

Article

Hydrochemical Variability in Karst Hypothermal Mineral Springs of Greece

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Abstract

In Greece, the geodynamics of karst hypothermal–mineral springs, in which often shallow fresh groundwater is intermixed, is not well known. This study aims to investigate the monthly hydrochemical variability of three karst hypothermal mineral springs in Greece named Kyllini (southern Greece), Agiasma (northern Greece), and Voskina (northern Greece). Hence, monthly samples were collected and an analysis of major and trace elements, ion ratios, and saturation indices was performed, as well as statistical analysis and cross correlation. Elevated concentrations of Ca^{2+} , Mg^{2+} , and HCO_3^- are present in all springs, indicating that the dissolution of calcite and dolomite constitutes the main water–rock interaction process. Additionally, the mobilization and transport of Mn, Fe, and As are favored by the negative ORP values. However, there are also differences between the three springs. The Kyllini spring is characterized by high salinity and dominated by Na–Cl– HCO_3 water, while the Agiasma spring exhibits a mixed water type with moderate salinity. The Voskina spring reflects a fresher, bicarbonate-dominated aquifer system with modest trace element mobilization. This study provides the first comprehensive monthly assessment of the hydrochemical response of karst hypothermal–mineral springs in Greece, offering new insights into seasonal geochemical dynamics.

Keywords: hydrochemistry; trace elements; saturation indices; hypothermal mineral groundwater; statistical analysis; Greece



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1. Introduction

Groundwater is one of the most valuable sources of fresh water [1]. It can flow naturally from springs on the Earth’s surface and be artificially pumped/extracted from boreholes and wells. Although groundwater may not always meet drinking water standards due to natural geochemical composition or anthropogenic contamination, it is widely used for domestic and agricultural purposes following appropriate treatment and conditioning.

Thermal–mineral springs are a characteristic example of groundwater that contains high concentrations of dissolved minerals due to deep hydrogeological processes and interaction with mineral-rich rocks under geothermal heat [2].

Thermal waters typically originate at shallow to intermediate depths and are heated by prolonged contact with comparatively warm geology or by regional geothermal gradients, typically 20–60 °C, while the temperature can reach above 100 °C in nearby zones with tectonic or volcanic activity [3]. Such waters tend to be more mineralized and contain higher concentrations of geothermal tracers like lithium and boron [4,5].

Karst aquifers, which store substantial groundwater reserves, are the source of numerous karst springs worldwide [6]. These springs often serve as significant water resources, particularly in arid and semi-arid regions, where they provide a primary water supply for human use [7]. The heterogeneity and anisotropy of karst springs result from the prolonged dissolution of soluble rocks, creating highly variable flow pathways [8]. Various methods are used to investigate the hydrological and hydrogeochemical features of karst springs. Monitoring spring discharges and water quality parameters, such as electrical conductivity and temperature, is a fundamental step towards understanding the hydrological regime of karst springs [9]. Environmental tracers, including stable isotopes of oxygen and hydrogen, are also utilized to determine recharge areas and quantify the characteristics of these springs [10]. Several studies have examined the hydraulic behavior and flow regimes of karst springs, which often exhibit a dual discharge pattern. During dry periods, the discharge is low and steady, while high, temporally variable discharges follow intense recharge events [11]. Hydrograph recession analysis has been used to estimate aquifer parameters and geometric properties [12]. Researchers have also explored the geomorphic, geological, and anthropogenic factors influencing the occurrence and distribution of karst springs [13].

Recent isotopic investigations in Mediterranean coastal karst aquifers have improved recharge and flow path understanding [14]. Karst mineral springs have distinctive chemical and physical characteristics that are crucial to their ecological, hydrological, and geological significance [15]. Furthermore, the hydrodynamic behavior of these springs is complex, exhibiting multifractal discharge patterns that reflect the intricate nature of karst systems. Factors like precipitation, geological structures, and the permeability of the aquifer strongly influence these dynamics [16,17]. Notably, the rapid discharge responses of karst aquifers to rainfall events underscore their significance for groundwater recharge and water resource management [18].

They are defined by their distinct geochemical composition, which is controlled by the geology they traverse and the groundwater residence time within the aquifer. Flow pathways and the character of rocks, principally limestone and dolomite, influence the mineral content of spring waters. This leads to differences in basic chemical characteristics, including pH, electrical conductivity, and concentrations of dissolved minerals, like calcium and magnesium [19–21]. The physical properties of karst thermal mineral springs are equally noteworthy [22,23]. These springs often maintain a stable temperature, which is crucial for supporting diverse aquatic ecosystems. For instance, stable thermal conditions favor the continuous reproduction of certain macroinvertebrates that have adapted to high-calcium environments typical of karst waters [23]. In some cases, mineral spring water originating from karst aquifers is characterized by seasonal hydrochemical variations [24]. In the hydrochemical composition of karst thermal mineral springs, a prevalence of bicarbonate ions can usually be found, with trace elements. Other springs, such as the sulfide spring of Zveplenica in Slovenia, exhibit a distinct mineralogical and isotope signature of complex geological interactions, including the dissolution of dolomite and organic matter [25].

Hypothermal springs are characterized by discharge temperatures that exceed ambient levels and remain below the typical geothermal threshold (approximately 20–35 °C). Nevertheless, they represent a significant geochemical component of low-enthalpy hydrothermal systems [26]. Although they lack the thermal intensity of hot springs, their

origin often involves the mixing of meteoric waters with deeper, gas-enriched fluids, commonly containing CO_2 and H_2S , that ascend along fault structures [27]. These springs are notable not for their heat but for their distinct hydrochemical profiles, and hence hydro-geochemical analysis can provide valuable information on the hydrochemical evolution of spring water. Elevated concentrations of total dissolved solids, particularly bicarbonate (HCO_3^-), calcium (Ca^{2+}), and trace elements, are commonly observed. Their development is typically linked to carbonate aquifers that intersect with both active and relict fault zones, which facilitate the vertical migration of mineralized fluids from deeper reservoirs [28]. In the Pontina Plain of Italy, three groups of karst springs were determined according to the electrical conductivity of groundwater due to the different degrees of mineralization, while most of the springs were characterized as hypothermal [29]. The spring water of Pontina Plain's hydrochemistry indicates a mixing process of Karst water (Ca-HCO_3) with deep Na-Cl water, which is supported by the elevated concentrations of trace elements (e.g., Li) [29]. In the Central Kamchatka Depression, near the active Kizimen volcano, the hydrochemical analysis revealed that the springs were characterized by high concentrations of Mg and Ca^{2+} , mainly formed from the interaction of carbonate-bearing rocks with CO_2 of igneous formations. The origin of Mg is mainly linked with serpentinites, carbonate rocks with magnesite, as well as magnesian basalts [30]. In the Kutai Basin of Indonesia, high concentrations of trace elements, such as iron, are linked to reducing conditions due to sluggish groundwater flow in low hydraulic gradient regimes [31]. In Tanzania, Kobare et al. (2025) compared hot, warm, and cold spring waters for hydrochemical evolution, revealing that calcite dissolution in combination with ion exchange constitute the processes forming the spring waters with dominant Na^+ and K^+ cations [32]. Additionally, the equilibrium indices showed that the spring waters were over-saturated with carbonate minerals. In Baden-Baden of Germany, the hydrochemical study revealed similarities in spring water evolution and characterization (Na-Cl -rich waters); however, the spring originated from different geological formations [33].

Hydrogeological barriers can influence the hydrochemical regime of groundwater. For instance, the Musov Zone on the Czech side and the Mailberg Fault on the Austrian side make up the border between the two portions [34]. The hydrochemical analysis indicated that while the groundwaters from both aquifer sections are of the same Na-Cl type, characterized by a predominance of Na^+ and Cl^- ions, their total dissolved solids (TDS) and relative main ion concentrations vary [34].

The Fiambalá Basin (Argentina) revealed that thermal springs transition from bicarbonate-type waters to chloride- and sulfate-rich compositions, adhering to groundwater flow routes and resulting in elevated total dissolved solids [35]. The movement of fluids with excess of CO_2 often results in excessive water-rock interactions, which leads to the production of carbonate minerals and impermeable caprock layers that restrict the flow of fluids [36].

Geological structures, rock types, and the flow of multi-aquifer systems determine the thermal and mineral waters in North Africa. Hydrochemical research in the Guelma Basin (northeast Algeria) shows that water chemistry varies along the pathways of groundwater flow [37]. For instance, the facies transitions from calcium-bicarbonate to calcium-chloride or calcium-sulfate types during water recharge. This occurs due to minerals being gradually incorporated into the water when it interacts with rocks [37]. The modifications occur because the substance is tougher, conducts electricity more efficiently, and contains higher levels of Na^+ and Cl^- . These demonstrate the changes in the aquifer and the interaction of various types of water. In central Brazil's Caldas Novas Thermal Complex, groundwater rises up under variable temperatures and mineralization levels, depending on the aquifer system and the type of rock it is in. The waters from Rio Quente springs have less total

dissolved solids, less Ca^{2+} , Mg^{2+} , and HCO_3^- , and a pH that is somewhat acidic. The waters from Caldas Novas, on the other hand, have more TDS, more Ca^{2+} and Mg^{2+} , and more bicarbonate [38].

Thermal and hypothermal mineral waters are also of great importance in Greece due to the country's unique geological structure, which provides it with a wealth of natural springs rich in minerals and geothermal energy [39]. These waters have been valued since ancient times for their healing properties, with notable figures like Herodotus and Hippocrates recommending them for a range of ailments, including arthritis, rheumatism, skin diseases, and respiratory issues [40]. Hydrotherapy remains popular, including mud baths, inhalation sessions, and even sipping mineral-rich water for digestive or immune support. Popular sites, such as Loutraki, Edipsos, and Kyllini, illustrate the cultural and therapeutic importance of thermal springs in Greece. In addition to wellness tourism, thermal waters are increasingly considered for geothermal energy exploitation and scientific research. Although these springs are commonly referred to as thermal in local usage, their temperatures classify them more accurately as hypothermal mineral springs (waters with elevated temperatures but below conventional thermal thresholds of 30 °C) [41].

The main objective of this study was to collect monthly samples from three hypothermal springs from different sites, perform a chemical analysis, and compare the data in order to highlight differences and similarities between the three springs. Hence, monthly samples were collected from mineral karst springs of Greece, and detailed hydrochemical analyses were conducted. Additionally, statistical analysis and Phreeqci hydrogeochemical reverse modeling were conducted to compare the different processes influencing the selected springs. Ionic ratios and plotting hydrochemical results in diagrams, such as Piper and Durov, revealed similarities and different processes controlling the hydrochemical regime of the springs. The literature is missing the identification of hydrochemical differences and similarities between hypothermal–mineral springs from different sites and hydrogeological conditions that control the mixing process of deeper groundwater with shallow fresh groundwater. Hence, it provides key differences and similarities between the three springs based on the monthly time series analysis, which can be the basis for deeper understanding and management of hypothermal karst springs.

2. Material and Methods

2.1. Study Area Description

2.1.1. General Overview

This research investigates three karst springs located in distinct regions in Greece. The first is located in the region of Kyllini, W Peloponnese, southern Greece, and the other two are located in the Anthemountas basin in northern Greece. The two study areas, Kyllini and Anthemountas basin, are located in distinct climatic zones of Greece. During the hydrological year 2023–2024, the mean annual precipitation in the Kyllini region was approximately 834 mm, with a mean annual air temperature of 17.5 °C. In contrast, the Anthemountas basin, which hosts the Agiasma and Voskina springs, experienced lower rainfall levels (619 mm) and a mean temperature of 15.0 °C. The elevation above sea level for each spring is as follows: Kyllini spring lies at 18 m, Voskina at 135 m, and Agiasma at 131 m. Kyllini, Voskina, and Agiasma constitute karst fractured uprising springs, while fresh groundwater from upper Karst aquifers is mixed with the uprising deep thermal mineral water. This fact led to the study of their hydrochemical regime, while their comparison can provide information on the common process of springs in different sites. Their mean discharges were recorded at 8.5 m³/h for Voskina, 0.28 m³/h for Agiasma [24], and 1.6 m³/h for Kyllini [42].

The climate of the study area is classified as a typical Mediterranean type, with dry summers and wet winters. Hence, sampling spring water samples per month constitutes the optimal strategy in such hydrological and hydrogeological conditions in order to determine variations within these periods. This was the first such sampling campaign in hypothermal mineral springs in Greece. This study establishes a base campaign and constitutes a guide to increase sampling frequency (e.g., one sample per week) in future studies.

2.1.2. Geological Setting

The geological background of the Kyllini region in the western Peloponnese is shaped by a complex interplay of tectonic, sedimentary, and geomorphological regimes. The region lies within the broader framework of the Hellenic Arc, a major tectonic feature formed by the convergence of the African and Eurasian plates. This convergence has produced a fold-and-thrust belt, prominently represented by the Pindos Fold-and-Thrust Belt, which extends into the western Peloponnese [43,44]. The predominant tectonic trend in the area follows a NNW–SSE orientation, reflecting the structural geometry of the External Hellenides and the modern Hellenic Arc [43].

The Kyllini region is distinguished by its notable geological formations, including Upper Cretaceous limestones that were extensively used in ancient architecture, such as in local temples [45]. These limestones belong to the Pindos geological unit, which has been subjected to significant tectonic activity (Figure 1a). This activity has led to the development of various sedimentary facies and structures [46]. The Pindos Flysch Formation, for instance, provides evidence of a foreland basin environment, where sedimentation processes were influenced by tectonic uplift and the dynamics of surrounding orogenic activity. Historical seismic activity has significantly shaped the geological landscape of the Kyllini area. The region has experienced numerous earthquakes, including the 2008 Achaia-Ilia earthquake, which underscored the tectonic instability and active faulting that characterize the area [47]. Active faults, such as those associated with the Kyllini horst, highlight the ongoing tectonic processes that continue to influence the region's morphology and sedimentary patterns (Figure 1b) [48]. In addition to tectonic forces, the Kyllini region has also been shaped by tsunami events. Geological evidence of past tsunamis has been identified along the coastline, revealing their contribution to the sedimentary record and coastal geomorphology [49,50]. These findings illustrate the dynamic geological history of the region and provide valuable insights into its evolving landscape.

The aquifer containing Kyllini's hypothermal–mineral waters is situated in a zone oriented west to east, perpendicular to the north–south faults. The mineral spring emerges at the northern boundary of this zone, which lies vertical to the tectonic axis of the anticline that steeply dips northward from the spring [42].

The Anthemountas basin is located in northern Greece, in the Prefecture of Central Macedonia, and covers a total area of 374 km² (Figure 2). The mean altitude is 259 m, while the highest elevation occurs in the Hortiatas Mountain, reaching 1201 m. The basin has a typical Mediterranean climate with average annual temperature and precipitation of 15.5 °C and 475 mm, respectively. The basin is determined through normal faults with W–E orientation, while the mountainous part is covered by metamorphic rocks in the north and carbonate rocks in the south. Neogene sedimental formations and Quaternary deposits occur in the lowlands. The springs of Agiasma and Voskina are located in the south–central part of Anthemountas basin and are related to the W–E fault [24]. The mineral springs are related to the karst Jurassic limestones, which are partially covered with conglomerates and red clays. The Pleistocene travertine reveals the activity of the hypothermal springs [51].

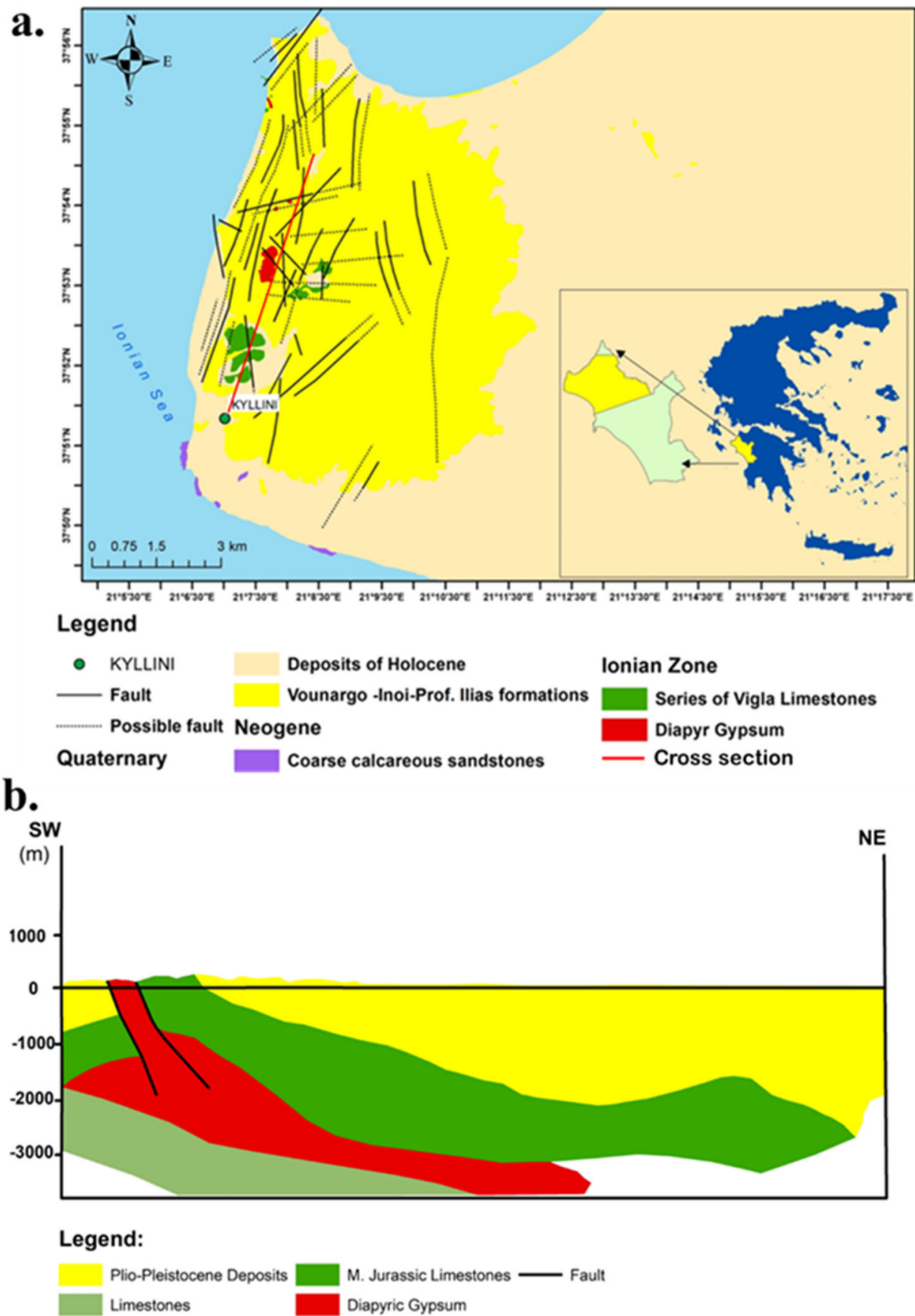


Figure 1. Geological map of Kyllini region (modified from IGME 1:50,000, Vartholomio sheet) (a), and geological cross-section across the region (b).

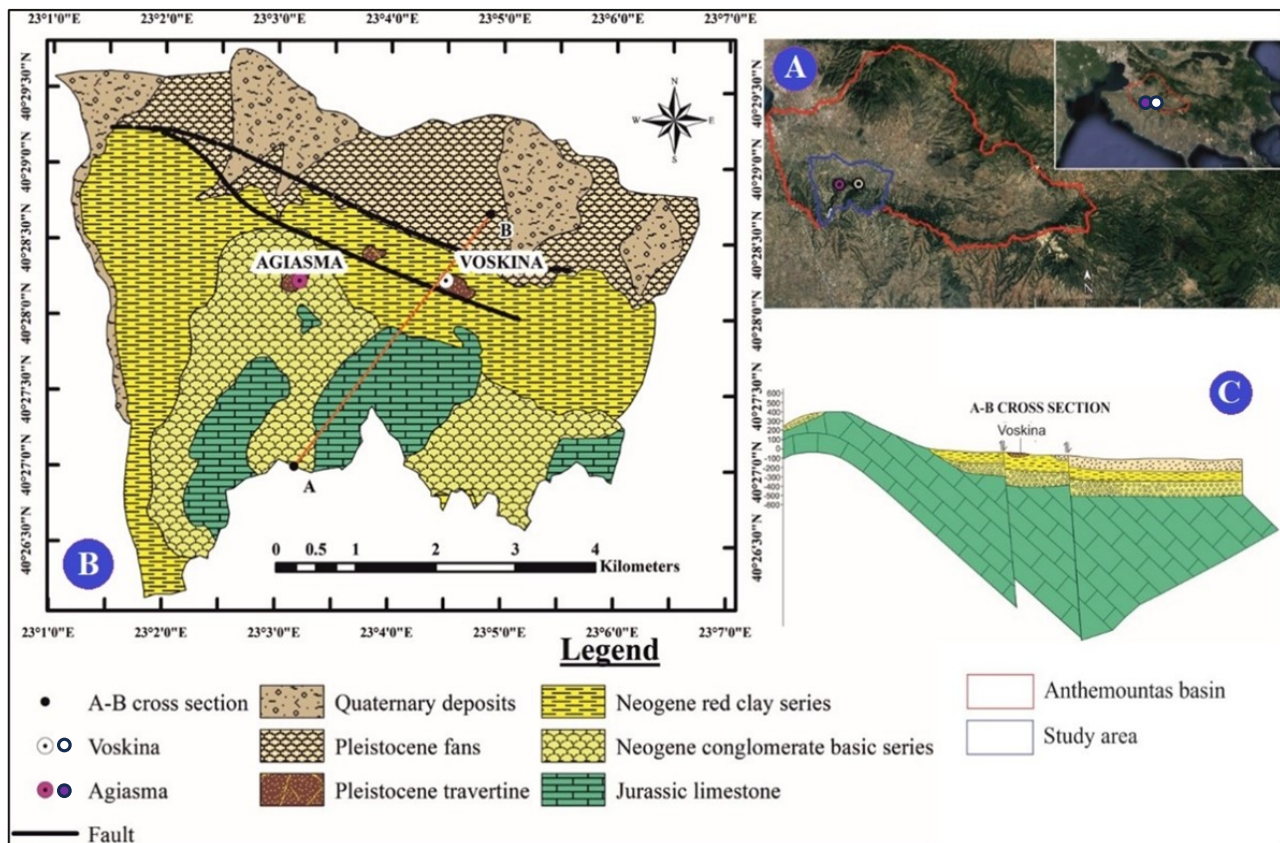


Figure 2. Satellite map of Anthemountas basin showing the locations of the studied springs (A); geological map of the study area (modified from IGME 1:50,000, Vasilika sheet) (B); and geological cross-section across the study area (C).

2.2. Hydrochemical Parameters and Analysis Methods

During the hydrogeological year 2023–2024, a total of 36 water samples were collected monthly from the mineral springs of Agiasma, Voskina, and Kyllini.

In Kyllini, the spring is exploited by an artesian borehole. In situ measurements of temperature, pH, electrical conductivity, and redox potential were conducted using a Hanna® HI9828, Woonsocket, USA portable multiparameter instrument. Alkalinity concentrations were measured in situ using a Hach® Digital Titrator, Loveland, CO. Chemical analyses were performed immediately after sample collection in the Laboratory of Hydrogeology, Department of Geology, University of Patras. For each sampling site, three distinct water samples were collected in pre-cleaned polyethylene bottles. The bottles were thoroughly acid-washed and rinsed with deionized water prior to use to ensure sample integrity. The first sample, with a volume of 1 L, was designated for the analysis of anions, including NO_3^- , NO_2^- , SO_4^{2-} , and Cl^- . The second and third samples, each 0.1 L in volume, were filtered through a 0.45 μm Whatman cellulose membrane. These samples were then treated with 0.3 mL of ultrapure HNO_3 to prepare for the determination of metal concentrations (Ca^{2+} , K^+ , Mg^{2+} , and Na^+) and trace elements. Major cations, including Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , were analyzed using atomic absorption spectrophotometry (AAS) to ensure high precision in metal quantification. Chloride (Cl^-) concentrations were determined through argentometric titration using a standard silver nitrate method. Nutrients, such as nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}), were measured using a Hach® DR3900 UV-Vis, Loveland, CO, spectrophotometer, following standard colorimetric procedures. Trace element concentrations were measured using inductively coupled plasma mass spectrometry (ICP-MS) in the Environmental Pollution Control Laboratory,

Department of Chemistry, Aristotle University of Thessaloniki. The accuracy of the major element analyses was verified through charge mass balance calculations, with the results deemed acceptable if the charge mass balance discrepancy was below 5%. Daily precipitation data used for the interpretation of hydrochemical variability were obtained from the National Observatory of Athens (NOA), which provides validated climatological records through its official hydrometeorological monitoring network.

For the Anthemountas basin, data were collected from the meteorological station located at Airport Macedonia (X: 412,684.61/Y: 4,485,697.40; EGSA '87 projection). For the Kyllini region, data originated from the NOA station situated near the coastal plain of Kyllini, at coordinates X: 1,948,367.32/Y: 2,408,545.43. These stations provide representative monthly precipitation records corresponding to the respective hydrological systems.

To understand common hydrogeochemical processes, the hydrochemical results of all springs and all periods were correlated. Following this, the highly correlated elements of all springs were then correlated pairwise for each spring. Spearman correlation coefficients were calculated. The general correlation matrix of all of the groundwater samples of the three springs was first obtained with the intention of tracking generalized trends in diverse hydrogeological settings. However, because Kyllini, Agiasma, and Voskina have different hydrochemical signatures according to the study's findings, inter-spring comparisons may mask site-specific geochemical trends. Thus, in addition to the general matrix, individual pairwise correlation analyses were also conducted for each spring separately. These correlations are illustrated in the Supplementary Materials (Tables S1–S3), yielding more specific information regarding geochemical controls at local scales.

Saturation index (SI) analysis was applied to evaluate the thermodynamic equilibrium between groundwater and selected mineral phases. The SI quantifies the tendency of water to either dissolve or precipitate minerals and is defined as $SI = \log \left(\frac{IAP}{K_{sp}} \right)$, where IAP is the Ion Activity Product of the dissolved mineral constituents and K_{sp} is the solubility product under given temperature and pressure conditions. $SI > 0$ indicates super-saturation (potential for precipitation), $SI = 0$ denotes equilibrium, and $SI < 0$ implies under-saturation (potential for dissolution) [52].

The saturation indices of minerals, such as calcite, dolomite, aragonite, and siderite, were computed using the software Phreeqci-3.7.3–15968 [53]. The saturation indices were derived from the sampling points using the most comprehensive available dataset, incorporating both major and trace elements.

3. Results and Discussion

3.1. Hydrochemical Characteristics of Groundwater

The statistical results of the physical and chemical parameters of the sampling points are shown in Tables 1–3. The physico-chemical parameters for Kyllini spring (Table 1) highlight its slightly alkaline nature, with pH values ranging from 7.2 to 7.4 and a low standard deviation of 0.08. This stability in pH suggests relatively stable geochemical conditions within the spring system. The average temperature of the Kyllini spring is 25.8 °C, with observed values varying between 24.7 °C and 27.7 °C, indicating relatively stable thermal conditions. The mean value of electric conductivity is 4376 µS/cm, reflecting high ionic content. Major cations like calcium and magnesium show average concentrations of 66.1 mg/L and 36.7 mg/L, respectively, while sodium concentrations are notably elevated at 824.2 mg/L. Chloride concentrations are substantial, averaging 987.5 mg/L, and bicarbonate is also prominent at 593.9 mg/L. These chemical characteristics correspond to a Na–Cl–HCO₃ water type, as illustrated by the Piper [54] and Durov [55] diagrams (Figure 3).

Table 1. Statistical analysis of physico-chemical parameters in the waters of Kyllini spring (*n*. 12).

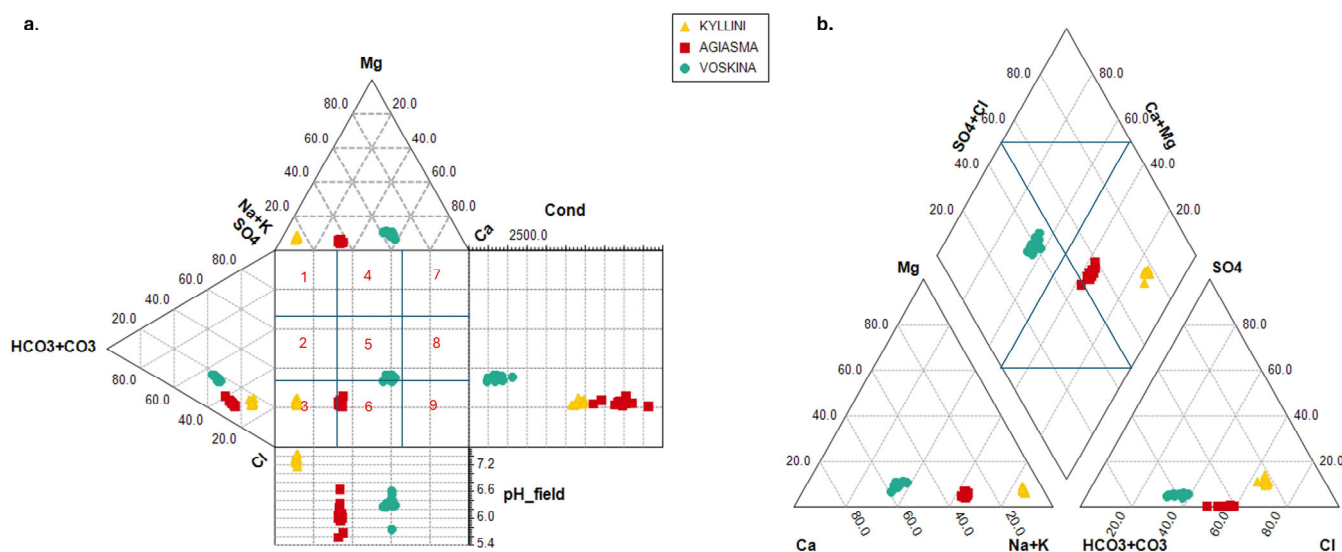
Parameters	Units	Min.	Max.	Average	Median	Standard Deviation
pH		7.2	7.4	7.3	7.3	0.08
T	°C	24.7	27.7	25.8	25.5	1.0
Conductivity	µS/cm	4183.0	4457.0	4313.8	4276.5	92.8
TDS	mg/L	2697.3	2865.8	2752.5	2747.3	45.7
Ca ²⁺	mg/L	62.8	72.8	66.1	65.8	2.5
Mg ²⁺	mg/L	30.0	45.9	36.7	35.8	4.7
Na ⁺	mg/L	800	870	824	810	26.1
K ⁺	mg/L	13.0	13.6	13.4	13.4	0.2
HCO ₃ [−]	mg/L	556.3	695.4	593.9	585.6	37.7
SO ₄ ^{2−}	mg/L	183.0	286.0	217.7	217.5	26.5
Cl [−]	mg/L	975	1000	987	987.5	7.8
NO ₃ [−]	mg/L	2.00	6.0	4.3	4.5	1.3
NO ₂ [−]	mg/L	0.00	0.03	0.01	0.01	0.01
NH ₄ ⁺	mg/L	6.57	9.51	8.56	8.66	0.8
PO ₄ ^{3−}	mg/L	0.30	0.50	0.38	0.37	0.07

Table 2. Statistical analysis of physico-chemical parameters in the waters of Agiasma spring (*n*. 12).

Parameters	Units	Min.	Max.	Average	Median	Standard Deviation
pH		5.6	6.6	6.1	6.0	0.28
T	°C	16.0	26.8	21.8	21.9	3.6
ORP		−46.3	−16.5	−31.6	−32	9.5
Conductivity	µS/cm	4843	5519	5224	5313	253.9
TDS	mg/L	3795	4135	3952	3958	97.6
Ca ²⁺	mg/L	348.0	390.0	368.0	367	11.1
Mg ²⁺	mg/L	26.4	47.6	37.1	35.4	7.2
Na ⁺	mg/L	760	880	835	840	29.7
K ⁺	mg/L	41.0	47.0	44.4	44.0	2.3
HCO ₃ [−]	mg/L	1360.3	1720.2	1535.7	1528.1	104.5
SO ₄ ^{2−}	mg/L	0.0	8.0	0.8	0.00	2.3
Cl [−]	mg/L	965	1200	1120	1130	58.8
NO ₃ [−]	mg/L	1.0	5.3	3.8	4.0	1.2
NO ₂ [−]	mg/L	0.00	0.02	0.00	0.0	0.01
NH ₄ ⁺	mg/L	6.90	8.60	7.60	7.6	0.5
PO ₄ ^{3−}	mg/L	0.03	1.66	0.47	0.35	0.5

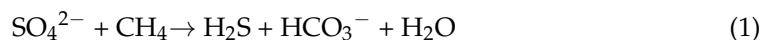
Table 3. Statistical analysis of physico-chemical parameters in the waters of Voskina spring (*n*. 12).

Parameters	Units	Min.	Max.	Average	Median	Standard Deviation
pH		5.8	6.6	6.3	6.3	0.2
T	°C	17.6	21.1	19.9	20.3	1.0
ORP		−46.3	−3.6	−17.3	−12.3	14.6
Conductivity	μS/cm	1983	2635	2251	2423	165.9
TDS	mg/L	1674.7	1937.3	1755.8	1754	73.1
Ca ²⁺	mg/L	263.2	286	272.5	272	6.1
Mg ²⁺	mg/L	25.61	33.7	29.2	29.9	2.8
Na ⁺	mg/L	190.0	225	198.8	190	12.1
K ⁺	mg/L	6.3	7.8	6.7	6.5	0.5
HCO ₃ [−]	mg/L	805.2	982.1	877.4	860.1	53.7
SO ₄ ^{2−}	mg/L	49.0	65.0	55.4	54.5	5.2
Cl [−]	mg/L	265.0	371.0	302.2	294	34.2
NO ₃ [−]	mg/L	6.3	13.0	11.3	12.0	2.3
NO ₂ [−]	mg/L	0.01	0.03	0.01	0.01	0.01
NH ₄ ⁺	mg/L	1.0	2.6	2.0	2.2	0.4
PO ₄ ^{3−}	mg/L	0.07	0.46	0.17	0.13	0.1

**Figure 3.** Chemical composition of springs' water presented as Durov diagram (a) and Piper diagram (b).

Waring (1965) [2] suggested a characterization method for mineral springs in which H₂S can be accounted for in the characterization of groundwater. According to this characterization, the Kyllini spring can be classified as a sulphur-rich hypothermal mineral water [56]. The occurrence of hydrogen sulfide (H₂S) concentrations up to 29.6 mg/L has been reported in previous studies [42]. The presence of abundant sulfate ions (SO₄^{2−}) supports conditions favorable for reduction processes, such as bacterial or thermochemical sulfate reduction (BSR/TSR). As described in similar systems, such as those in the Cerna Valley [57], hydrocarbons, particularly methane, may act as electron donors, en-

abling SO_4^{2-} reduction and leading to significant H_2S production. The TSR representative reaction involving methane is



TSR is an inorganic, non-biological process in which sulfate ions (SO_4^{2-}) are reduced to hydrogen sulfide (H_2S) through a reaction with hydrocarbons, primarily methane (CH_4), under high-temperature conditions (typically $>100^\circ\text{C}$) [57]. In the literature, there are several methods to link spring water interactions with natural hydrocarbon reservoirs [58]. In contrast, in coal mines, the presence of bacteria positively influences pyrite oxidation, producing sulfate ions [59].

The physico-chemical parameters of the Agiasma karst spring (Table 2) indicate a mildly acidic to near-neutral pH range of 5.6 to 6.6, with an average of 6.1 and a standard deviation of 0.28. Temperature ranges between 16°C and 26.8°C , with an average value of 21.8°C , suggesting a mix of shallow groundwater sources and possibly deeper geothermal influences, as evidenced by the relatively moderate temperatures. The oxidation–reduction potential (ORP) is negative, averaging -31.6 mV , indicative of reducing conditions. Conductivity values indicate high ionic content, averaging $5224.8\text{ }\mu\text{S/cm}$. Total dissolved solids (TDS) are substantial, with an average value of 3952.4 mg/L . According to the Piper diagram, the water type is predominantly Na–Cl (Figure 3a). Nevertheless, considering the elevated bicarbonate concentrations, the water can also be classified as Na–Cl– HCO_3 , reflecting a mixed influence resulting from carbonate weathering, ion exchange, and mixing with CO_2 -rich deep hydrothermal fluids, as indicated by trace element enrichment. The water type of the Agiasma spring is similar to groundwater of the geothermal field of Yangbajing in China, in which Na–Cl to Na–Cl– HCO_3 water types occur, while the deeper zone is influenced by granite rocks [60]. Furthermore, the extremely low concentrations of sulfate (SO_4^{2-}), averaging only 0.8 mg/L , suggest limited contributions from sulfate-bearing minerals, such as gypsum or anhydrite. This scarcity may also indicate the absence of significant sulfide oxidation or evaporitic influence, reinforcing the interpretation of Agiasma as a system dominated by carbonate dissolution and deep CO_2 -rich water mixing rather than sulfate processes.

The physico-chemical characteristics of Voskina spring water are shown in Table 3, encompassing parameters like pH, temperature, redox potential (ORP), electrical conductivity, total dissolved solids (TDS), and major ion concentrations. According to the Piper and Durov diagrams (Figure 3), the Voskina spring is classified as a Ca– HCO_3 -type water, indicating a fresher, less mineralized system dominated by carbonate dissolution.

In the Anthemountas basin, the porous aquifer is influenced by agricultural activities depicting elevated concentrations of nitrate pollution [61]. However, in both of the springs, nitrate concentrations are low, highlighting the low impact of agricultural activities on the spring's water.

The modified Durov diagram (Figure 3a) is divided into nine different classes, illustrating the influences of simple dissolution and linear mixing on groundwater chemistry [62]. The diagram combines a ternary plot for major anions and cations with a rectangular projection to incorporate additional parameters, such as pH and conductivity. Samples from the Agiasma spring predominantly cluster around mixed water types, characterized by relatively high conductivity and a balanced presence of Mg^{2+} and $\text{Na}^+ + \text{K}^+$ cations, as well as Cl^- and HCO_3^- anions. In contrast, Kyllini's groundwater samples show a greater dominance of $\text{Na}^+ + \text{K}^+$ and Cl^- , typical of saline or mineralized groundwaters, clustering near grid 3, which aligns with the elevated salinity observed in these samples. Groundwater samples from the Voskina plot are between grids 5 and 6, indicating

bicarbonate-dominated water with Ca^{2+} and Mg^{2+} as the dominant cations, typical of less mineralized or recharge-dominated groundwater.

Figure 4 illustrates the distribution of predominant ions (Ca^{2+} , Mg^{2+} , Na^+ , and Cl^-) among the three springs. Ca^{2+} concentrations are markedly elevated in the Agiasma spring, ranging from 350 to 390 mg/L, followed by Voskina (263–286 mg/L), while Kyllini has the lowest concentrations of approximately 65 mg/L. Magnesium (Mg^{2+}) concentrations show a similar trend, with Agiasma displaying the highest concentrations (30–50 mg/L), Voskina having moderate values (25–35 mg/L), and Kyllini showing minimal variability at around 30 mg/L. Na^+ and Cl^- concentrations are significantly higher in Kyllini and Agiasma (Na 800–900 mg/L, Cl^- 900–1200 mg/L), reflecting saline influences, such as evaporite dissolution. Conversely, Voskina presents significantly lower Na^+ (200 mg/L) and Cl^- (265–371 mg/L) concentrations, suggesting the presence of a relatively fresher groundwater system. A complete set of box plots illustrating the distribution of all major ions (K^+ , NO_3^- , NO_2^- , SO_4^{2-} , and HCO_3^-) for the three springs is provided in the Supplementary Materials, offering a more comprehensive overview of the hydrochemical variability across sites.

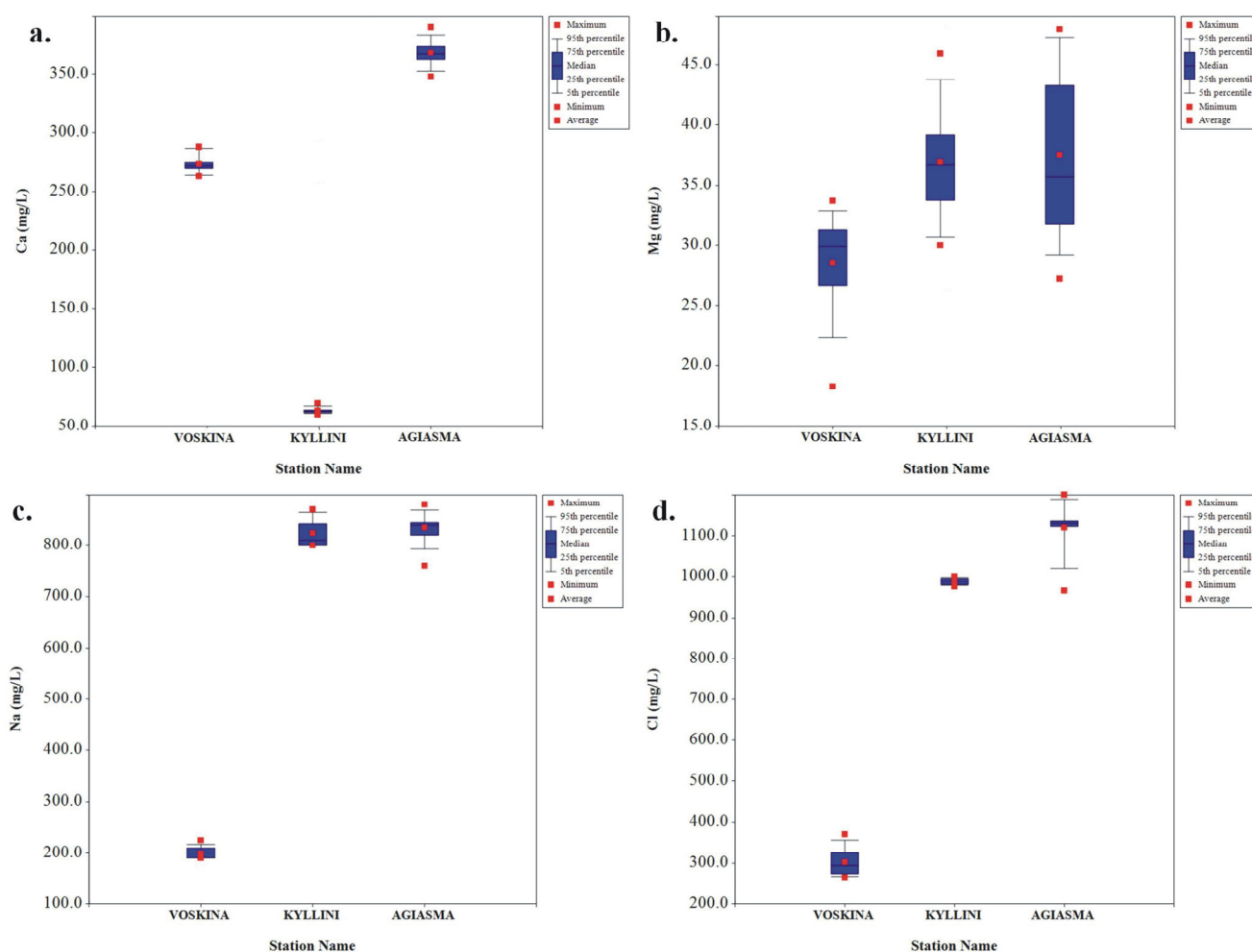


Figure 4. Box and Whisker plots of chemical parameters of the groundwater samples for Ca^{2+} (a), Mg^{2+} (b), Na^+ (c), and Cl^- (d).

The descriptive statistics of trace element concentrations in the hypothermal waters of Kyllini, Voskina, and Agiasma are presented in Table 4. Of the three sites, Agiasma spring water has higher concentrations of the majority of the elements, notably Li (average 2834.1 $\mu\text{g/L}$), B (46,410.9 $\mu\text{g/L}$), Mn (1520.0 $\mu\text{g/L}$), Fe (15,504.5 $\mu\text{g/L}$), and As (367.0 $\mu\text{g/L}$),

reflecting a greatly mineralized water composition. Voskina spring shows intermediate enrichment, particularly in B (mean 12,229.5 µg/L), Sr (613.4 µg/L), and Cs (43.6 µg/L). Kyllini spring shows the lowest concentrations for most elements, with a notable exception of Sr, which averages 1710.8 µg/L, higher than that observed in Voskina. Such differences highlight the importance of the local hydrogeological conditions that control the hydrochemical regime of springs.

Table 4. Descriptive statistics of trace elements (µg/L) recorded in the groundwater samples. (n.d. not detected).

Parameters	Kyllini Spring (n = 12)				Voskina Spring (n = 12)				Agiasma Spring (n = 12)			
	Minimum	Maximum	Average	Std. Dev.	Minimum	Maximum	Average	Std. Dev.	Minimum	Maximum	Average	Std. Dev.
Li	37.1	88.8	53.1	16.6	429.5	991.9	567.9	187.1	1985	4851	2834	936
Be	0.00	0.08	0.03	0.02	0.04	0.11	0.07	0.03	0.37	0.85	0.58	0.19
B	1289	1968	1566	201	9969	16,381	12,229	2042	36,675	58,879	46,411	8011
Al	1.3	454.0	60.3	125	1.27	43.8	12.4	16.5	4.92	11.8	7.99	2.78
P	0.0	110	45.1	32.8	0.01	39.0	18.3	12.3	0.06	284.4	188.8	115
Ti	209	295	245	32.6	980	1391	1136	176	1094	1820	1363	309
V	6.4	11.4	8.3	1.5	1.39	3.53	2.33	0.83	5.5	13.1	8.3	3.28
Cr	15.4	213.9	39.1	55.3	3.83	16.3	9.92	4.05	6.8	30.8	15.0	8.26
Mn	9.5	15.9	12.8	2.4	1.20	8.9	4.08	2.12	898	2166	1521	450
Fe	12.6	269.9	80.0	71.5	29.3	166.9	76.9	44.6	9571	21,695	15,505	4341
Co	0.1	0.3	0.2	0.1	0.55	1.09	0.78	0.20	7.06	12.8	10.0	1.87
Ni	0.6	2.0	1.2	0.4	10.4	22.2	15.1	4.0	17.8	31.7	23.1	4.54
Cu	12.3	88.1	30.9	23.8	4.96	55.0	22.5	15.7	11.8	118.2	54.2	37.3
Zn	0.64	20.6	7.42	6.79	11.2	687	156	180	31.6	146.3	72.5	36.4
As	0.63	4.33	2.13	1.40	9.27	21.3	13.4	4.22	314	651	418	105
Se	2.46	7.07	4.40	1.46	1.34	6.73	2.71	1.69	3.08	11.6	5.44	2.83
Rb	5.22	6.99	6.13	0.62	32.8	42.5	36.4	3.43	129	183	154	20.5
Sr	1386	2317	1711	305	474	889	613	145	1331	2684	1838	461
Nb	0.00	0.11	0.03	0.04	0.00	0.13	0.03	0.04	0.03	0.14	0.07	0.04
Mo	0.03	0.33	0.13	0.14	0.11	0.74	0.39	0.20	0.02	0.60	0.31	0.19
Cd	0.00	0.23	0.06	0.07	0.01	0.05	0.03	0.01	0.00	0.04	0.02	0.01
In	0.01	0.01	0.01	0.00	0.00	0.09	0.03	0.04	n.d	n.d	n.d	n.d
Sn	0.00	0.40	0.11	0.12	0.00	26.1	3.99	8.56	0.00	0.78	0.28	0.25
Sb	0.01	0.22	0.07	0.07	0.12	0.32	0.19	0.06	0.01	0.14	0.06	0.05
Cs	0.08	0.24	0.13	0.04	35.8	61.4	43.6	8.71	92.5	189.1	126.2	34.9
Ba	49.0	81.3	61.0	10.7	103.4	179.9	133.8	28.0	321.6	558.4	406.1	83.3
Pb	0.00	3.56	0.92	1.47	0.00	0.52	0.16	0.20	n.d	n.d	n.d	n.d
Bi	0.00	0.05	0.02	0.01	0.00	0.07	0.02	0.03	0.00	0.05	0.01	0.01
U	0.00	0.05	0.01	0.01	3.84	6.35	4.72	0.94	0.32	0.64	0.45	0.11

Boxplot analysis of trace element concentrations (Figure S2) reveals distinct geochemical signatures in the three springs. Agiasma consistently demonstrates significantly elevated levels of Ba, V, Ni, Sr, B, and Li in the aquifer matrix. Such enrichment is commonly associated with the dissolution of lithogenic minerals and potential mixing with deep geothermal fluids [63]. The concurrent elevation of Li and B supports the hypothesis of hydrothermal input, as these elements are known tracers of geothermal activity [64]. High concentrations of boron and lithium are linked to deep groundwater [65], while in some cases it is linked to brine lakes [66]. In the studied springs, the influence of deep groundwater is confirmed, while the higher concentrations of Li and B correspond to the Agiasma spring, highlighting the reduced mixing process with fresh shallow groundwater. The high Sr concentrations in both Agiasma and Kyllini further suggest enhanced carbonate weathering, which is typical in karst environments with active dissolution of limestone and dolomite [67]. In contrast, Voskina presents significantly lower trace element

concentrations and a narrower variability range, reflecting limited geochemical evolution and a predominantly fresh, bicarbonate-rich water composition. Kyllini has intermediate trace element levels, indicative of a transitional hydrochemical regime influenced by both saline and carbonate sources. These patterns are in agreement with prior geochemical characterizations of karst thermal systems, where trace element mobilization is regulated by redox conditions, mineral equilibria, and lithological heterogeneity [68].

Combining hydrochemical datasets from different sampling points for statistical analysis has been widely applied to gain a thorough understanding of hydrochemical processes [69]. Remarkably, the correlation analysis revealed numerous correlations between the elements, despite their different hydrogeological origins (Figure 5). This process can contribute to the determination of similar hydrochemical processes among the three springs. Several relationships were observed between elements with correlation coefficients higher than 0.7, and these reflect strong positive correlations among certain variables in all of the samples. These high correlations indicate that the paired components are likely to be regulated by the same geochemical sources, processes, or conditions. The Spearman correlation coefficient heatmap (Table S1) analysis detected numerous significant positive correlations ($r > 0.7$) between significant elements, which are indicative of shared geochemical sources and controls. Li and Ca^{2+} ($r \approx 0.87$), whose likely origin is carbonate dissolution [70], and Sr and V ($r \approx 0.97$), which may co-occur in the lithological sources or related mobilization processes, are strong correlations. Manaka et al. [71] observed a similar correlation in the aquifer spring of the Ganges-Brahmaputra river system. The mutual Mg and V relationship ($r = 0.86$) can be attributed to mutual geochemical controls, such as adsorption or co-precipitation [72].

The strong correlation between Cl and Mn ($r \approx 0.84$) suggests a possible evaporitic origin. The close near-unity correlation that exists between rubidium (Rb) and arsenic (As) ($r \approx 0.99$) highlights a close geochemical relationship, most likely caused by similar ionic characteristics, whereas the strong association between lithium (Li) and bicarbonate (HCO_3^-) ($r \approx 0.92$) is an indicator of the major role played by carbonate equilibria in dominating lithium mobility [73]. Zhou et al. [74] observed a similar correlation in the Bangor Co Salt Lake (central Tibet), where the findings indicate a strong correlation between the recharge water regime and lithium content ($R^2 = 0.94$). Chloride was also found to have a strong positive correlation with phosphorus (P) ($r = 0.80$) and selenium (Se) ($r = 0.698$), highlighting high temperature and high pressure water, indicating a common geochemical pathway or origin [75].

Manganese (Mn) also had highly positive correlations with iron (Fe) ($r = 0.83$) and strontium (Sr) ($r = 0.79$), indicating its common association with iron oxides and association with carbonate phases, as well as Neogen deposits. There were also strong correlations with cobalt (Co), nickel (Ni), copper (Cu), and selenium (Se), indicating its extensive geochemical interactions [76]. Liu et al. [70] observed that the methodologies of clustering analysis and compositional balance analysis were utilized to elucidate the multi-element association patterns associated with Ni–Co mineralization. The strong association of manganese with chloride and their mutual associations with other trace elements highlight the role of natural sources in shaping the water chemistry of the studied thermal springs. Hoque et al. observed significant positive correlations between chloride, sulfate, and sodium [77].

Arsenic (As) exhibited strong positive correlations with rubidium (Rb) ($r = 0.98$), cesium (Cs) ($r = 0.97$), and barium (Ba) ($r = 0.96$), suggesting that these elements likely share similar geochemical pathways or originate from source-related processes within the studied environment. A moderate positive correlation was also seen between As and U ($r = 0.53$) and therefore presumably indicates co-mobilization under certain geochemical conditions. The moderate positive correlation between As and U reflects their shared

dependence on the reductive dissolution of iron (hydr)oxides in aquifer sediments. Under reducing conditions that promote uranium immobilization via reduction from U(VI) to U(IV), arsenic becomes readily mobilized from mineral surfaces [78].

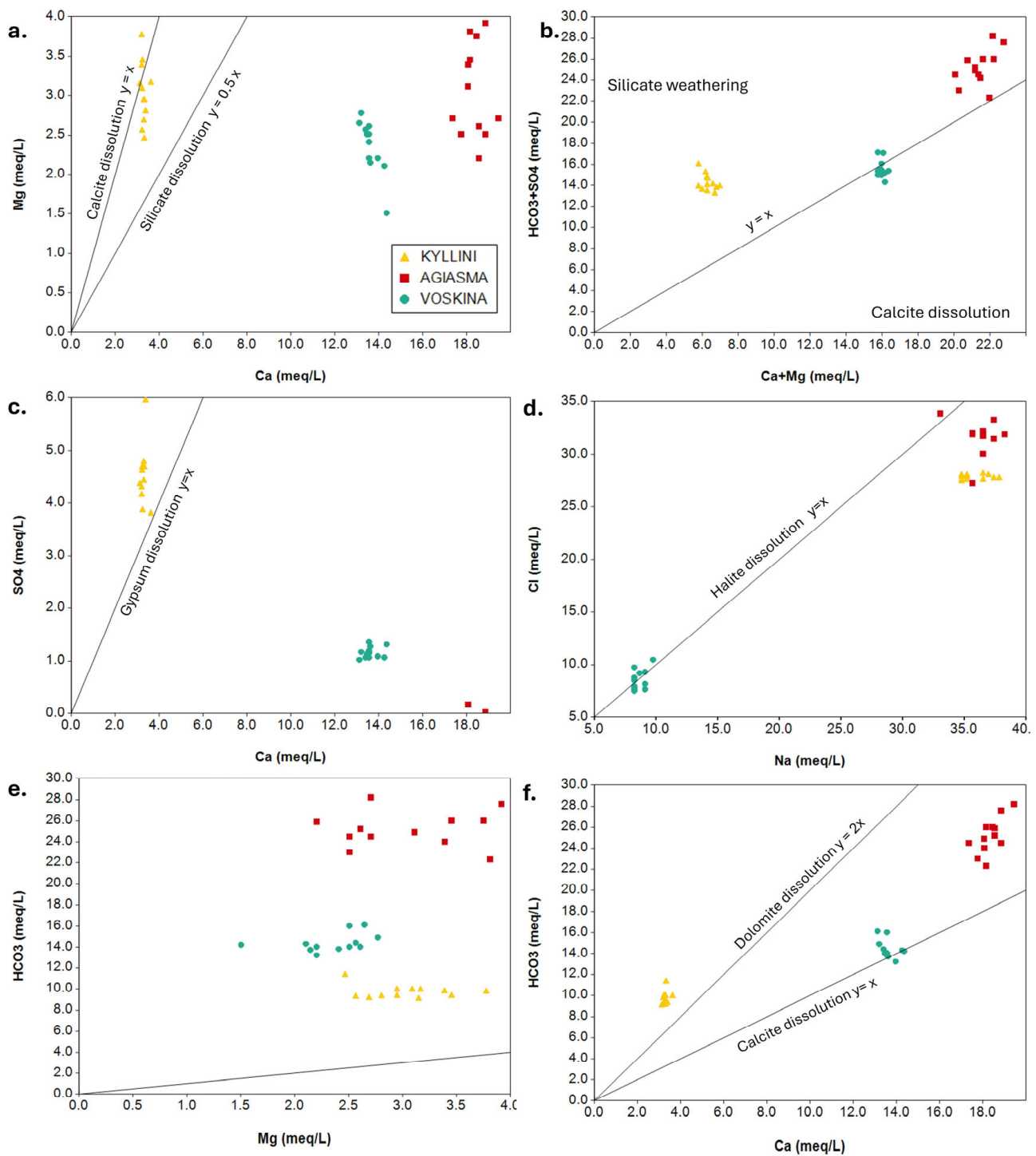


Figure 5. Scatter plots showing relationships between the concentrations of the major ions detected in the groundwater samples, Ca^{2+} vs. Mg^{2+} (a), $\text{HCO}_3^- + \text{SO}_4^{2-}$ vs. $\text{Ca}^{2+} + \text{Mg}^{2+}$ (b), SO_4^{2-} vs. Ca^{2+} (c), Cl^- vs. Na^+ (d), HCO_3^- vs. Mg^{2+} (e), and HCO_3^- vs. Ca^{2+} (f).

In contrast, sulfate (SO_4^{2-}) showed a strong negative correlation with As ($r = -0.93$), revealing an inverse trend where higher sulfate concentrations correspond to lower arsenic levels, possibly due to competitive adsorption or other geochemical controls. It was also negatively correlated with elements like lithium (Li) ($r = -0.92$), beryllium (Be) ($r = -0.95$),

and cobalt (Co) ($r = -0.94$), reflecting its complex geochemical processes and influence on trace element mobility. These correlations highlight the dominant role of sulfate in regulating arsenic and other metal concentrations in the system, with implications towards potential redox reactions and dissolution–precipitation. For example, O'Day et al. [79] pointed out that dissolved arsenic concentrations may remain difficult to predict quantitatively in specific cases because they are controlled by rates of dissolution and precipitation of iron and sulfide phases and their solubilities and also by competing pH-dependent adsorption reactions.

Barium (Ba) was highly positively related to bicarbonate (HCO_3^-) ($r = 0.89$), which indicates that these two components occur in tandem within the investigated system. This relationship suggests the possible significance of bicarbonate in mobilizing and transporting barium, possibly through carbonate mineral complexation or dissolution reactions. The degree of correlation specifies the dominance that carbonate equilibria have on Ba concentrations, highlighting the geochemical significance of bicarbonate in trace element cycling in the sampled environment. Strong positive correlations between Li, Ca^{2+} , and HCO_3^- further illustrate a close geochemical relationship. Bicarbonate was found to have a very strong positive correlation with calcium ($r = 0.90$) and lithium ($r = 0.91$), indicating that the two elements are influenced by carbonate equilibria, probably through carbonate mineral dissolution processes. Li and Ca^{2+} also had a strong positive relationship ($r = 0.86$), proof that related geological processes, including the dissolution of carbonate rocks or environmental ion exchange mechanisms, regulate their concentrations. The high inter-correlations among these three parameters provide additional evidence of the critical role carbonate chemistry plays in controlling the distribution of major cations within the system.

Following the correlation of all of the datasets, elements of specific interest were identified and correlated between two springs (Supplementary Materials Tables S1–S3). Emphasis was placed on evaluating the consistency of strong correlations between trace elements and major ions across spring pairs, as these reflect underlying geochemical processes, mineral–water interactions, and potential common hydrogeological pathways. Across all combinations of spring pairs, strong and recurrent positive correlations were observed among Na^+ , K^+ , and HCO_3^- , most prominently in the Kyllini–Voskina and Kyllini–Agiasma datasets. Moreover, consistently high correlations between Ca^{2+} and HCO_3^- in all cases highlight the presence of carbonate rock dissolution, pointing to a dominant contribution of limestone layers within the aquifer matrix [80].

One of the most consistent features across all datasets is the highly significant clustering of Li, B, Be, Cs, Rb, Ba, and U, showing strong positive correlations with each other. This recurrent pattern implies a shared geochemical control linked to lithologies or interaction with deep geothermal fluids. The high mobility of these elements in thermal, slightly alkaline, or CO_2 -rich waters supports the hypothesis of hydrothermal alteration or deep circulation as a common source mechanism [63]. In addition, transition and redox-sensitive metals, such as Mn, Fe, Co, Ni, Cu, Zn, As and Se, form a second, robust cluster of positively correlated elements in nearly all spring pairs. These elements are typically mobilized under reducing or mildly fluctuating redox conditions, pointing to groundwater environments that are at least partially suboxic [81]. The co-occurrence of As and Se with Fe and Mn suggests that desorption from iron/manganese hydroxides or reductive dissolution play an important role in their transport [82].

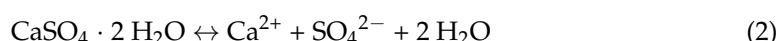
3.2. Ion Ratio Analysis

The scatter plots in Figure 5 illustrate hydrochemical relationships between the major ions, providing insights into the geochemical processes influencing the water chemistry of Kyllini, Agiasma, and Voskina springs. Each plot reflects distinct mineral dissolution

and weathering mechanisms of the respective spring systems. In Figure 5a, the relationship between Ca^{2+} and Mg^{2+} is used to assess the dissolution of carbonate and silicate minerals. The $y = x$ line indicates a 1:1 molar release of Ca^{2+} and Mg^{2+} , characteristic of dolomite dissolution. Samples plotting below this line, closer to a $y = 0.5x$ trend, suggest disproportionate Ca^{2+} enrichment, potentially derived from calcite or silicate weathering [52]. Notably, the Agiasma samples show elevated Ca-HCO_3 concentrations, suggesting substantial dissolution of carbonate minerals. In contrast, the samples from Kyllini and Voskina align predominantly with calcite dissolution patterns, indicating a relatively minor contribution from dolomite.

The bivariate diagram of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ versus $(\text{HCO}_3^- + \text{SO}_4^{2-})$ serves as a reliable tool for identifying ion exchange and reverse ion exchange processes (Figure 5b). Data plotting along the 1:1 line implies equilibrium governed primarily by the dissolution of carbonate and sulfate minerals. Points positioned above the line indicate that ion exchange is the dominant process, whereas those below the line suggest the occurrence of reverse ion exchange. When the $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$ ratio is 1:1, the groundwater's hydrogeochemical composition is primarily influenced by the dissolution of carbonate and sulfate minerals. Kyllini samples plot below the calcite dissolution trend ($y = x$), indicating a relative excess of $\text{Ca}^{2+} + \text{Mg}^{2+}$, possibly due to ion exchange or CO_2 degassing. In contrast, Agiasma samples lie above the line, suggesting a surplus of $\text{HCO}_3^- + \text{SO}_4^{2-}$, which may reflect enhanced carbonate weathering, geothermal CO_2 input, or additional sulfate sources. Meanwhile, the samples from Voskina have comparatively lower values, reflecting minimal involvement of either sulfate or extensive weathering processes.

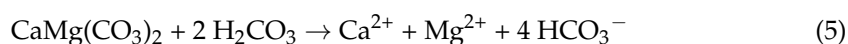
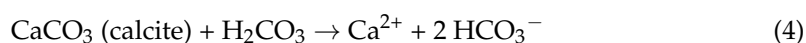
A $\text{Ca}^{2+}/\text{SO}_4^{2-}$ molar ratio of approximately one indicates gypsum dissolution, as described by Equation (2). In this study, most water samples exhibited an excess of Ca^{2+} , likely derived from the dissolution of carbonate minerals. In contrast, Kyllini samples aligned with or slightly deviated from the 1:1 equiline (Figure 5c), suggesting that gypsum dissolution was the predominant process. Notably, Kyllini groundwater samples exhibited significantly elevated SO_4^{2-} concentrations, possibly indicating additional influences from sulfide oxidation. Agiasma and Voskina have lower SO_4 concentrations, indicating limited gypsum involvement. Agiasma's deviation may imply other sulfate sources or mixing.



The Na^+/Cl^- plot reflects halite dissolution ($y = x$). If halite dissolution was the dominant process governing groundwater chemistry, the Na^+/Cl^- molar ratio would be expected to be one, as described by Equation (3). Agiasma and Kyllini groundwater samples align well with the halite trend (Figure 5d). Samples from Voskina spring show lower values, suggesting reduced halite contribution or dilution effects.



Figure 5e examines sources of Mg, such as dolomite dissolution. Kyllini samples align with carbonate dissolution trends, while Agiasma shows slightly elevated HCO_3^- values, likely from enhanced carbonate weathering. Voskina samples are distinct, indicating less Mg from dolomite.



The $\text{Ca}^{2+}/\text{HCO}_3^-$ ratio serves as a valuable indicator for assessing carbonate dissolution, with calcite dissolution following a 1:1 ratio and dolomite dissolution a 1:2 ratio

(Equations (4) and (5)). As shown in Figure 5f, Kyllini groundwater samples fall between the 1:1 and 1:2 equilines, confirming carbonate dissolution as the primary process. In contrast, Agiasma and Voskina samples deviate significantly from these equilines and exhibit excess Ca^{2+} , suggesting an additional source of Ca^{2+} beyond carbonate dissolution.

The Gibbs diagrams of the groundwater samples (Supplementary Materials Figure S3) illustrate the relationship between total dissolved salts (TDS) and two key hydrochemical ratios, $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$, aiding in the interpretation of salinity origins of groundwater. In the left plot, the $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio distinguishes between waters dominated by rock interactions, precipitation, and seawater influence [69]. Voskina samples fall within the rock dominance zone, suggesting significant interactions with carbonate rocks. Conversely, Agiasma and Kyllini samples plot near or within the seawater zone, indicating the influence of saline waters, such as remnant seawater intrusion or evaporite dissolution. According to previous studies, seawater intrusion in the Agiasma spring can be excluded [55]. The second plot uses $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ ratios to further evaluate salinity sources.

Marandi and Shand (2018) [83] indicate that the Gibbs diagram tends to oversimplify complex geochemical processes and cannot distinguish water–rock interaction from other contaminating processes, such as ion exchange. In the present study, Gibbs plots are used only as a general visual classificatory tool for the representation of salinity trends among the three springs. More robust indicators, like ion ratio plots, saturation indexes, and statistical analysis, were employed to enhance the identification of controlling geochemical processes. In the present study, the Gibbs diagrams are not conclusive in their assertions regarding the governing hydrogeochemical processes, as the mapped samples cut across different interpretive zones without any specific trend. This assertion supports the Marandi and Shand (2018) [83] criticism that the Gibbs diagram, initially designed for surface waters, might oversimplify or hide important processes in groundwater systems, particularly those governed by complex water–rock interactions, redox conditions, and mineral dissolution not accounted for by the limited $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ ratios.

The relationship between $(\text{Na}^+ + \text{K}^+) - \text{Cl}^-$ and $[(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]$ is commonly used to investigate the geochemical processes influencing water composition, particularly focusing on ion exchange, salinity, and water–rock interactions [70]. For instance, Liu et al., 2023 highlighted using the Schoeller index when analyzing cation exchange in groundwater systems, which is crucial for understanding hydrochemical dynamics [64].

Figure 6 highlights the relationship between the cation–anion balance, represented as $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})$, and the $(\text{Na}^+ + \text{K}^+) - \text{Cl}^-$ balance for groundwater samples from the three springs. The plotted data show a linear trend, with most samples from Kyllini and Agiasma aligning below the zero line of the y axis, thus indicating a deficit in cations relative to anions (likely due to processes like $\text{Na}^+ - \text{Cl}^-$ dominance or ion exchange). In contrast, Voskina samples cluster near the zero balance on both axes, suggesting a closer balance between cation and anion inputs. This distribution highlights geochemical heterogeneity, with Kyllini and Agiasma springs being more saline and chemically different in evolution, possibly as a result of evaporative concentration or geothermal activity, while Voskina shows fresher water.

The Langelier–Ludwig (LL) diagram (Figure 7) displays relative concentrations of the major ions of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), and chloride (Cl^-) on a square coordinate grid. The quadrants represent different types of waters, which can indicate processes influencing their water chemistry, such as mineral dissolution, ion exchange, and mixing of various waters [84]. In hydrochemistry, the LL diagram helps detect the occurrence of saline intrusion in coastal aquifers, as

illustrated in a study where water samples from different sources were plotted on the LL diagram to show changes in water chemistry resulting from mixing with seawater [85].

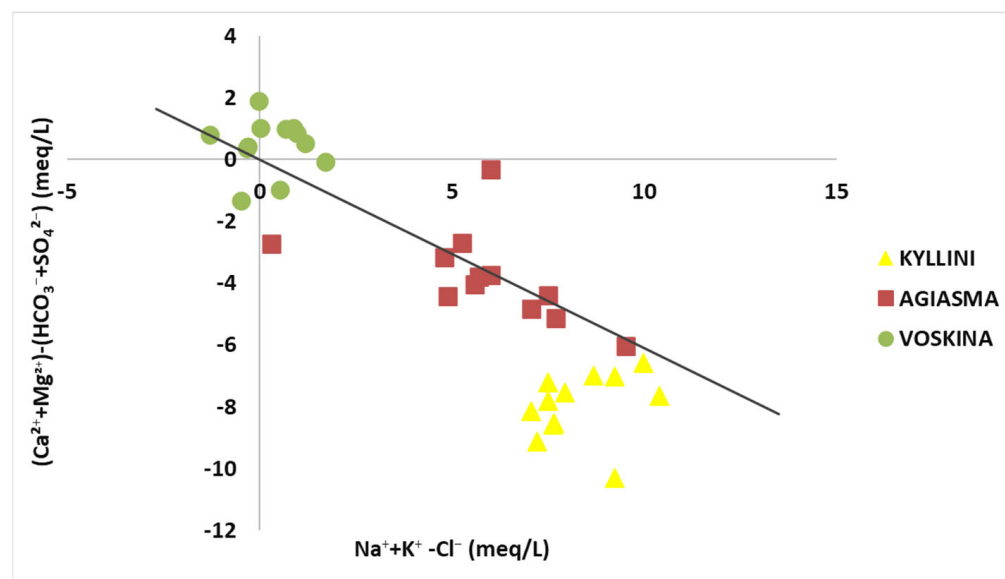


Figure 6. Relationship between the cation–anion balance for the groundwater samples based on molar ratio balance.

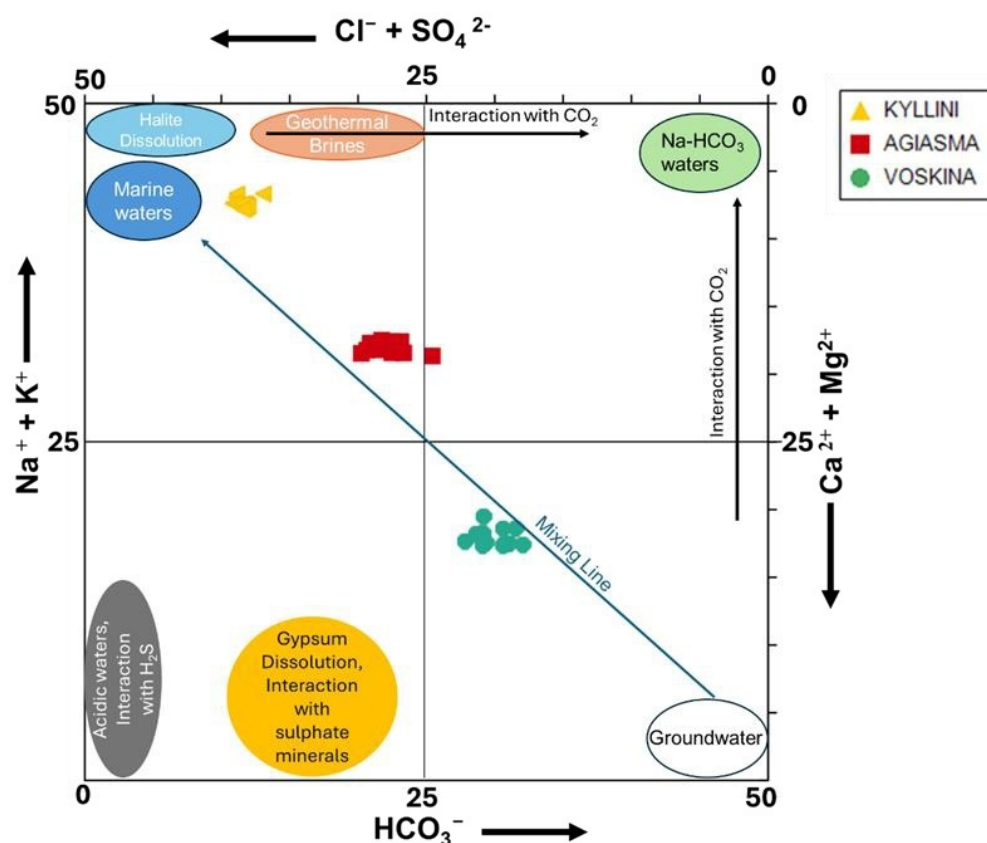


Figure 7. Langelier–Ludwig diagram of the three springs indicating some geological interpretations.

The geochemical character of the Kyllini groundwaters is typified by the high concentrations of Na^+ and Cl^- ions. This stability further supports the conclusion that the geochemical evolution of Kyllini spring waters is largely governed by marine-derived processes, with minimal interaction with CO_2 or other mineral sources. Agiasma groundwater

samples appear to be influenced by halite dissolution, CO₂ interactions, and carbonate weathering, as the presence of both Cl[−] and HCO₃[−] might also indicate mixing between saline and carbonate-enriched waters. On the other hand, Voskina samples are dominated by freshwater inputs with relatively low levels of mineralization. The proximity to the mixing line suggests that these waters may represent a transitional composition influenced by the dilution of more mineralized waters through mixing with freshwater sources. These results are in accordance with previous studies on the seawater pattern in Anthemountas basin [69] that conclude that the salinity of the Voskina and Agiasma springs is not caused by seawater intrusion.

Scatter plots are widely used in hydrogeochemical studies as a visual and analytical tool to explore the relationships between chemical constituents in groundwater. They help reveal trends, correlations, and potential geochemical processes, such as ion exchange, mineral dissolution, or mixing of different water sources. For instance, Nyirenda et al., 2016 used scatter plots to analyze the hydrogeochemical characteristics of groundwater at the Xikuangshan Antimony Mine, China, and demonstrated how these visual tools can reveal significant relationships between various chemical constituents, including Cl and trace elements [86]. This approach is particularly effective in identifying patterns that may indicate specific geochemical processes, such as ion exchange.

The geochemical relationships between the concentrations of chloride (Cl) (meq/L) and specific trace elements (Cs, Li, Sr, and Ba) in the three thermal springs under study are depicted in Figure 8. As shown in Figure 8a, Agiasma samples have significantly higher cesium (Cs) concentrations at higher Cl levels, whereas Kyllini and Voskina samples have consistently low Cs values. While Kyllini and Voskina exhibit noticeably lower and more stable lithium (Li) levels, Agiasma also has the highest Li concentrations, with significant variability throughout the hydrological year (Figure 8b). Concentrations of strontium (Sr) show a strong positive correlation with Cl in Figure 8c, especially in Agiasma and Kyllini samples, but they are consistently lower in Voskina samples. Similarly, Figure 8d shows that in Agiasma, barium (Ba) concentrations rise with Cl, with Voskina having the lowest values and Kyllini having moderate values. Overall, the high positive correlations found between Cl and trace elements, particularly in Agiasma, indicate that processes driven by salinity, such as evaporative concentration, water–rock interaction, or geothermal input, are important for trace element enrichment in these systems.

The trace element scatter plots in Figure 9 reveal strong linear relationships among selected trace elements within individual spring systems. These trends likely reflect co-mobilization under similar hydrogeochemical conditions. For example, the strong correlation between Cs and Rb ($r = 0.91$ – 0.97 in Agiasma and Voskina) suggests a shared origin or behavior during the weathering of feldspar- and mica-bearing lithologies (Figure 9a). Similarly, the Ba–Li (Figure 9b) and B–Li (Figure 9d) plots demonstrate very high correlation coefficients ($r > 0.93$) in Kyllini and Agiasma, indicating a possible association with deep hydrothermal fluid contributions or CO₂-enriched environments that enhance the mobility of these elements. The Sr–Rb relationship is also particularly strong across all three springs ($r = 0.94$ – 0.98), reinforcing the role of carbonate mineral dissolution and potential cation exchange processes in regulating strontium behavior (Figure 9c). The variation in correlation strength among springs (Ba–Li being weak in Voskina) further underlines the hydrochemical distinctiveness of each site, emphasizing the need for site-specific geochemical interpretations.

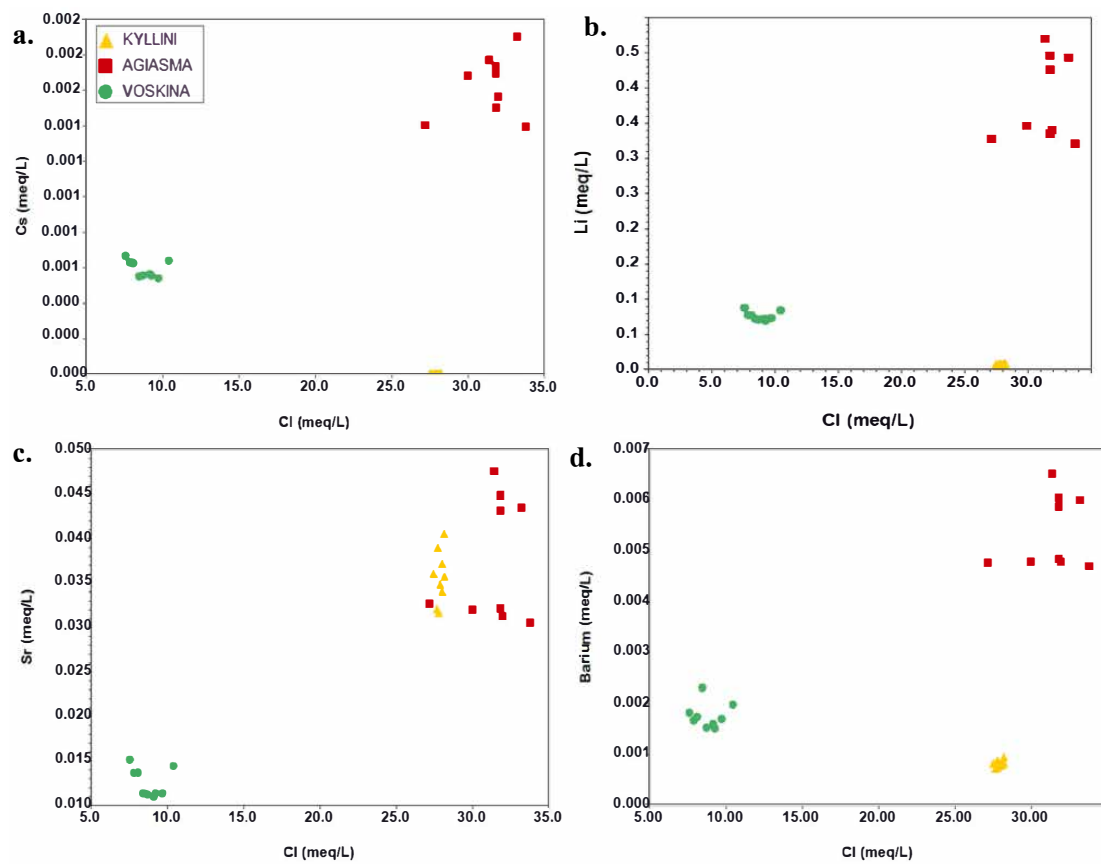


Figure 8. Plots of ratios for all groundwater samples: Cs vs. Cl (a), Li vs. Cl (b), Sr vs. Cl (c), and Ba vs. Cl (d).

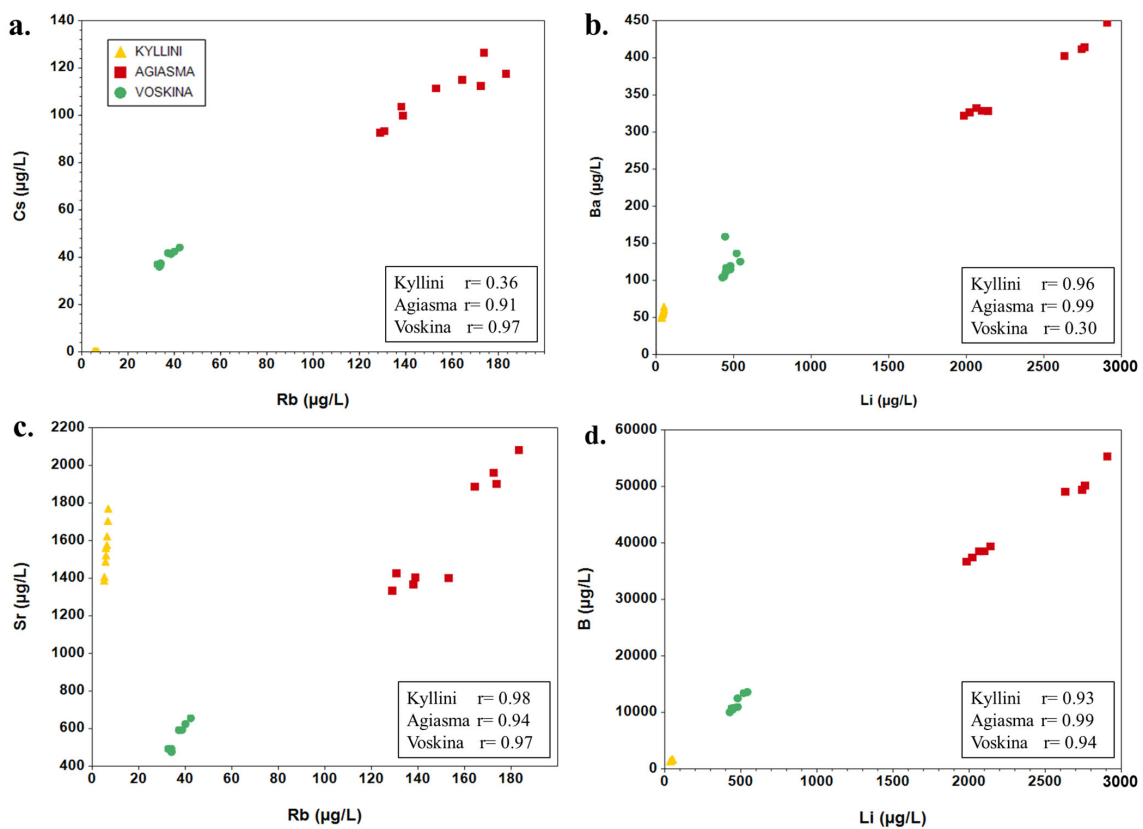


Figure 9. Plots of ratios for all groundwater samples: Cs vs. Rb (a), Ba vs. Li (b), Sr vs. Rb (c), and B vs. Li (d).

3.3. Saturation Indices

Saturation indices (SI) were calculated using the PHREEQC [53] code and then compared to analyze the dissolution and precipitation tendencies of minerals (Figure 10). Various geochemical environments influenced by the local geology and hydrology are revealed in the dissimilarities of mineral saturation behavior and TDS concentrations at varying locations. SI can be used to determine mineral stability in groundwater systems. In studies on carbonate minerals, SI can be used to determine if the precipitation conditions for calcite or dolomite are favorable, which is beneficial in studies of carbonate aquifer dynamics [64,67].

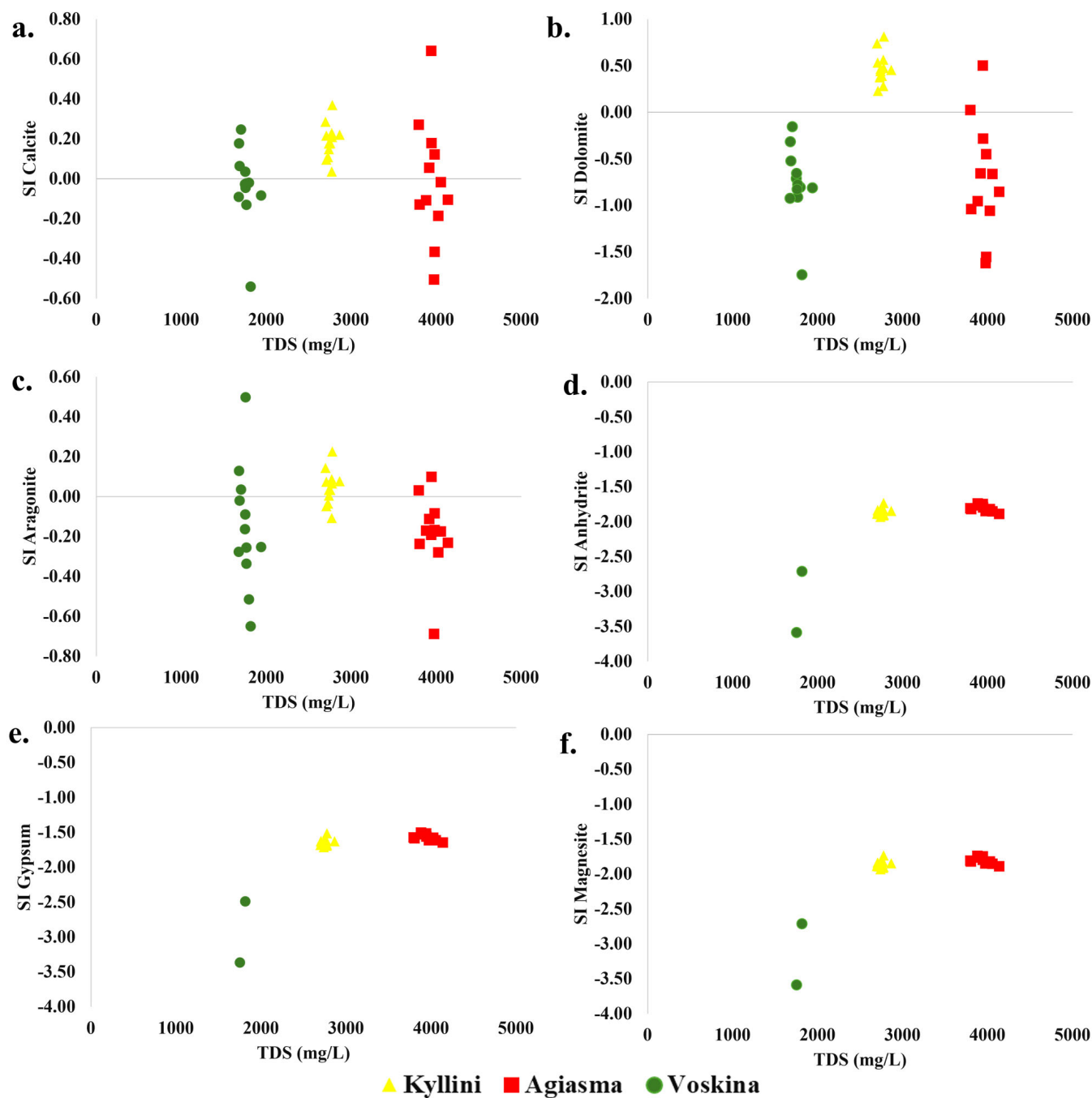


Figure 10. Scatter plots of saturation indices for calcite (a), dolomite (b), aragonite (c), anhydrite (d), gypsum (e), and magnesite (f) vs. TDS. The gray line is the equilibrium line (SI = 0).

The relationship between SI values and total dissolved solids (TDS) for each sample is shown in Figure 10. These color-coded clusters indicate mineral saturation variation among the three sites. In this study, saturation index (SI) values between -0.5 and $+0.5$ were considered indicative of near-equilibrium conditions, while values beyond this range were interpreted as either under-saturation or over-saturation. Voskina samples are mainly under-saturated for dolomite, whereas Kyllini and Agiasma samples are either over-saturated or near equilibrium levels, particularly with the higher TDS values. Anhydrite, gypsum, and magnesite exhibit a consistent trend of under-saturation in all stations, with minimal variation in SI values.

3.4. Time Series Data

The temporal analysis of temperature and electrical conductivity in relation to monthly precipitation reveals distinct seasonal dynamics among the three springs (Figures 11 and 12). Kyllini spring displays stable temperatures, which slightly decrease during the wet season (December–February) and recover towards the end of the summer. Electrical conductivity also shows minimal variation, suggesting a buffered, deep-circulating system with limited influence of meteoric recharge. This supports the interpretation of Kyllini as a shallow geothermal system with consistent mineral input.

In contrast, Agiasma spring exhibits significant seasonal temperature variability, with maxima in spring–summer and minima coinciding with peak rainfall. A similar but more subdued trend is observed in electrical conductivity, indicating dilution effects from recharge during the wet season. These patterns are consistent with a mixed system involving geothermal waters and variable meteoric input, where the ionic strength decreases during higher recharge periods. The system may be sensitive to seasonal hydrodynamics and ion exchange processes, as reflected in its trace element enrichment. Voskina shows relatively stable temperatures and conductivity throughout the monitoring period, though minor decreases in conductivity are observed during wetter months. The spring's hydrochemical behavior aligns with a shallow, karst-fed system dominated by bicarbonate and calcium, where geochemical evolution is minimal and rapid infiltration likely limits long residence times.

The variability of major ions recorded throughout one hydrological year is shown in Supplementary Materials Figure S4. Concentrations of chloride and sodium remained relatively stable, indicating consistent saline influence throughout the year, while HCO_3^- levels fluctuated, possibly reflecting interactions with carbonate rocks or seasonal recharge variations. Magnesium and calcium also had stable patterns, likely due to continuous dissolution processes or lithological consistency. The stability or variability of each ion highlights the influence of geological formations, evaporation, or anthropogenic activities [77].

Temporal variation in the saturation indices (SI) of the selected minerals recorded from October 2023 to September 2024 is presented in Supplementary Materials Figure S5. These trends provide insight into the geochemical conditions governing mineral stability, precipitation potential, and water–rock interaction processes in each aquifer. In Kyllini (Figure S5a), carbonate minerals, such as calcite, dolomite and aragonite, showed SI values near or slightly above equilibrium, indicating favorable conditions for carbonate precipitation. Sulfate minerals, including gypsum and anhydrite, remained consistently under-saturated ($\text{SI} < -2$), suggesting their continued dissolution.

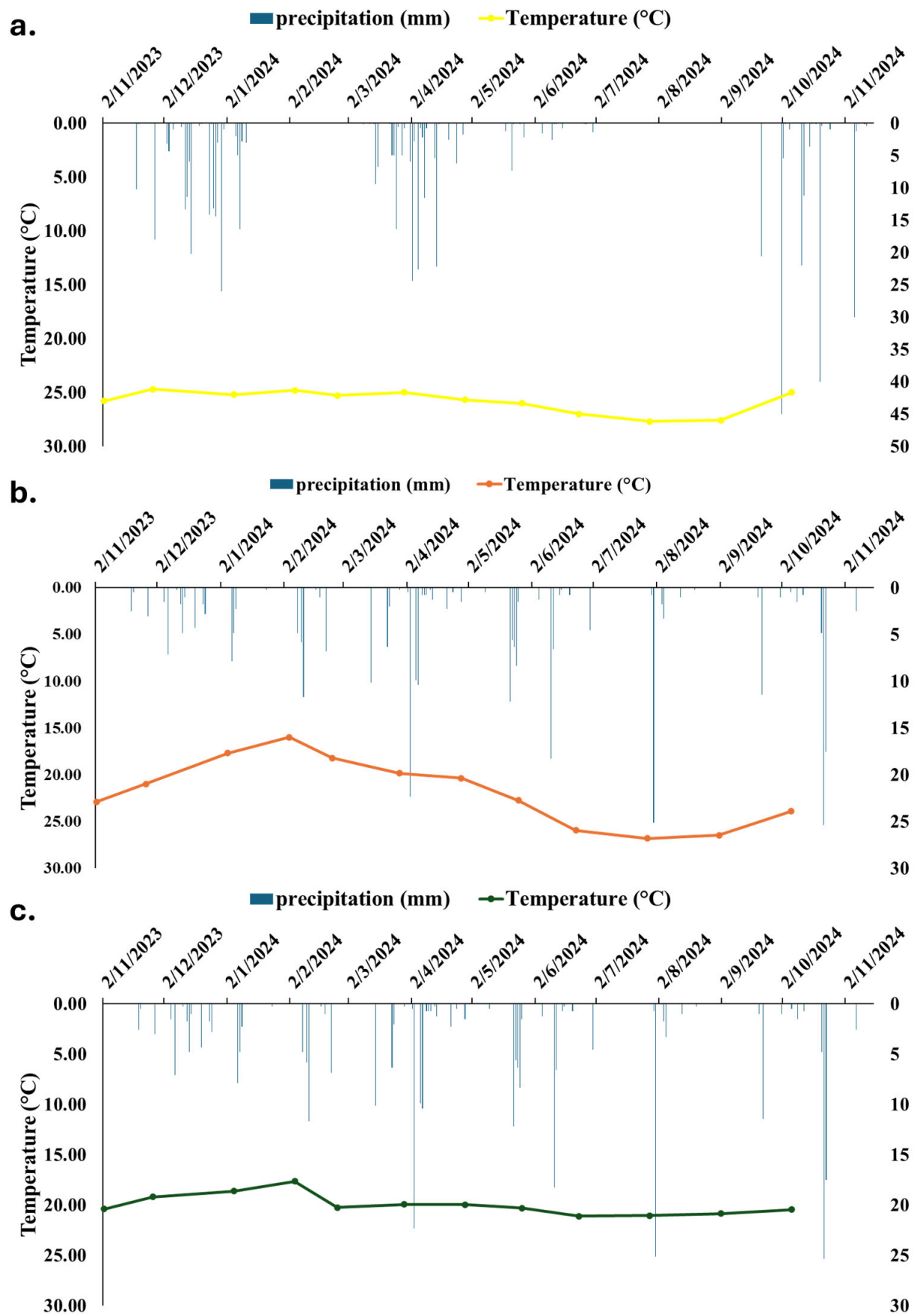


Figure 11. Time series plots of temperature for Kyllini (a), Agiasma (b), and Voskina (c).

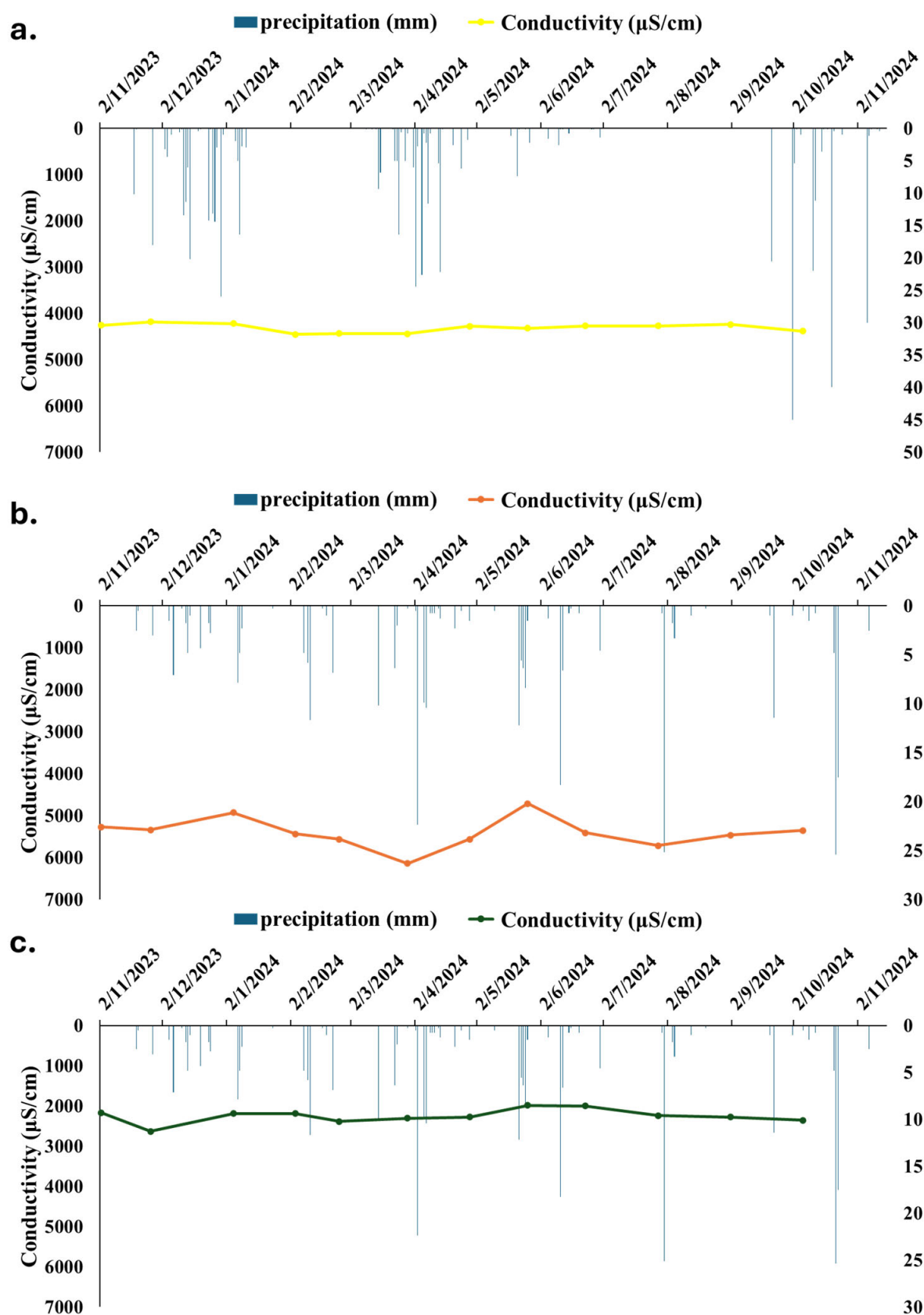


Figure 12. Time series plots of conductivity for Kyllini (a), Agiasma (b), and Voskina (c).

The stability of SI values over time reflects a geochemically buffered environment with sustained contributions from carbonate dissolution and possibly geothermal influences [52]. In Agiasma spring samples (Figure S5b), there is pronounced super-saturation of iron oxides

(maghemite, hematite, magnetite) with SI values exceeding +10, which indicate active iron cycling and redox-driven precipitation processes. Carbonate minerals also showed saturation or near-saturation behavior, while siderite and strontianite fluctuated near equilibrium. These trends suggest a complex geochemical environment characterized by both carbonate equilibrium and strong redox activity, likely enhanced by longer residence times and intense water–rock interactions [15]. In Voskina spring (Figure S5c), all minerals analyzed remained strongly under-saturated, especially halite, gypsum, and magnesite, indicating that dissolution dominates the hydrochemical regime. Carbonate minerals showed SI values well below equilibrium ($SI < -1$), suggesting minimal precipitation potential. The influence of halite in the hydrochemical evolution of groundwater has been highlighted in Fars Province of southern Iran [87]. The persistent under-saturation of sodium-rich evaporitic minerals, such as thenardite and natron, further supports the interpretation of a dilute groundwater system with limited geochemical evolution and a low ionic strength, consistent with the trace element and major ion data [67]. The seasonal consistency of SI values in all springs suggests limited short-term variability. However, the differences in SI levels and mineral behavior reflect distinct geochemical pathways: carbonate precipitation and geothermal input in Kyllini, iron oxide saturation and redox influence in Agiasma, and dominant dissolution under low-salinity conditions in Voskina.

3.5. Hydrochemical Relationship of the Studied Springs of Greece with Other Regions

The hydrochemical characteristics of the three studied springs in Greece align with broader patterns observed in Mediterranean hypothermal systems. For instance, the mineralized Na–Cl waters of Kyllini with moderate temperatures ($\approx 26^\circ\text{C}$) are comparable to those described in southwestern Tunisia, where deep aquifers exhibit Cl–Na signatures and are shaped by long circulation paths and mixing with connate or evaporitic waters [88]. Similarly, the Agiasma spring, showing evidence of thermal maturity, ionic exchange, and high HCO_3^- and Na^+ , presents geochemical affinities with the CO_2 -rich thermal waters of Chaves (Portugal), where fluid–rock interaction with granitic lithologies and deep-seated CO_2 input dominate the chemistry [89]. On the other hand, Voskina, characterized by relatively low TDS and bicarbonate dominance, aligns more closely with low-enthalpy karst systems reported in southern Italy, where infiltration processes and shallow flow paths control spring water quality [26]. This comparative analysis supports the internal differentiation proposed in our dataset: Agiasma as a mature geothermal source, Kyllini as a shallow thermal aquifer, and Voskina as a local recharge-dominated system. These insights contribute to refining the classification and resource potential of hypothermal springs in tectonically active Mediterranean terrains.

In Tyrma region of Russia, the thermal springs occur due to the favorable flow paths of the fault zone in combination with the stratigraphic features [90]. This environment is also verified in the studied springs in which hydrochemistry is governed by the fault zones flow paths, while the stratigraphy determines distinct mixing patterns with shallow fresh groundwater. Similarly, on the Algerian–Tunisian border, the hydrochemical evolution of the geothermal groundwater is governed by the geodynamic structure of the formations [91]. In the Chott-El-Gharbi basin of Algeria, groundwater hydrochemistry is influenced by the fault zone flow paths, leading to a mixing process of different geological formations [92].

The spatial differentiation of hydrochemical facies observed in the Anthemountas springs, particularly the transition between Ca- HCO_3 and Na-Cl water types, is consistent with regional-scale karst flow systems affected by CO_2 -rich deep fluids. Similar trends were observed by Temovski et al. (2021) [93] in the karst springs of North Macedonia, where isotopic and chemical evidence indicated variable mixing depths and residence

times related to geological structure and recharge elevation. The elevated TDS and HCO_3^- concentrations observed in the Kyllini and Agiasma springs likely result from prolonged interaction with CO_2 -rich fluids in deep karst systems. This is in line with findings by Gori et al. (2024) [29], who documented similar geochemical signatures in central Italy, where mixing between shallow and deep groundwater, enhanced by magmatic CO_2 input, contributed to high bicarbonate content and increased mineralization.

Groundwater quality is governed by the combination of physical and chemical parameters, which are characterized by natural processes, like geological formations as well as anthropogenic activities. Agricultural activities should also be among the pollution sources within the recharge zone of karst spring [94]. Thus, understanding hydrogeochemical processes is essential to assess rock–water interactions and the impacts of anthropogenic influences on groundwater quality [95]. Su et al. [96] point out that groundwater properties are controlled by a combination of natural processes, such as hydrogeological conditions, redox states, and mineral–mineral interactions, and anthropogenic activities, such as over-extraction, release of wastewaters, and fertilizer usage. Similarly, Gone et al. [97] underscore the significant influence of geochemical processes on water quality, including interactions with aquifer minerals and the mixing of groundwater along subsurface flow paths. All of these processes are accountable for the chemical evolution of groundwater, its physico-chemical and ecological roles, and its sustainable utilization, as it has been established within this study.

3.6. Future Work and Challenges

This study presented the results of a detailed hydrochemical statistical analysis and reverse modeling of three hypothermal mineral springs located in Greece. The analysis revealed both similarities and differences between the springs, which contribute to a more thorough understanding of hydrochemical processes in deep environments.

According to Paul et al. [98], groundwater quality is influenced by various geological and chemical factors, including precipitation, recharge quality, water–rock interactions, dissolution, mineralization, and ion exchange processes, all of which play a significant role in determining its suitability for drinking, irrigation, and industrial use. Planned future work on this dataset is the application of isotopic analysis (^3H , ^2H , ^{18}O , ^{11}B , ^6Li , ^{87}Sr , ^{86}Sr). The high salinity recorded in Agiasma spring is possibly caused by remnant seawater intrusion, and multi-isotope tracers, such as $^{87}\text{Sr}/^{86}\text{Sr}$ and ^{37}Cl , have been used effectively in similar cases to investigate the entrapment of paleo-seawater associated with past marine transgressions. Such events can lead to long-term salinization of inland aquifers, even those located more than two kilometers from the present coastline [99]. Hydrodynamic analysis of the three springs is especially challenging, while weekly spring water sampling and hydrochemical analysis can also help in further monitoring the springs. Seasonal monitoring of hydrochemistry is critically important in order to determine the influence of geohazards on groundwater quality, as well as extreme climatic conditions. For instance, the volcanic eruption in La Palma led to the increase in the concentrations of Na^+ , Ca^{2+} , SiO_2 , and SO_4^{2-} in fresh groundwater [100]. In India, the tropical monsoonal seasons influence the hydrochemistry of groundwater in the eastern Odisha [101]. Such datasets could be coupled and analyzed using principal component analysis in order to determine mechanisms and attract global interest in the approach provided in this manuscript. Karst aquifers exhibit high heterogeneity due to the long-term dissolution of rocks and the formation of complex subsurface flow channels [102]. Fluctuation in spring discharge reflects the complexity of the karst system, influenced by geologic structures, aquifer permeability, and precipitation. These processes are critical for evaluating the recharge capacity of groundwater [103]. Spring discharge is an important reflector of groundwater-

level changes through direct and indirect relationships with aquifer processes, climatic variables, and anthropogenic activities. Changes in precipitation might have significant effects on spring discharge by altering hydrological inputs of aquifers and surface systems. Additional precipitation increases infiltration and directly enhances aquifer recharge, which leads to greater spring discharge. Further programmed research will include an analysis of the hydrodynamics of the studied springs and cross-correlation with the available hydrochemical dataset. In particular, this will include linking the spring dynamics with lowland aquifers in which groundwater depletion occurs [104], while the vulnerability of the recharge zone should be considered in this conceptualization [105]. On balance, this study revealed the hydrochemical variability of three hypothermal mineral springs. These types of springs cannot be used for agricultural and domestic use; however, they can be used as centers for spa and nutrition therapy. We have to mention that Agiasma spring is partly used for nutrition therapy, while Kyllini spring was a spa center during the Roman age.

4. Conclusions

This study focused on the hydrochemical analysis and cross-comparison of three hypothermal mineral springs in Greece. According to the hydrogeochemical analysis, the following key differences between the springs are established:

- a. Kyllini: Characterized by high salinity, with Cl^- and Na^+ dominance, likely indicative of geothermal or hydrothermal activity.
- b. Agiasma: Exhibits a mixed water type with moderate salinity, representing an intermediate geochemical environment.
- c. Voskina: Marked by bicarbonate-rich groundwater, lower salinity, and a dominance of $\text{Ca}^{2+}/\text{Mg}^{2+}$, indicative of a more dilute system.

The three springs have distinct hydrogeochemical signatures, reflecting diverse controlling processes. However, the following similarities between the springs were also noted:

1. Dominance of carbonate dissolution processes: All springs had elevated concentrations of Ca^{2+} , Mg^{2+} , and HCO_3^- , indicating that water–rock interactions are primarily governed by the dissolution of calcite and dolomite.
2. Redox conditions and trace element mobilization: Negative ORP values in all sites suggest reducing environments, which favor the mobilization and transport of trace elements, such as Mn, Fe, and As.
3. Consistent saturation indices for carbonate minerals: The waters of all three springs show near-equilibrium to over-saturation states with respect to carbonate phases (calcite, dolomite), indicating a periodically shared geochemical tendency towards carbonate precipitation.

This study provided a comprehensive hydrochemical analysis and comparison of three hypothermal mineral springs in Greece. This approach can be applied to wider data sets from other springs to compare different hydrochemical processes of hypothermal mineral waters.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/hydrology12090237/s1>, Figure S1: Box and Whisker plots of trace elements of the groundwater samples; Figure S2: Box and Whisker plots of chemical parameters of groundwater samples; Figure S3: Gibbs diagrams for groundwater samples; Figure S4: Time series plots of major elements and precipitation for Agiasma (a), Voskina (b), and Kyllini (c) springs; Figure S5: Time series plots of saturation indices for Kyllini (a), Agiasma (b), and Voskina (c) springs; Table S1: Heatmap of Spearman correlation for all samples; Table S2: Heatmap of Spearman correlation for Agiasma Voskina; Table S3: Heatmap of Spearman correlation for Voskina Kyllini; Table S4:

Heatmap of Spearman correlation for Agiasma Kyllini; Table S5: Physico-chemical characteristics and concentrations (mg/L) of major elements for all groundwater samples.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding author due to that fact that under elaboration for a project report and publication. (specify the reason for the restriction).

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