Physics and Chemistry of the Earth 129 (2023) 103351

Contents lists available at ScienceDirect

Physics and Chemistry of the Earth

journal homepage: www.elsevier.com/locate/pce

Hydrogeochemical characteristics of groundwater in the Mediterranean region: A meta-analysis

Rachad Al Haj [a,b], Mohammad Merheb [a,c,*], Jalal Halwani [a], Baghdad Ouddane [b]

[a] Lebanese University, Water & Environment Science Lab, PHF 3, Tripoli, Lebanon
[b] Université de Lille, LASIRE-UMR CNRS 8516, 59655, Villeneuve d'Ascq cedex, France
[c] Institut Agro, INRAE, SAS, 65 Rue de Saint Brieuc, 35000 Rennes, France

A R T I C L E I N F O

Keywords:
Mediterranean
Hydrogeochemistry
Pollution
Isotopes

A B S T R A C T

The Mediterranean region is a water-stressed environment where groundwater, as main water source, is under a lot of anthropogenic pressure. This study aims to evaluate the baseline hydrogeochemical characteristics and water quality of groundwater in the region. For this purpose, 123 hydrogeochemical studies conducted in the area were examined. Information concerning the studies and concentrations of major, minor ions and isotopes were extracted. The data was divided into 3 major aquifers types: Quaternary, Jurassic and Cretaceous, and Tertiary. The data was analyzed qualitatively to identify the major topics of research and quantitatively using classical hydrogeochemical methods and multivariate analysis. The results show a disparity in the distribution of study topics across the region with minor ions and isotopes studies mostly concentrated in Europe. Moreover, the dominant hydro-chemical facies are Ca–Cl and Na–Cl in the Quaternary, Ca–HCO_3 and mixed in the Jurassic and Cretaceous and Ca–HCO_3 dominate the Tertiary aquifers. Furthermore, the major water forming process is the evaporation in the Quaternary and Tertiary aquifers, and rock-water interaction in the Jurassic and Cretaceous aquifers. Finally, nitrate pollution is found in 29% of aquifers while 15.3% of aquifers with minor ions data show high concentrations of at least one minor ion. The majority of aquifers with pollution problems are Quaternary. Indeed, these aquifers are highly affected by anthropogenic impact and seawater intrusion. Finally, this work is a preliminary assessment of groundwater characteristics in the region. Further works are needed to investigate specific aspects of Mediterranean region aquifers' groundwater hydrogeochemistry.

1. Introduction

The Mediterranean region is characterized by high temporal and spatial variability of water resources availability. This is mainly due to the dry summer's climate characteristic of the region, but also to discrepancies in the geographical distribution of water resources, and in the concentration of urban settlements along the coastlines of the area. Hence, water is a vulnerable and scarce resource in many areas across the region. This fact has resulted in an increase pressure on groundwater as a more stable source of water (Leduc et al., 2017). However, with the current rate of exploitation, combined with increasing demographic pressure especially in the coastal areas (Bakalowicz, 2018) and climate change impact, many countries around the Mediterranean will face water shortage problems in the upcoming years (Tramblay et al., 2020). Indeed, plan Bleu (2006) projected that by 2025, water per capita per year will decrease to less than 1000 m^3 in Egypt, Lebanon, Morocco, Syria and Turkey (Plan Bleu, 2006). Besides the decreasing quantities, groundwater quality in the region is also under a lot of pressure due mainly to anthropogenic impact (Kelepertsis, 2000; Siegel, 2002; Stamatis et al., 2001; Sullivan et al., 2005), especially on the coastal zones. For instance, many shallow aquifers could be affected by nitrate pollution due to the high agricultural activities accompanied by aggressive fertilization (Boumaiza et al., 2020; Dimopoulos et al., 2003; Weil et al., 1990). Moreover, the overexploitation is already affecting coastal aquifers with seawater intrusion (Alcalá and Custodio, 2008; Cary et al., 2014; Dazy et al., 1997; Mongelli et al., 2013). Furthermore, the infiltration of leachate from the municipal solid waste, collected in unregulated landfills, leads to the deterioration of groundwater quality (Castañeda et al., 2012; Christensen et al., 2001; Samadder et al., 2017).

All these challenges make hydrogeochemical studies a hot topic of

* Corresponding author. Institut Agro, INRAE, SAS, 65 Rue de Saint Brieuc, 35000 Rennes, France.
E-mail addresses: rachad.haj_1994@hotmail.com (R. Al Haj), mohammad.merheb@agrocampus-ouest.fr (M. Merheb), jhalwani@ul.edu.lb (J. Halwani), baghdad.ouddane@univ-lille.fr (B. Ouddane).

https://doi.org/10.1016/j.pce.2022.103351
Received 25 April 2022; Received in revised form 24 November 2022; Accepted 10 December 2022
Available online 13 December 2022
1474-7065/

research in the Mediterranean (Mongelli et al., 2019; Voutsis et al., 2015). Indeed, such studies are a key step to understand Mediterranean groundwater's chemistry in order to identify the natural and anthropogenic processes affecting its formation and quality (Asmael et al., 2014; Djebebe-Ndjiguim et al., 2013) and to identify pollution sources and extent (Corniello and Ducci, 2014). Furthermore, the evolution of knowledge will lead to a better understanding, and as a result, better management strategies for a sustainable exploitation of groundwater resources (Bourg and Richard-Raymond, 1994).

Nevertheless, even though hydrogeochemical studies in the Mediterranean are quite abundant. These studies are, most of the time, confined to a single aquifer or geographical location. Comparative studies that compare groundwater hydrogeochemical characteristics from various aquifers across the Mediterranean are scarce or focus on a specific aspect of the geochemical processes such as seawater intrusion (Telahigue et al., 2020). Thus, this work objective is to present an overview of the Mediterranean groundwater hydrogeochemical characteristics. For this purpose, 123 studies (Fig. 1) undertaken from various countries across the Mediterranean, were analyzed. The authors aim to answer the following questions:

- What are the main concerns that drive hydrogeochemical studies in the Mediterranean?
- What are the physico-chemical characteristics of groundwater in the Mediterranean?
- What are the general hydrogeochemical characteristics of groundwater in the Mediterranean region?
- What geochemical processes influence the water chemistry of the Mediterranean region's aquifers?
- What is the extent of nitrate and minor ions pollution in the Mediterranean?
- What can we learn from stables isotopes studies in the Mediterranean?

2. The mediterranean region

2.1. Boundary of the mediterranean region

Defining the boundary of the Mediterranean region is not an easy task and there is no worldwide consensus on the actual extent of this region (Hooke, 2006). Multiple definitions that define the Mediterranean region according to various characteristics exist in the literature. These can be related to climatic classification, hydrological classification, bio-climatic classification or administrative one (Merheb et al., 2016). Each of these classifications omits or add areas that are or are not generally considered Mediterranean. As an example, the climatic definition will totally exclude Egypt and the majority of Lybia and part of Southeastern Spain from the Mediterranean region, while adding regions further inland in the Middle East. Moreover, the hydrologic boundary will exclude areas that have typical Mediterranean climate characteristics such as Portugal and western Morocco. This is why, for the sake of this article, the boundary of the Mediterranean region was set as a combination of both climatic and hydrologic limits. The extent of the Mediterranean region as defined for the sake of this study is presented in Fig. 1.

2.2. Physical characteristics

The Mediterranean Sea occupy a surface equal to 2.5 million km^2 approximately, with a coastal area covering almost 1.5 million km^2 (Selenica, n.d.).

The region represents variable topography, from the high mountains, to the sandy beaches, and rocky shores, impenetrable scrub, coastal wetlands, myriad islands (Sundseth, 2000). While its climate is known for its hot dry summers and humid winters accompanied with heavy seasonal rain which are considered the main characteristics of the Mediterranean region climate (European Union, n.d.). Sometimes the seasonal rainfall accompanied with high evaporation leads to a predominant shortage in water. This observation was detected particularly in North African countries located in the southern part of the Mediterranean region (Selenica, n.d.). While the Mediterranean region is also characterized by a high biodiversity and could be considered one of the richest in the world (Vlachogianni et al., 2012). In fact, the Mediterranean basin occupies the third place of the most concentrated and richest regions in terms of its vegetation, where approximately 25,000 species can be found with more than 13,000 endemic species; which can be found exclusively in this area (CEPF, 2017).

2.3. Geology and hydrogeology

The Mediterranean basin was formed during the Tertiary and Quaternary due to the northward movement of the African and Arabian plates (Bakalowicz, 2015). In addition, the Alpine belt and high-elevation mountains surrounding the basin were shaped after intense tectonic activity due to the plates movement (Moores and Fairbridge, 1997). The mountains ranges surrounding the Mediterranean basin along with a complex geological structure has prevented the development of large aquifer systems (Aureli et al., 2008). The majority of the Mediterranean region's aquifers are small to medium sized sedimentary aquifers (Leduc et al., 2016). Among these are karstic carbonates aquifers which are common all around the region (Bakalowicz, 2014). The development of this local karst occurred during the late Jurassic, early Cretaceous, and Oligocene and since the end of the Miocene, and was attributed to the emersion periods (Bosák et al., 2015). In fact, the geological evidence points to the important role of the Messinian Salinity Crisis (MCS) in shaping the fluvial and karst landscapes well below the sea level (Clauzon, 1982; Rouchy et al., 2006). These karstic groundwater reservoirs that can form high altitude springs or coastal and even submarine springs tend to have uneven flow and volume (Bakalowicz, 2015). Another major type of sedimentary aquifers in the region is alluvial aquifers. These are generally associated with rivers valleys and deltas, but also coastal aquifers located in coastal plains and with direct contact with the sea (Aureli et al., 2008). Volcanic and crystalline aquifers also exist in the Mediterranean region. However, these are small scale local aquifers, mostly located on volcanic islands (Leduc et al., 2017).

3. Materials and methods

3.1. Description of the dataset

The collected data was extracted from 123 articles conducted from 2000 till 2019 (Fig. 1). These studies focus on the following Mediterranean countries: Algeria (9 articles) (Aouidane and Belhamra, 2017; Belfar et al., 2017; Bettahar et al., 2017; Bouderbala and Gharbi, 2017; Bouderbala et al., 2016; Chemseddine et al., 2015; Belkhiri and Mouni, 2014, 2012; Fehdi et al., 2009), Croatia (1) (Terzić et al., 2007), Cyprus (2) (Milnes, 2011; Neal and Shand, 2002), Egypt (5) (Eissa et al., 2018; Salem and Osman, 2017; Salem et al., 2017; Eissa et al., 2016; Gomaah et al., 2016), France (8) (Santoni et al., 2016; Maréchal et al., 2014; Bicalho et al., 2010; Charmoille et al., 2009; De Montety et al., 2008; Huneau and Blavoux, 2000; Bourg and Richard-Raymond, 1994; Bosch et al., 1986), Greece (4) (Filippidis et al., 2016; Tziritis et al., 2016; Voutsis et al., 2015; Skordas et al., 2013), Italy (15) (Biddau et al., 2019; Preziosi et al., 2019; Allocca et al., 2018; Busico et al., 2018; De Caro et al., 2017; Critelli et al., 2015; Corniello and Ducci, 2014; Pierotti et al., 2013; Brozzo et al., 2011; Giménez-Forcada et al., 2010; Ghiglieri et al., 2009; Cucchi et al., 2008; Manno et al., 2007; Barbieri and Morotti, 2003; Capaccioni et al., 2001), Lebanon (25) (Chaza et al., 2018; Hanna et al., 2018; Khadra and Stuyfzand, 2018; Khadra et al., 2017; Samad et al., 2017; Assaker, 2016; Kalaoun et al., 2016; Koeniger et al., 2016; Bakalowicz, 2015; Youssef et al., 2015; Bakalowicz, 2014;

Khadra and Stuyfzand, 2014; Daou et al., 2013; Saadeh et al., 2012; Awad, 2011; Assaf and Saadeh, 2009; Bakalowicz et al., 2008, 2007; Korfali and Jurdi, 2007; El Moujabber et al., 2006; El Hakim, 2005; Metni et al., 2004; Acra and Ayoub, 2001; Ghannam et al., 1998; Lababidi et al., 1987), Libya (2) (Alfarrah et al., 2016; Sadeg and Karahanoðlu, 2001), Morocco (6) (Chafouq et al., 2018; Mountadar et al., 2018; Karroum et al., 2017; Re et al., 2014, 2013; De Jong et al., 2008), Palestine (7) (Abu-alnaeem et al., 2018; Jebreen et al., 2018; Aliewi and Al-Khatib, 2015; Jabal et al., 2015; Da'as and Walraevens, 2013; Qahman and Larabi, 2006; Al-Agha, 2005), Portugal (8) (Freitas et al., 2019; Carreira et al., 2017; Marques et al., 2017; Barroso et al., 2015; Andrade and Stigter, 2011; Carreira et al., 2011; Fernandes et al., 2006; Van der Weijden and Pacheco, 2006), Spain (15) (Argamasilla et al., 2017; Merchán et al., 2015; Vallejos et al., 2015; Merchán et al., 2014; Molina-Navarro et al., 2014; Acero et al., 2013; Daniele et al., 2013; González-Ramón et al., 2012; Hidalgo et al., 2010; Lentini et al., 2009; Giménez Forcada and Morell Evangelista, 2008; Navarro and Carbonell, 2007; Gómez et al., 2006; López-Chicano et al., 2001; Pulido-Bosch et al., 1995), Syria (2) (Abou Zakhem, 2016; Abo and Merkel, 2015), Tunisia (10) (Hamdi et al., 2018; Mejri et al., 2018; Telahigue et al., 2018; Houatmia et al., 2016; Ben Cheikh et al., 2014; Farid et al., 2013; Hamed and Dhahri, 2013; Moussa et al., 2012; Hamzaoui-Azaza et al., 2011; Zghibi et al., 2014) and Turkey (4) (Varol and Şekerci, 2018; Somay, 2016; Tayfur et al., 2008; Demirel and Güler, 2006). For each study the key information that was systematically collected and analyzed include:

(1) Aquifer location (reference, study area, and coordinates)
(2) Study objective
(3) Aquifer characteristics including climate, land cover, geological and hydrogeological settings
(4) Sampling date, strategy and number of samples
(5) Methods of analysis
(6) Main results
(7) Samples physical characteristics including pH, temperature, electrical conductivity (EC) and total dissolved solids (TDS).
(8) Major ions concentrations including the concentrations of calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride and nitrate
(9) Minor ions concentrations including – but not limited to-the concentrations of manganese, silicate, iron, strontium, bromide, fluoride, lithium, etc
(10) Isotopes concentrations

It should be mentioned here, that not all studied articles contain data about all the aforementioned collected physico-chemical parameters. Fig. 1 shows the spatial distribution of the articles used in this work. It also identifies the types of data available in each study. More details about each article, along with the reference, country, study area, and sampling dates, the available physico-chemical data collected and used in this work are available in Appendix 1. Thirty-five articles contain detailed information on all physical characteristics, 84 articles include the major ions data of 92 aquifers, 38 articles contain data on various minor ions concentrations and only 16 articles contain data on the isotopes. From a geographical perspective, the data was organized in 3 main regions: North Africa (Algeria, Egypt, Libya, Morocco and Tunisia), Europe (Croatia, France, Greece, Italy, Portugal and Spain) and the Middle East (Cyprus, Lebanon, Palestine, Syria and Turkey). The physico-chemical data are distributed in 18 North African, 8 European and 9 Middle Eastern studies, while major ions are represented in 29, 32 and 23 studies conducted in each zone respectively. In addition, more than half of minor ions data is clustered in 23 European studies, while 8

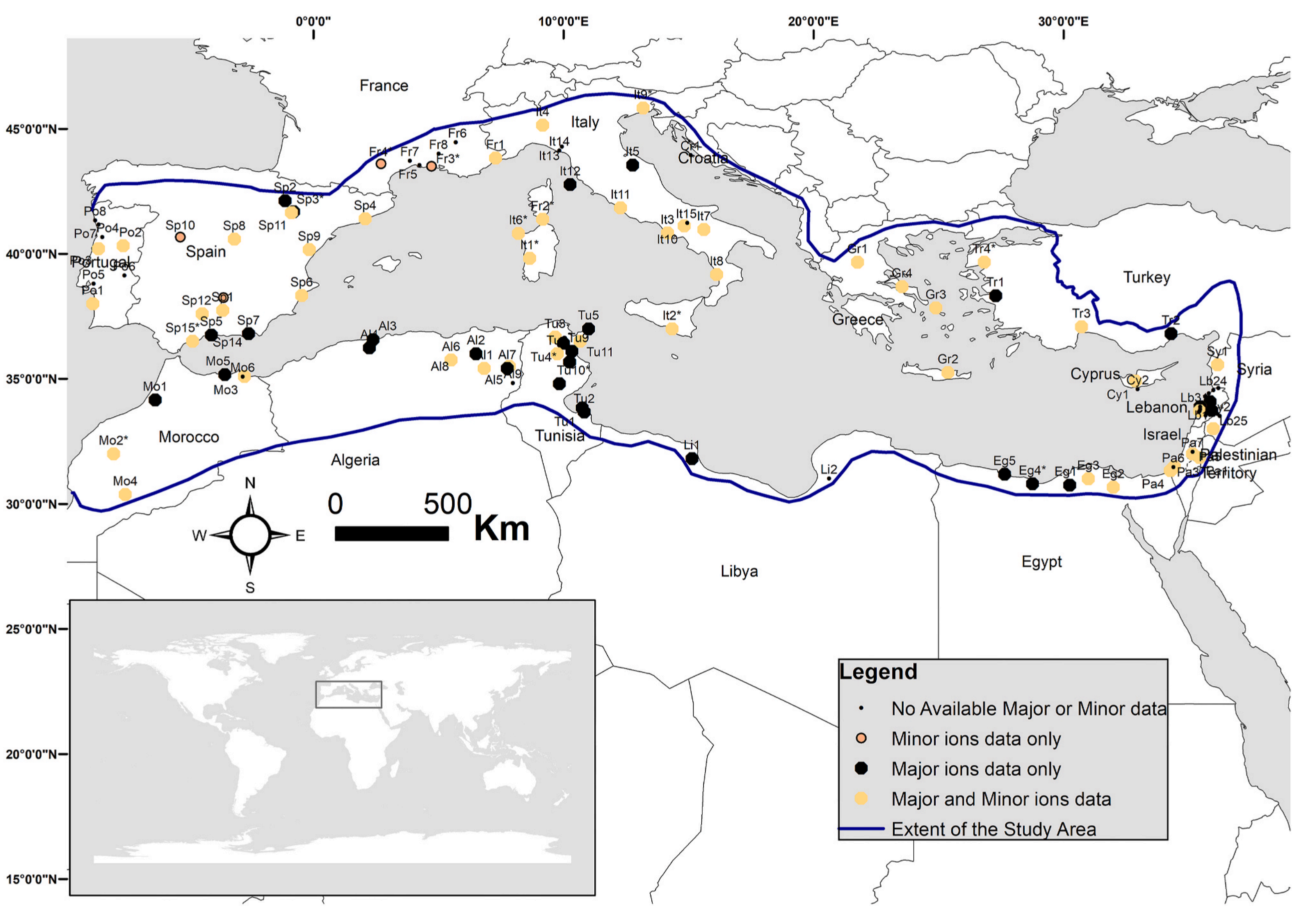

Fig. 1. Study area extent and distribution of studied articles with the types of data contained in each study. The article labelled with an * are those with isotopes data.

North African and 7 Middle Eastern studies hold minor ions data. Finally, most of the isotopic studies belong to the European region, where this type of data is observed in 9 studies, while the other 7 studies are distributed between the North African and Middle Eastern region with 4 and 3 studies respectively.

After collecting all the data, the units were homogenized. In order to facilitate the comparison, the Mediterranean data were grouped into 3 major sets of aquifers: “Quaternary”, “Jurassic and Cretaceous” and “Tertiary” aquifers. The Quaternary data contain 68 aquifers, the Tertiary data contain 18 aquifers, and the Jurassic and Cretaceous data contain 27 aquifers. Finally, the “coastal - non-coastal” attributes of each aquifer were also taken into consideration.

3.2. Methods of analysis

The analysis of the data was made on two levels. The first one consists of a qualitative analysis of the datasets. Here, the studied articles were classified according to the following topics: hydrogeology, hydrogeochemistry, isotopes, pollution, water quality, seawater intrusion, and modelling. This classification was made for the entire dataset and for each type of aquifers also taking into account the geographical distribution.

The second one is a quantitative analysis. For general hydrogeochemical characteristics, the mean of physico-chemical parameters and major ions concentrations were computed for each aquifer. This data was organized in a statistical table (Appendix 2). The same procedure was done for nitrate and isotopes. However, for the minor ions, the analysis was made on the entire samples and not just the mean. First, the authors compared the mean physico-chemical characteristics for all aquifers in the region and for each aquifer type separately. Similarly, major ions, minor ions, isotopes and nitrate concentrations were compared for all aquifers and for each type separately. Moreover, the Piper diagram (Piper, 1944) and the Gibbs diagrams (Gibbs, 1970) were used to identify the major hydro-chemical facies and groundwater processes respectively in each set of aquifers. Furthermore, agglomerative hierarchical clustering (AHC) was used in order to identify groups of aquifers across the Mediterranean that share similar behavior or characteristics. AHC is one of the most used classification methods in hydrogeochemistry (Güler et al., 2002; Steinhorst and Williams, 1985). It uses a dissimilarity matrix based on Euclidean distance in order to group samples into groups of relatively similar characteristics. It identifies the differences between samples and regroup them into several clusters based on their differences (Jiang et al., 2015). The clusters are generated by minimizing the sums of square distance to the center mean (Ward, 1963). The AHC was carried out using the standardized data via RStudio software version 1.3.1093. Finally, in order to simplify our dataset (Cloutier et al., 2008) and reduce its dimensionality while maintaining its variability (Zhang et al., 2008) a Principal Component Analysis was carried out. The interesting aspect of PCA is its capability in explaining the correlation between a big number of variables while reducing the loss in information (Shrestha and Kazama, 2007). In fact, it is designed to plot the principal components which are a whole new uncorrelated variable derived from the original ones as linear combinations (Shrestha and Kazama, 2007). Using RStudio software version 1.3.1093, the standardized data was plotted into 3 plots representing PC2 vs PC1 for the 3 sets of aquifers. These samples were distributed based on the dendrograms groups, while the correlations between the first 4 principal components (PC1 to PC4) and the values of major ions and pH were measured using the same software.

4. Results

4.1. Study topics

The studied articles were divided into 7 topics: hydrogeology, hydrogeochemistry, isotopes, modelling, pollution, seawater intrusion, and water quality. Fig. 2 presents the distribution of articles according to the study topic for the whole dataset (Fig. 2a) and by aquifer types (Fig. 2b and c, and d). Fig. 2 (a) indicates that the hydrogeochemistry and water quality presented in 48 and 23 studies respectively, are the major topics in this dataset. While 19 and 14 articles focus on pollution and hydrogeology respectively. Moreover, 13 studies deal with seawater intrusion and only 4 and 2 studies focus on the isotope and modelling topics respectively. Hydrogeochemistry and water quality are also the dominant topics in the Quaternary data (Fig. 2b) with 28 and 15 studies respectively, while the hydrogeochemistry and hydrogeology topics dominate the Jurassic and Cretaceous aquifers (Fig. 2c) with 9 and 6 studies respectively. The water quality topic is represented also in 5 Jurassic and Cretaceous articles. Same as Jurassic data, the Tertiary aquifers (Fig. 2d) are also dominated by the same topics where the hydrogeochemistry was found in 8 studies, followed by hydrogeology in 3 studies. Moreover, 11, 9 and 4 Quaternary aquifers focus on the pollution, seawater intrusion and hydrogeology respectively, while only 1 addresses the modelling topic and none the isotopes. In the Jurassic and Cretaceous data, 4 studies deal with pollution, while isotopes and seawater intrusion topics are represented in 1 and 2 articles respectively. Finally, the number of studies focusing on isotopes in the tertiary data is 3, while, modelling, pollution, water quality and seawater intrusion topics are represented only in 1 Tertiary aquifer. From geographical perspective, the North African studies focus on the hydrogeochemistry and water quality topics represented in 10 and 9 studies in this region respectively, followed by the pollution topic occupying 5 studies, while 3 and 4 studies tackle the hydrogeology and seawater intrusion respectively and only 1 study deals with the modelling subject. For the European region, the hydrogeochemistry topic remains the main focus represented in 26 studies, followed by the pollution and hydrogeology topics highlighted in 9 and 5 articles respectively, while the water quality, isotopes and seawater intrusion are distributed in 4, 3 and 3 studies respectively, when only 1 article deals with modelling. Finally, the main focus of the Middle Eastern studies resembles the North African ones, with 12 and 10 studies tackling the hydrogeochemistry and water quality topics respectively, followed by the hydrogeology, seawater intrusion and pollution topics represented in 6, 6 and 5 studies respectively, while only one study focuses on the isotopes.

4.2. Groundwater characteristics

4.2.1. Physical characteristic

This section, presents the main results for the following 4 physico-chemical parameters: pH, temperature, total dissolved solids (TDS) and electrical conductivity (EC). The average pH values for all aquifers range from 6.8 in a Quaternary aquifer located in the Portuguese Serra da Estrela mountain to 9 in a Quaternary aquifer of Koruteli located in Turkey with a mean value of 7.6. Moreover, the EC values range between 3.6 and 8126 μS/cm with a mean value of 2106.6 μS/cm. The lowest EC value belongs to a Quaternary aquifer located in an agricultural and urban area in north western Tunisia, while the highest value is for the Tertiary aquifer of Ras El-Hekma in Egypt. Finally, the lowest temperature value equal to 10.8 °C in a Jurassic and Cretaceous aquifer located in the Italian Mt. Catria-Mt. Nerone ridge, while the highest one is 25.1 °C for an agricultural Jurassic and Cretaceous aquifer located in south east of Tunisia; the mean temperature for all aquifers is 19.7 °C.

4.2.1.1. Quaternary aquifers. For Quaternary aquifers, pH means range from 6.8 in the Portuguese Serra da Estrela mountain's study to 9 in a Turkish study conducted on a Quaternary aquifer located in the Korkuteli district in Antalya. The mean pH values for all Quaternary aquifers is 7.6. EC values range between 3.6 and 5093 μS/cm with a mean value of 1996.4 μS/cm. Both lowest and highest EC means were calculated for agricultural areas aquifers in Tunisia. The former located in the north western part of the country, while the latter is in central Tunisia.

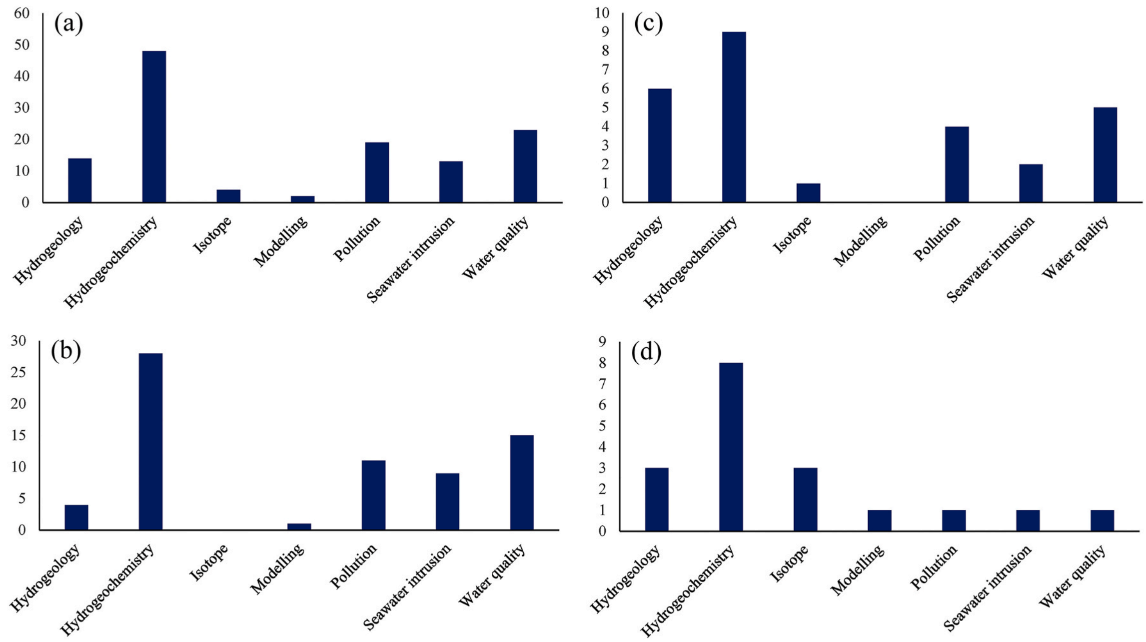

Fig. 2. Histograms representing the number of articles focusing on the 7 main identified topics in: **(a)** all the data, **(b)** the Quaternary, **(c)** Jurassic & Cretaceous and **(d)** Tertiary data.

Similarly, the highest TDS value belongs to the aforementioned aquifer in central Tunisia with 3710 mg/L, while Serra da Estrela mountain of Portugal holds the lowest mean equal to 80.6 mg/L. The mean TDS values for all Quaternary aquifers is 1434.2 mg/L. Temperature values range from 15.1 °C in the Turkish aquifer located in the Korkuteli district, to 24.1 °C in Egyptian agricultural areas located in some central Nile delta villages. Mean groundwater temperature for all aquifers is 20 °C.

4.2.1.2. Jurassic and Cretaceous aquifers. In the Jurassic and Cretaceous aquifers, pH values range from 6.9 in the northwestern Sardinia, Italy, while the highest mean equal to 8 belongs to the Tunisian Sisseb El Alem basin. Mean pH value for all aquifers is 7.6. Moreover, the EC means range between 349.2 μS/cm and 3796 μS/cm with a mean value of 1396.1 μS/cm. The lowest value belongs to the Monte Catria and Monte Nerone in Italy, where oil drilling is the main economic activity, while the aquifer system in the agricultural area of south east Tunisia holds the highest value. TDS values range from 264.7 mg/L in a karstic aquifer in the central West Bank of Palestine to 2970 mg/L in south east of Tunisia. Both regions are agricultural areas. The mean TDS value is 1215.9 mg/L. Finally, temperature values range from 10.8 °C in the same Italian study holding the lowest EC to 25.1 °C in an agricultural area in south east of Tunisia. The Mean Temperature is 18.8 °C.

4.2.1.3. Tertiary aquifers. In the Tertiary aquifers, pH means range between 7.4 and 7.8, with the lowest value found in an Egyptian area known as Bagoush area and the highest value in Ras El-Hekma aquifer in Egypt. The mean pH value is 7.6. Ras El-Hekma aquifer also has the highest EC mean equal to 8127 μS/cm and the highest TDS value at 5494 mg/L, while the industrial area of Friuli Venezia Giulia plain aquifers of Italy holds the lowest values of EC and TDS equal to 471.5 μS/cm and 430.7 mg/L respectively. Average EC and TDS values for all Tertiary aquifers are 3996 μS/cm and 3188.5 mg/L respectively. Finally, the temperature means range between 18.5 °C and 21.7 °C, the highest value is the mean of the Bagoush area located in Egypt, while the lowest mean belongs to a Turkish aquifer located in the Torbali Region covered by agricultural and urban areas; mean temperature is 20.1 °C.

4.2.2. Major ions

Major ions concentrations are presented here for all aquifers, then for each type of aquifer separately. Calcium concentration ranges from 2.9 mg/L in a Quaternary Portuguese aquifer in Serra da Estrela mountain to 849.4 mg/L in a coastal Quaternary aquifer in south eastern Tunisia. Average Ca^{2+} concentration is 124.4 mg/L. Mean magnesium concentrations ranges from 0.6 to 259.4 mg/L with an average of 60 mg/L. The lowest value is calculated for the Quaternary aquifer in Serra da Estrela mountain of Portugal while the highest mean is represented by Ras El-Hekma Tertiary aquifer. Sodium concentrations range from 1.8 mg/L in a Jurassic aquifer in the southern Alps of France, to 1501 mg/L in the aforementioned Ras El-Hekma aquifer. Average Na^{+} concentration is 217.4 mg/L. The Potassium concentrations range between 0.1 and 60.8 mg/L in Quaternary aquifers. In fact, Elba island in Italy has the lowest value, while the coastal aquifer south of Tunisia holds the highest. Mean K^{+} concentration is 9.8 mg/L. In addition, the lowest bicarbonate mean equal to 5.3 mg/L exists in the Quaternary Italian aquifer located in Elba island. However, the highest HCO_3^- concentration of 1199.7 mg/L was measured in the Tunisan study conducted on the Jurassic and Cretaceous basin of Sisseb El Alem. Average HCO_3^- is 294.5 mg/L. In addition, the chloride means range from 2.5 mg/L to 2862 mg/L. Same as the sodium, the lowest value is found in the Jurassic aquifer in the Southern Alps of France, while the highest value, is found as for the Na^{+} in the Egyptian Ras El-Hekma aquifer. Mean Cl^{-} value is 356.3 mg/L. Finally, the Quaternary aquifer has both the lowest and highest mean of sulfate equal to 2.4 and 1728 mg/L respectively, with the Elba island of Italy and the coastal aquifer south east of Tunisia showing the minimal and maximal mean respectively. Mean SO_4^{2-} is 235 mg/L.

4.2.2.1. Quaternary formation. For the Quaternary aquifers, Ca^{2+} means range from 2.9 mg/L in Serra da Estrela mountain in Portugal to 849.4 mg/L in the coastal aquifer south east of Tunisia. Average Ca^{2+} value for the Quaternary formations is 150.5 mg/L. The highest and lowest means of Mg^{2+} belongs to the same aforementioned studies respectively. Values range between 0.6 mg/L and 248.8 mg/L with an average of 70 mg/L. Average Na^{+} concentrations for Quaternary aquifers is 276.8 mg/L. The lowest Na^{+} mean equal to 4.6 mg/L belongs to the Italian study located in the Elba island where 85% of its surface is occupied by semi-natural and natural environment, while the aforementioned coastal aquifer in south eastern Tunisia also has the highest Na^+ mean equal to 1131 mg/L. This Tunisian aquifer holds the highest average concentrations of K^+, Cl^-, and SO_4^{2-} with 60.8 mg/L, 2516.2 mg/L and 1728 mg/L respectively. Similarly, the lowest values of these ions were found in one aquifer located in the Elba Island in Italy with concentrations 0.1 mg/L, 5.3 mg/L and 2.4 mg/L respectively. Average concentrations of these ions are 11.8 mg/L, 466.4 mg/L and 292.5 mg/L respectively. Finally, the lowest HCO_3^- value is also recorded in the Elba island with a value of 5.3 mg/L while the highest value equal to 509.8 mg/L is found in a Moroccan study conducted on Bou-Areg coastal aquifer located north of the country. Average HCO_3^- concentration for quaternary formations is 291.8 mg/L.

4.2.2.2. Jurassic and Cretaceous formations. In the Jurassic and Cretaceous formations, Ca^{2+} means range between 7.3 mg/L and 319.2 mg/L, where the Italian aquifer located in the agricultural Nurra region and the aquifer of the agricultural area located south east of Tunisia holds the lowest and highest values respectively. Mean Ca^{2+} concentration is 88.1 mg/L. Mg^{2+} and HCO_3^- lowest values were also found in the Nurra region with values of 4.6 mg/L and 6.3 mg/L respectively. While the agricultural Sisseb El Alem basin in Tunisia has the highest means of both ions with 191.7 mg/L for Mg^{2+} and 1199.7 mg/L for HCO_3^-. Average Mg^{2+} and HCO_3^- concentrations for all aquifers is 53.7 mg/L and 342.3 mg/L respectively. Furthermore, the lowest Na^+ mean equal to 1.8 mg/L is found in the Coaraze spring in the southern Alps of France, while the aquifers located south east of Tunisia holds the highest mean equal to 400.8 mg/L. Average Na^+ concentration is 96.4 mg/L. Highest K^+ concentration is also found in the aforementioned aquifer of south east Tunisia with 21.9 mg/L. However, the lowest mean of 0.3 mg/L is attributed to an Italian aquifer in north western Nurra region. Average K^+ value for all aquifers is 5.7 mg/L. Similarly, the same aquifers hold the lowest and highest sulfate concentrations with values of 3.9 mg/L and 1272.5 mg/L respectively. Average SO_4^{2-} concentration is 183.5 mg/L. Finally, the lowest Chloride mean equal to 2.5 mg/L is found in the Italian Nurra region characterized by its intensive agricultural activities, while the highest one equal to 665.3 mg/L belongs the aquifer of south east of Tunisia. Average Cl^- concentration for the Jurassic and Cretaceous aquifers is 134.4 mg/L.

4.2.2.3. Tertiary formation. In the Tertiary formations, the lowest calcium concentration equal to 19 mg/L is found in Cyprus with a study conducted on large part of the mid-to south-eastern side of the island characterized by agriculture and light industry, while the Ebro Valley in Spain holds the highest mean of 293.5 mg/L. Average Ca^{2+} for these aquifers is 91.8 mg/L. For the magnesium and potassium ions, the lowest means are found in the same agricultural zone of northern Bekaa in Lebanon, while their highest means belongs to Ras El-Hekma aquifer in Egypt. Furthermore, the magnesium means vary from 12 mg/L to 259.4 mg/L with an average equal to 41.8 mg/L and the potassium values range between 0.7 and 60.6 mg/L with average equal to 8 mg/L. Na^+ values range from 2.5 to 1501, with the lowest found in the Spanish Pareja basin dominated by natural vegetation, while the highest belongs to Ras El-Hekma aquifer. This aquifer also holds the highest Cl^- value of 2862 mg/L, while the lowest value is found in a mountainous karstic aquifer on Morocco with a value of 5.3 mg/L. Mean Na^+ and Cl^- values are 168.4 mg/L and 275.3 mg/L respectively. The lowest HCO_3^- is also found in the aforementioned Moroccan aquifer with 115.9 mg/L while the Italian aquifer located in Mt. Vulture holds the highest Bicarbonate mean equal to 448.5 mg/L. Average HCO_3^- concentration is 264.6 mg/L. Finally, the minimal sulfate mean equal to 8.1 mg/L is found the agricultural land of northern Bekaa, while the maximal mean of 645.7 mg/L belongs to the Spanish study of Ebro valley. Average SO_4^{2-} concentration for all Tertiary aquifers is 135.6 mg/L.

4.2.3. Minor ions

This part focuses on the following 13 minor ions: Mn, Fe, F, NH4, Br, Zn, Ba, Al, As, B, Ni, Pb and Cu and compares the samples' concentrations with the WHO threshold (WHO, 2017). This data includes 38 studies distributed between the following 3 types of aquifers: 24 Quaternary, 7 Jurassic & Cretaceous and 7 Tertiary aquifers. It is important to note that in this part the authors will take into consideration each sample in the dataset instead of the studies' means. For instance, the Ba, Ni and Cu concentrations are considered low where all of their concentrations represented by 103, 59 and 29 samples respectively fall below the threshold, while only 1 sample belonging to a Quaternary aquifer holds a concentration of Pb trespassing the WHO limit. For the NH4, Zn and Al ions, which are represented in 39, 92 and 60 samples respectively, a low number of concentrations are considered high where only 5, 2 and 4 samples respectively fall above the threshold. In fact, all NH4 and Zn concentrations falling above the limit were found in Quaternary regions, while the concentrations of Al were distributed equally between Quaternary and Tertiary aquifers. For the ions Mn and Fe represented by 167 and 209 samples respectively, only 16 and 18 concentrations fall above the limit, where most of them belong to the Quaternary data and only 1 Mn and 1 Fe samples are represented by the Jurassic and Cretaceous regions. In addition, only 4 Mn samples belong to the Tertiary data. Furthermore, the 3 minor ions F, As and B hold the highest number of samples trespassing the WHO thresholds. For F, 33 Quaternary and 1 Tertiary sample hold concentrations higher than the limit and represent 18.6% of the data, while all the concentrations of As falling above the threshold are Quaternary samples, equal to 38 and represent approximatively half of the data with percentage equal to 43.2%. Moreover, 54 B samples out of 154 trespass the limit where most of them belong to the Quaternary data and only 1 and 10 samples belong to the Jurassic & Cretaceous and Tertiary data respectively. In addition, almost all of 169 Br concentrations fall above the threshold with percentage equal to 98.2%. In fact, the Br ion could serve as an indicator of salinization processes. Besides the 13 ions mentioned before, it is important to note that many studies measure the concentrations of Li and Sr, represented by 162 and 364 samples respectively, however, the authors were unable to find the WHO threshold for these ions.

In order to analyze the geographical distribution of this data, the 338 high concentration samples were organized into 3 distinctive groups, the European, Middle Eastern and North African samples, following the continents where the studies occur. Since 160 North African samples trespass the threshold, this region dominates the data with a percentage equal to 47.3%. This value was followed by the European then the Middle Eastern ones with percentages equal to 35.8% and 16.9% respectively. Despite the high number of concentrations falling above the thresholds in the North African region, it is important to note that a high number of them were Br concentrations and represent 98 out of the 160 samples, while the European and Middle eastern region hold 31 and 37 samples falling above the Br limit. In addition, the 3 minor ions holding the highest numbers of concentrations exceeding the limits are F, B and As. Most of the sample trespassing the F and B thresholds are conducted on the Quaternary aquifers in North Africa with values equal to 20 out of 34 samples and 40 out of 54 samples respectively, while the European and Middle Eastern studies hold 37 and 1 As samples respectively falling above the WHO limit.

4.2.3.1. Quaternary aquifers. Following the aquifer's type, the Quaternary samples stand out as the most polluted one compared to the Jurassic & Cretaceous and the Tertiary samples. In fact, the Quaternary data holds the highest numbers of Br, B, As, F, Fe and Mn concentrations trespassing the WHO thresholds, where their values are equal to 130, 43, 38, 33, 17 and 11 samples respectively. In addition, it holds only 5, 2, 2 and 1 samples exceeding the WHO limits of NH4, Zn, Al and Pb, while none of its samples exceed the thresholds of Ba, Ni and Cu.

4.2.3.2. Jurassic and Cretaceous aquifers. For the Jurassic & Cretaceous aquifers, its data includes only 1 sample falling above the thresholds of the following ions: Mn, Fe and B, while 16 ones trespass the limit for Br. Beyond these 4 ions, none of its samples exceed the thresholds of the others minor ions.

4.2.3.3. Tertiary aquifers. For the Tertiary aquifers, only 37 concentrations fall above the limits of 5 minor ions, which are distributed as following: 20 Br samples, 10 B, 4 Mn, 2 Al and 1 F sample. For the rest of minor ions none of the Jurassic & Cretaceous samples fall above the thresholds.

4.2.4. Isotopes

Two isotopes, $\delta^{18}O$ and $\delta^{2}H$ were taken into account in this work. The $\delta^{18}O$ minimal and maximal means for all aquifers, are found in Quaternary aquifers. The composition ranges from −7.9‰ to −0.4‰, with the minimal value in the Lebanese study of Nahr Ibrahim area characterized by intense industrial activities, and the maximal mean in the agricultural area of "Biviere di Gela" in Italy. Furthermore, the lowest mean of $\delta^{2}H$ equal to −50.3‰ belongs also to the Quaternary aquifer of Lerma basin in Spain, while the highest mean equal to −9.2‰ was found in the study conducted on the Tertiary aquifer in Bagoush, Egypt. Average composition of $\delta^{18}O$ and $\delta^{2}H$ are −5.6‰ and −36.4‰ respectively.

4.2.4.1. Quaternary aquifers. For the Quaternary aquifers, the means of $\delta^{18}O$ values are mentioned in the previous paragraph. As same as before, the Lerma basin located in Spain show the minimum mean of $\delta^{2}H$ equal to −50.3‰. Moreover, the highest mean of $\delta^{2}H$ equal to −27.1‰ is found in the Spanish Pareja basin characterized by rural features and natural vegetation. Average content of $\delta^{18}O$ and $\delta^{2}H$ for the Quaternary aquifers are −5.3‰ and −36.7‰ respectively.

4.2.4.2. Jurassic and Cretaceous aquifers. In the Jurassic and Cretaceous aquifers, $\delta^{18}O$ means range between −7‰ and −5.2‰ in south-eastern Tunisia and the Turkish Edremit-Dalyan coastal wetland respectively. While the $\delta^{2}H$ means range from −37.8‰ to −24.2‰ in the same aforementioned Turkish wetland and the Lebanese Damour coastal aquifer respectively. Finally, average content of $\delta^{18}O$ and $\delta^{2}H$ for the Jurassic and Cretaceous aquifers are −5.8‰ and −31.8‰ respectively.

4.2.4.3. Tertiary aquifers. For the Tertiary formations, the minimal and maximal means of $\delta^{2}H$ equal to −34.9‰ and −9.2‰ In fact, the lowest $\delta^{2}H$ mean belongs to the French aquifer of Bonifacio, while the highest one represents the Egyptian Bagoush area. In addition, the $\delta^{18}O$ stable isotope content ranges from −7.9‰ to −2.6‰. The lowest one in the Italian Friuli Venezia Giulia plain, while the highest mean is represented in the aforementioned Egyptian study conducted on Bagoush area. Average content of $\delta^{18}O$ and $\delta^{2}H$ for Tertiary aquifers are −5.5‰ and −22‰ respectively.

4.2.5. Nitrate

Despite that most of the chosen studies focus on the hydrogeochemical topic, a low number take into consideration or focus solely on the pollution problem. The low or high nitrate concentrations is one of the first indication of this problem. For instance, the highest mean of nitrate equal to 348.7 mg/L belongs to the Tunisian Quaternary aquifer of Cap-Bon, while the lowest nitrate mean equal to 0.2 mg/L was measured in an Italian study conducted on the Quaternary aquifer of Elba Island, where 85% of the surface is occupied by natural or semi-natural environment. Average concentrations of NO_3^- for all aquifers is 43.6 mg/L.

4.2.5.1. Quaternary aquifers. In fact, the Quaternary aquifers holds the lowest and highest mean of nitrate. The average of NO_3^- concentrations for all Quaternary aquifers is equal to 54.1 mg/L.

4.2.5.2. Jurassic and Cretaceous aquifers. The Jurassic and Creatceous data show that the means of nitrate vary between 0.6 and 78.1 mg/L. In fact, the minimal and maximal values of nitrate belong to the French Coaraze spring located in the southern Alps and the agricultural Italian region in north western Sardinia respectively. Moreover, the average concentrations for all Jurassic and Cretaceous aquifers is equal to 14.1 mg/L.

4.2.5.3. Tertiary aquifers. For the Tertiary aquifers, the minimal value equal to 4.1 mg/L belongs to the Moroccan study concerning a mountainous karst area, while a Lebanese aquifer located in north Bekaa and Anti-Lebanon revealed the highest value equal to 112.5 mg/L. Average concentration of NO_3^- for all Tertiary aquifers is 27.8 mg/L.

4.3. Hydrochemical facies

In order to identify the major water types in the Mediterranean region aquifers, the mean of major ions and TDS concentrations were measured, and 79 aquifers were plotted into 3 Piper diagrams (Piper, 1944). Each diagram represents one aquifer type: Quaternary (Fig. 3a), Jurassic and Cretaceous (Fig. 3b) and Tertiary (Fig. 3c). The 3 diagrams show that 3 water types dominate the Mediterranean groundwater. These are Ca–HCO_3, mixed and Ca–Cl facies, with 76.3% of the aquifers falling into one of these 3 facies. The dominance of calcareous formation in the Mediterranean, could be the main cause of this pattern (FAO, 1973). While the rest belong to the Na–Cl and Na–HCO_3 facies, which may be caused by the seawater intrusion in the coastal areas and the anthropogenic activities. In addition, most of the studies falling into the Na–Cl and Na–HCO_3 facies are the North African and European studies. In fact, North Africa has 26.7% of its studies falling into the Na–Cl and Na–HCO_3. However, only 15% of Middle eastern studies respectively belong to the same categories. The previous findings indicate that seawater intrusion accompanied with the agricultural pollution along with higher evaporation rates in North Africa may be the cause of this distinctive pattern.

4.3.1. Quaternary aquifers

The Piper diagram of Quaternary aquifers (Fig. 3a) indicates that many of its point are falling toward the Na–Cl (26.5%) and Ca–Cl (36.7%) facies indicating the effect of seawater intrusion on the regions occupied by this type of formation, hence most of the zones holding a Quaternary aquifer are coastal. 30.6% of the Quaternary articles fall into the Ca–HCO_3 and mixed zones, where the mixed facies has a percentage equal to 18.4% higher than the percentage of Ca–HCO_3 equal to 12.2%. Finally, Na–HCO_3 holds the lowest number of studies with a percentage equal to 6.1%, Moreover, many countries follow a distinctive pattern. For instance, all of Algerian, Moroccan, Egyptian and Tunisian studies fall into the mixed, Ca–Cl and Na–Cl zones. In addition, 7 out of 8 Spanish studies belong to the same facies, while the rest falls into the Ca–HCO_3 zone. The mixed and Ca–HCO_3 facies also incorporates 2 out of 2 and 2 out of 7 studies conducted in Turkey and Italy respectively. In addition, 2 Italian studies belong to the Na–HCO_3 area. Furthermore, 3 Italian studies fall into the Na–Cl and Ca–Cl zones.

4.3.2. Jurassic and Cretaceous aquifers

The Piper diagram of Jurassic and Cretaceous aquifers (Fig. 3b) shows that all of its points fall into the Ca–HCO_3, mixed and Ca–Cl facies. In Fact, 84.69% of the Jurassic and Cretaceous aquifers belong to the Ca–HCO_3 and mixed facies. This observation is normal since the main mineral-forming Jurassic and Cretaceous rocks are calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Moreover, such aquifers are highly karstified system with complex structure that allow long rock-water interaction. For the Middle East region, most of its studies with a percentage of 75%

was plotted into the mixed area and only one study falls into the $Ca–HCO_3$ facies. Moreover, 50% of the European studies belong to the $Ca–HCO_3$ zone, while the rest of its studies lies equally in the mixed and Ca–Cl facies. In addition, the studies conducted in the North Africa was plotted mainly in the mixed facies and only 1 study fall into the Ca–Cl facies.

Furthermore, some countries' studies follow specific pattern. For example, all the studies of Algeria and Greece belong to the mixed and $Ca–HCO_3$ facies respectively, the same is true for 2 Lebanese studies. While, the 3 Tunisian studies were divided between two facies, two studies fall into the mixed zone and only one falls into the Ca–Cl facies.

4.3.3. Tertiary aquifers

The Piper diagram of the Tertiary aquifers (Fig. 3c) indicates that the $Ca–HCO_3$ facies is dominant. For instance, 64.7% of the studies focusing belong to this facies, while the mixed and Na–Cl facies occupy 23.5% and 11.8% of the Tertiary studies respectively. This aspect could be a consequence of the rock-water interaction dominance in modifying the water's chemistry, hence the major geological formation in the Mediterranean zone is calcareous. Moreover, 87.5% of the Middle East studies fall into the $Ca–HCO_3$ zone. In addition, 66.7% of the studies conducted in North Africa was plotted into the Na–Cl zone, while 33.3% of its studies belong to the mixed facies which could be considered as a signal for major problem such as seawater intrusion. Moreover, the European studies fall into 2 facies, $Ca–HCO_3$ and mixed with percentages equal to 66.7% and 33.3% respectively. Furthermore, some countries show a specific pattern. In fact, all the Lebanese studies lies in the $Ca–HCO_3$ zone. While all the studies conducted in Egypt belong to the Na–Cl facies. Finally, the Italian studies were plotted into the $Ca–HCO_3$.

4.4. Geochemical processes

In order to identify the main geochemical processes governing groundwater formation in the Mediterranean, the mean values of each studied aquifer were plotted on the Gibbs diagram (Fig. 4). Fig. 4 shows that the evaporation is the main process that affect the groundwater's chemistry in most of the country and studies, where 72.7% of the studies were affected by this type of process, while only 24.2% of all the means fall into the rock-water interaction area. Only one study conducted on the Portuguese Quaternary aquifer of the mountainous region in Serra da Estrela has precipitation as a major water forming process. In fact, the decrease in temperature due to the elevation, which could reach 1993 m, leads to higher precipitation in this area. In addition, the geographical distribution indicates that 37.5% of the studies conducted in the Middle East region present water's chemistry affected mainly by rock-water interaction process. As same as before, almost third of the

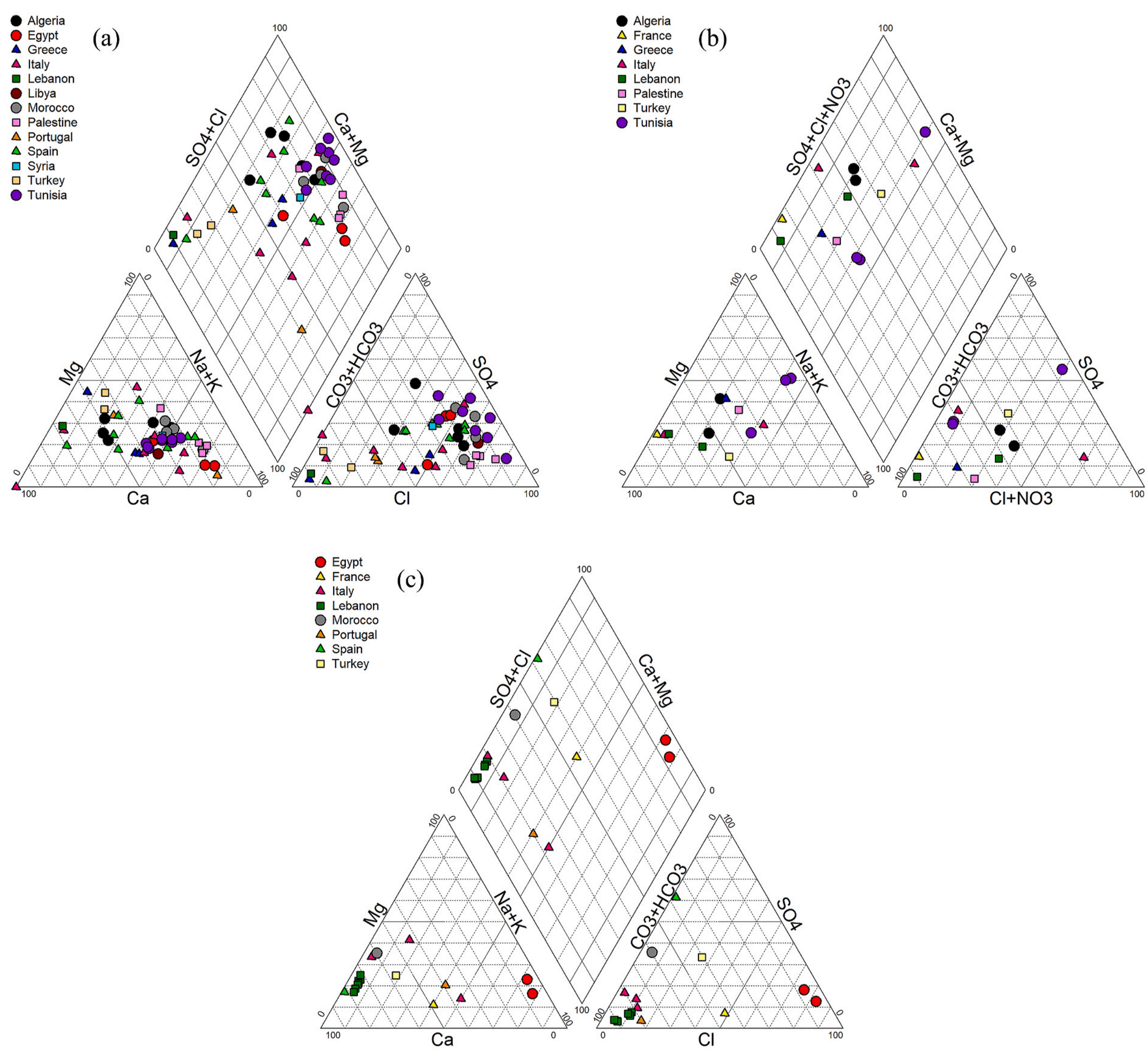

Fig. 3. Piper diagrams representing the distribution of hydrochemical facies in the 3 types of aquifers: (a) Quaternary, (b) Jurassic & Cretaceous and (c) Tertiary.

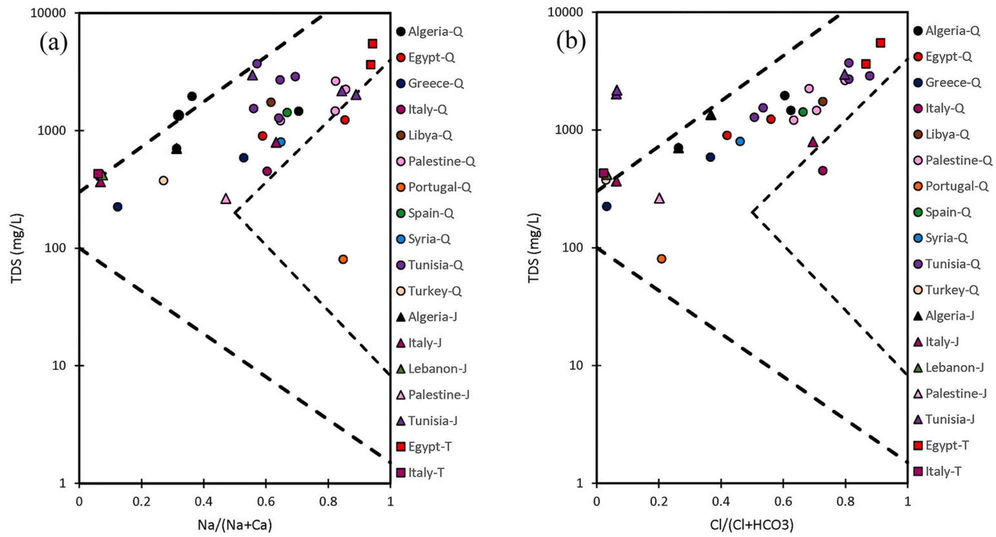

Fig. 4. Gibbs diagrams representing; **(a)** TDS Vs $Na^+/(Na^+ + Ca^{2+})$ and **(b)** TDS Vs $Cl^-/(Cl^- + HCO_3^-)$.

Europe studies were affected by the same process with a similar percentage equal to 37.5%. However, the North African studies shows a different pattern where almost all them fall into the evaporation section with a percentage equal to 88.2%, while the rock-water interaction is considered the main process in modifying the water's chemistry only in 2 North African studies. This distinctive pattern could be attributed to the difference in temperature, where it is higher in North Africa in comparison with the Middle East or Europe. Furthermore, from the aquifers' perspective, half of the Jurassic and Cretaceous aquifers fall into the rock-water interaction zone. In addition, the same previous process affects the water's chemistry of only 33.3% of the Tertiary Studies. Finally, most of the Quaternary aquifers were affected by evaporation process where only 13.6% of Quaternary data fall into the rock-water interaction area. This difference between the aquifer could be attributed to the difference of the groundwater depth in the different types of aquifers. Indeed, Jurassic and Cretaceous aquifers, and many Tertiary aquifers are characterized by high karstification creating deep and complex groundwater system that permit higher degree of rock-water interaction. Moreover, the depth of these aquifers makes it harder for evaporation to have a major role in the groundwater forming process. Whereas, the majority of Quaternary aquifers are shallow coastal or plain aquifer which might explain the greater evaporation impact.

4.5. Multivariate analysis

For further analyzing, the data were standardized and analyzed using AHC and PCA. In fact, 72 aquifers divided in 3 different data based on their aquifer types, were plotted in 3 dendrograms (Fig. 5) and 3 PCA (Fig. 6). For AHC, Ward's method was used and the squared Euclidean distance was chosen as a measure of similarity between every pair of objects. As for PCA, and based on the Scree plots, the first 4 principal components, from PC1 to PC4, were interpreted, with cumulative percent variance equal to 92.8%, 98.9% and 98.3% for the Quaternary, Jurassic& Cretaceous and Tertiary data respectively. In order to classify our data, the correlations between the principal components and the variables were observed (Table 1). The Quaternary data showed high and significant negative correlations between PC1 and Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^- and SO_4^{2-}, while PC2 was positively correlated with PH and HCO_3^-. Moreover, the Jurassic and Cretaceous data showed a high and significant positive correlation between PC1 and Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^- and SO_4^{2-}, and PC2 was negatively correlated with pH and HCO_3^-. Finally, the Tertiary data showed a significant positive correlation between PC1 and Mg^{2+}, Na^+, K^+, Cl^- and SO_4^{2-}, a significant positive correlation between PC2 and HCO_3^- and a significant negative correlation between PC2 and pH.

The Dendrogram of quaternary aquifers presents 5 groups. These 5 groups were labelled as Q1, Q2, Q3, Q4 and Q5 from left to right (Fig. 5a). First of all, the group Q1 represents 10 studies affected slightly by anthropogenic activities, with most of its studies holding PC1 and PC2 equal to 0 expect for an Algerian study (Aouidane and Belhamra, 2017), conducted on the Remila aquifer located north-east of the country, with lower PC2 score indicating lower pH and bicarbonate values. The group Q2 contains 13 studies, affected mainly by rock-water interaction, with most of its studies showing slightly positive PC1 scores and PC2 nearly equal to 0. In addition, the groundwater of this group is slightly affected by anthropogenic impact. While a Portuguese study conducted on Serra da Estrela mountain area (Carreira et al., 2011) holds the highest and lowest PC1 and PC2 respectively in Q2, indicating lower values of the 7 major ions and pH.

Furthermore, Q3 holds only 1 study conducted on a south eastern Tunisian zone (Telahigue et al., 2018), and has a PC2 score slightly

Table 1.1
the correlations between the 5 PCs from one hand and the 4 physicochemical parameters with the 9 major ions from the other hand.

		T	TDS	EC	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	PO_4^{3-}	NO_3^-	HCO_3^-	Cl^-
Wet	**PC1**	**−0.76**	**−0.83**	**−0.93**	**0.83**	**−0.79**	−0.61	**−0.89**	−0.53	−0.64	−0.23	−0.46	**−0.83**	**−0.86**
	PC2	−0.23	−0.31	−0.18	0.22	−0.12	0.62	0.22	0.58	**0.72**	0.1	−0.51	−0.3	−0.13
	PC3	−0.23	0.21	−0.05	−0.13	0.02	0.09	−0.11	−0.17	−0.13	**0.94**	−0.26	0.12	−0.28
	PC4	0.26	0.09	−0.01	0.02	−0.54	0.29	−0.26	0.14	−0.05	−0.06	−0.12	0.35	0.03
Dry	**PC1**	**0.77**	**0.95**	**0.96**	**−0.82**	**0.72**	0.65	**0.84**	0.55	**0.87**	0.11	0.54	**0.85**	**0.92**
	PC2	0.14	0.26	0.25	−0.14	0.58	−0.37	−0.36	−0.56	−0.19	0.37	0.65	0.17	−0.21
	PC3	0.1	−0.09	−0.08	0.11	−0.05	−0.5	−0.17	0.59	−0.09	0.2	0.43	−0.34	0.06
	PC4	−0.57	0.03	0.02	0.05	0.04	0.16	0.2	0.01	0.32	0.46	0.24	−0.13	−0.05

below 0, while it shows a very low score on PC1 indicating an increasing in calcium, magnesium, sodium, chloride and sulfate concentrations. Moreover, the group Q4 which contains 6 aquifers, shows an abundance in coastal studies and is affected by the increase in water salinity. In addition, the PCA indicate that most of the group's studies fall near PC2 equal to 0 except for the Moroccan study conducted on Bou-Areg aquifer, which hold a positive PC2 score indicating an exceptional high pH and bicarbonate values in comparison to other aquifers in this group. Moreover, all Q4 aquifers fall slightly toward a negative PC1, which indicate an increasing in Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-} especially in the Moroccan and Tunisian studies concerning the Bou-Areg coastal aquifer and an irrigated land in central Tunisia respectively (Farid et al., 2013; Re et al., 2013). The group Q5 holds 11 aquifers including 6 coastal aquifers. Most of these aquifers hold slightly positive PC1 and PC2 scores. In fact, a huge increase in salinity affect this group where almost all of its aquifers' chemical composition were altered due to seawater intrusion or evaporite dissolution.

For the Jurassic data, the dendrogram indicate 4 groups labelled J1, J2, J3 and J4 from left to right (Fig. 5b). The group J1 represented by only one Algerian study conducted on the Ain Azel area (Belkhiri and Mouni, 2014). In fact, this group is affected by salinization and holds a slightly positive PC1 indicating a higher calcium, magnesium, sodium, potassium, chloride and sulfate since they are positively correlated, and low bicarbonate and pH values indicated by the slightly positive PC2. In addition, the group J2 contains 9 studies with PC2 nearly 0 and a slightly negative PC1 indicating low concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-}, since they are positively correlated with PC1. Moreover, the J3 group includes one study conducted on an aquifer located in south eastern Tunisia (Ben Cheikh et al., 2014). This group holds extremely high PC1 and PC2 correlation scores, reflecting high concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-} and low values of pH and HCO_3^{-}. Furthermore, only 2 Tunisian aquifers belong to the J4 group. These aquifers were analyzed in a Tunisian study conducted on Sisseb El Alem basin (Houatmia et al., 2016), which holds a high PC1 and an extremely low PC2 indicating high concentrations of the 7 major ions and pH.

Finally, the Tertiary aquifers were divided into 3 groups, labelled T1, T2 and T3 from left to right (Fig. 5c). In addition, PC1 is positively correlated with Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-}, while PC2 is positively and negatively correlated with HCO_3^{-} and pH respectively. In fact, the T1 group, holding 2 studies, is characterized by PC2 nearly null and a positive PC1. While the second group holds only 3 studies with slightly negative PC1 and positive PC2. Most of the Tertiary aquifers are clustered in the T3 group holding 12 studies with PC1 and PC2 nearly null for the majority of the studies, except for the Italian study conducted on Lago located south of the country (Critelli et al., 2015) holding a slightly higher PC2 score and a Moroccan study conducted in a karstic mountainous area (De Jong et al., 2008) with a high PC2. This higher PC2 scores reflect the higher bicarbonate concentrations and lower pH values in these 2 studies.

5. Discussions

5.1. What are the main concerns that drive the hydrogeochemical studies in the mediterranean?

The hydrogeochemical studies in our dataset focus on seven main topics: the hydrogeology, hydrogeochemistry, isotope, modelling, pollution, seawater intrusion and water quality. Despite this diversity in topics, the group of countries in each continent indicate a distinctive interest. For instance, 28.1% of North Africa's studies discussed the water quality problem hence its countries focus mainly on agriculture as the main activity (Siebert et al., 2010). Furthermore, the seawater intrusion represents a serious Middle Eastern problem due to overpopulation and the close distant to sea with 15% of its studies focusing on this topic, for example Kalaoun et al. indicate in 2016 that the overexploitation and intensive pumping are causing this problem in the coastal city of Tripoli, Lebanon and it will aggravate if pumping rates are maintained. In addition, the European countries focus on the hydrogeochemistry aspect and the pollution problem with percentages equal to 51% and 17.6% respectively. In fact, this interest in pollution topic comes from the contamination of groundwater resource from different sources, such as agricultural practices, urban areas and industries (Cucchi et al., 2008). Finally, the modelling is represented only in 3.1% and 2% of North African and European studies respectively, while the isotope topic is represented by 5.9% and 2.5% of European and Middle Eastern studies respectively.

The low number of studies tackling the isotopic and modelling topics was clear. In fact, 2 articles focus on the modelling, 1 of them is a North African study located in Morocco and 1 is a European Portuguese study, while 1 of the 4 isotopic studies focus on Lebanon and the rest were conducted in the following European countries: Spain, France and Italy. This pattern represented by the isotope topic could be explained by the cost factor, where the expensive studies were found mostly in the European studies. In opposite of the 2 previous topics, the hydrogeochemical topic was considered the most important one with 48 articles tackling this subject. Furthermore, more than half of the studies focusing on this topic are European ones (54.2%), while the other half is distributed equally between the North African (20.8%) and Middle Eastern (25%) region. Moreover, a close number of articles focus on the remaining topics. Indeed, the water quality, pollution, hydrogeology and seawater intrusion topics were covered by 23, 19, 14 and 13 articles respectively. Focusing on the hydrogeology, a quasi-equal number of European (5 studies) and Middle Eastern articles (6 studies) was observed, while the number of North African studies addressing this topic equal to 3 articles was lower compared to the previous two regions. While the focus of the North African region was directed toward the water quality subject, with 9 studies focusing on this topic, compared to the 4 European studies focusing on this subject. In addition, 10 Middle Eastern studies tackle this topic. From the European perspective, we could see clearly that their focus is directed toward the pollution topic with 9 studies, while 10 studies located equally in the other two regions focus on this topic. The previous finding considering the hydrogeology, pollution and water quality topics could be explained by the fact that the European region is industrial oriented region leading to a higher focus on the hydrogeology and pollution topics, while the North African region is an agricultural one leading to increase the interest in water quality topic. Last but not least, the 7 studies focusing on the seawater intrusion were distributed quasi-equally between the North African and European regions with 4 and 3 articles respectively, while the Middle Eastern articles focusing on this subject are equal to 6 studies (46.2%), which could be explained by the fact that most of the middle Eastern countries are overpopulated with many major coastal cities and as a result the focus of this region on the seawater intrusion is distinctive.

5.2. What are the physico-chemical characteristics of groundwater in the mediterranean?

Groundwater in the Mediterranean region exhibit similarities but also differences between the 3 major types of aquifers discussed in this work. Hence, the physical parameters data shows that average pH values for the 3 aquifers is similar with the values equal to 7.6. The slightly alkaline pH in all aquifers is normal since alkaline element are the major chemical components of all groundwater samples in the region. Mean temperature values range from 18.8 °C in the Jurassic to 20.1 °C in the Tertiary with a mean value of 20 °C in the Quaternary. The lower temperature of the Jurassic and Cretaceous aquifers groundwater may stem from the fact that these aquifers are generally located in mountainous areas whereas a large proportion of Tertiary and Quaternary aquifers are located in lower altitude. Moreover, the highest TDS and EC means were found in the Tertiary data with values of 3188.5 mg/L and 3996 μS/cm, followed by the Quaternary with values of 1434.2 mg/L and 1996.4 μS/cm respectively. Whereas the lowest values are found in the Jurassic with 1215.9 mg/L for TDS and 1396.1 μS/cm for EC. The high values of EC and the TDS in the Tertiary and Quaternary data can be attributed to both evaporation and seawater intrusion problems given the prevalence of coastal aquifers in these formations. For instance, the evaporation process is prevalent in some studies (Karroum et al., 2017; Manno et al., 2007; Telahigue et al., 2018; Zghibi et al., 2014) as visualized in the Gibbs plot (Fig. 4).

Monitoring groundwater physico-chemical characteristics is essential because of their potential hazards on both human and agriculture. According to WHO 2017 guidelines, the high and low groundwater pH values do not impose any health issues on consumers. However, groundwater with high pH values tends to yield poor quality water after treatment for human consumption while the groundwater with pH < 7 are corrosive. Hence, for distribution and treatment purposes, the groundwater of the 3 Mediterranean aquifers' types hold moderate pH values. As for the TDS, high values don't affect the human health directly, however it is recommended to avoid drinking water with TDS higher than 500 or 600 mg/L according to EPA (2018) and WHO (2017) respectively. Following these thresholds, the groundwater of the 3 aquifers are considered not suitable for drinking.

The aforementioned analysis refers to mean aquifer values. Regarding physico-chemcial parameters extreme values, only 1 Quaternary study holds pH value outside the normal range, which vary between 6.5 and 8.4 (Ayers and Westcot, 1985). This study is a Turkish one conducted on Korkuteli water resources located in Antalya (Varol and Şekerci, 2018). The results indicate that most of the samples are considered unsuitable for drinking and irrigation. In fact, using this water could cause imbalance in the plants' nutrients and may even holds hazardous ions affecting the plants. In addition, only 5 Quaternary, 3 Jurassic and Cretaceous and 2 Tertiary studies holds TDS means higher than 2000 mg/L which deemed them unsuitable for irrigation (Ayers and Westcot, 1985). In fact, 4 Quaternary and 2 Tertiary aquifers (Abu-alnaeem et al., 2018; Eissa et al., 2018, 2016; Jabal et al., 2015; Zghibi et al., 2014; Farid et al., 2013) were affected by seawater intrusion. In addition to seawater intrusion, wastewater infiltration (Jabal et al., 2015; Zghibi et al., 2014) and nitrate contamination (Abu-alnaeem et al., 2018) also increase TDS values of 3 Quaternary aquifers. Moreover, the halite and evaporate minerals dissolution is responsible for increasing the salinity of a Quaternary and 2 Jurassic & Cretaceous aquifers (Houatmia et al., 2016; Hamzaoui-Azaza et al., 2011). Furthermore, the outcropping of salt deposits is the main source of Jurassic and Cretaceous aquifer's contamination in Tunisia (Ben Cheikh et al., 2014).

5.3. What are the general hydrogeochemical characteristics of groundwater in the mediterranean region?

Major ions concentrations show different patterns across various aquifers. For the Quaternary aquifer, the cation concentrations are as follow $[Na^+]>[Ca^{2+}]>[Mg^{2+}]>[K^+]$, similar aspect is found in the Tertiary and Jurassic and Cretaceous aquifers. However, in the Jurassic aquifers the major cation Na^+ represents very close concentrations to Ca^{2+} while this difference is bigger in the other 2 types of aquifers. For major anions, the HCO_3^- is the major anion in the Jurassic and Cretaceous aquifers, whereas, the Cl^- in the major anions in the Quaternary and Tertiary data. The anions concentrations for the Quaternary, Jurassic and Cretaceous and Tertiary data are as follow: $[Cl^-]> [SO_4^{2-}]> [HCO_3^-]$, $[HCO_3^-]>[SO_4^{2-}]>[Cl^-]$, and $[Cl^-]>[HCO_3^-]>[SO_4^{2-}]$ respectively. Moreover, the dominant hydro-chemical facies in the Quaternary is Ca–Cl and Na–Cl facies. In the Jurassic and Cretaceous, the dominant facies is by far $Ca–HCO_3$, mixed and Ca–Cl owing to the high concentration of Ca that is a major element in the mineral-forming rocks of these aquifers. Similarly, the $Ca–HCO_3$ is the dominant facies in the Tertiary followed by the mixed facies.

Finally, for the groundwater formation process, the major water forming process in the Mediterranean region is evaporation followed by rock-water interaction. Precipitation is only a factor in one study. As for the various aquifers, the large majority of Quaternary groundwater chemistry, and to a lesser extent Tertiary aquifers water chemistry is governed by evaporation processes. However, this is not the case for the Jurassic and Cretaceous aquifers where rock-water interaction is the primary water forming process.

5.4. What geochemical processes influence the water chemistry of the mediterranean region's aquifers?

Based on the previous findings, certain patterns could be attributed to some regions. In fact, the European and Middle Eastern countries' studies are distributed in the following 4 facies: $Ca–HCO_3$, mixed, Ca–Cl and Na–Cl, with a high number of aquifers tending to cluster into the $Ca–HCO_3$ and mixed zones. While, the considerable number of studies falling into the Ca–Cl could be attributed to the fact that some of the developed countries are suffering from pollution and anthropogenic contaminations. For instance, Italian groundwater are affected by the effect of fertilizers and manure disposal in agriculture area (De Caro et al., 2017; Manno et al., 2007) and the low depth of its water leading to higher vulnerability due to over pumping and/or contamination in some areas (Cucchi et al., 2008), while some Spanish aquifers suffer from a high pollution due to the infiltration of domestic and industrial wastewater from sewage networks, septic tanks (Navarro and Carbonell, 2007) and industrial activities (Giménez Forcada and Morell Evangelista, 2008). In addition, the contamination of Sines coastal aquifer in Portugal was attributed to the intense agricultural exploitations (Fernandes et al., 2006). While the North African countries focus aggressively on the agriculture activity. On one hand, this activity will cause the infiltration of the contaminants from the surface to the groundwater (Karroum et al., 2017; Mejri et al., 2018; Re et al., 2014). On the other hand, in order to meet the agriculture's needs, the water consumption increase dramatically in this region, depleting the groundwater's supply and as a result increasing the seawater intrusion in the coastal area (Mountadar et al., 2018; Moussa et al., 2012; Zghibi et al., 2014). In fact, the 2 previous problems are considered as major factors in deteriorating the groundwater on the quality and quantity scale, and as a result most of the North African studies are plotted in the mixed, Ca–Cl and Na–Cl zones with the dominance of Ca–Cl and Na–Cl facies. Moreover, according to the Gibbs plot, these countries located in North Africa are more affected by the evaporation process in comparison with the European and Middle Eastern region. For instance, in Telahigue et al. (2018) proved that the evaporations process is one of the factors increasing the groundwater's salinity in a Tunisian aquifer southern of the country, while the Sminja aquifer located in Tunisia suffers from the same process. This finding was proved in an isotopic study by Mejri et al. (2018). In fact, the higher evaporation effect on the North African countries could be simply attributed to the temperature linked with the geographical location, where the African continent suffer from a higher temperature leading to a higher evaporation in comparison with the European and Middle Eastern region.

Various factors, natural and anthropogenic, impact the water chemistry of the aquifers in the Mediterranean. These factors are discussed for each type of aquifers taking into account the results of the Piper and Gibbs plots along with the cluster analysis.

To facilitate the analysis, the previously identified groups of studies using AHC were plotted on the Piper diagram. Fig. 7 shows, for each type of aquifers, the distribution of these groups on the various hydrochemcial facies. The Quaternary data shows that many zones, in the coastal and non-coastal areas, are affected by the weathering process. In fact, the Piper diagram (Fig. 7, a) shows that many studies belong to the $Ca–HCO_3$ and mixed facies while the dendrogram (Fig. 5, a) indicates the important role of this process in shaping the water chemistry especially in the group Q2. In fact, 11 Q2 aquifers are distributed between $Ca–HCO_3$ and mixed facies which are affected mainly by rock-water interaction. Only 2 studies fall outside of these zones. The first one is

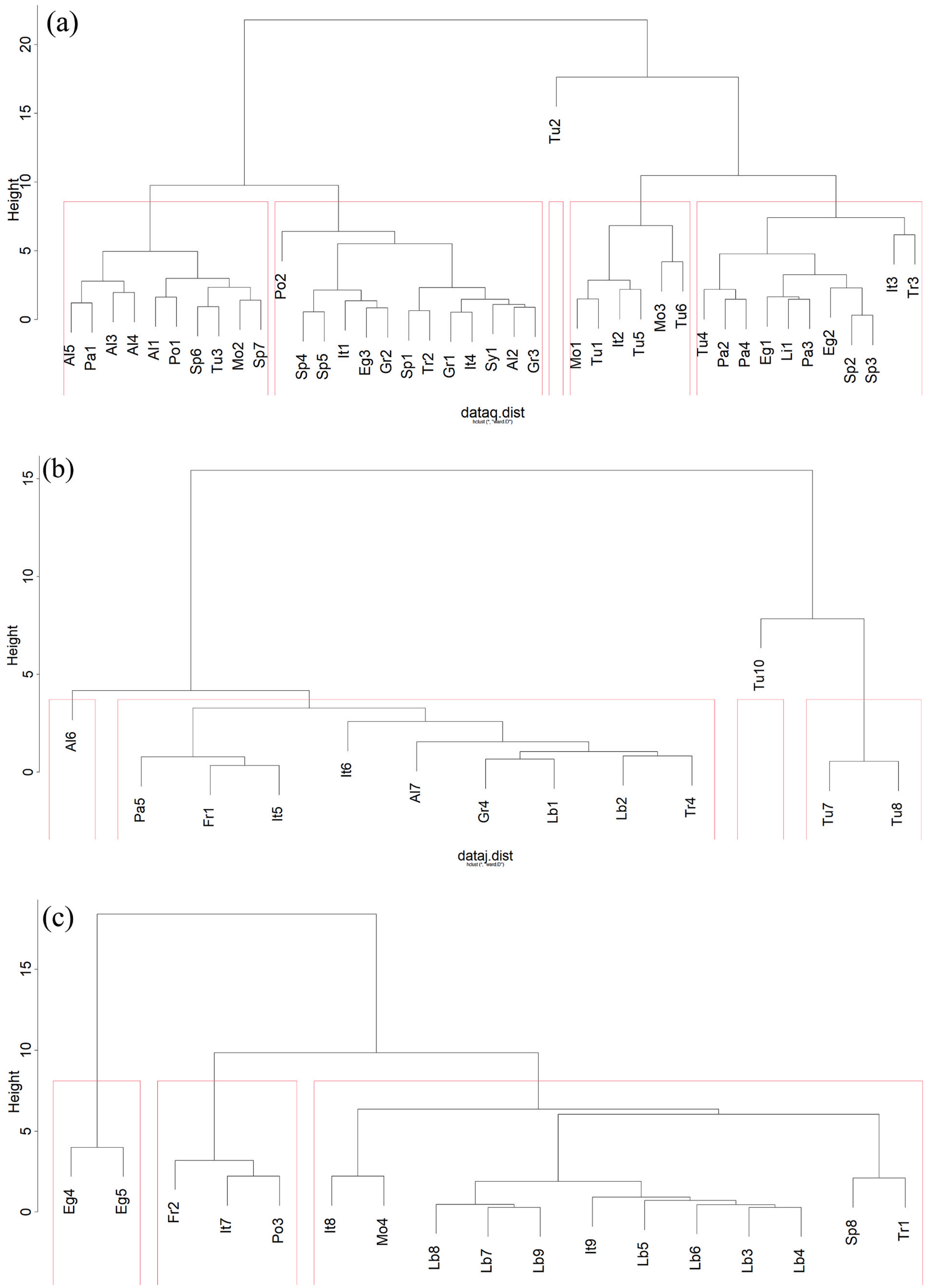

Fig. 5. Dendrograms from hierarchical cluster analysis conducted on: (**a**) the Quaternary, (**b**) the Jurassic & Cretaceous and (**c**) the Tertiary aquifers.

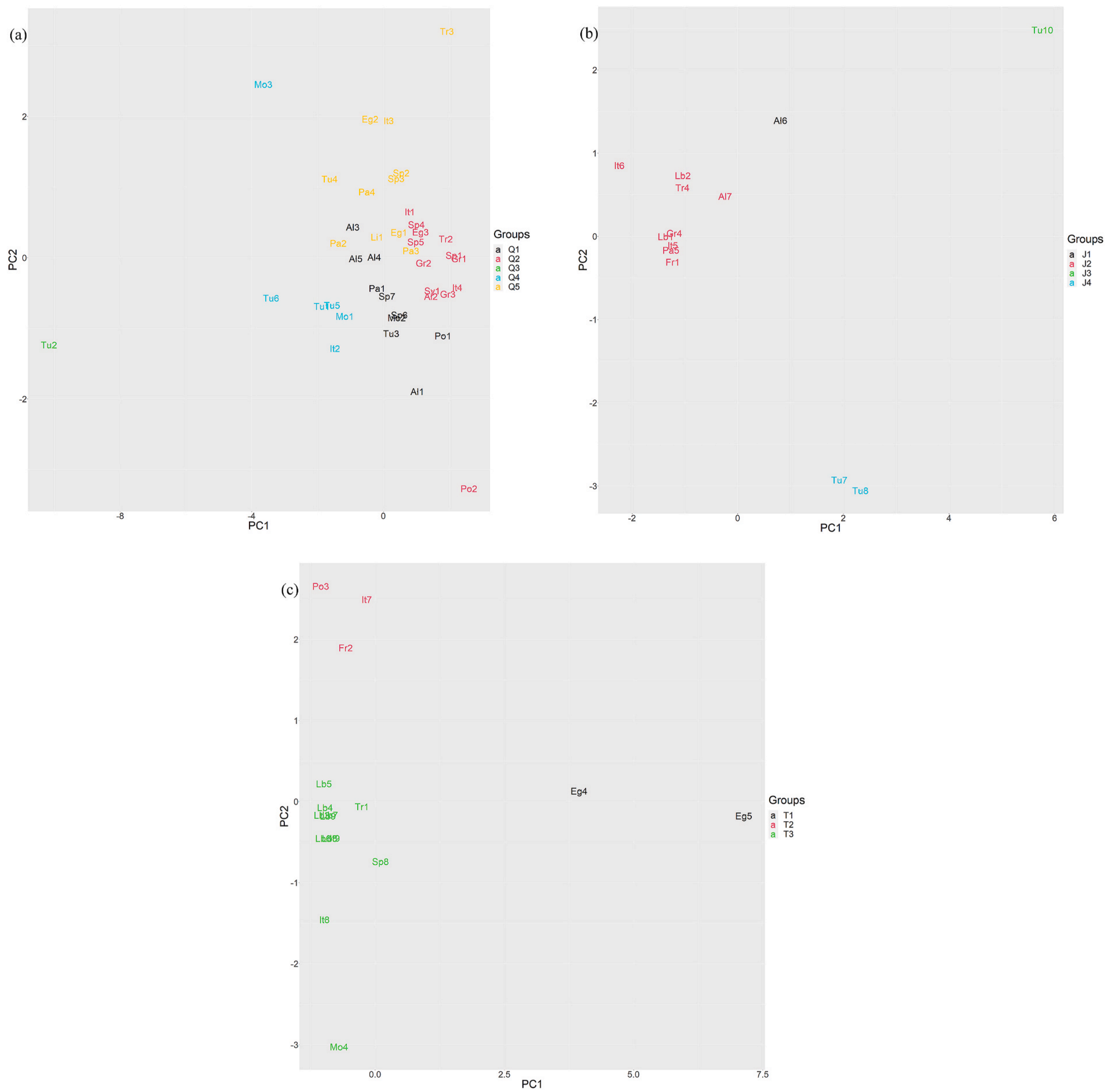

Fig. 6. Loading plots of PC1 versus PC2: (a) the Quaternary, (b) Jurassic & Cretaceous and (c) Tertiary aquifers.

the Portuguese study (Carreira et al., 2011) conducted on Serra da Estrela mountain area falls into the Na–HCO_3 zone and holds the highest and lowest PC1 and PC2 respectively in Q2, indicating lower values of the 7 major ions and pH. In fact, its groundwater is shallow and located at high altitude leading to a lower residence time. The other one is the Italian study (Biddau et al., 2019) conducted on Arborea plain. This study falls into the Na–Cl zone and holds slightly higher PC2 compared to the rest of Q2 studies. In fact, the groundwater was found to be contaminated due to agricultural activities. Despite the importance of weathering, other processes also affect the water's chemistry of Quaternary aquifers. For instance, the group Q4, which holds 6 studies with abundance of coastal aquifers were affected by salinity. This group is dominated by Ca–Cl facies, where 5 studies fall into this facies compared to the other 1 falling into the Na–Cl. The pattern of this group in PCA indicates an increasing in Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-} in some studies especially in a Moroccan and Tunisian studies. In fact, the agricultural pollution and the dissolution of evaporates in Morocco's Bou-Areg coastal aquifer (Re et al., 2013) increases the sodium and chloride concentrations while the Tunisian study (Farid et al., 2013) focusing on an agricultural land in the center of the country is clearly influenced by a mixing process with Sabkhas salt groundwater. Moreover, the group Q5, dominated by coastal aquifers, high concentrations of sodium and chloride has most of its dots falling into the Na–Cl facies. This huge increase in salinity was the result of different processes such as: the seawater intrusion due to excessive pumping (Al-Agha, 2005; Allocca et al., 2018; Sadeg and Karahanoðlu, 2001), the evaporite dissolution (Mejri et al., 2018; Merchán et al., 2014), the mixing with deep saline water (Merchán et al., 2014), etc. Furthermore, most of Q1 studies fall into the Ca–Cl facies, expect for a Portuguese study (Fernandes et al., 2006), conducted on Sines coastal aquifer, falling into the mixed facies. In fact, this region was mainly affected by rock-water interaction. wIn this region, groundwater quality was maintained by respecting the protection limits. Most of these studies were affected by anthropogenic impact due to agricultural activities (Da'as and Walraevens, 2013; Hamed and Dhahri, 2013; Karroum et al., 2017), domestic wastewater and leaks from septic tanks in urban areas (Bouderbala and Gharbi, 2017; Da'as and Walraevens, 2013) and overexploitation leading to seawater intrusion (Daniele et al., 2013; Fernandes et al., 2006). Finally, Q3 holds only 1 study conducted on a coastal south-eastern Tunisian zone (Telahigue et al., 2018), where its main hydrochemical

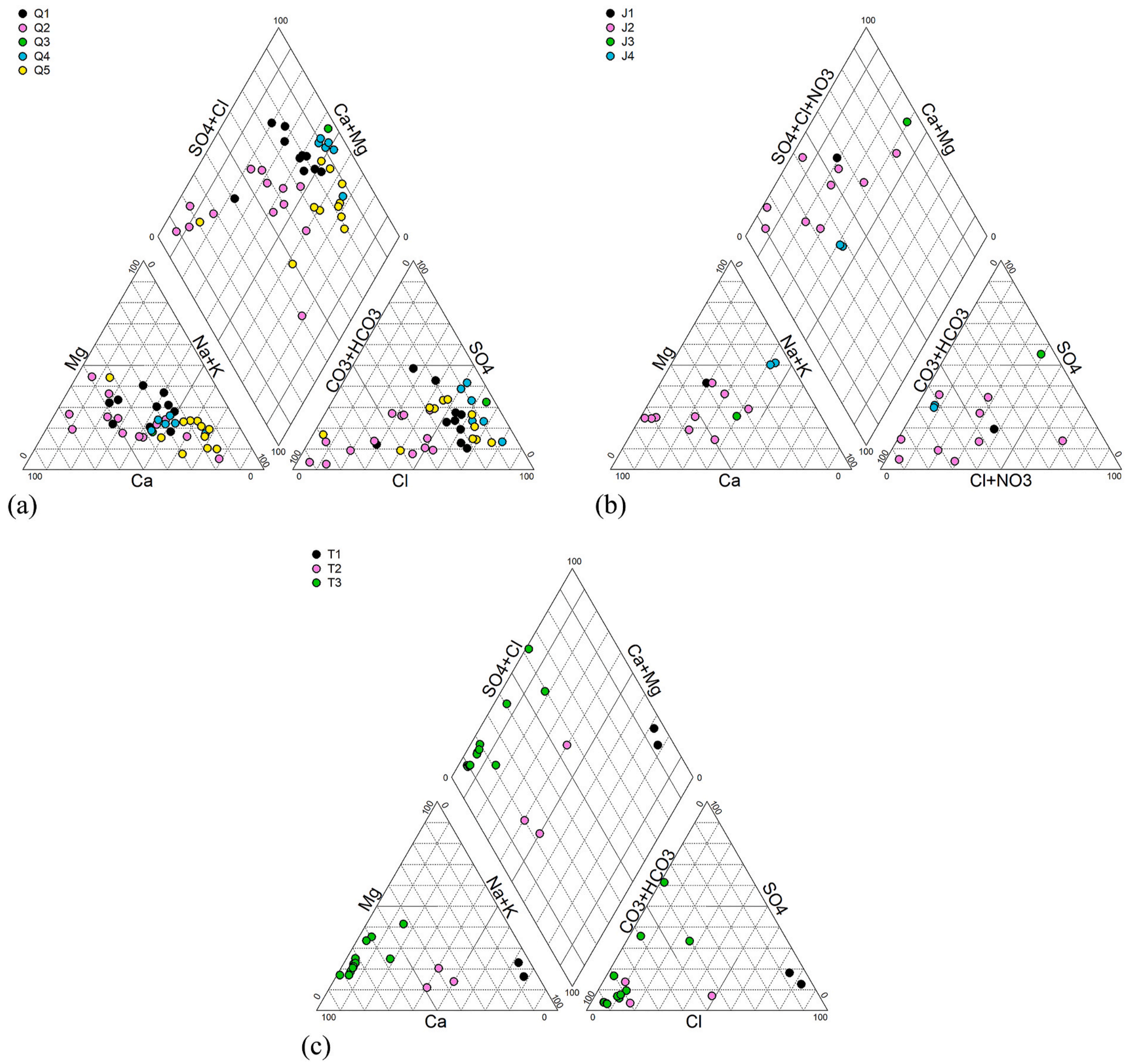

Fig. 7. Piper diagrams representing the distribution of hydrochemical facies for the various groups identified using cluster analysis in the 3 types of aquifers: (a) Quaternary, (b) Jurassic & Cretaceous and (c) Tertiary.

facies is Ca–Mg–Cl–SO_4. The seawater intrusion into the coastal zones and in some parts having low topographic and piezometric levels, in addition to the gypsum and carbonate dissolution are the main culprits of this modification. The fact that many Quaternary aquifers where affected by this problem and hold the highest concentrations of Na and Cl leading to a high number of aquifers falling into the Ca–Cl and Na–Cl zones (Fig. 3, a) could be attributed to the location, where many of the coastal Mediterranean regions belong to the Quaternary formation.

The Jurassic & Cretaceous data indicates that the salinization affects a low number of aquifers, especially in the group J2 dominated by coastal ones. For instance, the studies in Greece and Lebanon by Voutsis et al., in 2015 and Khadra et al., in 2014 respectively show that their groundwater's chemistry is affected to a certain degree by this process. The difference of seawater intrusion occurrence between the Quaternary and Jurassic and Cretaceous aquifers could be observed in the Piper diagram (Fig. 7, b), where a small number of Jurassic and Cretaceous aquifers fall into the Ca–Cl area. Despite the impact of seawater intrusion on J2, these aquifers are mainly affected by rock-water interaction with a slightly negative PC1 and most of them fall into Ca–HCO_3 and Ca–Mg–HCO_3 zones in the Piper diagram. According to PCA, the group J1, which includes solely the Algerian study conducted on the Ain Azel area (Belkhiri and Mouni, 2014), represents high calcium, magnesium, sodium, potassium, chloride and sulfate concentrations and low bicarbonate concentrations. In addition, this study is located in the mixed facies according to the Piper diagram. In fact, the geochemical modelling explained this slight increase in salinity based on the weathering process. In addition, the group J4 holds only 2 Tunisian aquifers of Sisseb El Alem basin (Houatmia et al., 2016). Following PCA, high values of the 7 major ions and pH was observed in this study. In fact, this group is dominated by mixed facies, while the Gibbs diagram showcase the importance of evaporation in shaping their groundwater's chemistry. In fact, the water was very hard, to the extent that two-thirds of the samples were considered poor. Finally, J3 includes 1 Tunisian study (Ben Cheikh et al., 2014). This group holds high concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-} and low concentrations of pH and HCO3. This group is affected mainly by rock-water interaction and falls into the Ca–Cl zone. In fact, Ben Cheikh et al. (2014) proved in 2014 that the dissolution of halite is the main culprit for high salinity in the studied aquifer located south eastern of the country. According to Gibbs diagram, the evaporation process also plays a limited role in this group.

As same as the Jurassic and Cretaceous data, the seawater intrusion problem is rarely affecting the Tertiary aquifers. Most of the Tertiary data falls into the $Ca–HCO_3$ and mixed zone in the Piper diagram (Fig. 7, c). The group T3 is the biggest group with 12 aquifers dominated by $Ca–HCO_3$ and mixed facies due to the important role played by rock-water interaction. In addition, the PC1 and PC2 nearly null except for an Italian study conducted on Lago located south of the country (Critelli et al., 2015) where the chemistry fluctuation is controlled by the dissolution of metabasalts and serpentinites. Besides the previous study, a Moroccan one conducted on mountainous karst area (De Jong et al., 2008) has high PC2 where the groundwater mixing is the main source of chemistry modification. Meanwhile, 2 coastal Egyptian studies conducted on Ras El-Hekma aquifer (Eissa et al., 2018) and Bagoush area (Eissa et al., 2016) belong to the group T1, characterized by Na–Cl facies. According to Gibbs plots, Ras el-Hekma aquifer was affected mainly by evaporation. The seawater intrusion is one of the main culprits in increasing water's salinity in both studies. For the group T2, all PC1 scores are slightly negative while PC2 are positive. According to Piper diagram, the mixed facies is the dominant one. In fact, many anthropogenic and natural factors affect the T2 salinity. For instance, the weathering of carbonate or volcanic rocks could contribute in some studies (Barbieri and Morotti, 2003; Santoni et al., 2016), while the contamination due to fertilization and irrigation could also play an important role in other studies (Andrade and Stigter, 2011).

In summary, the Quaternary and Jurassic and Cretaceous aquifers were affected mostly by the weathering process. Moreover, the seawater intrusion is also present in some studies tackling the two previous types of aquifers but to a lesser extent in the Jurassic and Cretaceous data. Furthermore, the Tertiary aquifers were rarely affected by seawater intrusion and most of its aquifers are affected by rock-water interaction to a lesser extent along with anthropogenic contamination.

In terms of the practical significance of the PCs. PC1 is a good indicator of salinity and contamination because of it is correlation with the calcium, magnesium, sodium, potassium, chloride and sulfate. While PC2 is an indicator of alkalinity due to its correlation with the bicarbonate. Hence, Q4, Q5, J3 and T1 groups that are highly correlated with PC1 might have negative impacts on agriculture activities, where high concentrations of sodium compared to other major ions could cause major permeability and structural damage of soil (Sparks, 2003). In addition, the water used for irrigation holding high concentrations of calcium, bicarbonate and sulfate, such as Q1, Q3, J4 and T2, may lead to leaves and flowers' white scale formation. Such problems can be aggravated by particular irrigation techniques such as sprinklers. Salts from the water droplets will precipitate leading to higher concentrations (Ayers and Westcot, 1985).

5.5. What is the extent of nitrate and minor ions pollution in the mediterranean?

In this work we followed the concentration of minor ions across the Mediterranean aquifers. Two major pollutant types were considered: nitrate pollution and minor ions. In fact, 69 aquifers (46 in the Quaternary, 14 in the Tertiary, and 9 in the Jurassic and Cretaceous formations) and 38 aquifers (24 in the Quaternary, 7 in the Tertiary, and 7 in the Jurassic and Cretaceous) where at least one minor ion was studied were taken into consideration for nitrate pollution and minor ions pollution respectively. Fifteen minor ions that are discussed here. These ions are: manganese (Mn), iron (Fe), fluoride (F), ammonia (NH4), bromide (Br), zinc (Zn), barium (Ba), aluminum (Al), arsenic (As), boron (B), nickel (Ni), lead (Pb), and copper (Cu). The mean aquifer's concentrations of nitrate and the minor ions' concentrations of each sample in the studied aquifers were compared to international standard (especially WHO) in order to identify the regions where groundwater pollution might be considered a health hazard. Fig. 8 represents the studies where pollution was recorded for either nitrate or at least one minor ion.

For nitrate pollution, 20 aquifers out of 69 presented mean concentration values higher than 50 mg/L (WHO, 2017). Almost all of these aquifers are Quaternary, with only one Jurassic and Cretaceous and 3 Tertiary aquifers presented high values of nitrate. The prevalence of nitrate pollution in Quaternary aquifer can be attributed to the fact that most agriculture areas are indeed alluvium deposits from the Quaternary. In addition, the agriculture is a major source of nitrate pollution in the Mediterranean. Moreover, NO_3^- pollution is not distributed equally around different countries and geographic regions. In fact, North African

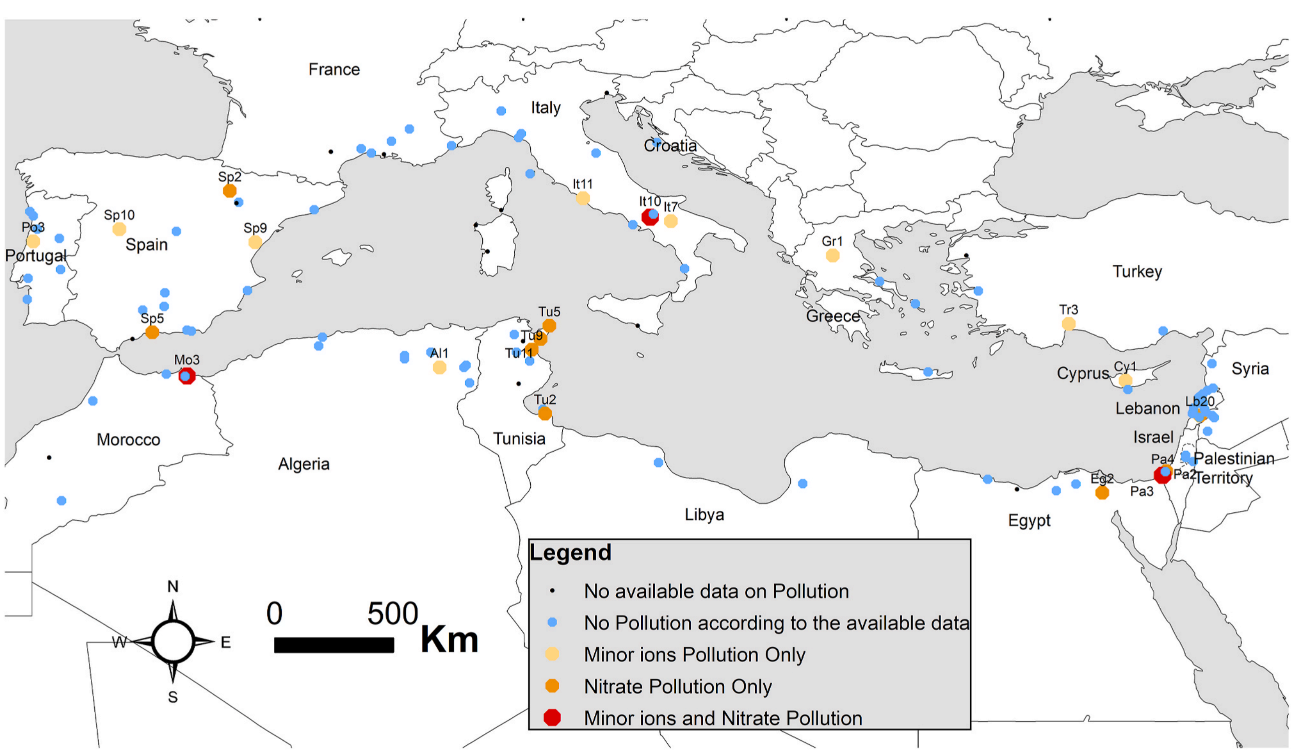

Fig. 8. Distribution of studies with recorded Nitrate or Minor ions pollution.

countries hold the largest number of aquifers with nitrate pollution in our dataset with 8 aquifers located in Tunisia (Hamdi et al., 2018; Mejri et al., 2018; Moussa et al., 2012; Telahigue et al., 2018; Zghibi et al., 2014), Morocco (Re et al., 2013) and Egypt (Gomaah et al., 2016). The African region is followed by 5 aquifers located in Europe with 3 in Italy (Biddau et al., 2019; Corniello and Ducci, 2014; Ghiglieri et al., 2009) and 2 in Spain (Lentini et al., 2009; Merchán et al., 2014). The remaining 7 aquifers are located in the eastern Mediterranean region, 4 aquifers were located in Lebanon (Assaf and Saadeh, 2009; El Hakim, 2005) and 3 in Palestine (Abu-alnaeem et al., 2018; Al-Agha, 2005; Jabal et al., 2015). All aquifers with high nitrate concentrations are located in agricultural areas, except the study conducted by Jabal et al. (2015) concerning the Palestinian urban area of Khan Younis city, where the wastewater contamination is the main result of this pollution indicated by the positive correlation factor between calcium and nitrate equal to +0.64.

As for Minor ions pollution, F, As and B show the highest number of concentrations trespassing the thresholds in the Quaternary aquifers. In addition, 97.4% of the samples with high As concentrations belong exclusively to the European region while a high number of F and B values trespassing the WHO limits belong to the North African region with percentages equal to 60.6% and 93% respectively. In fact, the presence of B ions could serve as an indicator of the increasing in salinity (Brandt et al., 2016) which explain its high abundance in the North African region. For instance, the Moroccan study conducted on Bou-Areg coastal aquifer by (Re et al., 2013) confirmed the high salinity affecting its groundwater, while this increase was attributed to natural and anthropogenic processes such as the weathering process of evaporite and the agriculture activity. Moreover, the Spanish study conducted by Giménez Forcada and Morell Evangelista (2008) concerning the coastal detritic aquifer of Castellón plain also used the B as an indicator of salinity, where a low number of its samples shows high concentrations. In fact, it was proven that the seawater intrusion process affects some of its samples. Meanwhile, 33 samples hold F concentrations falling above WHO threshold. Furthermore, these samples were distributed as follows: 7 European, 6 Middle Eastern and 20 North African samples. In fact, this random distribution could be explained by the source of fluorite which is in most of the time a natural process. In addition, the studies holding the high values of F indicate the importance of weathering process and minerals dissolution in modifying their groundwater's chemistry (Al-Agha, 2005; Gómez et al., 2006; Jabal et al., 2015; Karroum et al., 2017; Manno et al., 2007). For the arsenic component, the main source seems to be anthropogenic, where the high concentrations represented by the Italian study conducted on an aquifer located central of the country could be attributed to the fact that this area is a landfill (Preziosi et al., 2019), while the high values presented on another Italian study focusing on the Arborea plain were attributed to 2 shallow groundwater's samples where an intensive farming activity dominate the region (Biddau et al., 2019). After analyzing the previous 3 ions, Mn and Fe comes as minor ions represented in a decent number of samples with concentrations trespassing the limit with values equal to 11 and 17 samples respectively. For the manganese ion, 3 articles hold the 11 samples with high concentration. In fact, the 2 same Italian studies observed before holding high concentrations for arsenic (Biddau et al., 2019; Preziosi et al., 2019) also hold 4 samples with Mn trespassing the limit distributed equally between the 2. In addition, 7 of these samples belong to a study conducted on an aquifer located in southern France (Maréchal et al., 2014). In fact, the main source of this ion is the weathering process of certain minerals. For instance, the Italian study conducted by Preziosi et al. (2019) proves the importance of this process in increasing the Mn concentrations using PCA. Furthermore, the samples with high Fe concentrations were distributed between 2 studies. The first one is a Spanish study conducted on deep groundwaters of the Hesperian massif holding 15 samples with weathering process as main source of iron (Gómez et al., 2006), while the other study is the Italian study holding the high concentrations for Mn and As conducted by Preziosi et al. (2019), where the main sources were attributed to sulfide oxidation and the precipitation of the Fe oxyhydroxides processes. Finally, most of the Quaternary samples hold concentrations of NH4, Zn, Al and Pb lower than the thresholds, where only 5, 2, 2 and 1 samples respectively exceed those limits. It is important to note that none of the samples in the 3 different types of aquifers trespass the WHO guidelines for Ba, Ni and Cu.

The Jurassic & Cretaceous data indicates that all of its samples holding concentrations for F, NH4, Zn, Al, As and Pb fall below the limits put by WHO. While only one concentration of Mn, Fe and B exceeding the thresholds is presented in these samples. In fact, Mn and Fe concentrations belong to an Italian study conducted on the Nurra region located in Sardinia (Ghiglieri et al., 2009), while the B concentrations belong to a Lebanese study conducted on the Damour coastal aquifer (Khadra and Stuyfzand, 2014). Ultimately, no important pollution was observed in this type of aquifers.

For the Tertiary aquifers, its data indicate minor pollution in its samples except for the B ion, where 10 samples belong to a study conducted on the Cyprus ophiolites by Neal and Shand (2002) and hold concentrations exceeding the WHO threshold due to sea-salt. While the concentrations of Mn, F and Al trespassing the WHO limits belong to 4, 1 and 2 samples respectively. In fact, the Mn concentration were found in a Portuguese study concerning an aquifer located in the centre of the country (Andrade and Stigter, 2011), while the F concentration was found in an Italian study conducted on Monte Vulture volcano (Barbieri and Morotti, 2003), and last but not least the same Cyprus study mentioned before, holding the high concentrations of B, also hold the Al ones exceeding the guidelines (Neal and Shand, 2002).

Finally, pollution in the Mediterranean seems to be a source of concern and an understudied problem especially in the south and especially in term of trace elements. Nitrate pollution was detected in 29% of aquifers that are mostly agricultural, while 15.3% of the minor ions' samples showed values higher than the recommended WHO thresholds. Moreover, the limited number of such studies and their concentration mainly in the northern part of the Mediterranean makes it even harder to identify the extent of this pollution in the groundwater of the Mediterranean aquifers especially in North Africa and the eastern Mediterranean.

5.6. *What can we learn from stables isotopes studies in the mediterranean?*

The isotopic data is measured in 16 studies in order to enlarge the border of investigation while revealing the water origin and water fluxes (Clark, 1997; Gat, 1996). For instance, the Lebanese study conducted on Nahr Ibrahim by Hanna et al. (2018) indicates that the snowmelt recharge is a key process in this aquifer, especially during the dry season and identify Nahr Ibrahim river as a groundwater-dominated river even during the wet season. While in Merchán et al. (2014) proved via isotopic signatures that the main origin of the increase in nitrate concentrations of the Spanish "Lerma" Quaternary basin is the application of ammonia/urea fertilizers more than nitrate fertilizer inputs. In addition, the nitrate contamination occurring at local scale was proved by Biddau et al. (2019) in the Italian study conducted on the Arborea plain's Quaternary aquifer. Furthermore, the freshwater/seawater mixing in Rhône delta's Quaternary aquifer located southern France was confirmed by De Montety et al., in 2008 where the sample plots form a line following the equation $\delta^2H = 7\delta^{18}O - 0.7$; which fall beneath the global meteoric water line (GMWL; $\delta^2H = 8\delta^{18}O + 10$). Furthermore, in the Tunisian study conducted by Ben Cheikh et al. (2014) concerning the Cretaceous aquifer located south eastern of the country, the isotopic signature reveals the groundwater's age by plotting δ^2H versus chloride, which reveal two groups: old water as a result of the mix with continental intercalaire groundwater and the recent recharge via rainwater infiltration. Moreover, the seawater intrusion was proved via isotopic study by Somay (2016) concerning the Jurassic aquifer located in the

Turkish Edremit-Dalyan coastal wetland, where this process only affects the coastal zone's water. In addition, the Italian study conducted by Cucchi et al. (2008) on the Venezia Giulia plain's Tertiary aquifers located north eastern of the country shows an isotopic data similar to local rainfall indicating that the rainfall plays an important role in recharging the groundwater. Finally, the groundwater located in the Bagoush area's Tertiary Egyptian aquifer is recharged by modern fresh water with several sources of salinity affecting a paleo-water part (Eissa et al., 2016).

6. Conclusion

This study aimed at analyzing the hydrogeochemical characteristics of groundwater in the Mediterranean region. For this purpose, 123 articles were collected from the literature and their qualitative and/or quantitative data were extracted when available. The data were divided by aquifers type: Jurassic and Cretaceous, Tertiary and Quaternary. And the analysis took into account the geographical location of the studies with a focus on 3 main geographical regions: Europe, North Africa and the Middle East.

On one hand, the qualitative analysis focuses on the studies' topics. For the entire dataset, the main topics were identified as the hydrogeochemistry and water quality topics. The same aspect was observed in the Quaternary data, while the Jurassic and Cretaceous, and Tertiary data were dominated by the hydrogeochemistry and hydrogeology topics. On the other hand, the groundwater characteristics, hydrogeochemical facies, geochemical processes and multivariate analysis were inspected in the quantitative analysis.

In term of general hydrogeochemical characteristics, the data indicates that the Quaternary aquifers hold the highest and lowest values of Ca^{2+} and Mg^{2+} respectively and the highest and lowest values of K^+ and SO_4^{2-} respectively. Meanwhile, the lowest Ca^{2+} value, the extreme values of HCO_3^- and lowest values of Na^+ and Cl^- belong to the Jurassic and Cretaceous aquifers. In addition, the Tertiary data holds the highest values of Mg^{2+}, Na^+ and Cl^-. In addition, major ions concentrations show different patterns across various aquifers. For the Quaternary aquifer, the cation concentrations are as follow $[Na^+]>[Ca^{2+}]>[Mg^{2+}]>[K^+]$, similar aspect is found in the Tertiary and Jurassic and Cretaceous aquifers. Meanwhile, the anions concentrations in the Quaternary, Cretaceous and Jurassic, and Tertiary are as follow: $[Cl^-]>[SO_4^{2-}]>[HCO_3^-]$, $[HCO_3^-]>[SO_4^{2-}]>[Cl^-]$, and $[Cl^-]>[HCO_3^-]>[SO_4^{2-}]$ respectively.

The Piper diagrams shows that 76.3% of the aquifers falling into one of these 3 following facies: are Ca–HCO_3, mixed and Ca–Cl. While the rest belong to the Na–Cl and Na–HCO_3 facies, especially for the North African studies. In fact, the hydrochemical facies of groundwater dominating the Quaternary aquifers are as follow: Ca–Cl > Na–Cl > mixed > Ca–HCO_3>Na–HCO_3. While the Jurassic and Cretaceous aquifers are dominated by the following facies: mixed > Ca–HCO_3>Ca–Cl. In addition, the Tertiary aquifers are distributed between 3 facies as follow: Ca–HCO_3>mixed > Na–Cl. Furthermore, the Gibbs plots revealed that the evaporation followed by rock-water interaction are the main geochemical processes affecting the Mediterranean aquifers. In addition, almost third of the European and Middle eastern aquifers are affected by rock-water interaction. Meanwhile, almost all of North African studies fall into the evaporation zone. This pattern could be attributed to the higher temperature in the North Africa region.

Furthermore, the multivariate analysis showed that the Quaternary aquifers are divided in 5 groups, Jurassic and Cretaceous aquifers in 4 groups and Tertiary aquifers in 3 groups. This analysis ensures that the Quaternary aquifers are governed by the anthropogenic impact and seawater intrusion. Meanwhile, a high number of Jurassic and Cretaceous aquifers are affected mainly by rock-water interaction, while the high salinity observed in a small number of aquifers is attributed to the evaporites dissolution. In addition, the Tertiary aquifers are affected by rock-water interaction.

Moreover, the nitrate data indicates that 20 aquifers out of 69 hold values higher than 50 mg/L (WHO, 2017). Almost all of these aquifers are Quaternary, with only one Jurassic and Cretaceous and 3 Tertiary aquifers presented high values of nitrate. As for the minor ions, 15.3% of the minor ions' samples show values higher than the recommended WHO thresholds. Moreover, 83.4% of these concentrations exceeding the limits belong to Quaternary aquifers, while the Tertiary and Jurassic and Cretaceous aquifers hold smaller percentages equal to 10.9% and 5.6% respectively. Finally, the isotope data indicates that the average composition of δ18O and δ2H are −5.6‰ and −36.4‰ respectively. In fact, the δ18O composition ranges from −7.9‰ to −0.4‰. Meanwhile, the δ2H composition varies between −50.3‰ and −9.2‰.

In the end, this work is a preliminary assessment of baseline hydrogeochemical characteristics of groundwater in the Mediterranean region. It only focuses on average concentrations and does not take into account seasonal variability or specific interactions in various types of aquifers such as coastal aquifers. Indeed, this work highlighted some of the major problems facing groundwater in the Mediterranean region. Among these, saltwater intrusion and pollution appear to be some of the main issues especially in coastal and agricultural aquifers respectively. Hence, the need for the implication of different stakeholders and authorities at all levels to find solutions that permit the sustainable exploitation of groundwater resources. First, continuous monitoring of groundwater quality is certainly a necessity. Such activity will sometimes require north-south cooperation in terms of both funding and scientist mobility especially when it comes to sophisticated chemical analysis that are not always possible in the south. Furthermore, authorities need to monitor the implementation of different water quality directives. Not only that, but there is the need to develop new directives that can take into consideration the ever-changing situations. In addition, the use of alternative and non-conventional water resources such as treated wastewater or desalinated water can also reduce pressure on groundwater. Artificial recharge can also be a possible solution to reestablish depleted water tables or to reduce pollution. More case specific remedies can and are being used to deal with certain aspects of quality deterioration especially when dealing with irrigation.

Finally, the authors do believe that comparative studies at a regional scale such as this one are indispensable to advance our understanding in the field of hydrogeochemistry. Further works are certainly needed in order to extend our knowledge on the groundwater formation processes in a region where groundwater is the main water source for various economic sectors.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: AL HAJ Rachad reports financial support was provided by Azm and Saade Association.

Data availability

The authors would like to publish the data if funding to do so is available.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.pce.2022.103351.

References

Abo, R.K., Merkel, B.J., 2015. Comparative estimation of the potential groundwater recharge in Al Zerba catchment of Aleppo basin, Syria. Arabian J. Geosci. 8, 1339–1360. https://doi.org/10.1007/s12517-013-1222-9.

Abou Zakhem, B., 2016. Using principal component analysis (PCA) in the investigation of aquifer storage and recovery (ASR) in Damascus Basin (Syria). Environ. Earth Sci. 75, 1123. https://doi.org/10.1007/s12665-016-5923-8.

Abu-alnaeem, M.F., Yusoff, I., Ng, T.F., Alias, Y., Raksmey, M., 2018. Assessment of groundwater salinity and quality in Gaza coastal aquifer, Gaza Strip, Palestine: an integrated statistical, geostatistical and hydrogeochemical approaches study. Sci. Total Environ. 615, 972–989. https://doi.org/10.1016/j.scitotenv.2017.09.320.

Acero, P., Gutiérrez, F., Galve, J., Auqué, L., Carbonel, D., Gimeno, M., Gómez, J.B., Asta, M., Yechieli, Y., 2013. Hydrogeochemical characterization of an evaporite karst area affected by sinkholes (Ebro Valley, NE Spain). Geol. Acta: an international earth science journal 11, 389–407.

Acra, A., Ayoub, G.M., 2001. Indicators of coastal groundwater quality changes induced by seawater infiltration. Int. J. Environ. Stud. 58, 761–769. https://doi.org/10.1080/00207230108711367.

Al-Agha, M.R., 2005. Hydrogeochemistry and carbonate saturation model of groundwater, khanyounis governorate—gaza strip, Palestine. Environ. Geol. 47, 898–906. https://doi.org/10.1007/s00254-004-1211-0.

Alcalá, F.J., Custodio, E., 2008. Using the Cl/Br ratio as a tracer to identify the origin of salinity in aquifers in Spain and Portugal. J. Hydrol. 359, 189–207. https://doi.org/10.1016/j.jhydrol.2008.06.028.

Alfarrah, N., Hweesh, A., van Camp, M., Walraevens, K., 2016. Groundwater flow and chemistry of the oases of Al Wahat, NE Libya. Environ. Earth Sci. 75, 985. https://doi.org/10.1007/s12665-016-5796-x.

Aliewi, A., Al-Khatib, I.A., 2015. Hzard and risk assessment of pollution on the groundwater resources and residents' health of Salfit District, Palestine. J. Hydrol.: Reg. Stud. 4, 472–486. https://doi.org/10.1016/j.ejrh.2015.07.006.

Allocca, V., Coda, S., De Vita, P., Di Rienzo, B., Ferrara, L., Giarra, A., Mangoni, O., Stellato, L., Trifuoggi, M., Arienzo, M., 2018. Hydrogeological and hydrogeochemical study of a volcanic-sedimentary coastal aquifer in the archaeological site of Cumae (Phlegraean Fields, southern Italy). J. Geochem. Explor. 185, 105–115. https://doi.org/10.1016/j.gexplo.2017.11.004.

Andrade, A.I.A.S.S., Stigter, T.Y., 2011. Hydrogeochemical controls on shallow alluvial groundwater under agricultural land: case study in central Portugal. Environ. Earth Sci. 63, 809–825. https://doi.org/10.1007/s12665-010-0752-7.

Aouidane, L., Belhamra, M., 2017. Hydrogeochemical processes in the plio-quaternary Remila aquifer (khenchela, Algeria). J. Afr. Earth Sci. 130, 38–47. https://doi.org/10.1016/j.jafrearsci.2017.03.010.

Argamasilla, M., Barberá, J.A., Andreo, B., 2017. Factors controlling groundwater salinization and hydrogeochemical processes in coastal aquifers from southern Spain. Sci. Total Environ. 580, 50–68. https://doi.org/10.1016/j.scitotenv.2016.11.173.

Asmael, N.M., Huneau, F., Garel, E., Celle-Jeanton, H., Le Coustumer, P., Dupuy, A., 2014. Hydrochemistry to delineate groundwater flow conditions in the mogher Al mer area (damascus basin, southwestern Syria). Environ. Earth Sci. 72, 3205–3225. https://doi.org/10.1007/s12665-014-3226-5.

Assaf, H., Saadeh, M., 2009. Geostatistical assessment of groundwater nitrate contamination with reflection on DRASTIC vulnerability assessment: the case of the upper litani basin, Lebanon. Water Resour. Manag. 23, 775–796. https://doi.org/10.1007/s11269-008-9299-8.

Assaker, A., 2016. Hydrologie et biogéochimie du bassin versant du fleuve Ibrahim : Un observatoire du fonctionnement de la zone critique au Liban (phd).

Aureli, A., Ganoulis, J., Margat, J., 2008. Groundwater resources in the Mediterranean region: importance, uses and sharing. Water Mediterr, pp. 96-105.

Awad, S., 2011. Hydrochimie et faciès géochimiques des eaux souterraines, Plaine de Bekaa. Hydrol. Sci. J. 56, 334–348. https://doi.org/10.1080/02626667.2011.559331.

Ayers, R.S., Westcot, D.W., 1985. Water Quality for Agriculture, vol. 29. Food and Agriculture Organization of the United Nations, Rome, p. 174.

Bakalowicz, M., 2014. Karst at depth below the sea level around the Mediterranean due to the Messinian crisis of salinity. Hydrogeological consequences and issues. Geol. Belg. 17, 96–101.

Bakalowicz, M., 2015. Karst and karst groundwater resources in the Mediterranean. Environ. Earth Sci. 74, 5–14. https://doi.org/10.1007/s12665-015-4239-4.

Bakalowicz, M., 2018. Coastal karst groundwater in the mediterranean: a resource to Be preferably exploited onshore, not from karst submarine springs. Geosciences 8, 258. https://doi.org/10.3390/geosciences8070258.

Bakalowicz, M., El-Hajj, A., El Hakim, M., Al Charideh, A., Al-Fares, W., Kattaa, B., Fleury, P., Brunet, P., Dörfliger, N., Seidel, J., others, 2007. Hydrogeological settings of karst submarine springs and aquifers of the Levantine coast (Syria, Lebanon). Towards their sustainable exploitation. TIAC 7, 721–732.

Bakalowicz, M., El Hakim, M., El-Hajj, A., 2008. Karst groundwater resources in the countries of eastern Mediterranean: the example of Lebanon. Environ. Geol. 54, 597–604. https://doi.org/10.1007/s00254-007-0854-z.

Barbieri, M., Morotti, M., 2003. Hydrogeochemistry and strontium isotopes of spring and mineral waters from Monte Vulture volcano, Italy. Appl. Geochem. 18, 117–125. https://doi.org/10.1016/S0883-2927(02)00069-0.

Barroso, M.F., Ramalhosa, M.J., Olhero, A., Antão, M.C., Pina, M.F., Guimarães, L., Teixeira, J., Afonso, M.J., Delerue-Matos, C., Chaminé, H.I., 2015. Assessment of groundwater contamination in an agricultural peri-urban area (NW Portugal): an integrated approach. Environ. Earth Sci. 73, 2881–2894. https://doi.org/10.1007/s12665-014-3297-3.

Belfar, D., Fehdi, C., Baali, F., Salameh, E., 2017. Results of a hydrogeological and hydrogeochemical study of a semi-arid karst aquifer in Tezbent plateau, Tebessa region, northeast of Algeria. Appl. Water Sci. 7, 1099–1105. https://doi.org/10.1007/s13201-015-0357-0.

Belkhiri, L., Mouni, L., 2012. Hydrochemical analysis and evaluation of groundwater quality in El Eulma area, Algeria. Appl. Water Sci. 2, 127–133. https://doi.org/10.1007/s13201-012-0033-6.

Belkhiri, L., Mouni, L., 2014. Groundwater geochemistry of Ain Azel area, Algeria. Geochemistry 74, 99–106. https://doi.org/10.1016/j.chemer.2013.09.009.

Ben Cheikh, N., Zouari, K., Abidi, B., 2014. A hydrogeochemical approach for identifying salinization processes in the Cenomanian–Turonian aquifer, south-eastern Tunisia. Carbonates Evaporites 29, 193–201. https://doi.org/10.1007/s13146-013-0166-1.

Bettahar, A., Nezli, I.E., Kechiched, R., 2017. Evolution and mineralization of water chemistry in the aquifer systems of the terminal complex of the wadi righ valley. Energy Proc. 119, 318–324. https://doi.org/10.1016/j.egypro.2017.07.115.

Bicalho, C.C., Batiot-Guilhe, C., Seidel, J.L., Van-Exter, S., Jourde, H., 2010. Investigation of groundwater dynamics in a mediterranean karst system by using multiple hydrogeochemical tracers. In: Andreo, B., Carrasco, F., Durán, J.J., LaMoreaux, J.W. (Eds.), Advances in Research in Karst Media, Environmental Earth Sciences. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 157–162. https://doi.org/10.1007/978-3-642-12486-0_24.

Biddau, R., Cidu, R., Da Pelo, S., Carletti, A., Ghiglieri, G., Pittalis, D., 2019. Source and fate of nitrate in contaminated groundwater systems: assessing spatial and temporal variations by hydrogeochemistry and multiple stable isotope tools. Sci. Total Environ. 647, 1121–1136. https://doi.org/10.1016/j.scitotenv.2018.08.007.

Bleu, Plan, 2006. Faire face aux crises et pénuries d'eau en Méditerranée. Les notes du Plan Bleu: environnement et développement durable en Méditerranée, 4.

Bosák, P., Ford, D.C., Glazek, J., Horácek, I., 2015. Paleokarst: a Systematic and Regional Review. Elsevier.

Bosch, B., Leleu, M., Oustrière, P., Sarcia, C., Sureau, J.-F., Blommaert, W., Gijbels, R., Sadurski, A., Vandelannoote, R., Van Grieken, R., Van 'T Dack, L., 1986. Hydrogeochemistry in the zinc—lead mining district of "Les Malines" (Gard, France). Chem. Geol. 55, 31–44. https://doi.org/10.1016/0009-2541(86)90125-7.

Bouderbala, A., Gharbi, B.Y., 2017. Hydrogeochemical characterization and groundwater quality assessment in the intensive agricultural zone of the Upper Cheliff plain, Algeria. Environ. Earth Sci. 76, 744. https://doi.org/10.1007/s12665-017-7067-x.

Bouderbala, A., Remini, B., Saaed Hamoudi, A., Pulido-Bosch, A., 2016. Application of multivariate statistical techniques for characterization of groundwater quality in the coastal aquifer of nador, tipaza (Algeria). Acta Geophys. 64, 670–693. https://doi.org/10.1515/acgeo-2016-0027.

Boumaiza, L., Chesnaux, R., Drias, T., Walter, J., Huneau, F., Garel, E., Knoeller, K., Stumpp, C., 2020. Identifying groundwater degradation sources in a Mediterranean coastal area experiencing significant multi-origin stresses. Sci. Total Environ. 746, 141203 https://doi.org/10.1016/j.scitotenv.2020.141203.

Bourg, A.C.M., Richard-Raymond, F., 1994. Spatial and temporal variability in the water redox chemistry of the M27 experimental site in the Drac River calcareous alluvial aquifer (Grenoble, France). J. Contam. Hydrol. 15, 93–105. https://doi.org/10.1016/0169-7722(94)90012-4.

Brandt, M.J., Johnson, K.M., Elphinston, A.J., Ratnayaka, D.D., 2016. Twort's Water Supply. Butterworth-Heinemann.

Brozzo, G., Accornero, M., Marini, L., 2011. The alluvial aquifer of the Lower Magra Basin (La Spezia, Italy): conceptual hydrogeochemical–hydrogeological model, behavior of solutes, and groundwater dynamics. Carbonates Evaporites 26, 235–254. https://doi.org/10.1007/s13146-011-0066-1.

Busico, G., Cuoco, E., Kazakis, N., Colombani, N., Mastrocicco, M., Tedesco, D., Voudouris, K., 2018. Multivariate statistical analysis to characterize/discriminate between anthropogenic and geogenic trace elements occurrence in the Campania Plain. Southern Italy. Environmental Pollution 234, 260–269. https://doi.org/10.1016/j.envpol.2017.11.053.

Capaccioni, B., Didero, M., Paletta, C., Salvadori, P., 2001. Hydrogeochemistry of groundwaters from carbonate formations with basal gypsiferous layers: an example from the Mt Catria–Mt Nerone ridge (Northern Appennines, Italy). J. Hydrol. 253, 14–26. https://doi.org/10.1016/S0022-1694(01)00480-2.

Carreira, P.M., Marques, J.M., Espinha Marques, J., Chaminé, H.I., Fonseca, P.E., Santos, F.M., Moura, R.M., Carvalho, J.M., 2011. Defining the dynamics of groundwater in Serra da Estrela Mountain area, central Portugal: an isotopic and hydrogeochemical approach. Hydrogeol. J. 19, 117–131. https://doi.org/10.1007/s10040-010-0675-0.

Carreira, P.M., Neves, M.O., Figueiredo, P., Marques, J.M., Nunes, D., Rei, J.C.M., Caracho, A.J.E., 2017. Geochemistry and environmental isotopes as natural tracers of groundwater flow in shallow aquifer systems within lisbon volcanic complex (Portugal). Procedia Earth and Planetary Science 17, 634–637. https://doi.org/10.1016/j.proeps.2016.12.170.

Cary, L., Benabderraziq, H., Elkhattabi, J., Gourcy, L., Parmentier, M., Picot, J., Khaska, M., Laurent, A., Négrel, Ph, 2014. Tracking selenium in the Chalk aquifer of northern France: Sr isotope constraints. Appl. Geochem. 48, 70–82. https://doi.org/10.1016/j.apgeochem.2014.07.014.

Castañeda, S.S., Sucgang, R.J., Almoneda, R.V., Mendoza, N.D.S., David, C.P.C., 2012. Environmental isotopes and major ions for tracing leachate contamination from a municipal landfill in Metro Manila, Philippines. J. Environ. Radioact. 110, 30–37. https://doi.org/10.1016/j.jenvrad.2012.01.022.

CEPF, (Critical Ecosystem Partnership Fund), 2017. Mediterranean Basin Biodiversity Hotspot [WWW Document]. URL. https://www.cepf.net/sites/default/files/mediterranean-basin-2017-ecosystem-profile-summary-english.pdf, 10.22.21.

Chafouq, D., El Mandour, A., Elgettafi, M., Himi, M., Chouikri, I., Casas, A., 2018. Hydrochemical and isotopic characterization of groundwater in the Ghis-Nekor plain (northern Morocco). J. Afr. Earth Sci. 139, 1–13. https://doi.org/10.1016/j.jafrearsci.2017.11.007.

Charmoille, A., Binet, S., Bertrand, C., Guglielmi, Y., Mudry, J., 2009. Hydraulic interactions between fractures and bedding planes in a carbonate aquifer studied by means of experimentally induced water-table fluctuations (Coaraze experimental site, southeastern France). Hydrogeol. J. 17, 1607–1616. https://doi.org/10.1007/s10040-009-0470-y.

Chaza, C., Sopheak, N., Mariam, H., David, D., Baghdad, O., Moomen, B., 2018. Assessment of pesticide contamination in Akkar groundwater, northern Lebanon. Environ. Sci. Pollut. Res. 25, 14302–14312. https://doi.org/10.1007/s11356-017-8568-6.

Chemseddine, F., Dalila, B., Fethi, B., 2015. Characterization of the main karst aquifers of the Tezbent Plateau, Tebessa Region, Northeast of Algeria, based on hydrogeochemical and isotopic data. Environ. Earth Sci. 74, 241–250. https://doi.org/10.1007/s12665-015-4480-x.

Christensen, T.H., Kjeldsen, P., Bjerg, P.L., Jensen, D.L., Christensen, J.B., Baun, A., Albrechtsen, H.-J., Heron, G., 2001. Biogeochemistry of landfill leachate plumes. Appl. Geochem. 16, 659–718. https://doi.org/10.1016/S0883-2927(00)00082-2.

Clark, I., 1997. Tracing the hydrological cycle. Environmental isotopes in hydrogeology 35–61.

Clauzon, G., 1982. Le canyon messinien du Rhone; une preuve decive du "desiccated deep-basin model" (Hsue, Cita and Ryan, 1973). Bulletin de la Société Géologique de France S7-XXIV, pp. 597–610. https://doi.org/10.2113/gssgfbull.S7-XXIV.3.597.

Cloutier, V., Lefebvre, R., Therrien, R., Savard, M.M., 2008. Multivariate statistical analysis of geochemical data as indicative of the hydrogeochemical evolution of groundwater in a sedimentary rock aquifer system. J. Hydrol. 353, 294–313. https://doi.org/10.1016/j.jhydrol.2008.02.015.

Corniello, A., Ducci, D., 2014. Hydrogeochemical characterization of the main aquifer of the "litorale domizio-agro aversano NIPS" (campania — southern Italy). J. Geochem. Explor. 137, 1–10. https://doi.org/10.1016/j.gexplo.2013.10.016.

Critelli, T., Vespasiano, G., Apollaro, C., Muto, F., Marini, L., De Rosa, R., 2015. Hydrogeochemical study of an ophiolitic aquifer: a case study of Lago (Southern Italy, Calabria). Environ. Earth Sci. 74, 533–543. https://doi.org/10.1007/s12665-015-4061-z.

Cucchi, F., Franceschini, G., Zini, L., 2008. Hydrogeochemical investigations and groundwater provinces of the Friuli Venezia Giulia Plain aquifers, northeastern Italy. Environ. Geol. 55, 985–999. https://doi.org/10.1007/s00254-007-1048-4.

Daniele, L., Vallejos, Á., Corbella, M., Molina, L., Pulido-Bosch, A., 2013. Hydrogeochemistry and geochemical simulations to assess water–rock interactions in complex carbonate aquifers: the case of Aguadulce (SE Spain). Appl. Geochem. 29, 43–54. https://doi.org/10.1016/j.apgeochem.2012.11.011.

Daou, C., Salloum, M., Mouneimne, A., Legube, B., Ouaini, N., 2013. Multidimensionnal analysis of two Lebanese surface water quality: Ibrahim and el-Kalb rivers. J. Appl. Sci. Res. 9, 2777–2787.

Dazy, J., Drogue, C., Charmanidis, P., Darlet, Ch, 1997. The influence of marine inflows on the chemical composition of groundwater in small islands: the example of the Cyclades (Greece). Environ. Geol. 31, 133–141. https://doi.org/10.1007/s002540050172.

Da'as, A., Walraevens, K., 2013. Hydrogeochemical investigation of groundwater in jericho area in the Jordan valley, West Bank, Palestine. J. Afr. Earth Sci. 82, 15–32. https://doi.org/10.1016/j.jafrearsci.2013.01.010.

De Caro, M., Crosta, G.B., Frattini, P., 2017. Hydrogeochemical characterization and natural background levels in urbanized areas: milan metropolitan area (northern Italy). J. Hydrol. 547, 455–473. https://doi.org/10.1016/j.jhydrol.2017.02.025.

De Jong, C., Cappy, S., Finckh, M., Funk, D., 2008. A transdisciplinary analysis of water problems in the mountainous karst areas of Morocco. Eng. Geol. 99, 228–238. https://doi.org/10.1016/j.enggeo.2007.11.021.

De Montety, V., Radakovitch, O., Vallet-Coulomb, C., Blavoux, B., Hermitte, D., Valles, V., 2008. Origin of groundwater salinity and hydrogeochemical processes in a confined coastal aquifer: case of the Rhône delta (Southern France). Appl. Geochem. 23, 2337–2349. https://doi.org/10.1016/j.apgeochem.2008.03.011.

Demirel, Z., Güler, C., 2006. Hydrogeochemical evolution of groundwater in a Mediterranean coastal aquifer, Mersin-Erdemli basin (Turkey). Environ. Geol. 49, 477–487. https://doi.org/10.1007/s00254-005-0114-z.

Dimopoulos, M., Chalkiadaki, M., Dassenakis, M., Scoullos, M., 2003. Quality of groundwater in western Thessaly the problem of nitrate pollution. Global Nest 5, 185–191.

Djebebe-Ndjiguim, C.L., Huneau, F., Denis, A., Foto, E., Moloto-a-Kenguemba, G., Celle-Jeanton, H., Garel, E., Jaunat, J., Mabingui, J., Le Coustumer, P., 2013. Characterization of the aquifers of the Bangui urban area, Central African Republic, as an alternative drinking water supply resource. Hydrol. Sci. J. 58, 1760–1778. https://doi.org/10.1080/02626667.2013.826358.

Eissa, M.A., Mahmoud, H.H., Shouakar-Stash, O., El-Shiekh, A., Parker, B., 2016. Geophysical and geochemical studies to delineate seawater intrusion in Bagoush area, Northwestern coast, Egypt. J. Afr. Earth Sci. 121, 365–381. https://doi.org/10.1016/j.jafrearsci.2016.05.031.

Eissa, M.A., de Dreuzy, J.-R., Parker, B., 2018. Integrative management of saltwater intrusion in poorly-constrained semi-arid coastal aquifer at Ras El-Hekma, Northwestern Coast, Egypt. Groundwater for Sustainable Development 6, 57–70. https://doi.org/10.1016/j.gsd.2017.10.002.

El Hakim, M., 2005. Les aquiferes karstiques de l'anti-Liban et du nord de la plaine de la Bekaa : caractéristiques, fonctionnement, évolution et modélisation, d'après l'exemple du système karstique Anjar-Chamsine (Liban) (These de doctorat), vol. 2. Montpellier.

El Moujabber, M., Samra, B.B., Darwish, T., Atallah, T., 2006. Comparison of different indicators for groundwater contamination by seawater intrusion on the Lebanese coast. Water Resour. Manag. 20, 161–180. https://doi.org/10.1007/s11269-006-7376-4.

EPA, 2018. 2018 Edition of the Drinking Water Standards and Health Advisories Tables.

European Union. The mediterranean region. n.d, [WWW Document]. URL. https://ec.europa.eu/environment/nature/natura2000/biogeog_regions/mediterranean/index_en.htm, 3.18.21.

FAO, 1973. Agriculture Organization of the United Nations (FAO): Calcareous Soils: Report of the FAO/UNDP Regional Seminar on Reclamation and Management of Calcareous Soils (FAO Soils Bulletin 21) (Cairo, Egypt).

Farid, I., Trabelsi, R., Zouari, K., Abid, K., Ayachi, M., 2013. Hydrogeochemical processes affecting groundwater in an irrigated land in Central Tunisia. Environ. Earth Sci. 68, 1215–1231. https://doi.org/10.1007/s12665-012-1788-7.

Fehdi, Ch, Rouabhia, Aek, Baali, F., Boudoukha, A., 2009. The hydrogeochemical characterization of Morsott-El Aouinet aquifer, Northeastern Algeria. Environ. Geol. 58, 1611. https://doi.org/10.1007/s00254-008-1667-4.

Fernandes, P.G., Carreira, P., da Silva, M.O., 2006. Identification of anthropogenic features through application of principal component analysis to hydrochemical data from the Sines coastal aquifer, SW Portugal. Math. Geol. 38, 765–780. https://doi.org/10.1007/s11004-006-9040-1.

Filippidis, F., Stamatis, G., Mantaloufa, I., 2016. Hydrogeochemistry for the assessment of groundwater quality of springs on andros: an island of the cyclades complex, Greece. geosociety 50, 691. https://doi.org/10.12681/bgsg.11775.

Freitas, L., Afonso, M.J., Pereira, A.J.S.C., Delerue-Matos, C., Chaminé, H.I., 2019. Assessment of sustainability of groundwater in urban areas (Porto, NW Portugal): a GIS mapping approach to evaluate vulnerability, infiltration and recharge. Environ. Earth Sci. 78, 140. https://doi.org/10.1007/s12665-019-8167-6.

Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. Annu. Rev. Earth Planet Sci. 24, 225–262. https://doi.org/10.1146/annurev.earth.24.1.225.

Ghannam, J., Ayoub, G.M., Acra, A., 1998. A profile of the submarine springs in Lebanon as a potential water resource. Water Int. 23, 278–286. https://doi.org/10.1080/02508069808686783.

Ghiglieri, G., Oggiano, G., Fidelibus, M.D., Alemayehu, T., Barbieri, G., Vernier, A., 2009. Hydrogeology of the Nurra Region, Sardinia (Italy): basement-cover influences on groundwater occurrence and hydrogeochemistry. Hydrogeol. J. 17, 447–466. https://doi.org/10.1007/s10040-008-0369-z.

Gibbs, R.J., 1970. Mechanisms controlling world water chemistry. Science 170, 1088–1090. https://doi.org/10.1126/science.170.3962.1088.

Giménez Forcada, E., Morell Evangelista, I., 2008. Contributions of boron isotopes to understanding the hydrogeochemistry of the coastal detritic aquifer of Castellón Plain, Spain. Hydrogeol. J. 16, 547–557. https://doi.org/10.1007/s10040-008-0290-5.

Giménez-Forcada, E., Bencini, A., Pranzini, G., 2010. Hydrogeochemical considerations about the origin of groundwater salinization in some coastal plains of Elba Island (Tuscany, Italy). Environ. Geochem. Health 32, 243–257. https://doi.org/10.1007/s10653-009-9281-2.

Gomaah, M., Meixner, T., Korany, E.A., Garamoon, H., Gomaa, M.A., 2016. Identifying the sources and geochemical evolution of groundwater using stable isotopes and hydrogeochemistry in the Quaternary aquifer in the area between Ismailia and El Kassara canals, Northeastern Egypt. Arabian J. Geosci. 9, 437. https://doi.org/10.1007/s12517-016-2444-4.

Gómez, P., Turrero, M., Garralón, A., Peña, J., Buil, B., De la Cruz, B., Sánchez, M., Sánchez, D., Quejido, A., Bajos, C., others, 2006. Hydrogeochemical characteristics of deep groundwaters of the Hesperian Massif (Spain). J. Iber. Geol. 32, 113–131.

González-Ramón, A., López-Chicano, M., Rubio-Campos, J.C., 2012. Piezometric and hydrogeochemical characterization of groundwater circulation in complex karst aquifers. A case study: the Mancha Real-Pegalajar aquifer (Southern Spain). Environ. Earth Sci. 67, 923–937. https://doi.org/10.1007/s12665-012-1529-y.

Güler, C., Thyne, G.D., McCray, J.E., Turner, K.A., 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. Hydrogeol. J. 10, 455–474.

Hamdi, M., Zagrarni, M.F., Jerbi, H., Tarhouni, J., 2018. Hydrogeochemical and isotopic investigation and water quality assessment of groundwater in the Sisseb El Alem Nadhour Saouaf aquifer (SANS), northeastern Tunisia. J. Afr. Earth Sci. 141, 148–163. https://doi.org/10.1016/j.jafrearsci.2017.11.035.

Hamed, Y., Dhahri, F., 2013. Hydro-geochemical and isotopic composition of groundwater, with emphasis on sources of salinity, in the aquifer system in Northwestern Tunisia. J. Afr. Earth Sci. 83, 10–24. https://doi.org/10.1016/j.jafrearsci.2013.02.004.

Hamzaoui-Azaza, F., Ketata, M., Bouhlila, R., Gueddari, M., Riberio, L., 2011. Hydrogeochemical characteristics and assessment of drinking water quality in Zeuss–Koutine aquifer, southeastern Tunisia. Environ. Monit. Assess. 174, 283–298. https://doi.org/10.1007/s10661-010-1457-9.

Hanna, N., Lartiges, B., Kazpard, V., Maatouk, E., Amacha, N., Sassine, S., El Samrani, A., 2018. Hydrogeochemical processes in a small eastern mediterranean karst watershed (Nahr Ibrahim, Lebanon). Aquat. Geochem. 24, 325–344. https://doi.org/10.1007/s10498-018-9346-x.

Hidalgo, M.C., Rey, J., Benavente, J., Martínez, J., 2010. Hydrogeochemistry of abandoned Pb sulphide mines: the mining district of La Carolina (southern Spain). Environ. Earth Sci. 61, 37–46. https://doi.org/10.1007/s12665-009-0318-8.

Hooke, J.M., 2006. Human impacts on fluvial systems in the Mediterranean region. Geomorphology 79, 311–335. https://doi.org/10.1016/j.geomorph.2006.06.036.

Houatmia, F., Azouzi, R., Charef, A., Bédir, M., 2016. Assessment of groundwater quality for irrigation and drinking purposes and identification of hydrogeochemical mechanisms evolution in Northeastern, Tunisia. Environ. Earth Sci. 75, 746. https://doi.org/10.1007/s12665-016-5441-8.

Huneau, F., Blavoux, B., 2000. Isotopic hydrogeology within the Miocene basin of Carpentras-Valreas (southeastern France). Tracers and modelling in hydrogeology.

In: Proceedings of TraM'2000, the International Conference on Tracers and Modelling in Hydrogeology Held at Liège, Belgium, May 2000, pp. 433–438.

Jabal, M.S.A., Abustan, I., Rozaimy, M.R., El Najar, H., 2015. Groundwater beneath the urban area of Khan Younis City, southern Gaza Strip (Palestine): hydrochemistry and water quality. Arabian J. Geosci. 8, 2203–2215. https://doi.org/10.1007/s12517-014-1346-6.

Jebreen, H., Wohnlich, S., Banning, A., Wisotzky, F., Niedermayr, A., Ghanem, M., 2018. Recharge, geochemical processes and water quality in karst aquifers: central West Bank, Palestine. Environ. Earth Sci. 77, 261. https://doi.org/10.1007/s12665-018-7440-4.

Jiang, Y., Guo, H., Jia, Y., Cao, Y., Hu, C., 2015. Principal component analysis and hierarchical cluster analyses of arsenic groundwater geochemistry in the Hetao basin, Inner Mongolia. Geochemistry 75, 197–205. https://doi.org/10.1016/j.chemer.2014.12.002.

Kalaoun, O., Al Bitar, A., Gastellu-Etchegorry, J.-P., Jazar, M., 2016. Impact of demographic growth on seawater intrusion: case of the Tripoli aquifer, Lebanon. Water 8, 104. https://doi.org/10.3390/w8030104.

Karroum, M., Elgettafi, M., Elmandour, A., Wilske, C., Himi, M., Casas, A., 2017. Geochemical processes controlling groundwater quality under semi arid environment: a case study in central Morocco. Sci. Total Environ. 609, 1140–1151. https://doi.org/10.1016/j.scitotenv.2017.07.199.

Kelepertsis, A., 2000. Applied Geochemistry (in Greek).

Khadra, W.M., Stuyfzand, P.J., 2014. Separating baseline conditions from anthropogenic impacts: example of the Damour coastal aquifer (Lebanon). Hydrol. Sci. J. 59, 1872–1893. https://doi.org/10.1080/02626667.2013.841912.

Khadra, W.M., Stuyfzand, P.J., 2018. Simulation of saltwater intrusion in a poorly karstified coastal aquifer in Lebanon (Eastern Mediterranean). Hydrogeol. J. 26, 1839–1856. https://doi.org/10.1007/s10040-018-1752-z.

Khadra, W.M., Stuyfzand, P.J., van Breukelen, B.M., 2017. Hydrochemical effects of saltwater intrusion in a limestone and dolomitic limestone aquifer in Lebanon. Appl. Geochem. 79, 36–51. https://doi.org/10.1016/j.apgeochem.2017.02.005.

Koeniger, P., Toll, M., Himmelsbach, T., 2016. Stable isotopes of precipitation and spring waters reveal an altitude effect in the Anti-Lebanon Mountains, Syria. Hydrol. Process. 30, 2851–2860. https://doi.org/10.1002/hyp.10822.

Korfali, S.I., Jurdi, M., 2007. Assessment of domestic water quality: case study, Beirut, Lebanon. Environ. Monit. Assess. 135, 241–251. https://doi.org/10.1007/s10661-007-9646-x.

Lababidi, H., Shatila, A., Acra, A., 1987. The progressive salination of groundwater in Beirut, Lebanon. Int. J. Environ. Stud. 30, 203–208. https://doi.org/10.1080/00207238708710394.

Leduc, C., Pulido Bosch, A., Remini, B., Massuel, S., 2016. Sub-chapter 2.3.5. Changes in Mediterranean groundwater resources. In: Moatti, J.-P., Thiébault, S. (Eds.), The Mediterranean Region under Climate Change. IRD Éditions, pp. 327–333. https://doi.org/10.4000/books.irdeditions.23583.

Leduc, C., Pulido-Bosch, A., Remini, B., 2017. Anthropization of groundwater resources in the Mediterranean region: processes and challenges. Hydrogeol. J. 25, 1529–1547. https://doi.org/10.1007/s10040-017-1572-6.

Lentini, A., Kohfahl, C., Benavente, J., García-Aróstegui, J.L., Vadillo, I., Meyer, H., Pekdeger, A., 2009. The impact of hydrological conditions on salinisation and nitrate concentration in the coastal Velez River aquifer (southern Spain). Environ. Geol. 58, 1785–1795. https://doi.org/10.1007/s00254-008-1677-2.

López-Chicano, M., Bouamama, M., Vallejos, A., Pulido-Bosch, A., 2001. Factors which determine the hydrogeochemical behaviour of karstic springs. A case study from the Betic Cordilleras, Spain. Appl. Geochem. 16, 1179–1192. https://doi.org/10.1016/S0883-2927(01)00012-9.

Manno, E., Vassallo, M., Varrica, D., Dongarrà, G., Hauser, S., 2007. Hydrogeochemistry and water balance in the coastal wetland area of "biviere di Gela," sicily, Italy. Water Air Soil Pollut. 178, 179–193. https://doi.org/10.1007/s11270-006-9189-8.

Maréchal, J.C., Lachassagne, P., Ladouche, B., Dewandel, B., Lanini, S., Le Strat, P., Petelet-Giraud, E., 2014. Structure and hydrogeochemical functioning of a sparkling natural mineral water system determined using a multidisciplinary approach: a case study from southern France. Hydrogeol. J. 22, 47–68. https://doi.org/10.1007/s10040-013-1073-1.

Marques, J.M., Neves, M.O., Miller, A.Z., Rocha, C., Vance, S., Christensen, L., Etiope, G., Carreira, P.M., Suzuki, S., 2017. Water-rock interaction ascribed to hyperalkaline mineral waters in the cabeço de Vide serpentinized ultramafic intrusive massif (Central Portugal). Procedia Earth and Planetary Science 17, 646–649. https://doi.org/10.1016/j.proeps.2016.12.173.

Mejri, S., Chekirbene, A., Tsujimura, M., Boughdiri, M., Mlayah, A., 2018. Tracing groundwater salinization processes in an inland aquifer: a hydrogeochemical and isotopic approach in Sminja aquifer (Zaghouan, northeast of Tunisia). J. Afr. Earth Sci. 147, 511–522. https://doi.org/10.1016/j.jafrearsci.2018.07.009.

Merchán, D., Otero, N., Soler, A., Causapé, J., 2014. Main sources and processes affecting dissolved sulphates and nitrates in a small irrigated basin (Lerma Basin, Zaragoza, Spain): isotopic characterization. Agric. Ecosyst. Environ. 195, 127–138. https://doi.org/10.1016/j.agee.2014.05.011.

Merchán, D., Auqué, L.F., Acero, P., Gimeno, M.J., Causapé, J., 2015. Geochemical processes controlling water salinization in an irrigated basin in Spain: identification of natural and anthropogenic influence. Sci. Total Environ. 502, 330–343. https://doi.org/10.1016/j.scitotenv.2014.09.041.

Merheb, M., Moussa, R., Abdallah, C., Colin, F., Perrin, C., Baghdadi, N., 2016. Hydrological response characteristics of Mediterranean catchments at different time scales: a meta-analysis. Hydrol. Sci. J. 61, 2520–2539. https://doi.org/10.1080/02626667.2016.1140174.

Metni, M., El-Fadel, M., Sadek, S., Kayal, R., Lichaa El Khoury, D., 2004. Groundwater resources in Lebanon: a vulnerability assessment. Int. J. Water Resour. Dev. 20, 475–492. https://doi.org/10.1080/07900620412331319135.

Milnes, E., 2011. Process-based groundwater salinisation risk assessment methodology: application to the Akrotiri aquifer (Southern Cyprus). J. Hydrol. 399, 29–47. https://doi.org/10.1016/j.jhydrol.2010.12.032.

Molina-Navarro, E., Sastre-Merlín, A., Vicente, R., Martínez-Pérez, S., 2014. Hydrogeology and hydrogeochemistry at a site of strategic importance: the Pareja Limno-reservoir drainage basin (Guadalajara, central Spain). Hydrogeol. J. 22, 1115–1129. https://doi.org/10.1007/s10040-014-1113-5.

Mongelli, G., Monni, S., Oggiano, G., Paternoster, M., Sinisi, R., 2013. Tracing groundwater salinization processes in coastal aquifers: a hydrogeochemical and isotopic approach in the Na-Cl brackish waters of northwestern Sardinia. Italy. Hydrol. Earth Syst. Sci. 17, 2917–2928. https://doi.org/10.5194/hess-17-2917-2013.

Mongelli, G., Argyraki, A., Lorenzo, M.L.G., Shammout, M.W., Paternoster, M., Simeone, V., 2019. Groundwater quality in the mediterranean region. Geofluids 1–4. https://doi.org/10.1155/2019/7269304, 2019.

Moores, E.M., Fairbridge, R.W., 1997. Encyclopedia of European and Asian Regional Geology. Chapman & Hall.

Mountadar, S., Younsi, A., Hayani, A., Siniti, M., Tahiri, S., 2018. Groundwater salinization process in the coastal aquifer sidi abed-ouled ghanem (province of el jadida, Morocco). J. Afr. Earth Sci. 147, 169–177. https://doi.org/10.1016/j.jafrearsci.2018.06.025.

Moussa, A.B., Zouari, K., Valles, V., Jlassi, F., 2012. Hydrogeochemical analysis of groundwater pollution in an irrigated land in Cap bon peninsula, north-eastern Tunisia. Arid Land Res. Manag. 26, 1–14. https://doi.org/10.1080/15324982.2011.631688.

Navarro, A., Carbonell, M., 2007. Evaluation of groundwater contamination beneath an urban environment: the Besòs river basin (Barcelona, Spain). J. Environ. Manag. 85, 259–269. https://doi.org/10.1016/j.jenvman.2006.08.021.

Neal, C., Shand, P., 2002. Spring and surface water quality of the Cyprus ophiolites. Hydrol. Earth Syst. Sci. 6, 797–817. https://doi.org/10.5194/hess-6-797-2002.

Pierotti, L., Botti, F., Bracaloni, S., Burresi, I., Cattaneo, M., Gherardi, F., 2013. Hydrogeochemistry of magra valley (Italy) aquifers: geochemical background of an area investigated for seismic precursors. Procedia Earth and Planetary Science 7, 697–700. https://doi.org/10.1016/j.proeps.2013.03.081.

Piper, A.M., 1944. A graphic procedure in the geochemical interpretation of water-analyses. Eos, Transactions American Geophysical Union 25, 914–928. https://doi.org/10.1029/TR025i006p00914.

Preziosi, E., Frollini, E., Zoppini, A., Ghergo, S., Melita, M., Parrone, D., Rossi, D., Amalfitano, S., 2019. Disentangling natural and anthropogenic impacts on groundwater by hydrogeochemical, isotopic and microbiological data: hints from a municipal solid waste landfill. Waste Manag. 84, 245–255. https://doi.org/10.1016/j.wasman.2018.12.005.

Pulido-Bosch, A., Morell, I., Andreu, J.M., 1995. Hydrogeochemical effects of groundwater mining of the sierra de Crevillente aquifer (alicante, Spain). Geo 26, 232–239. https://doi.org/10.1007/BF00770473.

Qahman, K., Larabi, A., 2006. Evaluation and numerical modeling of seawater intrusion in the Gaza aquifer (Palestine). Hydrogeol. J. 14, 713–728. https://doi.org/10.1007/s10040-005-003-2.

Re, V., Sacchi, E., Martin-Bordes, J.L., Aureli, A., El Hamouti, N., Bouchnan, R., Zuppi, G. M., 2013. Processes affecting groundwater quality in arid zones: the case of the Bou-Areg coastal aquifer (North Morocco). Appl. Geochem. 34, 181–198. https://doi.org/10.1016/j.apgeochem.2013.03.011.

Re, V., Sacchi, E., Mas-Pla, J., Menció, A., El Amrani, N., 2014. Identifying the effects of human pressure on groundwater quality to support water management strategies in coastal regions: a multi-tracer and statistical approach (Bou-Areg region, Morocco). Science of The Total Environment 500– 501, 211–223. https://doi.org/10.1016/j.scitotenv.2014.08.115.

Rouchy, J.-M., Suc, J.-P., Ferrandini, J., Ferrandini, M., 2006. The Messinian Salinity Crisis Revisited. Sedimentary Geology, 188/189. ELSEVIER.

Saadeh, M., Semerjian, L., Amacha, N., 2012. Physicochemical evaluation of the upper litani river watershed, Lebanon. Sci. World J. 2012, e462467 https://doi.org/10.1100/2012/462467.

Sadeg, S., Karahanoðlu, N., 2001. Numerical assessment of seawater intrusion in the Tripoli region, Libya. Environ. Geol. 40, 1151–1168. https://doi.org/10.1007/s002540100317.

Salem, Z.E.-S., Osman, O.M., 2017. Use of major ions to evaluate the hydrogeochemistry of groundwater influenced by reclamation and seawater intrusion, West Nile Delta, Egypt. Environ. Sci. Pollut. Res. 24, 3675–3704. https://doi.org/10.1007/s11356-016-8056-4.

Salem, Z.E., Elsaiedy, G., ElNahrawy, A., 2017. Hydrogeochemistry and quality assessment of groundwater under some central nile delta villages, Egypt. In: Negm, A.M. (Ed.), Groundwater in the Nile Delta, the Handbook of Environmental Chemistry. Springer International Publishing, Cham, pp. 625–645. https://doi.org/10.1007/698_2017_111.

Samad, O.E., Baydoun, R., Aoun, M., Slim, K., 2017. Investigation of seawater intrusion using stable and radioisotopes at coastal area south of Beirut, the Capital of Lebanon. Environ. Earth Sci. 76, 187. https://doi.org/10.1007/s12665-017-6514-z.

Samadder, S.R., Prabhakar, R., Khan, D., Kishan, D., Chauhan, M.S., 2017. Analysis of the contaminants released from municipal solid waste landfill site: a case study. Sci. Total Environ. 580, 593–601. https://doi.org/10.1016/j.scitotenv.2016.12.003.

Santoni, S., Huneau, F., Garel, E., Aquilina, L., Vergnaud-Ayraud, V., Labasque, T., Celle-Jeanton, H., 2016. Strontium isotopes as tracers of water-rocks interactions, mixing processes and residence time indicator of groundwater within the granite-carbonate coastal aquifer of Bonifacio (Corsica, France). Sci. Total Environ. 573, 233–246. https://doi.org/10.1016/j.scitotenv.2016.08.087.

Selenica, A.. n.d. The Mediterranean region: an Hydrological Overview [WWW Document]. URL. http://medhycos.mpl.ird.fr/en/t1.resi&gn=res.inc&menu=fresimf.inc.html, 3.18.21.

Shrestha, S., Kazama, F., 2007. Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji river basin, Japan. Environmental Modelling & Software, Special section: Environmental Risk and Emergency Management 22, 464–475. https://doi.org/10.1016/j.envsoft.2006.02.001.

Siebert, S., Burke, J., Faures, J.M., Frenken, K., Hoogeveen, J., Döll, P., Portmann, F.T., 2010. Groundwater use for irrigation – a global inventory. Hydrol. Earth Syst. Sci. 14, 1863–1880. https://doi.org/10.5194/hess-14-1863-2010.

Siegel, F.R., 2002. Environmental Geochemistry of Potentially Toxic Metals. Springer, Berlin ; New York.

Skordas, K., Papastergios, G., Tziantziou, L., Neofitou, N., Neofitou, C., 2013. Groundwater hydrogeochemistry of Trikala municipality, central Greece. Environ. Monit. Assess. 185, 81–94. https://doi.org/10.1007/s10661-012-2535-y.

Somay, M.A., 2016. Importance of hydrogeochemical processes in the coastal wetlands: a case study from Edremit-Dalyan coastal wetland, Balıkesir-Turkey. J. Afr. Earth Sci. 123, 29–38. https://doi.org/10.1016/j.jafrearsci.2016.07.003.

Sparks, D.L., 2003. Environmental soil chemistry: an overview. Environmental soil chemistry 2, 1–42.

Stamatis, G., Voudouris, K., Karefilakis, F., 2001. Groundwater pollution by heavy metals in historical mining area of lavrio, attica, Greece. Water, air. & Soil Pollution 128, 61–83. https://doi.org/10.1023/A:1010337718104.

Steinhorst, R.K., Williams, R.E., 1985. Discrimination of groundwater sources using cluster analysis, MANOVA, canonical analysis and discriminant analysis. Water Resour. Res. 21, 1149–1156. https://doi.org/10.1029/WR021i008p01149.

Sullivan, P., Agardy, F.J., Clark, J.J.J., 2005. The Environmental Science of Drinking Water. Elsevier.

Sundseth, K., 2000. Natura 2000 in the Mediterranean Region. European Commission.

Tayfur, G., Kirer, T., Baba, A., 2008. Groundwater quality and hydrogeochemical properties of torbalı region, izmir, Turkey. Environ. Monit. Assess. 146, 157–169. https://doi.org/10.1007/s10661-007-0068-6.

Telahigue, F., Agoubi, B., Souid, F., Kharroubi, A., 2018. Assessment of seawater intrusion in an arid coastal aquifer, south-eastern Tunisia, using multivariate statistical analysis and chloride mass balance. Phys. Chem. Earth, Parts A/B/C 106, 37–46. https://doi.org/10.1016/j.pce.2018.05.001.

Telahigue, F., Mejri, H., Mansouri, B., Souid, F., Agoubi, B., Chahlaoui, A., Kharroubi, A., 2020. Assessing seawater intrusion in arid and semi-arid Mediterranean coastal aquifers using geochemical approaches. Phys. Chem. Earth, Parts A/B/C 115, 102811. https://doi.org/10.1016/j.pce.2019.102811.

Terzić, J., Šumanovac, F., Buljan, R., 2007. An assessment of hydrogeological parameters on the karstic island of Dugi Otok, Croatia. J. Hydrol. 343, 29–42. https://doi.org/10.1016/j.jhydrol.2007.06.008.

Tramblay, Y., Llasat, M.C., Randin, C., Coppola, E., 2020. Climate change impacts on water resources in the Mediterranean. Reg. Environ. Change 20, 83. https://doi.org/10.1007/s10113-020-01665-y s10113-020-01665-y.

Tziritis, E., Arampatzis, G., Hatzigiannakis, E., Panoras, G., Panoras, A., Panagopoulos, A., 2016. Quality characteristics and hydrogeochemistry of irrigation waters from three major olive groves in Greece. Desalination Water Treat. 57, 11582–11591. https://doi.org/10.1080/19443994.2015.1057869.

Vallejos, A., Díaz-Puga, M.A., Sola, F., Daniele, L., Pulido-Bosch, A., 2015. Using ion and isotope characterization to delimitate a hydrogeological macrosystem. Sierra de Gádor (SE, Spain). J. Geochem. Explor. 155, 14–25. https://doi.org/10.1016/j.gexplo.2015.03.006.

Van der Weijden, C.H., Pacheco, F.A.L., 2006. Hydrogeochemistry in the vouga river basin (central Portugal): pollution and chemical weathering. Appl. Geochem. 21, 580–613. https://doi.org/10.1016/j.apgeochem.2005.12.006.

Varol, S., Şekerci, M., 2018. Hydrogeochemistry, water quality and health risk assessment of water resources contaminated by agricultural activities in Korkuteli (Antalya, Turkey) district center. J Water Health wh2018003. https://doi.org/10.2166/wh.2018.003.

Vlachogianni, T., Vogrin, M., Scoullos, M., 2012. Biodiversity in the Mediterranean Region.

Voutsis, N., Kelepertzis, E., Tziritis, E., Kelepertsis, A., 2015. Assessing the hydrogeochemistry of groundwaters in ophiolite areas of Euboea Island, Greece, using multivariate statistical methods. J. Geochem. Explor. 159, 79–92. https://doi.org/10.1016/j.gexplo.2015.08.007.

Ward, J.H., 1963. Hierarchical grouping to optimize an objective function. J. Am. Stat. Assoc. 58, 236–244. https://doi.org/10.1080/01621459.1963.10500845.

Weil, R.R., Weismiller, R.A., Turner, R.S., 1990. Nitrate contamination of groundwater under irrigated coastal plain soils. J. Environ. Qual. 19, 441–448. https://doi.org/10.2134/jeq1990.00472425001900030015x.

Who, 2017. Guidelines for Drinking-Water Quality: First Addendum to the Fourth Edition.

Youssef, L., Younes, G., Kouzayha, A., Jaber, F., 2015. Occurrence and levels of pesticides in South Lebanon water. Chem. Speciat. Bioavailab. 27, 62–70. https://doi.org/10.1080/09542299.2015.1023092.

Zghibi, A., Merzougui, A., Zouhri, L., Tarhouni, J., 2014. Understanding groundwater chemistry using multivariate statistics techniques to the study of contamination in the Korba unconfined aquifer system of Cap-Bon (North-east of Tunisia). J. Afr. Earth Sci. 89, 1–15. https://doi.org/10.1016/j.jafrearsci.2013.09.004.

Zhang, Q., Li, Z., Zeng, G., Li, J., Fang, Y., Yuan, Q., Wang, Y., Ye, F., 2008. Assessment of surface water quality using multivariate statistical techniques in red soil hilly region: a case study of Xiangjiang watershed, China. Environ. Monit. Assess. 152, 123. https://doi.org/10.1007/s10661-008-0301-y.