intruded syenites, which is about 80 km² elongated along a ENE-WSW direction, outcrop through the argillaceous envelope. This geological setting, especially the syenitic intrusions and their associated spring systems, is analogous to other globally studied spring systems where geothermal, volcanic and hydrothermal activities significantly influence the chemical composition of water (Asnin et al., 2022; Guo and Wang, 2012; Negri et al., 2018). In SW Portugal, this has resulted in an exceptional topography peaking at 902 m at Fóia, geographically situated at the intersection of the Atlantic and the Mediterranean district regions (Fig. 1). The hydrogeological phenomena observed here demonstrate how diverse geological formations can give rise to varied spring systems, each with unique chemical compositions and ecological impacts (Benavente et al., 2016; Paikaray and Mahajan, 2023). The high precipitation, reaching up to 1000 mm per annum, in combination with the faulted, fractured
and altered syenites on the higher topography, has given rise to a varied spring system including the well-known Monchique thermal springs, valley-fill aquifers and a few radial rivers. This diversity facilitates investigation of the intricate connections between geology, hydrology and environmental health, which has global implications.

The balneological use of natural geothermal waters for healing and leisure has been around for thousands of years (Naraindas and Bastos, 2011). The famous geothermal springs of Monchique, known since Roman times, are harvested for recreational purposes in natural thermal baths and spas, making Monchique a major tourist destination in the Algarve and Portugal as a whole (Bastos, 2011). The geothermal spring referred to as “Fonte Santa”, literally translated as “holy spring”, is still believed to have healing properties on the grounds of both natural therapeutic benefits and traditional beliefs (Naraindas and Bastos, 2011). Additionally, water from the Monchique springs is bottled as a natural mineral water, a practice common in many other springs in Portugal (Lourenço et al., 2010) and Spain (García-Marín et al., 2020). However, the sustainability of water from these springs remains largely unexplored.

Of current global interest is the elevated sodium levels in such springs with concentrations reaching upwards of 100 mg/L and even exceed 1000 mg/L in some regional counterparts and elsewhere (Azoulay et al., 2001; Grasby et al., 2019; Lourenço et al., 2010; Vigni et al., 2022). This prevalence of sodium, as noted in recent studies (de Carvalho et al., 2015; Mao et al., 2023; Tapias et al., 2022), raises concerns regarding its health implications, which are not yet fully understood. The presence of sodium in drinking water is increasingly recognised as a potential health risk, contributing to overall dietary sodium intake and thereby posing a potential threat to cardiovascular health (Calabrese and Tuthill, 1981; Hoque and Butler, 2016; Khan et al., 2011; Khan et al., 2014; Nwankwo et al., 2020; Scheelbeek et al., 2017). While in coastal regions, elevated sodium levels in drinking water are often attributed to coastal hydrodynamics and storm surges (Hoque et al., 2016; Islam et al., 2019; Michael et al., 2017), the sources of sodium in inland springs remain less clear. This scenario is observed in other spring systems with elevated sodium levels, like those in the East African Rift (Asnin et al., 2022) and the high-sodium mineral springs in the Andes (Carrera-Villacrés et al., 2016), which offer comparative perspectives on the geological factors influencing sodium concentrations. With sodium concentrations consistently surpassing 100 mg/L, the springs of Monchique offer valuable insights, serving as a comparative model for similar springs both in the region and in North America (Azoulay et al., 2001; Lourenço et al., 2010). Furthermore, the geological settings of Monchique, characterized by syenitic intrusions and argillaceous country-rock, reflect findings from globally studied geothermal systems, where such formations have significant impacts on the chemical composition of spring waters, particularly sodium levels (de Carvalho et al., 2015; Tapias et al., 2022; White, 1957).

The Monchique springs also offer a source of good quality potable water for drinking and local domestic purposes, as is the case in other hilly localities of the Iberian Peninsula and Mediterranean basins (García-Marín et al., 2020; Lourenço et al., 2010). In Monchique and the neighbouring Caldas de Monchique, most inhabitants depend on groundwater collected from numerous springs in the township as their main source of water supply. The springs also have important cultural, social, religious and economic significance (Bastos, 2011; Naraindas and
Bastos, 2011). They also have an important role in local agriculture, including the irrigation of crops such as sweet potatoes. Given their lower management costs compared to treated water, these springs are economically attractive. Their productivity, however, is not always reliable, often faltering due to insufficient rainfall. This makes them susceptible to the impacts of future climate change, a pressing concern as Portugal is considered one of the regions most vulnerable to climate shifts in southern Europe (Mourato et al., 2014).

In this study, our overarching aim is to explain the complexities of the Monchique springs by analysis of hydrochemical and isotopic profiles. We employ a diverse dataset, sourced from sampling across springs, streams, and waterfalls, further augmented by aquifer characteristics, rock compositions and radiogenic dating results. While our inquiry encompasses the origin, hierarchy and general water quality of these springs, we place a particular emphasis on the mechanisms or sources behind the elevated sodium levels. By adopting this comprehensive approach, we aim to provide insights into the long-term sustainability and public health implications of the Monchique spring system, and to offer valuable perspectives that could be applicable to similar spring systems elsewhere.

2 Geological setting

The geology of southern Portugal in Western Iberia is characterised by Carboniferous mudstones, siltstones and greywackes (i.e., sandstone with a significant mud component) of marine origin deformed and mildly metamorphosed during the Variscan orogeny. The region enjoys a varied landscape, from the mountainous Serra areas to the coastal plains, accompanied by a diverse climate that ranges from Mediterranean in the south to more temperate conditions in the north. Large patches of Mesozoic and Cenozoic limestones, marls, sandstones and other shallow marine deposits with sub-volcanic intrusions occupy the western and southernmost regions (Menezes and Rodrigues Da Silva, 1988; Pinheiro et al., 1996; Quesada, 1990). Overlying Neogene sediments with radiometric ages of <23 Ma are generally present as thin, discontinuous outcrops throughout the region, but are better expressed in the south (Cabral, 2012).

Multi-phase Mesozoic magmatism resulted in the Monchique syenite massif, which has been dated at 72 Ma (Bernard-Griffiths et al., 1997; Ribeiro et al., 2014). It is the largest (63 km x 16 km) of the Portuguese alkaline massifs (Grange et al., 2010), devoid of well-defined structures (Rock, 1978) and composed of around 95% “miaskitic” syenite (Bernard-Griffiths et al., 1997; Rock, 1978). The syenites are composed of feldspars (microcline, albite and/or oligoclase), micas, amphiboles, pyroxenes, feldspathoids (particularly nepheline) and accessory titanite plus apatite (Abad et al., 2014). There are substantial variations in syenite composition (Rock, 1978): those occurring at the margins are characterised by finer grain size, low to no nepheline content, highly sodic pyroxenes and more variable Na$_2$O (5.5-10.2 %) compared to internal syenites (7.5-8.7 % Na$_2$O).

Fig. 1. Study Area and Sampling Locations with Geological and Climatic Context. a) The
The figure illustrates the elevation gradients and highlights the prevailing wind direction from NW to SE, as represented in the elevation profile. Geological conceptualisation, featuring Carbonaceous and Syenite formations, provides a high-level understanding of the subsurface conditions along the elevation profile. Elevation data is sourced from the SRTM dataset. b) A zoomed-in section shows areas of high-density springs, including thermal springs, and incorporates geological lineaments and faults as identified by Valadares (Valadares, 2004a). The 300 m contour line delineates the approximate boundary of the exposed igneous (Syenite) rock.

The two prominent intrusions are Picota, (774 m) in the east, and Serra de Monchique (Fóia, 902 m) in the west, forming a mountainous barrier between the Algarve and Alentejo provinces (Fig. 1). A significant southward-trending fault line exists between these intrusions hosting mainland Portugal's most seismically active cluster of low magnitude quakes (M < 4). Intriguingly, these seismic events concentrate at depths between 5 and 20 kilometres suggesting that the structural complexity of the area is both deep-seated and vertically oriented (Carvalho et al., 2006). This deep-seated fault system along with irregular fracturing and variable weathering of the protective carapace plays a critical role in shaping the fault-controlled and fracture-modulated hydrogeology of the region, particularly in Monchique, by contributing to the formation of minor aquifers.

3 Materials and methods

In this section, we elaborate on the sampling procedures and analytical methods employed to generate the data. All the data generated during this study are included as supplementary information.

3.1 Sampling

Water samples were taken from publicly accessible springs during a four-week period from April to May 2018, a time when most perennial springs in the region are typically active and characterized by relatively stable hydrological conditions. The locations range from the highest point at Fóia to low elevations on the coast of around Aljezur. Post-winter, the springs in the Monchique region exhibit consistent flow rates and the influence of direct rainfall on water chemistry is reduced leading to more stable chemical and isotopic compositions. This stability is crucial for accurately assessing the springs' baseline characteristics without the confounding effects of significant seasonal hydrological shifts, such as those caused by heavy rainfall or drought conditions. To ensure a robust depiction of their origin and associated water quality, especially for cold springs, we ensured comprehensive geographical coverage by sampling across representative elevations. There is a total of 37 samples: 32 of which are water samples and 5 rock samples. The 32 water samples comprise 21 samples of cold springs, 4 from geothermal springs, 5 samples from streams/rivers and 1 sample each from a waterfall and from a borehole at a depth of 80 m (Fig. 1). The rock samples are pieces of the intrusive syenite carapace at different stages of weathering, and these were collected from a road-side cliff near Fóia (Fig. 1).
A standard, systematically applied sampling procedure was followed at each location. Field parameters (DO, pH, Temperature and EC) were measured prior to sample collection. Alkalinity (i.e. HCO$_3$) was determined on site by colorimetry and titration with 1.4N H$_2$SO$_4$ solution. The ChemMetrics K-7512 colorimetric DO test kit, calibrated Hanna HI 9033 multi-range conductivity meter and Hanna HI 98190 pH/ORP electrode and thermometer were used.

Three sets of samples were collected, one sample each for isotopic, anion and plus cation analyses into 30 ml high-density polyethylene (HDPE) bottles. Samples collected for trace/major and cation analysis were filtered with 0.45 μm pore-sized Whatman polydisc GW in-line filters. These were acidified with 0.15 ml concentrated nitric acid (HNO$_3$) to reduce pH to <2, thus avoiding precipitation and adsorption of metals into container walls and to minimize microbial degradation. Samples collected for isotopic and anion analyses were neither filtered nor acidified but were refrigerated to below 5 °C. One sample for $^{13}$C/$^{12}$C and $^{14}$C activity determination was collected into a thick-walled plastic bottle.

Finally, a Solinst data logger and RG rain gauge monitoring station were established at the No.15 sampling site, which recorded rainfall and monitored EC of the water at the spring outlet at hourly intervals for 8 months (April 2018 to Jan 2019).

### 3.2 Geochemical analysis

A Thermo Scientific Dionex ion chromatograph (IC) was used to analyse Cl, NO$_3$ and SO$_4$, at Imperial College London. Major cations (Ca, Mg, Na and K) and trace elements (Fe, Mn, As, Sr) were determined with a SpectroBlue ICP-OES at the University of Portsmouth. Both instruments were calibrated across appropriate concentration ranges with commercially-available multi-element solutions. Precision and accuracy of analyses were monitored with CRMs and replicate determinations, and these estimated as approximately 10% and 5% respectively.

Oxygen and hydrogen isotope ratios ($\delta^{18}$O, $\delta^2$H) were measured at the University of East Anglia using a Picarro Cavity Ring-Down Spectroscopy (CDRS) laser instrument, and these are expressed in standard ‘per mil’ notation relative to Vienna Standard Mean Ocean Water (%VSMOW). Data were collected by measuring 2.2 µl aliquots of the sample six times, to overcome memory effects. Repeat analyses of standard Norwich Tap Water (NTW), Greenland Ice Sheet Precipitation (GISP), USGS67400 and USGS64444 gave a measurement precision of 0.16‰ for $\delta^{18}$O and 1.05‰ for $\delta^2$H.

$^{14}$C in pMC and $\delta^{13}$C were determined by current industry standard method Accelerator Mass Spectrometry (AMS) at the Beta lab (Miami, USA) (https://www.radiocarbon.com/). A simple correction based on $^{13}$C values, as outlined in Hoque & Burgess (2012), is used here to determine the age of the groundwater.

A Rigaku Primus ZXII x-ray fluorescence instrument (XRF) was used for elemental analyses of rock samples at the University of Portsmouth. Fused glass discs and pressed powder pellets
were prepared for major elements and trace elements respectively. The XRF was calibrated using a range of rock and soil Certified Reference Materials (CRMs). Accuracy and precision were monitored with additional CRMs and replicate analyses, and both are estimated to be better than ca. 5%.

4 Results

4.1 Physicochemical and field parameters

Temperatures in the water samples exhibit a broad range, from roughly 13 to over 30°C and were clearly influenced by water type. A correlation was observed between temperature and electrical conductivity (EC) in cold springs with a correlation coefficient of 0.431, although this correlation was not statistically significant. In geothermal springs, the correlation coefficient between temperature and EC was -0.71, also not statistically significant. Regarding electrical conductivity (EC), which ranges from approximately 50 to over 1000 μS/cm, and a notable inverse correlation with elevation was observed. In cold springs, the elevation versus EC correlation coefficient was -0.69 indicating a statistically significant relationship with higher elevations generally demonstrating lower EC values. In contrast, for geothermal springs, the elevation versus EC correlation was -0.860, but it was not statistically significant.

These relationships along with pH levels that vary from around 5 to 10, are shown in Fig. 2, which illustrates the relationships between temperature, EC and elevation for the different water types.

Fig. 2. Scatter plots depicting how EC correlates with key parameters in geothermal springs and other water types: a) Temperature vs EC, b) pH vs EC, c) Elevation vs EC.

All springs were situated at elevations below 300 m and characterised by elevated EC values ranging between 378 and 1004 μS/cm, as well as higher pH levels, falling within a 7 to 10 range. Among the cold springs, a few exhibited higher temperatures, though these temperatures were still below those of the geothermal springs. The cold springs with higher temperatures also recorded increased EC values that overlapped with the data from geothermal springs.

Long-term, hourly monitoring at the site corresponding to sample No. 15, located at a 506 m elevation on the Eastern slope of the Fóia block with a larger catchment and perennial flow, indicates a generally stable trend in EC values with discernible fluctuations. While these fluctuations appeared to show a pattern in relation with rainfall events, the correlation was not statistically strong (Fig. 3). During periods of low rainfall, there were observed increases in EC. Notably, EC measurements from all water sources including surface water, consistently registered values above the regional rainfall (Ferreira-Gomes et al., 2022) baseline EC, of approximately 70 μS/cm, suggesting additional influences affecting the precipitation as it moves through the subsurface.
Fig. 3. Time-series representation of electrical conductivity (EC) in µS/cm (depicted in green) at the site corresponding to sample No. 15. Concurrent measurements of rainfall in mm/hr (illustrated in blue) and temperature in degrees Celsius (depicted in red) were also taken at hourly intervals. The inset plot presents a refined analysis where only EC values greater than 70 µS/cm are considered in relation to the cumulative rainfall total for the three days preceding each EC measurement event. Despite the Pearson correlation coefficient being relatively low at -0.1978, the plot reveals a subtle inverse relationship, suggesting a degree of interdependence between rainfall and EC values.

4.2 Hydrochemical facies

A comprehensive evaluation of major ion chemistry, illustrated by a Piper diagram (Fig. 4), delineates geothermal springs and cold surface- and groundwaters into two discrete categories. Geothermal springs predominantly occupy the extreme bounds of the NaCl to NaHCO₃ spectrum suggesting differing influences compared to cold springs. Cold waters are dispersed across the Ca-HCO₃-Cl to Ca-Na-HCO₃-Cl range. This spread hints at a variety of sources for the cold waters, while the geothermal springs' chemistry may point towards a distinct, possibly deeper, source. Notably, two outliers—samples 31 and 32, which are, respectively, from a cold spring and a stream water location—closely align with the geothermal springs. These samples, however, are located 83 and 45 metres downslope from geothermal springs samples 29 and 30 respectively (Fig. 1a), possibly indicating some interaction or influence from the geothermal springs.

Fig. 4. Piper diagram delineating the major ion chemistry across water samples. Thermal springs manifest distinct ion profiles, markedly segregating them from other water types. While direct rainwater analysis at our site is unavailable, we reference similar regional data (Ferreira-Gomes et al., 2022) from 55 km inland suggesting rock-water interaction leading to observed mineral-rich spring water.

4.3 Cations

The geothermal springs, identified as samples Nos. 26, 24, 30 and 29, exhibit the highest sodium concentrations ranging between 94 and 351 mg/l. These springs also display temperatures between 23 and 31°C. The excess sodium, calculated as $Na_{ex} = Na_{sample} - R_{sea} \times Cl_{sample}$ with $R_{sea}$ representing the Na/Cl ratio in seawater (0.56 according to Moller, 1990) — vary from 80 to 295 mg/l (Fig. 5a). A strong correlation emerged between excess sodium and sodium, and between temperature and sodium (Fig. 5a, b). The median Na/Cl mass ratio for the spring samples was found to be 0.46 diverging from the seawater standard of 0.56.
Additionally, several cold springs (Nos. 9, 22, 1, 2, and 31) and a stream (No. 32) recorded sodium concentrations that exceed the US EPA drinking water guideline value of 20 mg/l, along with elevated temperatures between 16 and 22°C.

In stark contrast, calcium concentrations in geothermal springs were notably low (Fig. 5e). While calcium was detectable across all samples, the majority exhibit concentrations below 20 mg/l. Only three samples (Nos. 2, 16, and 14) have higher concentrations reaching up to 96 mg/l. A negative correlation was observed between sodium and both calcium and magnesium, but a positive correlation was noted with boron (r=0.9).

Observed iron and aluminium concentrations do not exceed recommended values for potable water in any of the samples. Among all water sources, Sample 8, the sole borehole with a metal casing, presents the highest iron concentration at 2150 μg/l. A limited number of other samples exceed 10 μg/l. In terms of aluminium concentrations, geothermal springs averaged higher levels (mean 10.8 μg/l) with Sample 24 registering the highest at 48.2 μg/l. Only four cold springs have reported aluminium levels above 10 μg/l.

**Fig. 5.** Scatter plots elucidating the unique sodium (Na) levels in geothermal springs via diverse parameters: a) Excess Na vs Na, b) Temperature vs Na, c) Electrical Conductivity (EC) vs Na, d) Boron (B) vs Na, e) Calcium (Ca) vs Na, f) Chloride (Cl) vs Na.

Principal Component Analysis (PCA), following Trauth (2022), reveals distinct variance patterns between cold springs and geothermal springs. For cold springs and surface water samples, five components collectively account for 90% of the observed variance. Contrastingly, in geothermal springs, a mere two components suffice to explain over 90% of the variance, underscoring the hydrochemical simplicity of these geothermal systems (Fig. 6).

**Fig. 6.** Principal Component Analysis (PCA) biplot with loadings illustrating the variance in ion composition for both cold and geothermal springs. The first two principal components predominantly feature ions such as Na, SO₄, B, Cl, HCO₃ which are notably prevalent in geothermal springs.

**Fig. 7.** Interactions between electrical conductivity and ion concentrations, highlighting distinct ion-conductivity profiles in geothermal springs: a) Cl vs EC, b) SO₄ vs EC, c) Na/Cl vs EC, d) Ca vs EC, e) Mg vs EC, f) HCO₃ vs EC.

Pearson's correlation analyses (Figs. S.1 and S.2 in supplementary information), reveal distinct
ion-conductivity relationships for cold springs and geothermal springs. For cold springs and surface water, a significant positive correlation was observed between Electrical Conductivity (EC) and the ions Cl, HCO₃, Na, Ca, Mg, and B, each yielding a correlation coefficient (r) of approximately 0.9. In geothermal springs, a strong positive correlation was only found between EC and the ions Cl, SO₄, Na, and B, as substantiated by Figs. 5 and 7.

### 4.4 Anions

The distribution of chloride (Cl) concentrations across all samples exhibits a mean value of approximately 35 mg/l with three-quarters of the samples ranging from 12 to 40 mg/l. Notably, the highest Cl concentration with 106 mg/l was observed in a cold spring (Sample 2), which also exhibited the highest levels of calcium (Ca), magnesium (Mg), boron (B) and barium (Ba). Geothermal springs generally display elevated Cl concentrations, particularly evident in samples 29 and 30 with values of 99.8 and 88.2 mg/l respectively.

For sulphate (SO₄), the peak concentration of 143 mg/l was identified in geothermal spring sample 29, while the remaining geothermal springs also show relatively high levels. Cold springs at higher elevations, however, have the lowest SO₄ concentrations ranging from 2.3 to 4.8 mg/l.

Significant positive correlations were observed between chloride, sulphate and sodium, as corroborated by Figs. 5 and 7. In contrast to the prevalence of these anions, nitrate (NO₃) was undetectable (below the 0.02 mg/l detection limit) in five samples. The mean NO₃ concentration stood at 5.6 mg/l with the highest concentration found in cold spring sample 16 at 33.8 mg/l.

### 4.5 Oxygen and hydrogen isotope ratios

The isotopic composition of oxygen ($\delta^{18}$O) and hydrogen ($\delta^2$H) varies across the sampled waters, registering ranges of -4.86 to -4.10‰ and -23.92 to -16.90‰ relative to V-SMOW respectively. These data align closely yet are elevated compared to the Global Meteoric Water Line (GMWL) shown in Fig. 8. As there is no Global Network of Isotopes in Precipitation (GNIP) station near our study area to establish a Local Meteoric Water Line (LMWL), we used the GNIP dataset to create meteoric water lines for three sites around Monchique. These were Faro, a coastal location situated about 60 km southeast, Lagoa, a coastal town situated about 20 km south and Lisbon, 160 km north, at elevations of 7, 12 and 2 m above sea level respectively. Our evaluated stable isotope data includes comparisons with Meteoric Water Lines (MWLS) from Faro, Lagoa and Lisbon along with the Global Meteoric Water Line (GMWL) and the Eastern Mediterranean Water Line (EMWL). Lagoa and Lisbon are at similar distances to the west coast as the study area and may, therefore, receive moisture from similar sources. This broader comparison helps to contextualize our findings within the regional climatic variations. Significantly, we observed that while our samples align more closely with the MWLs of Lisbon and Lagoa, there is a noticeable divergence from the Faro
MWL. This divergence suggests different moisture sources, or at least a dominant moisture source, compared to Faro. Notably, our lower elevation samples align with the Lisbon and Lagoa MWLs, while samples from higher elevations show a clear altitude effect indicated by their placement above these lines. This aligns with the expected isotopic depletion at higher altitudes of between -0.15 and -0.5‰ per 100-m rise for oxygen and 1 to 4‰ per 100-m rise for hydrogen.

The dataset yielded a mean $\delta^{18}O$ of -4.57‰, clustering most samples between -4.60 and -4.30‰, and a mean $\delta^2H$ of -21.08‰ with the majority falling between -22 and -19‰. When contrasted with annual average values from the GNIP database ($\delta^{18}O$: -4.3, $\delta^2H$: -22.8), our averages appear slightly lower for $\delta^2H$ but elevated for $\delta^{18}O$. It is noteworthy that GNIP data reveal an expected seasonality manifesting as isotopically depleted values in the early part of the hydrological year (Nov to March, $\delta^{18}O$: -4.6, $\delta^2H$: -24.7) transitioning to isotopically heavier values later. Despite the lightest sample (No. 11; $\delta^{18}O$: -4.82, $\delta^2H$: -23.39) being from a cold spring, geothermal springs generally exhibited lighter isotopic signatures than their cold counterparts. Among cold waters, streams tend to be isotopically heavier than springs. The most depleted $\delta^{18}O$ value of -4.86‰ was found in a geothermal spring (Sample No. 29), while the least depleted value of -4.10‰ was identified in a cold spring (Sample No. 13).

Additionally, the analyses show samples’ parallel alignment with the nearest and relevant MWLs i.e. with Lagoa and Lisbon, may indicate no significant evaporation-induced enrichment. This alignment rather suggests a primary influence of altitude over evaporative processes in determining the isotopic composition of our samples. Furthermore, the influence of heavier winter precipitation is evident in our data, as most samples lean towards the depleted end indicating the weighting of isotopic ratios towards periods of more significant precipitation.

**Fig. 8.** Isotopic distribution of water samples with multiple meteoric water lines. These samples are plotted against the Global Meteoric Water Line (GMWL), Eastern Mediterranean Water Line (EMWL), and Local Meteoric Water Lines (MWLs) from Faro, Lagoa and Lisbon. Samples from lower elevations closely align with the Lagoa and Lisbon MWLs indicating altitude effects. Geothermal springs typically exhibit lighter isotopic signatures compared to cold springs. Streams generally display heavier isotopic values.

Geothermal springs, characterised by more depleted $\delta^{18}O$ values ranging from -4.85 to -4.56‰, exhibit higher pH levels between 7.8 and 9.6. In contrast, samples with less depleted $\delta^{18}O$ values between -4.80 and -4.10‰ manifest lower pH ranges of 5.5 to 8.0. Notably, streams, despite their higher pH levels from 7.3 to 8.0, do not correspond with similarly depleted $\delta^{18}O$ values. An inverse correlation between Electrical Conductivity (EC) and $\delta^{18}O$ is observed in geothermal springs indicates prolonged water-rock interactions, while a positive correlation is noted in streams and rivers suggests minimal such interactions, with $\delta^{18}O$ values varying mainly due to altitude differences (Fig. 9a).
The comparison with elevation presented in Fig. 9b and c must be interpreted with caution. The elevations used represent the points at which springs emerge, which may differ from their actual recharge elevations, potentially at multiple levels. Given the terrain's complexity, it is plausible that the recharge areas for the springs are at a similar altitude leading to minor elevation differences. For $\delta^{18}$O, geothermal springs exhibit more depleted values at lower elevations, while such a pattern is not evident for cold springs and streams (Fig. 9b).

A prevailing trend emerges: d-excess values of $\delta^2$H that would be expected based on the $\delta^{18}$O (Clark and Fritz, 1997) increase with rising elevation, albeit with significant variability at each elevation level. It appears that for the geothermal springs, d-excess values decrease with elevation, conversely, they tend to increase for cold springs and streams, no distinct pattern is observed (Fig. 9c). It is known that high elevation d-excess values are more associated with reduced subcloud evaporation, and local processes significantly alter d-excess in coastal and lowland areas but not at elevated regions (Bershaw, 2018; Natali et al., 2022). We take that d-excess values from springs at the lower and higher elevation extremes more accurately reflect their recharge conditions due to their smaller, more defined catchment areas with minimal elevation variation. This assumption allows for a comparison of intermediate elevation samples against a linear gradient established by lower and higher elevation d-excess values, facilitating the estimation of their recharge altitudes (Fig. 10). Linear extrapolation of data points, as shown in Fig. 10, suggests that springs between 400 to 500 meters may have isotopic signatures indicative of recharge from a variety of elevations, pointing to potentially complex recharge zones. Similarly, projections for geothermal springs, identified as outliers in Fig. 10, indicate their recharge occurs between elevations of 480 and 660 meters.

Fig. 9. The interplay between isotopic values, electrical conductivity, and elevation: a) electrical conductivity vs $\delta^{18}$O, b) elevation vs $\delta^{18}$O, and c) elevation vs deuterium excess.

Fig. 10. The variation in d-excess values across different altitudes (similar to Fig. 1) in the recharge source area of the geothermal springs. Springs located at altitudes of 400 to 500 meters may display isotopic signatures reflecting a blend of recharge elevations suggesting the possibility of more intricate or expansive recharge zones. The recharge of geothermal springs is estimated to occur predominantly at elevations between 480 and 660 meters, primarily confined to the Picota block, especially when considering the NE-SW fault and lineaments.

4.6 Rock geochemistry

Rock samples, all syenites with varying degrees of alteration, were collected from a road cutting (location shown in Fig. 1a) to establish a baseline elemental flux attributable to alteration processes and thereby available to groundwater. The extent of alteration was approximated by Loss on Ignition (LOI) at 1000°C, as outlined in Table 1. Notably, sample B2404/6A exhibited the highest LOI at 7.48%, indicating it as the most altered, while sample B2404/6D with the lowest LOI at 1.16%, was identified as the least altered. The latter was used
as a normalizing factor for the elemental values of the other, more altered samples.

Table 1: Results of Loss on Ignition (LOI) Tests.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>LOI %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2404-06A</td>
<td>7.48</td>
</tr>
<tr>
<td>B2404-06B</td>
<td>6.24</td>
</tr>
<tr>
<td>B2404-06C</td>
<td>3.69</td>
</tr>
<tr>
<td>B2404-06D</td>
<td>1.16</td>
</tr>
<tr>
<td>B2404-06E</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Upon normalization using B2404/6D, the elemental composition of the samples reveals distinct patterns. More altered samples exhibited enrichment in aluminium (Al) and iron (Fe), while showing depletion in silicon (Si) and phosphorus (P). For instance, the relatively less altered sample B2404/6E was enriched in sodium (Na), calcium (Ca), Al, potassium (K), manganese (Mn), Fe, sulphur (S) and strontium (Sr), but depleted in magnesium (Mg), Si, and P. Conversely, the progressively altered samples (B2404/6A, B2404/6B, and B2404/6C) show a gradual decrease in concentrations of Na, Ca, cobalt (Co), Sr, Si, and P, and an increase in levels of Al and Fe (Fig. 11).

Fig. 11. Elemental concentrations normalized against the least weathered sample B2404/6D, as determined by X-ray fluorescence (XRF) analyses. The more altered samples B2404-06A, B2404-06B, and B2404-06C display depletion in sodium (Na) and calcium (Ca), while the relatively unweathered sample B2404-06E exhibits enrichment in these elements.

4.7 C-14 dating of thermal springs

A single geothermal spring, notably known and located at Caldas (sample No. 24), was subjected to radiocarbon dating. The measured percent Modern Carbon (pMC) was 34.60 ± 0.10, accompanied by a δ¹³C value of -18.1‰. The unadjusted 'apparent' radiocarbon age calculated from these data stands at 8,774 years Before Present (BP). It is essential to note that this age has not been modified for any hydrogeochemical influences on meteoric water ¹⁴CO₂. Nevertheless, upon applying a simple correction based on ¹³C values, as per Hoque & Burgess (2012), the estimated reservoir residence time for this geothermal water is revised to 4,953
years BP. This correction assumes a 1:1 equivalence in DIC concentrations between the mixing components, which may not accurately reflect the dynamics of the system. Nevertheless, this corrected age estimates highlighting the long-term water-rock interactions while acknowledging potential variations in DIC concentration could affect this estimate.

5 Discussion

The findings from this study allow a detailed exploration of the Monchique springs and an in-depth analysis of their hydrochemical and isotopic complexities. The hydrogeological framework and mechanisms driving sodium enrichment in geothermal springs lead to discussion of the long-term sustainability and public health implications of the springs’ water. The following sections will explore these aspects systematically and comprehensively.

5.1 Complex faults and fractures define hydrogeological framework

Contrary to the conventional notion that igneous massifs like Monchique and the Carboniferous metasediments it intrudes are largely impermeable the results of our empirical studies show that intricate fracture systems, along with significant macro- and mesoscale faults, render the syenites locally porous and permeable (Valadares, 2004b). This porosity is influenced by the dominant NE-SW orientation of faults and lineaments in the area (Fig. 1b). These and, in particular, the major fault line between Fóia and Picota, previously identified as a seismic hotspot (Carvalho et al., 2006), highlight the area's deep-seated and vertically oriented structural complexity. This alignment suggests a more complex hydrogeological dynamic than previously understood, where these structures facilitate both localized and deeper subsurface groundwater movement (Bense et al., 2013).

The dominant NE-SW orientation of faults and lineaments in the area, particularly the major dislocation between Fóia and Picota (Fig. 10), suggests that major subsurface groundwater movement is likely parallel to these geological dislocations. Drawing from Barbosa(1999), the formation of Fóia and Picota from the same magma chamber at different times, Fóia forming first and limiting Picota’s spread towards the west, implies distinct hydrogeological systems with limited hydraulic connectivity. However, the presence of geological features crossing and perpendicular to this dominant trend indicates a more nuanced groundwater flow pattern. Given the predominant structural control in the area, substantial subsurface flow between the Picota and Fóia blocks appears less likely. This structural control, coupled with the elevation differences between the two blocks, supports the hypothesis that water infiltrating at higher elevations likely emerges as springs in lower elevation areas in respective blocks. In the Picota block, especially, deeper percolation along these structurally controlled pathways may lead to the emergence of geothermal springs suggesting a complex interplay between structural geology and hydrogeology.
Our findings build upon and expand the fundamental understanding provided by the previous studies (Araujo et al., 2017; Calado, 2003; Carvalho et al., 2018), offering new data and insights into the hydrogeology of the Serra de Monchique syenites. This work underscores the complex interplay of variably altered carapace, lineaments, micro-fractures near the surface and complex fracturing and possible fault zones at depth presenting a more detailed picture of the geological mosaic influencing the region's hydrogeological characteristics. Water from higher elevations infiltrates these structures until encountering zones of low permeability, such as unfractured rock or pelitic horizons within the metasediments. Additionally, much of the rainwater that infiltrates the ground briefly circulates through the regolith (Pruess, 1999; Ruiz et al., 2010). This layer is composed of altered rock, alluvium, colluvium, and soil and connects to fractures in the bedrock below including fractured syenite. As the recharge continues, the phreatic surface rises. When it reaches a level where water can no longer be stored within the geological structure, it emerges at the surface through numerous cold springs.

For geothermal springs, the hydrogeochemical behaviour is even more complex (Figs. 6 and 8). The results support the hypothesis that increased temperatures are a result of water circulating to significant depths (Andrews et al., 1982). This raises the question of how the heat is gained. A possible explanation, as suggested by Manga & Kirchner (2004), is either through advection at high velocities or from the reservoir's inherent geothermal properties. The syenites in Monchique have relatively high concentrations of U, Th, and K (Rock, 1978), potentially increasing the region's geothermal gradient due to radioactive decay (Gomes et al., 2015). In the absence of large volumes of water at depth to dissipate the heat, one might interpret these results as evidence that the geothermal springs' elevated temperatures are largely a result of geothermal heat.

Groundwater temperature serves as an invaluable tool both for constraining the geological processes occurring below the surface and for validating conceptual models of hydrogeology (Andrews et al., 1982). In the Monchique system, the geothermal springs' average temperature of 25.6°C surpasses the annual average atmospheric temperature by approximately 10°C. Based on a standard geothermal gradient of 30°C/km, one would ordinarily infer that the water has descended to a minimum depth of 500 metres below the recharge level to acquire this additional geothermal energy. The warmer groundwater becomes less dense. This change in density coupled with the pressure dynamics induces the heated water to ascend. However, considering the high-altitude recharge points of these springs and the potential for heat loss through advection during discharge, the water is likely circulating to even greater depths (Bense et al., 2013). The presence of fractures and fault zones within the massif serves as probable high-velocity discharge pathways, minimising excessive heat loss during ascent (Atkinson and Davison, 2002). This interpretation supports previous research, which has frequently attributed the surface discharge of hydrothermal systems to fault structures that affect temperature, discharge rates and locations (Asnin et al., 2022; Fairley, 2009; Negri et al., 2018). Thus, the hydrogeological intricacies of Monchique's springs can be traced back to a complex interplay between structural geology and thermal dynamics, each of which contributes to the distinct flow patterns and water quality within this unique system.
5.2 High-altitude meteoric recharge dynamics shape spring systems in Monchique

Our study reveals a complex recharge and flow system for the Monchique springs (Fig 12), underpinned by both isotopic and age constraints atop the structural control previously discussed. The isotopic data align closely with the MWLs of Lisbon and Lagoa, which, similar to our study area, are influenced by similar Atlantic moisture sources (Fig 8). This alignment, particularly evident in our lower elevation samples, reflects a dominant altitude control with isotopic compositions consistently above the MWLs and the GMWL indicating high-altitude recharge areas ranging between 300 and 800 m. (Clark and Fritz, 1997; Tazioli et al., 2019).

Moreover, the absence of significant evaporation-induced enrichment in our isotope data emphasizes the primary influence of altitude rather than evaporative processes in shaping the isotopic signature (Carreira et al., 2009; Jódar et al., 2016; Lee and Kim, 2007). This is further aligned with the isotopic ratios' weighting towards the winter precipitation period suggesting substantial recharge during this time (Lee and Kim, 2007).

Our empirical results reveal that geothermal springs, manifesting lighter isotopic values, suggest a recharge mechanism from elevations between 480 and 660 meters, predominantly within the Picota block. The NE-SW fault and lineament orientations offer insights into the directional flow of water (Taillefer et al., 2017) with geothermal springs on the eastern part of Picota potentially receiving water from the eastern side, while spring (sample) no. 26 may be influenced by the western side. High chloride content in geothermal springs may indicate the leaching of sea spray aerosols deposited during drier seasons (Fernández-Martínez et al., 2019), coupled with evidence of more extensive water-rock interactions, particularly in springs (sample) no. 29-30 compared to spring (sample) no. 24, suggesting longer travel times possibly along north-south dislocations parallel to the eastern side of the Picota block (Jefferson et al., 2006; Mancini et al., 2018).

Our isotopic analyses, and radiocarbon dating that indicates a recharge age of around 5000 years for these geothermal springs, offer a revised conceptualisation of the region's recharge and flow systems. This age dimension confirms prolonged water-rock interactions and underscore the implications for sustainability (Hoque and Burgess, 2012). The long residence times highlight a stable, enduring recharge mechanism, enhancing the resilience of the springs against natural variability, anthropogenic climate forces, and human exploitation. This comprehensive perspective sets the stage for future research, highlighting the potential for using additional environmental tracers to further elucidate the system's detailed characteristics (Thiros et al., 2023).

The average temperature of cold springs, along with other types of water, is 16.3°C, closely
approximating the annual average atmospheric temperature of Monchique. This observation suggests a shorter residence time for water in the shallow subsurface, particularly within the regolith (Szczucińska and Wasielewski, 2013). Such a pattern is consistent with the idea that water in cold springs follows a more direct pathway through the subsurface before surfacing (e.g., Fujimoto et al., 2014). Furthermore, empirical evidence supports this interpretation through elevational data: as 75% of cold springs were sampled at altitudes greater than 400 m above sea level, thus reinforcing the concept of upslope recharge and swift water movement through the regolith. By contrast, geothermal springs were predominantly located at lower elevations, below 300 m (Fig. 1).

The isotopic profiles of these cold springs provide additional layers of understanding. While some water from these springs does contribute to streams and rivers, this contribution is likely to be marginal compared to isotopically heavier surface runoff, which may explain why streams appear to have heavier isotopic ratios compared to the springs (Fig. 8). This observation prompts questions about the potential influence of cold springs on larger hydrological systems with ensuing implications for watershed management strategies.

The timing of recharge is a crucial aspect, and our data on isotopic and ion composition provide compelling evidence in this regard. Geothermal springs primarily recharge between November and March, a period aligned with more isotopically depleted δ18O and δ2H values. This is consistent with the seasonality observed in the Global Network of Isotopes in Precipitation (GNIP) database (IAEA, 2007). During this interval, deep fissures and fault cavities fill with water, flushing away evaporation-induced chloride ions. The isotopic values of these geothermal springs further corroborate this pattern ranging from -4.85 to -4.56‰ for δ18O (Fig. 8). This narrow range of isotopic signatures and the PCA analysis, where only a few components account for most of the variance, suggest a homogenised composition (Fig. 6), most likely resulting from the long travel time of geothermal spring water, which has been resident in the reservoir for approximately 5000 years. Elevated chloride concentrations in these geothermal springs reinforce the notion that recharge primarily occurs after periods of increased evaporation and soil ion concentration (Russell and Minor, 2002). This seasonal alignment between isotopic and chloride/EC data substantiates the hypothesis that geothermal springs recharge early in the hydrological year and subsequently undergo extended water-rock interactions, which are further corroborated by high sulfur content (Apollaro et al., 2012), essential for ion exchange and isotopic homogenisation (Fig. 9).

In sharp contrast, cold springs exhibit a wider range of isotopic compositions from -4.80 to -
4.10‰ for δ18O, likely indicating recharge throughout the year and varied elevation range of
their recharge (Fig. 8). This isotopic variability, alongside the springs’ higher elevations,
suggests a rapid diverse flow through the subsurface implying discrete cold springs rather than
extensive mixing between cold and geothermal springs. Unlike their thermal counterparts, cold
springs generally show lower chloride concentrations (Fig. 5f), attributable to their quicker
turnover rate. Cold springs are usually recharged after initial rainfall has washed away
evaporated ions and filled deeper cracks and pores. Subsequently, these saturated deeper
features limit further deep infiltration, leading to shallower infiltration, characterising cold
springs that have undergone less extensive water-rock interactions.

The differing isotopic values between geothermal and cold springs raise intriguing questions
around sustainability (Bahadori et al., 2019; Panwar, 2020). For example, the narrower, more
depleted isotopic range of geothermal springs suggests a more stable and isolated system,
potentially with implications for long-term aquifer sustainability and water quality. On the
other hand, the wider isotopic range in cold springs, coupled with their generally quicker
recharge times, could render them more vulnerable to short-term environmental changes. It is
worth noting that the isotopic composition of the single borehole sample resembles
geothermal springs, yet its hydrochemistry aligns with cold springs, adding complexity to this
interpretation reflecting the multifaceted hydrogeology of the region.

5.3 Sodium enrichment comes from ion exchange and heat induced
dissolution

Elevated concentrations of sodium (Na), a hallmark of Monchique's geothermal springs, can
reach up to 350 mg/l at temperatures of 31°C (Fig. 5b). Additionally, springs in peripheral
argillaceous country rocks (samples no. 1 and 2) exhibit relatively higher chloride and
sodium contents compared to cold springs in syenite terrain, though lower than that of
geothermal springs. Their enrichment is most likely associated with the marine nature of the
sediments (Soest et al., 2003).

This raises the question of the underlying mechanisms contributing to Na enrichment in
geothermal springs (Fig. 5e). Elemental data, as evidenced by Fig. 11, reveal that Na and
calcium (Ca) can be selectively leached from the aquifer rocks during advanced alteration
processes (e.g., Amrhein and Suarez, 1991). Rainwater infiltrating through Na-rich syenites
appears to facilitate a geochemical setting conducive to low-Ca, high-Na groundwater,
especially when prolonged water-rock interactions are considered (Morán-Ramírez et al.,
2016). Although Ca is not a major constituent of syenites (Rock, 1978), its presence in the
form of plagioclase feldspar and hornblende can not be disregarded, contributing to alteration
dynamics.

The water data present an interesting dichotomy: cold springs demonstrate a relatively higher
Ca to Na ratio, whereas geothermal springs are characterized by markedly low Ca levels. This
differential geochemical fingerprint, manifested as excess Na and a unique Na/Cl molar ratio in geothermal springs (Figs. 5 and 7), supports the hypothesis of ion-exchange mechanisms being at play (Morán-Ramírez et al., 2016). Specifically, water relinquishes Ca ions in favour of Na ions, culminating in a NaHCO$_3$ water type. This phenomenon aligns with established fundamental science on ion exchange processes (Appelo and Postma, 2005), where similar mechanisms were observed in groundwater studies. The positive correlation between excess Na and thermal spring temperature suggests that heat-induced dissolution of nepheline syenites at depth contributes (Bagani et al., 2021; Mao et al., 2023). This might result from the longer subsurface travel time of geothermal spring water, providing ample opportunity for mineral-water cation exchange. Thus, high Na concentrations in geothermal springs reflect a complex interplay between cation exchange, heat-induced dissolution and the unique geochemical make-up of the Monchique aquifer system.

5.4 Attention is needed for a drinking water guideline value for sodium

While most constituents in the springs under study conform to WHO and EU drinking water standards, the elevated sodium (Na) concentrations in some thermal springs, reaching up to 350 mg/l, pose substantial public health concerns. Elevated levels of sodium are widely acknowledged to be associated with hypertension and cardio-metabolic diseases (Farquhar et al., 2015; Hoque and Butler, 2016; Sacks et al., 2001; Scheelbeek et al., 2017). The average Na concentration of 204 mg/l not only marginally surpasses the taste thresholds established by WHO (2011) and the EU (1998), but also raises pressing questions about the broader European context. In Europe, some bottled waters can contain nearly half of the daily recommended sodium intake in a single litre (Azoulay 2001). Given the rising consumption of bottled water, this is particularly alarming. One of the geothermal springs in question is commercially exploited for bottling with ten-year average Na concentrations reported as 106 mg/l and 108 mg/l by two different laboratories.

The World Health Organisation (WHO) currently has no health-based guideline value for sodium in drinking water. Instead, it establishes a taste threshold at 200 mg/l, paralleled by similar EU guidelines. Yet, a contrasting narrative emerges from the WHO's dietary guidelines, which recommend a maximum daily salt intake of 5 g with 2 g designated as sodium (WHO, 2003, 2012). In formulating this dietary recommendation, the WHO team assumed that an individual would consume approximately 2 litres of water per day contributing to around 40 mg of daily sodium intake. This assumption implies a guideline value of about 20 mg/l in drinking water, a figure that is also in line with the recommendation set by the U.S. Environmental Protection Agency (USEPA). However, this seemingly low threshold has been challenged by recent studies, such as Nwankwo et al., (2020), which reveal that many water wells globally easily surpass this level. This finding underscores the pressing need for an immediate re-evaluation of the existing guidelines.

Interestingly, these geothermal springs are also characterised by high bicarbonate concentrations and elevated pH levels. While high bicarbonate concentrations have been
proposed to counteract sodium's negative health impacts, these claims are based on limited research involving only 500 mL of water (Santos et al., 2010). The co-existence of high levels of Na, bicarbonate, and pH in the same water source presents an intricate hydrogeochemical condition that remains largely unexplored from a health perspective. Further research is needed to fully understand the implications of this complex interaction for both cardiovascular and overall health.

The findings of this study raise two issues: they emphasise the urgent need for a re-evaluation of public health guidelines concerning sodium in both tap and bottled water, and they open up new avenues for research into the combined health effects of water high in sodium, bicarbonate, and pH.

5.5 Cold springs pose vulnerability, whereas geothermal springs exhibit sustainability

The findings of this study offer a nuanced understanding of the resilience and vulnerabilities of geothermal and cold springs in the Monchique region. Geothermal springs primarily recharge between November and March and that likely happens at elevation between 480 and 680 m, as evidenced by their narrow isotopic range. The radiocarbon dating extends back approximately 5000 years indicating a remarkable stability that implies strong resistance to the impacts of human-induced climate change (van Geldern et al., 2014). In stark contrast, cold springs, which recharge throughout the wet season, display a broader isotopic range. This variability signifies a greater vulnerability to shifts in precipitation patterns (Panwar, 2020; Pepin et al., 2022), a susceptibility exacerbated by the presence of anthropogenic pollutants such as nitrates (Infusino et al., 2022; Kendall et al., 2007). As a result, the long-term sustainability of these cold springs is potentially threatened by both climate change and human activities.

This contrasting behaviour raises questions about the most effective management strategies for these disparate water resources. While the geothermal springs with their historic stability may require less immediate intervention, the more vulnerable cold springs call for rigorous monitoring and perhaps even stricter source zone protection to ensure their long-term sustainability (Barquín and Scarsbrook, 2008). Additionally, as highlighted in a related study on the changes in land cover in Monchique between 1995 and 2018 (Raposo et al., 2023), considering land use improvements and their impact on the surrounding environment could be crucial. Overall, the findings underscore the urgent need for adaptive management strategies finely tuned to the unique characteristics and challenges presented by each type of spring.

6 Conclusions

Our study provides a comprehensive investigation into the hydrogeochemistry, sustainability, and public health implications of geothermal and cold springs in the Monchique region. Our insights into
the 5000-year water-rock interactions in geothermal springs and the sustenance provided by high-altitude meteoric water underscore the hydrogeochemical complexity of the Monchique springs. The detection of nitrate contamination due to local recharge and land use, alongside elevated sodium levels driven by syenites and ion-exchange processes, emphasizes the critical need for targeted environmental and public health strategies. These findings highlight the unique vulnerabilities of cold springs and the remarkable resilience of geothermal springs within the Monchique region. While our findings are robust, we acknowledge that the temporal scope of our sampling may not capture the full variability of hydrogeochemical conditions, and future studies could expand upon this with a more extended sampling timeline. Additionally, the potential influence of undetected geophysical processes on the hydrochemistry remains an uncertainty that could be explored in subsequent research.

These findings lead to two immediate implications. First, the need for adaptive management strategies to ensure the long-term sustainability of these springs, especially the more vulnerable cold ones. Second, and importantly, the urgent need for a re-evaluation of public health guidelines concerning sodium levels in both tap and bottled water. This re-evaluation becomes even more pressing when considering that European bottled waters can contain nearly half of the daily recommended sodium intake in just one litre. The WHO's existing taste-based threshold of 200 mg/l for sodium in drinking water starkly contrasts with its own dietary guidelines, which suggest a much lower value of around 20 mg/l. Given the potential public health risks, our study joins recent research in calling for an immediate review of these standards.

Overall, this study not only enhances our understanding of the unique hydrogeochemical conditions of the Monchique springs but also serves as a clarion call for policy changes in both water quality guidelines and sustainable management practices.

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**Declaration of Competing Interest:**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability:**

The authors have shared all data as a supplementary table.

**Declaration of AI Assistance**
The authors employed ChatGPT (GPT-4 version), a comprehensive language model developed by OpenAI, exclusively to enhance the grammatical accuracy and argumentative clarity of this manuscript. The manuscript was submitted to the model through an API call to ensure the confidentiality of the data. The authors rigorously examined all suggestions made by ChatGPT, incorporating only those that aligned with their intended meaning and scientific conclusions. The authors bear full responsibility for the content's accuracy, validity, and originality.

CRediT authorship contribution statement:

M. A. Hoque: Conceptualization; data curation; fieldwork; formal analysis; original draft; project administration; funding acquisition; resources; software; supervision; visualization; validation; writing - review & editing. K. B. Amponsah: Fieldwork; data curation; formal analysis; original draft; investigation; visualization; Writing - review & editing. A. Blum: fieldwork; resources; writing - review & editing. N. Walton: fieldwork; validation; writing - review & editing. P. Dennis: Data curation; resources; methodology; writing - review & editing. A. P. Butler: data curation; resources; methodology; writing - review & editing. S. Hugman: fieldwork; writing - review & editing. A. Bamberger: fieldwork; resources; writing - review & editing. M. Fowler: Conceptualization; fieldwork; original draft; data curation; fieldwork; supervision; methodology; validation; Writing - review & editing.

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The Origin and Water Quality of Spring Systems in Monchique, Portugal: A Focus on Long-Term Sustainability and Elevated Sodium Levels

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Highlights:

- Thermal springs in Monchique exhibit a 5000-year water-rock interaction.
- High-altitude meteoric water sustains geothermal and cold springs in Monchique.
- Local recharge and land use linked to nitrate contamination in cold springs.
- Syenite host rock and ion-exchange processes drive elevated sodium in geothermal springs.