Cotutelle Thesis

To obtain the PhD degree issued by

University of Lille

&

Lebanese University

Specialty: Earth and environmental sciences

Presented and defended publicly by

Rachad AL HAJ

17 December 2021

Hydrogeochemical study of Abu Ali watershed's groundwater (Lebanon)

Jury Members

President:	Dr. Moumen BAROUDI (Lebanese University, Tripoli, Lebanon)
Rapporteurs :	Dr. Chadi ABDALLAH (CNRS, Beirut, Lebanon)
	Dr. Julien DELOFFRE (University of Rouen, Rouen, France)
Examiners :	Dr. Fréderic BARREZ (Paris Water, Paris, France)
	Dr. Ulrich MASCHKE (CNRS – University of Lille, Lille, France)
Supervisors :	Dr. Baghdad OUDDANE (University of Lille, Lille, France)
	Dr. Jalal HALWANI (Lebanese University, Tripoli, Lebanon)
Co-Supervisor :	Dr. Mohammad MERHEB (Lebanese University, Tripoli, Lebanon)
Invited Doctors :	Dr. Sopheak NET (University of Lille, Lille, France)

Thèse en cotutelle

Pour obtenir le diplôme de doctorat délivré par

L'Université de Lille

Et

L'Université Libanaise

Spécialité : Sciences de la terre et de l'environnement

Ecole doctorale : Sciences de la Matière du Rayonnement et de l'Environnement - N°104

Présentée et soutenue publiquement par

Rachad AL HAJ

17 décembre 2021

Etude hydrogéochimique des eaux souterraines du bassin versant de la rivière Abou Ali (Liban)

Membres du jury

Président : Dr. Moumen BAROUDI (Université Libanaise, Tripoli, Liban)

Rapporteurs : Dr. Chadi ABDALLAH (CNRS, Beyrouth, Liban)

Dr. Julien DELOFFRE (Université de Rouen, Rouen, France)

Examinateurs : Dr. Fréderic BARREZ (Eau de Paris, Paris, France)

Dr. Ulrich MASCHKE (CNRS – Université de Lille, Lille, France)

Directeurs : Dr. Baghdad OUDDANE (Université de Lille, Lille, France)

Dr. Jalal HALWANI (Université Libanaise, Tripoli, Liban)

Co-encadrant : Dr. Mohammad MERHEB (Université Libanaise, Tripoli, Liban)

Docteurs invités : Dr. Sopheak NET (Université de Lille, Lille, France)

Acknowledgment

First of All, I want to express my sincere gratitude to my thesis supervisors, Pr. Jalal HALWANI and Pr. Baghdad OUDDANE, and co-supervisor Dr. Mohammad MERHEB for their guidance, patience, endless support, encouragement and immense knowledge. They welcomed me in their team and gave me all their support and time, therefore I am very grateful. I could not have dreamed of better advisors and mentors.

I would like to thank the Jury members: Dr. Chadi ABDALLAH, Dr. Julien DELOFFRE, Dr. Moumen BAROUDI, Dr. Frédéric BARREZ and Dr. Ulrich MASCHKE for giving their time and effort to evaluate my work.

Also, I am thankful to Dr. Sopheak NET for attending my defense.

A special thanks to the director of the "Ecole Doctorale en Sciences et Technologie" (EDST-UL) in Tripoli, Lebanon, Pr. Mohamad KHALIL and the director of the "Ecole Doctorale SMRE", Univeristy of Lille, France, Pr. Frédéric PAROL for their convenience.

I would also like to thank the laboratory technicians of the L.S.E.E laboratory in the Lebanese University, faculty of public health, of the Biotechnology laboratory in the EDST-UL, the Biology laboratory in the Lebanese university faculty of sciences and the laboratory LASIRE-UMR CNRS in the University of Lille, especially Ms. Nadia EID, Ms. Rayan EL CHAHAL and Ms. Souad HUSSEINI, for helping me and smoothen the workflow.

Also, I am grateful to all the members of CNF team of Tripoli in Lebanon, especially the director Dr. Imad AL KASSAA.

A massive thanks to Dr. Dalya GEREIGE for her priceless help.

I would also like to thank to the "AZM-UL" organization for providing funding this PhD Thesis.

I would also like to thank my friends, Khaled, Ezzeddine, Jowana, Ali, Adnan, Maya and Ahmad, for their endless support and encouragement throughout my life.

Finally, a warm thanks goes to my family, especially my mother, my sister and my brother, to whom I dedicate this thesis. My mother always stood by my side, even in the toughest periods of

my life, and drowned me with love unconditionally. No words can express my love to my family. I feel extremely lucky to have you in my life.

Abstract

Groundwater is an important natural resource heavily impacted by human activities which can degrade its quality. The Mediterranean basin is water stressed environment and subject to strong anthropogenic pressure. This makes groundwater the main water resource for several Mediterranean countries, including Lebanon. This thesis aims to study the hydrogeochemical characteristics of groundwater in the Abu Ali watershed, located in northern Lebanon, and to compare them with the hydrogeochemical characteristics of groundwater in the Mediterranean region. The first chapter of this thesis is a hydrogeochemical meta-analysis study of the Mediterranean region, while the second and third chapters focus on Abu Ali's watershed in order to analyze the hydrogeochemical characteristics and assess its groundwater quality.

In the first chapter, information about the studies and concentrations of major, minor ions and isotopes were taken from 123 Mediterranean hydrogeochemical studies. Then, the data was analyzed qualitatively and quantitatively. In fact, a disparity in the distribution of study topics was observed. In addition, the dominant hydrochemical facies are Ca-Cl in the Quaternary and Ca-HCO_3 in the "Jurassic and Cretaceous" and "Tertiary". In addition, the main geochemical process modifying the groundwater's chemistry is the evaporation in Quaternary and Tertiary aquifers, and rock-water interaction in Jurassic and Cretaceous aquifers. Finally, 29% and 15.3% of aquifers are polluted by nitrates and at least one of the minor ions respectively.

In the second chapter, 65 groundwater's samples were collected from Abu Ali's watershed between the wet and dry seasons of 2019 and 2020. The physicochemical parameters and concentrations of 9 major ions were measured. The data has been analyzed. The results show that Ca-HCO_3 with Ca-Mg-HCO_3 and rock-water interaction are the main hydrochemical facies and geochemical process respectively. In addition, hierarchical cluster analysis and PCAs divide samples into 5 groups affected by high sulphate concentrations, agricultural activity, low values of physicochemical parameters and major ions, reverse ions exchange and moderate chemical composition. Finally, the comparison with other studies in the Mediterranean basin indicates that Abu Ali's study does not represent any extreme value compared to the published data. In the last chapter, different indices and plots were calculated and constructed from the same 65 samples' concentrations. In addition, the concentrations of 24 minor ions were measured by ICP-OES. For domestic use, some samples have concentrations higher than the limits for TDS, nitrates, arsenic,

antimony, thallium and lead. According to RSC, Donen plot and magnesium ratios, 4, 10 and 7 samples respectively were considered inappropriate. Meanwhile, based on sodium percentages and Kelly's ratios, the majority of samples are excellent. The Wilcox diagram indicates that 13 samples, located from low to medium elevation, were considered good to acceptable. In addition, the same samples represent a high salinity risk according to the USSL diagram. Ultimately, most of the samples were considered suitable for irrigation.

Finally, this work presents a primary assessment of average hydrogeochemical characteristics of groundwater in the Mediterranean region and a baseline hydrogeochemical assessment of groundwater in Abu Ali basin. More comparative Mediterranean studies, focusing on seasonal variations and different types of aquifers are essential for advancement in the field of hydrogeochemistry. In addition, isotopic and microbiological studies of Abu Ali's groundwater are needed in order to analyze the groundwater's origin and assess the risk of Abu Ali's groundwater respectively.

Résumé

L'eau souterraine est une ressource naturelle importante fortement impactée par les activités anthropiques qui peuvent dégrader sa qualité. Le bassin méditerranéen est un environnement sous stress hydrique et soumis à une forte pression anthropique. Ce qui fait que les eaux souterraines représentent la principale ressource en eau pour plusieurs pays méditerranéens, le Liban inclut. Cette thèse vise à étudier les caractéristiques hydrogéochimiques des eaux souterraines du bassin versant de Abu Ali, situé au nord du Liban, et de les comparer avec les caractéristiques hydrogéochimiques des eaux souterraines dans la région méditerranéenne.

Par conséquent, le premier chapitre de cette thèse présente une méta-analyse hydrogéochimique de la région méditerranéenne et le deuxième et troisième chapitre se concentrent sur le bassin versant d'Abu Ali afin d'analyser les caractéristiques hydrogéochimiques et évaluer la qualité de ses eaux souterraines. Dans le premier chapitre, les études et les concentrations d'ions majeurs, mineurs et d'isotopes ont été extraites de 123 études hydrogéochimiques méditerranéennes. Ensuite, Les données ont été analysées qualitativement et quantitativement. Une disparité dans la répartition des sujets d'étude a été observer. De plus, les faciès hydrochimiques dominants sont Ca-Cl au Quaternaire et Ca-HCO_3 au « Jurassique et Crétacé » et « Tertiaire ». De plus, le principal processus géochimique modifiant l'eau souterraine est l'évaporation dans les aquifères quaternaires et tertiaires, et l'interaction roche-eau dans les aquifères jurassique et crétacé. Enfin, 29 % et 15.3% des aquifères sont pollués par les nitrates et un des ions mineurs respectivement.

Dans le deuxième chapitre, 65 échantillons d'eau souterraine d'Abu Ali ont été collectés entre les saisons humides et sèches de 2019 et 2020. Les paramètres physico-chimiques et les concentrations de 9 ions majeurs ont été mesurées. Les données ont été analysées. Les résultats montrent que Ca-HCO_3 avec Ca-Mg-HCO_3 et l'interaction roche-eau sont respectivement le principal faciès hydrochimique et le processus géochimique respectivement. De plus, l'analyse en grappes hiérarchiques et les PCA divisent les échantillons en 5 groupes affectés par des concentrations élevées de sulfate, l'activité agricole, faibles valeurs de paramètres physico-chimiques et d'ions majeurs, une réaction inverse d'échange d'ions et une composition chimique modérée respectivement. Enfin, la comparaison avec les autres études dans le bassin méditerranéen indique que l'étude d'Abu Ali ne représente aucune valeur extrême par rapport aux données publiées. Dans le dernier chapitre, différents indices et graphes ont été calculés et construits à partir

des concentrations des mêmes 65 échantillons. De plus, les concentrations de 24 ions mineurs ont été mesurées par ICP-OES. Pour l'évaluation d'usage domestique, certains échantillons ont des concentrations plus élevées que les limites en TDS, nitrates, arsenic, antimoine, thallium et plomb. Selon RSC, Donen plot et ratios de magnésium, 4, 10 et 7 échantillons respectivement ont été considérés comme inappropriés. En plus, selon les pourcentages de sodium et les ratios de Kelly, la majorité des échantillonnes sont excellents. Le diagramme de Wilcox indique que 13 échantillons, situés de basse à moyenne altitude, ont été considérés comme bons à admissibles, mais représentent un risque de salinité élevé selon le diagramme USSL. Finalement, la plupart d'échantillons ont été considérés comme appropriés pour l'irrigation.

Enfin, ce travail présente une évaluation primaire des caractéristiques hydrogéochimiques moyennes des eaux souterraines dans la région méditerranéenne et une évaluation hydrogéochimique de base des eaux souterraines dans le bassin d'Abu Ali. Des études méditerranéennes comparatives, axées sur les variations saisonnières et les différents types d'aquifères sont indispensables pour avancer les connaissances dans le domaine de l'hydrogéochimie. En plus des études isotopiques et microbiologiques concernant les eaux souterraines d'Abu Ali sont nécessaires afin d’analyser respectivement l’origine et le risque de l’usage des eaux souterraines d'Abu Ali.

Extended Abstract

World widely, the groundwater is an important natural resource, where several pollutants decreasing its quantity or quality. In fact, The Mediterranean region is a water-stressed environment where groundwater, as main water source, is under a lot of anthropogenic pressure. And the Lebanese aquifers are no exception. In fact, they are also impacted by several pollutants. Therefore, this thesis focuses on three main objectives. The first chapter includes a meta-analysis study on the Mediterranean region, where the hydrogeochemical characteristics of the region were inspected. The second chapter focuses on Abu Ali's watershed, located north of Lebanon. The main objective of this part is to analyses the hydrogeochemical characteristics and geochemical processes affecting this understudied aquifer. The third chapter focuses on assessing Abu Ali's groundwater quality for domestic use and agricultural activities.

The first chapter aims to evaluate the baseline hydrogeochemical characteristics and water quality of groundwater in the Mediterranean 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.

Meanwhile the second chapter focuses on revealing the hydrogeochemical characteristics of Abu Ali's groundwater and compare it with the Mediterranean characteristics analyzed in the previous

chapter. Therefore, 65 groundwater samples were collected between 2019 and 2020's wet and dry seasons. The following physicochemical parameters: Temperature, pH, total dissolved solids (TDS) and electrical conductivity (EC), were measured on the field. While the concentrations of 9 major ions, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-}, and PO_4^{3-} were measured via titration, colorimetric and potentiometric methods and Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). The data was analyzed using hydrogeochemical plots and multivariate analysis. Results show that Ca-HCO_3 with Ca-Mg-HCO_3 and rock-water interaction are the main hydrochemical facies and geochemical process respectively, while carbonate weathering is the main ions' source. Moreover, the cluster analysis and PCA divide the samples into 5 groups. The first group is characterized by high sulfate concentrations and higher gypsum saturation index, while the second group holds high values of physicochemical parameters and major ions due to the excessive use of fertilizers. In addition, the third group holds low physicochemical parameters and major ions values. In fact, the majority of its samples are springs located at high altitude, which result in a lower residence period. Moreover, the fourth group holds higher reverse ions exchange. Furthermore, the fifth group holds moderate chemical composition. Finally, The Lebanese comparison indicates that Abu Ali's study holds both the lowest and highest ions concentrations, while it doesn't hold any extreme value when compared to the Mediterranean data.

The final part of Abu Ali's study focuses on the groundwater quality assessment for domestic and irrigation purposes. This part was analyzed and discussed in chapter 3. In fact, different indexes, ratios and plots were computed and constructed using the concentrations of the 65 samples extracted between 2019 and 2020. In addition, the concentrations for 24 minor ions were measured using ICP-OES. For the domestic usage quality assessment, 1, 1, 2, 8, 13 and 30 samples fall above the limits of TDS, nitrate, arsenic, antimony, thallium and lead respectively. The irrigation quality of Abu Ali's groundwater was assessed after computing the following 7 parameters: RSC, %Na, SAR, PI, total concentrations, KR and MR. According to RSC, 6.2% of the samples were considered unsuitable, due to the infiltration during wet season. Meanwhile, according to sodium percentages, only 3 samples are considered just good and not excellent. The Wilcox diagram indicates that 13 samples, located at low to mid altitude, were considered good to permissible. The same 13 samples hold high salinity hazard according to USSL diagram, while 8 and 44 samples hold low and medium level respectively. In addition, no sodium hazard was observed. According

to Doneen Plot, 10 samples were identified as unsuitable. Furthermore, all samples are safe according to Kelly's ratios. Finally, only 7 samples hold high magnesium ratio. Ultimately, most of the ions, except lead, fall below the thresholds. Meanwhile, following the 7 parameters and several plots, a high number of samples were considered suitable for irrigation.

In the end, the first chapter is a preliminary assessment of baseline hydrogeochemical characteristics of groundwater in the Mediterranean region. It only focuses on average concentrations. Comparative Mediterranean studies, focusing on the seasonal variation and different types of aquifers are indispensable in the hydrogeochemistry field. Further works are certainly needed in order to extend our knowledge on the groundwater. Meanwhile the second chapter is a hydrogeochemical study focusing on Abu Ali's aquifer. Despite that, it only take into consideration the hydrogeochemical characteristics of this basin, while a number of knowledge remains a mystery such as: the water origin, residence time, water fluxes…etc. Further isotopic studies concerning Abu Ali's groundwater is needed. Finally, the third chapter focuses on Abu Ali's groundwater quality for domestic and irrigation use. Despite analyzing a relatively big data, this study focuses only on the chemical aspect of this groundwater, therefore, microbiological studies for this aquifer are needed in order to reveal the extent of bacterial and viral contamination in Abu Ali's groundwater.

Résumé étendu

L’eau souterraine est une ressource naturelle importante fortement impactée dans les zones urbanisées où plusieurs polluants dégradent sa qualité. Le bassin méditerranéen est un environnement sous stress hydrique soumis à une forte pression anthropique où les eaux souterraines sont considérées comme la principale ressource en eau. Les aquifères libanais ne sont pas une exception, en effet, ils sont également impactés par plusieurs polluants. Par conséquent, les travaux de cette thèse visent trois objectifs principaux. Le premier chapitre comprend une étude méta-analyse, où les caractéristiques hydrogéochimiques de la région méditerranéenne ont été inspectées. Le deuxième chapitre se concentre sur le bassin versant d'Abu Ali, situé au nord du Liban. L'objectif principal de cette partie est d'analyser les caractéristiques hydrogéochimiques et les processus géochimiques affectant cet aquifère peu étudié. Le troisième chapitre comprend une évaluation de la qualité des eaux souterraines d'Abu Ali pour les usages domestiques et les activités agricoles.

Le chapitre 1 vise à évaluer les caractéristiques hydrogéochimiques et la qualité des eaux souterraines méditerranéenne. Pour cette raison, 123 études hydrogéochimiques menées dans la zone ont été examinées. Les informations concernant les études et les concentrations d'ions majeurs, mineurs et d'isotopes ont été extraites. Les données ont été divisées en 3 grands types d'aquifères : Quaternaire, Jurassique et Crétacé et Tertiaire. Les données ont été analysées qualitativement pour identifier les principaux sujets de recherche et quantitativement en utilisant des méthodes hydrogéochimiques classiques avec une analyse multivariée. Les résultats montrent une disparité dans la répartition des sujets d'étude à travers la région, les études sur les ions mineurs et les isotopes étant principalement concentrées en Europe. De plus, les faciès hydrochimiques dominants sont Ca-Cl et Na-Cl au Quaternaire, Ca-HCO_3 et mixtes au Jurassique et Crétacé et Ca-HCO_3 domine les aquifères tertiaires. De plus, le principal processus géochimique modifiant l'eau souterraine est l'évaporation dans les aquifères quaternaires et tertiaires, alors que l'interaction roche-eau est le principal processus dans les aquifères jurassique et crétacé. Enfin, la pollution par les nitrates se retrouve dans 29 % des aquifères tandis que 15.3 % des aquifères contenant au moins une concentration d’ions mineurs élevées. La majorité des aquifères présentant des problèmes de pollution sont Quaternaire. En effet, ces aquifères sont fortement affectés par l'impact anthropique et l'intrusion d'eau de mer. Enfin, ce travail est une évaluation préliminaire des caractéristiques des

eaux souterraines dans la région. Des travaux supplémentaires sont nécessaires pour étudier des aspects spécifiques de l'hydrogéochimie des eaux souterraines des aquifères de la région méditerranéenne.

Le deuxième chapitre est consacré à l'analyse des caractéristiques hydrogéochimiques des eaux souterraines d'Abu Ali, et de les comparer avec les caractéristiques méditerranéennes analysées dans le chapitre précédent. Ainsi, 65 échantillons d'eau souterraine ont été collectés entre les saisons humides et sèches de 2019 et 2020. Les paramètres physico-chimiques suivants : température, pH, teneur totale en matières dissoutes (TDS) et conductivité électrique (EC), ont été mesurés sur le terrain. Alors que les concentrations de 9 ions majeurs, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-} et PO_4^{3-} ont été mesurées par titrage, méthodes colorimétriques et potentiométriques et spectroscopie d'émission optique de plasma à couplage inductif (ICP -OES). Les données ont été analysées à l'aide de tracés hydrogéochimiques et d'une analyse multivariée. Les résultats montrent que Ca-HCO_3 avec Ca-Mg-HCO_3 et l'interaction roche-eau sont respectivement le principal faciès hydrochimique et le processus géochimique, tandis que l'altération carbonatée est la principale source d'ions. De plus, l'analyse en grappes hiérarchiques et les PCA divisent les échantillons en 5 groupes. Le premier groupe est caractérisé par des concentrations élevées de sulfate et un indice de saturation en gypse plus élevé, tandis que le second groupe représente des valeurs élevées des paramètres physico-chimiques et d'ions majeurs en raison de l'utilisation excessive d'engrais dans l'agriculture. De plus, le troisième groupe représente de faibles valeurs de paramètres physico-chimiques et d'ions majeurs. En effet, la majorité de ses échantillons sont des sources situées à haute altitude, ce qui ramène la période de résidence au plus court. De plus, le quatrième groupe a été affecté par une réaction inverse d'échange d'ions plus élevé. Le cinquième groupe a une composition chimique modérée. Enfin, la comparaison avec les autres études dans le bassin méditerranéen indique que l'étude d'Abu Ali représente les concentrations les plus faibles de certains ions et les plus élevées d'autres ions, alors qu'elle ne représente aucune valeur extrême par rapport aux données publiées.

La dernière partie de l'étude d'Abu Ali porte sur l'évaluation de la qualité des eaux souterraines et l'impact d'usages domestiques et agricole. Cette partie a été analysée et discutée au chapitre 3. En effet, différents indices, ratios et graphes ont été calculés et construits à partir des concentrations des mêmes 65 échantillons prélevés entre 2019 et 2020. De plus, les concentrations de 24 ions

mineurs ont été mesurées par ICP-OES. Pour l'évaluation d'usage domestique, 1, 1, 2, 8, 13 et 30 échantillons ont des concentrations plus élevées que les limites en TDS, nitrates, arsenic, antimoine, thallium et plomb respectivement. La qualité des eaux souterraines d'Abu Ali a été évaluée après avoir calculé les 7 paramètres suivants : RSC, %Na, SAR, PI, concentrations totales, KR et MR. Selon RSC, 6.2% des échantillons ont été considérés comme inappropriés, en raison de l'infiltration pendant la saison des pluies. Pendant ce temps, selon les pourcentages de sodium, seuls 3 échantillons sont considérés comme juste bons et pas excellents. Le diagramme de Wilcox indique que 13 échantillons, situés de basse à moyenne altitude, ont été considérés comme bons à admissibles. Les mêmes 13 échantillons ont un risque de salinité élevé selon le diagramme USSL, tandis que 8 et 44 échantillons ont respectivement un niveau faible et moyen. De plus, aucun danger lié au sodium n'a été observé. Selon Doneen Plot, 10 échantillons ont été identifiés comme inappropriés. De plus, tous les échantillons sont appropriables pour l'irrigation selon les ratios de Kelly. Enfin, seuls 7 échantillons ont un taux de magnésium élevé. Finalement, la plupart des concentrations d'ions, excepte les concentrations du plomb, sont au-dessous des seuils. Pendant ce temps, suivant les 7 paramètres et plusieurs graphes, un grand nombre d'échantillons ont été considérés comme appropriés pour l'irrigation.

Enfin, le dernier chapitre est une évaluation préliminaire des caractéristiques hydrogéochimiques de base des eaux souterraines dans la région méditerranéenne. Il analyse uniquement les concentrations moyennes. Des études méditerranéennes comparatives, axées sur les variations saisonnières et les différents types d'aquifères sont indispensables dans le domaine de l'hydrogéochimie. Des travaux supplémentaires sont certainement nécessaires afin d'étendre nos connaissances sur les eaux souterraines. En plus, le troisième chapitre est une étude hydrogéochimique axée sur l'aquifère d'Abu Ali. Malgré cela, il ne prend en considération que les caractéristiques hydrogéochimiques de ce bassin, alors qu'un certain nombre de connaissances restent un mystère comme : l'origine de l'eau, le temps de séjour, les flux d'eau…etc. D'autres études isotopiques concernant les eaux souterraines d'Abu Ali sont nécessaires. En fin de chapitre, une analyse de la qualité des eaux souterraines d'Abu Ali pour les utilisations domestiques et agricoles a été réalisée. Malgré l'analyse d'une base de données, relativement importantes, cette étude se concentre uniquement sur l'aspect chimique des eaux souterraines, par conséquent, des

études de la contamination microbiologique et virale pour cet aquifère seront nécessaires afin d’analyser le risque de l’usage des eaux souterraines d'Abu Ali.

Abbreviations

%Na	Sodium percentage
AHC	Agglomerative hierarchical clustering
Al	Aluminium
As	Arsenic
B	Bore
Ba	Barium
Be	Beryllium
Bi	Bismuth
Br	Bromine
Ca	Calcium
CAI-1	Chloro-alkaline indices 1
CAI-2	Chloro-alkaline indices 2
Cd	Cadmium
CEPF	Critical ecosystem partnership fund
Cl^-	Chloride
CNRS	National Council for Scientific Research
Co	Cobalt
Cr	Chromium
Cu	Copper
D.L.	Dectecion limit
EC	Electrical conductivity
EPA	Environmental Protection Agency

F	Fluorine
FAO	Food and agriculture organization
Fe	Iron
GMWL	Global meteoric water line
HCO_3^-	Bicarbonate
ICP-OES	Induced Coupled Plasma – Optical Emission Spectroscopy
K	Potassium
KR	Kelly's ratio
Li	Lithium
MCS	Messinian salinity crisis
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
MR	Magnesium ratio
N.A.	Not available
N.D.	Not determined
Na	Sodium
NH_4^+	Ammonium
Ni	Nickel
NO_3^-	Nitrate
P	Phosphorus
Pb	Lead

PCA	Principal component analysis
PI	Permeability index
PO_4^{3-}	Phosphate
RSC	Residual sodium carbonate
SAR	Sodium absorption ratio
Sb	Antimony
Se	Selenium
SO_4^{2-}	Sulfate
SP	Supplementary materials
Sr	Strontium
T	Temperature
T. conc.	Total concentration of cations
TDS	Total dissolved solids
Ti	Titanium
Tl	Thallium
USSL	US salinity laboratory
V	Vanadium
WHO	World health organization
Zn	Zinc

Table of Contents

List of Figures

List of Tables

General Introduction

General Introduction

Water is, without a doubt, one of the most important natural resources on our planet. However, several natural and anthropogenic factors are affecting the quantity or quality of this valuable resource. In fact, the huge population growth and the increasing needs for water to cover some activities such as agriculture (Bhat et al., 2018), cause the emergence of many problems threatening this valuable resource. For instance, climate change (Kløve et al., 2014), pollution (Mekonnen & Hoekstra, 2018) and seawater intrusion in coastal aquifers (Bear et al., 1999) put pressure on both the quantity and quality of water worldwide (Das et al., 2010). Meanwhile, the usage of fertilizers, pesticides, and other chemical compounds during the agricultural practices affect its quality (Nag & Lahiri, 2012; Singh et al., 2020).

I. Groundwater in the Mediterranean region

The Mediterranean region is characterized by high temporal and spatial variability of water resources availability; which makes it a fragile natural resource (Iglesias et al., 2007). This is mainly due to the high inter and intra-annual variability of rainfall with long dry summer, 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). This has led to overexploitation of groundwater especially in densely populated coastal areas where seawater intrusion is considered as real concern (Daniele et al., 2013; Korfali & Jurdi, 2007; Tziritis et al., 2016), while seawater intrusion already affects several coastal aquifers (Alcalá & Custodio, 2008; Cary et al., 2014; Dazy et al., 1997; Mongelli et al., 2013). In addition to sea water intrusion, many aquifers around the Mediterranean are polluted (Fernandes et al., 2006; Giménez Forcada & Morell Evangelista, 2008;

Manno et al., 2007; Merhabi et al., 2021), which put even more pressure on an already vulnerable resource. The intensive industrial activities, services and tourism of the developed countries could be the culprits leading to this problem (Daniele et al., 2013). Moreover, 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). 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). In fact, the Mediterranean studies are quite abundant. However, 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).

II. Groundwater in Lebanon

Like many other Mediterranean countries, groundwater in Lebanon is the main water source. The water authorities exploit many springs and public wells and many more illegal wells spread out all across the Lebanese territory, leading to a dramatic decrease in groundwater levels in the majority of the Lebanese aquifers (MoEW, 2014). In fact, this overexploitation affected by the population growth and hastened by the civil war between 1975 and 1992 (Acra & Ayoub, 2001) led to seawater intrusion (Halwani et al., 2001; Kalaoun et al., 2018; Samad et al., 2017) in many coastal areas. In addition, the groundwater in Lebanon faces many challenges. Indeed, climate change (Saadeh et al., 2012) and water pollution (Assaf & Saadeh, 2008; Bakalowicz, 2015; Fan et al., 2010; Koeniger et al., 2016) due to the presence of sewers and uncontrolled septic tanks, the existence of untreated household waste (M. A. Massoud et al., 2006) and the intensive agricultural and domestic activities putting more and more strain on this valuable resource, inducing a quality problem and leading to scarcity in these resources (Baroudi et al., 2012). Furthermore, in urban areas, wastewater intrusion or sewer pipes crossing could be a source of groundwater contamination (Kjellen, 2000; Korfali & Jurdi, 2007; Saghir et al., 2000). All these challenges make hydrogeochemical studies a hot topic of research in the Mediterranean (Mongelli et al., 2019; Voutsis et al., 2015) in general and in Lebanon in particular.

Despite all these above-mentioned problems, groundwater hydrogeochemical studies in Lebanon remain scarce. In addition, many anthropogenic pollutants affect the groundwater. As a result, besides the hydrogeochemical studies, the quality assessment studies became an important tool. This type of studies increases the knowledge concerning the safeness of aquifers' groundwater usage in domestic and agricultural practices. In fact, the Lebanese study of this Thesis focuses on the hydrogeochemical characteristics and water quality assessment of Abu Ali's basin. This understudied watershed is located east and southeast of Tripoli in the Lebanese North Governorate. It covers a total area of approximately 489 Km2 and reach an elevation of 3038 m, which is the highest elevation in Lebanon.

III. Thesis structure

This PhD thesis includes a general introduction, 3 chapters, general conclusion and perspectives:

1. First, a general introduction focusing on the Mediterranean and Lebanese groundwater.

2. The first chapter is a meta-analysis study. This work focuses on giving an overview of the Mediterranean groundwater hydrogeochemical characteristics. For this purpose, 123 studies undertaken from various countries across the Mediterranean, were analyzed. This part aim to tackle several aspects. For instance, the main concerns that drive hydrogeochemical studies in the region were discussed. In addition, the general hydrogeochemical characteristics of groundwater and geochemical processes affecting the Mediterranean resources were revealed. Then, the extent of nitrate and minor ions pollution in the Mediterranean was inspected. Finally, the stables isotopes studies were mentioned briefly in the chapter (Submitted to Hydrogeology Journal).

3. The second chapter focuses on the under-studied groundwater of Abu Ali watershed, located in northern Lebanon. The main objective of this part is to reveal the hydrogeochemical characteristics of Abu Ali's groundwater and compare it to the hydrogeochemical characteristics of the Lebanese and Mediterranean aquifers observed in the first chapter (Submitted to Groundwater Journal).

4. The third chapter focuses on assessing Abu Ali's groundwater quality, in order to inspect its viability in domestic and agricultural practices, since several villages use its groundwater in their both activities (In Preparation).

5. The final part represents a general conclusion enfolding the whole thesis.

Chapter 1: Hydrogeochemical characteristics of groundwater in the Mediterranean region: a meta-analysis

Chapter 1: Hydrogeochemical characteristics of groundwater in the Mediterranean region: a meta-analysis

Rachad AL HAJ[1,2], Mohammad MERHEB[1,3*], Jalal HALWANI[1], Baghdad OUDDANE[2]

[1]Lebanese University, Water & Environment Science Lab, PHF 3, Tripoli, Lebanon

[2]Université de Lille, LASIRE-UMR CNRS 8516, 59655 Villeneuve d'Ascq cedex, France

[3]Lebanese University, Faculty of Sciences 3, Campus Mont Michel, 1352, Ras Maska, El Koura, Lebanon

Rachad AL HAJ: https://orcid.org/0000-0002-4977-6876, mail: rachad.haj_1994@hotmail.com

Mohammad MERHEB: https://orcid.org/0000-0003-0233-9334, email: mohammad.merheb.1@ul.edu.lb

Jalal HALWANI: https://orcid.org/0000-0001-9049-2309, email: jhalwani@ul.edu.lb

Baghdad OUDDANE: https://orcid.org/0000-0002-3778-9696, email: baghdad.ouddane@univ-lille.fr

*Corresponding author : Mohammad MERHEB, email: mohammad.merheb.1@ul.edu.lb

Abstract

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.

Keywords: Mediterranean, hydrogeochemistry, pollution, isotopes.

1.1 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 & 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 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 & 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 & 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. 1.1) 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 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?

1.2 The Mediterranean Region

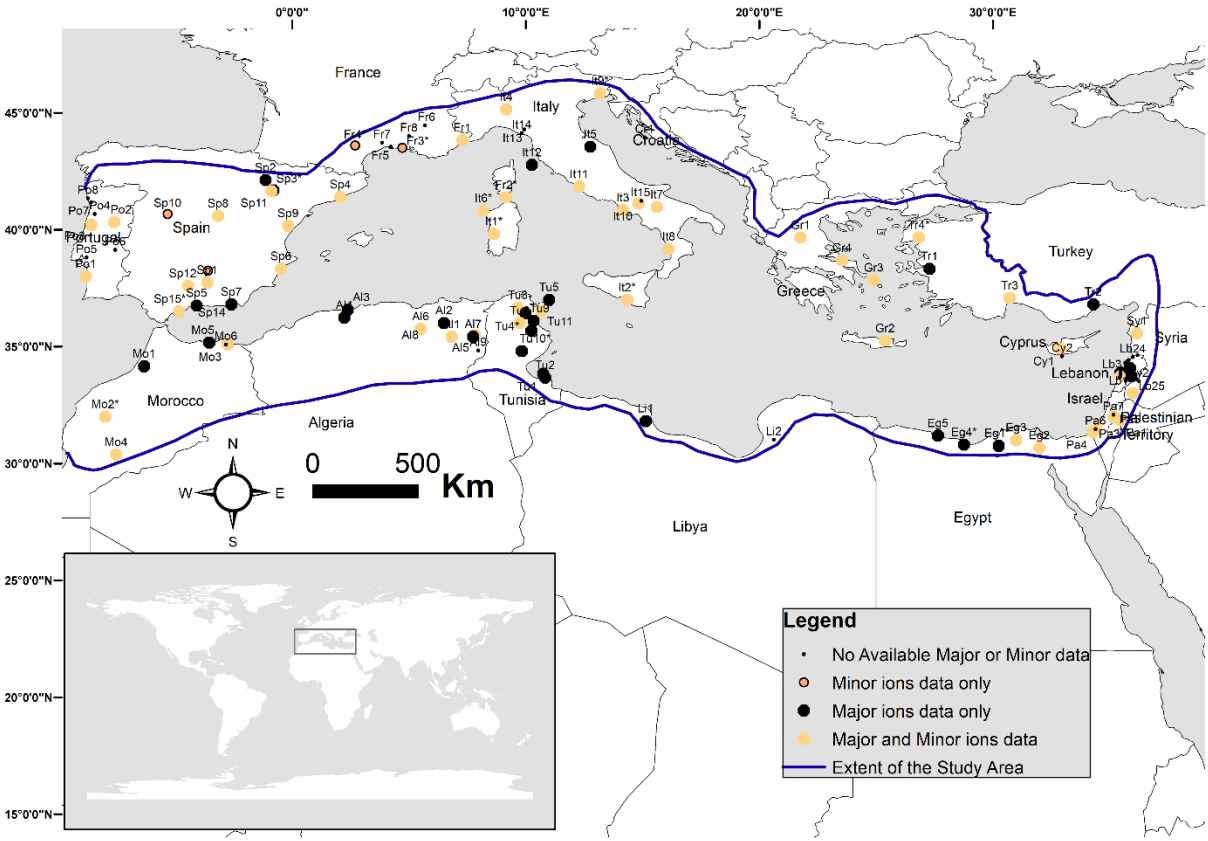


Figure 1.1 Study area extent and distribution of studied articles with the types of data contained in each study. The article labeled with an * are those with isotopes data.

1.2.1 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. 1.1.

1.2.2 Physical characteristics

The Mediterranean Sea occupy a surface equal to 2.5 million km² approximately, with a coastal area covering almost 1.5 million km² (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).

1.2.3 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 plate movement (Moores & 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).

1.3 Materials and Methods

1.3.1 Description of the dataset

The collected data was extracted from 123 articles conducted from 2000 till 2019 (Fig. 1.1). These studies focus on the following Mediterranean countries: Algeria (9 articles), Croatia (1), Cyprus (2), Egypt (5), France (8), Greece (4), Italy (15), Lebanon (25), Libya (2), Morocco (6), Palestine (7), Portugal (8), Spain (15), Syria (2), Tunisia (10) and Turkey (4). 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. Figure 1.1 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 data is clustered in 23 European studies, while 8 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.

1.3.2 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 & 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 & 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 & 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.

1.4 Results

1.4.1 Study topics

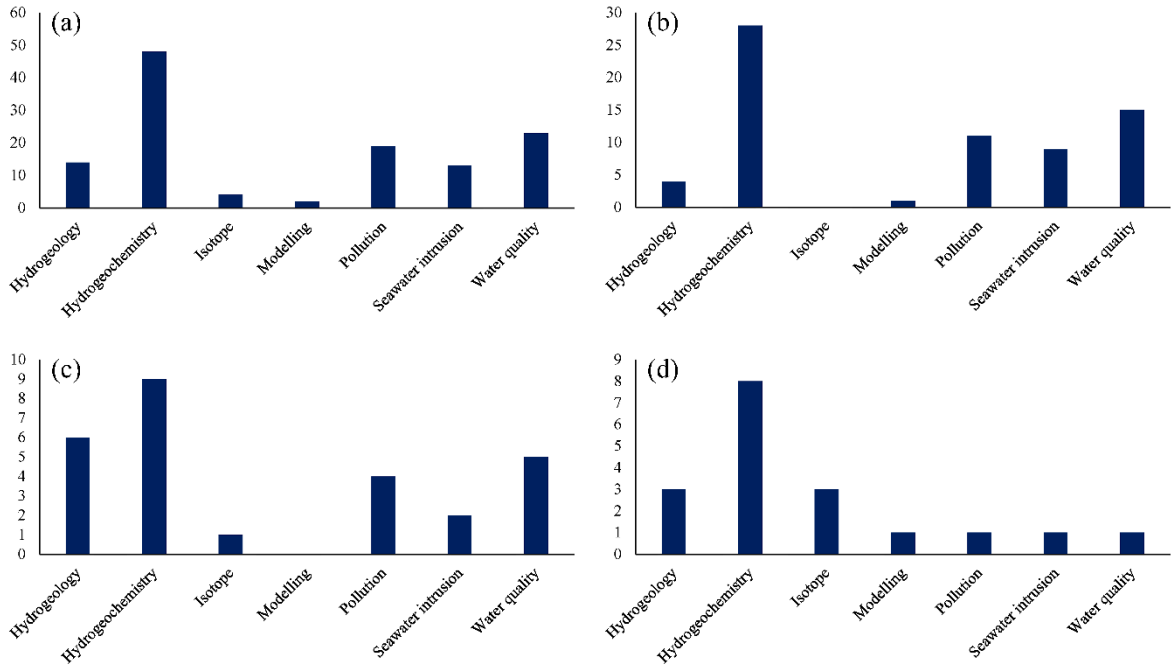


Figure 1.2 Histograms representing the number of articles focusing on the 7 main identified topics in: (**a)** all the data, (**b)** the Quaternary, (**c)** Jurassic & Cretaceous and (**d)** Tertiary data.

The studied articles were divided into 7 topics: hydrogeology, hydrogeochemistry, isotopes, modeling, pollution, seawater intrusion, and water quality. Figure 1.2 presents the distribution of articles according to the study topic for the whole dataset (Fig. 1.2a) and by aquifer types (Fig. 1.2 b, c, and d). Figure 1.2 (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. 1.2b) with 28 and 15 studies respectively, while the hydrogeochemistry and hydrogeology topics dominate the Jurassic and Cretaceous aquifers (Fig. 1.2c) 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 1.2d) 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.

1.4.2 Groundwater characteristics

1.4.2.1 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.

1.4.2.1.1 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. 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.

1.4.2.1.2 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.

1.4.2.1.3 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.

1.4.2.2 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.

1.4.2.2.1 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.

1.4.2.2.2 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.

1.4.2.2.3 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.

1.4.2.3 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.

1.4.2.3.1 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.

1.4.2.3.2 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.

1.4.2.3.3 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.

1.4.2.4 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.

1.4.2.4.1 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.

1.4.2.4.2 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.

1.4.2.4.3 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.

1.4.2.5 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.

1.4.2.5.1 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.

1.4.2.5.2 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.

1.4.2.5.3 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.

1.4.3 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. 1.3a), Jurassic and Cretaceous (Fig. 1.3b) and Tertiary (Fig. 1.3c). 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.

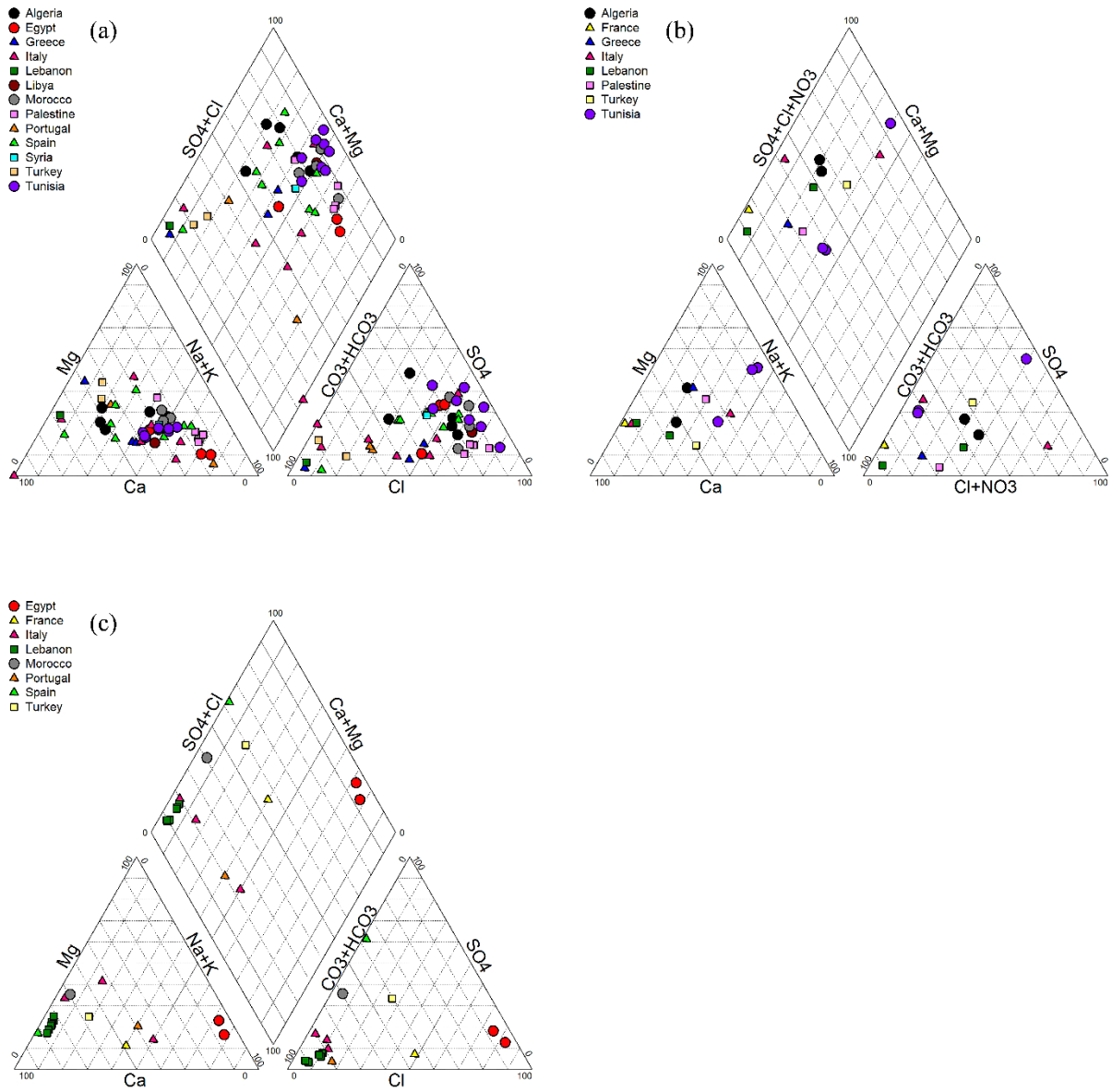


Figure 1.3 Piper diagrams representing the distribution of hydrochemical facies in the 3 types of aquifers: (a) Quaternary, (b) Jurassic & Cretaceous and (c) Tertiary.

1.4.3.1 Quaternary aquifers

The Piper diagram of Quaternary aquifers (Fig. 1.3a) 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.

1.4.3.2 Jurassic and Cretaceous aquifers

The Piper diagram of Jurassic and Cretaceous aquifers (Fig. 1.3b) 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.

1.4.3.3 Tertiary aquifers

The Piper diagram of the Tertiary aquifers (Fig. 1.3c) 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.

1.4.4 Geochemical processes

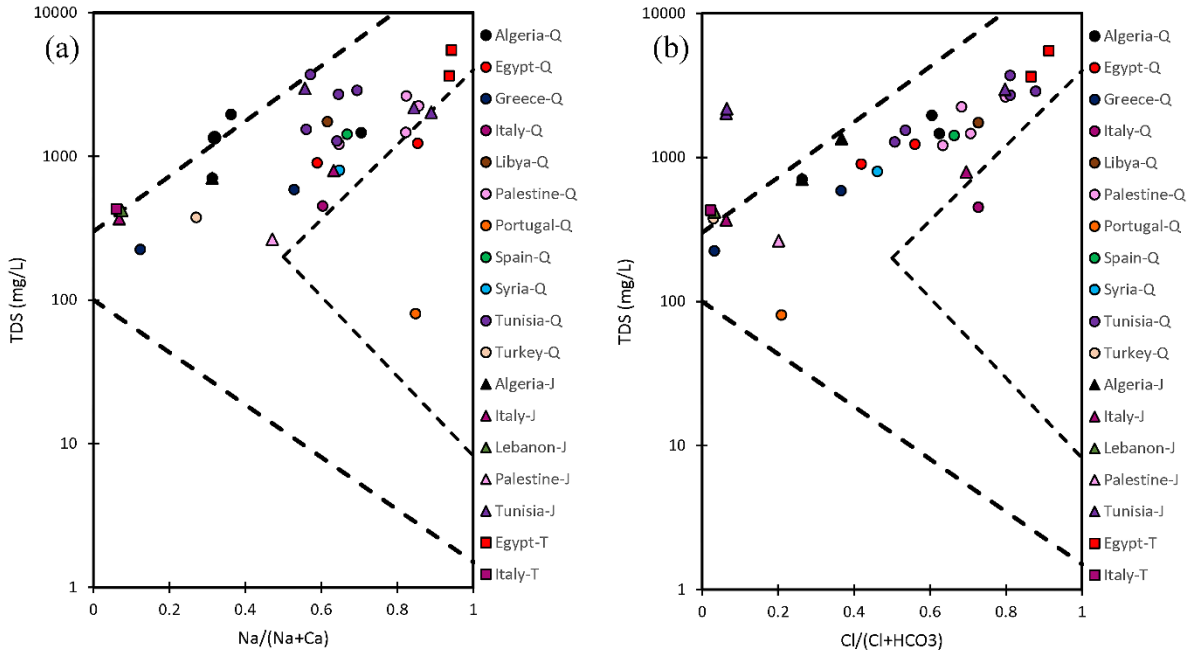
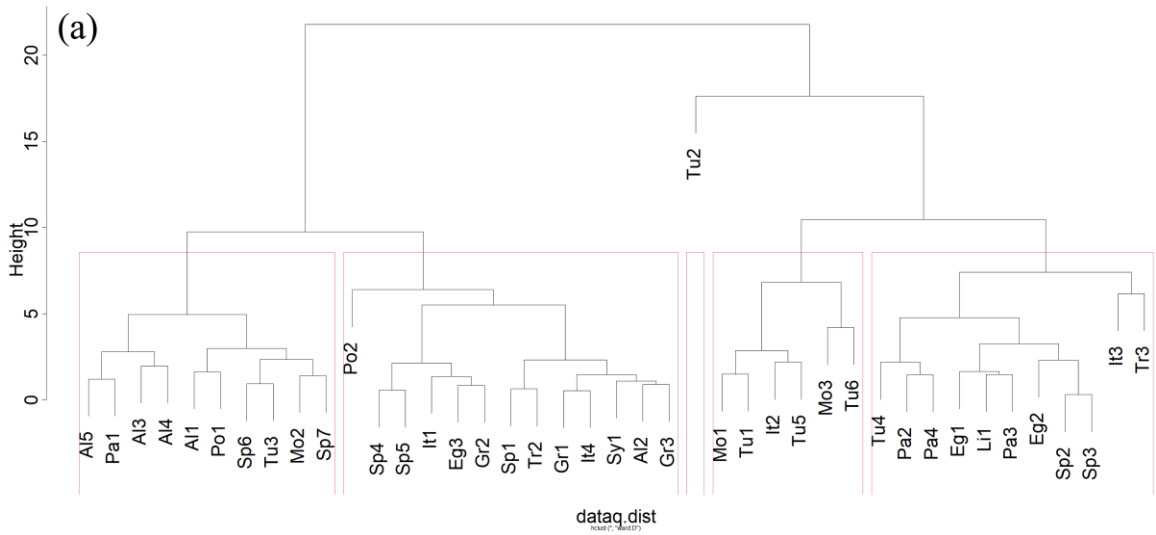


Figure 1.4 Gibbs diagrams representing; (**a**) TDS Vs $Na^+/(Na^++Ca^{2+})$ and (**b**) TDS Vs $Cl^-/(Cl^-+HCO_3^-)$

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. 1.4). Figure 1.4 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 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.

1.4.5 Multivariate analysis



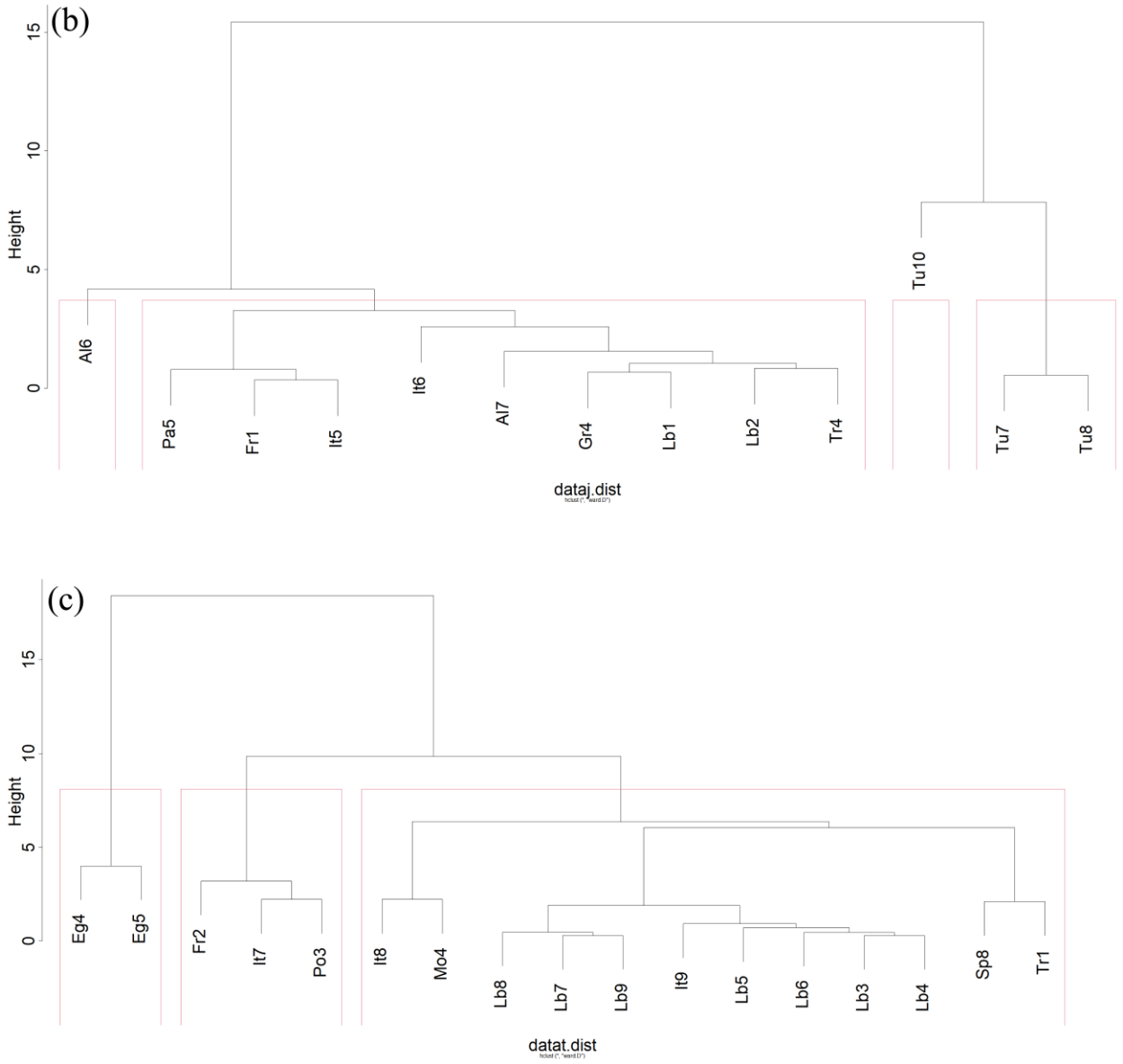


Figure 1.5 Dendrograms from hierarchical cluster analysis conducted on: (**a)** the Quaternary, (**b)** the Jurassic & Cretaceous and (**c)** the Tertiary aquifers.

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. 1.5) and 3 PCA (Fig. 1.6). 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 1.1). 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.

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

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. 1.5a). 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 & 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.

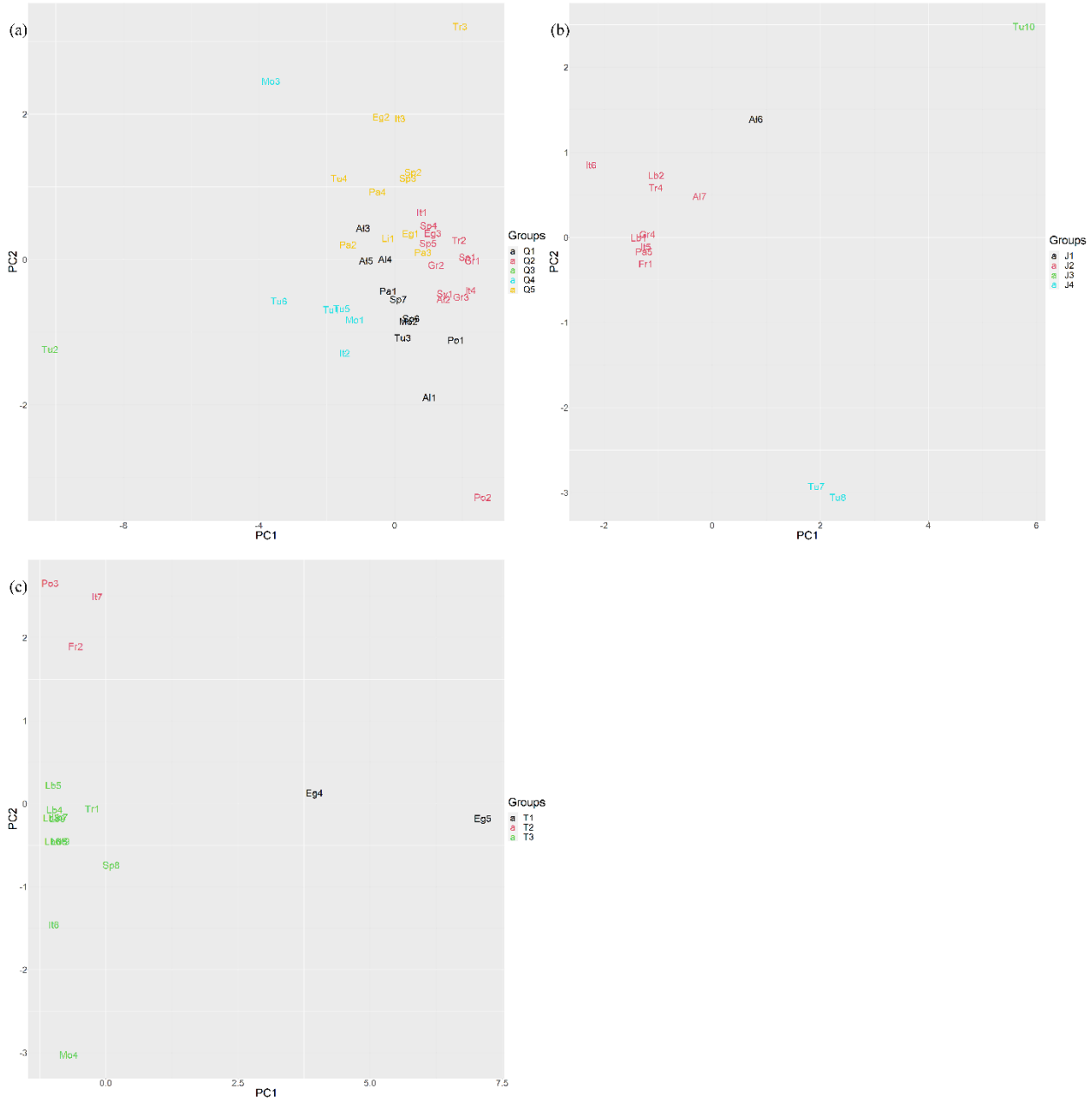


Figure 1.6 Loading plots of PC1 versus PC2: (a) the Quaternary, (b) Jurassic & Cretaceous and (c) Tertiary aquifers.

Furthermore, Q3 holds only 1 study conducted on a south eastern Tunisian zone (Telahigue et al., 2018), and has a PC2 score slightly 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. 1.5b). The group J1 represented by only one Algerian study conducted on the Ain Azel area (Belkhiri & 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 1.5c). 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.

1.5 Discussions

1.5.1 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.

1.5.2 What are the general hydrogeochemical characteristics of groundwater in the Mediterranean region?

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 18.8ºC in the Jurassic to 20.1ºC in the Tertiary with a mean value of 20ºC 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. 1.4).

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.

1.5.3 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 & Carbonell, 2007) and industrial activities (Giménez Forcada & 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. From 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). From the other hand, in order to meet the agriculture's needs, the water consumption increase dramatically in this region, leading to deplete 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 2018 Telahigue et al. proved that the evaporations process is one of the factors increasing the groundwater's salinity in the 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. in 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.

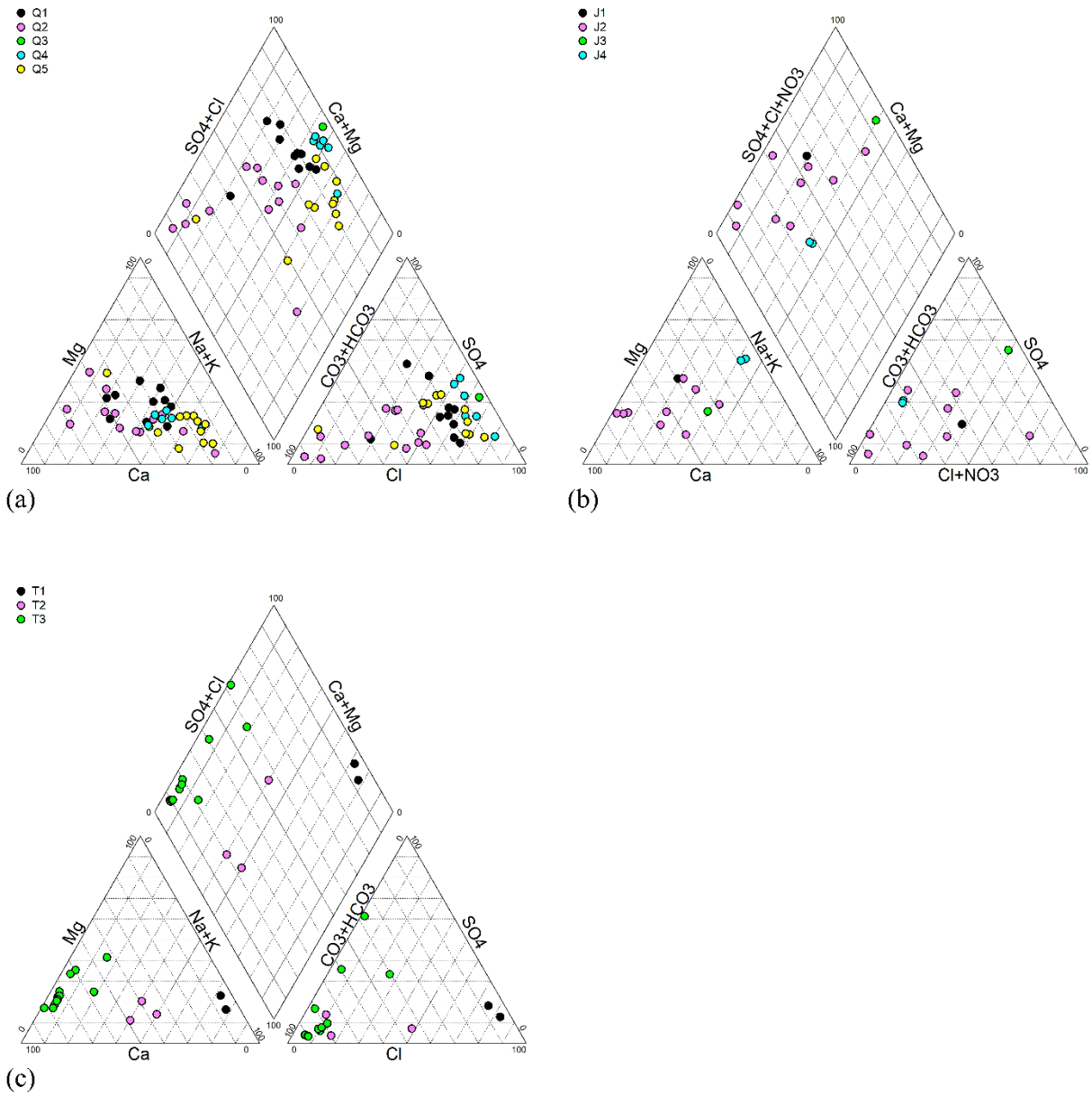


Figure 1.7 Piper diagrams representing the distribution of hydrochemical facies for the various groups identified using cluster analysis in the 3 types of aquifers: (a) Quaternary, (b) Jurassic & Cretaceous and (c) Tertiary.

To facilitate the analysis, the previously identified groups of studies using AHC were plotted on the Piper diagram. Figure 1.7 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. 1.7, a) shows that many studies belong to the Ca-HCO_3 and mixed facies while the dendrogram (Fig. 1.5,

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 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 were spotted where most of its dots fall 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 & 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, where they ensure that the groundwater quality was maintained by respecting the protection limits. Most of these studies were affected by anthropogenic impact due to agricultural activities (Da'as & Walraevens, 2013; Hamed & Dhahri, 2013; Karroum et al., 2017), domestic wastewater and leaks from septic tanks in urban areas (Bouderbala & Gharbi, 2017; Da'as & 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 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 dots falling into the Ca-Cl and Na-Cl zones (Fig. 1.3, 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 in 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. 1.7, 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 & 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. 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. 1.7, 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 & Morotti, 2003; Santoni et al., 2016), while the contamination due to fertilization and irrigation could also play an important role in other studies (Andrade & Stigter, 2011).

Ultimately, 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.

1.5.4 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) were 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. Figure 1.8 represents the studies where pollution was recorded for either nitrate or at least one minor ion.

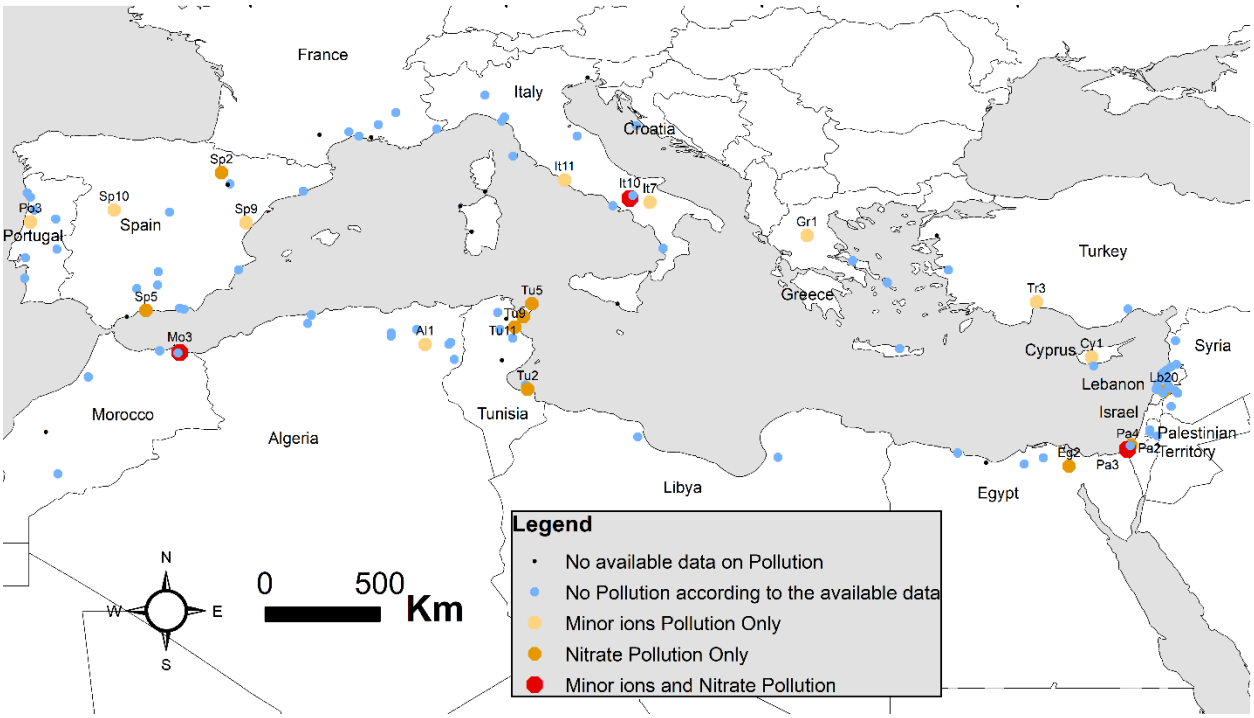


Figure 1.8 Distribution of studies with recorded Nitrate or Minor ions pollution

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 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 & 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 & 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. in 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 & Morell Evangelista in 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 following: 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 an 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 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., in 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 & 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 et al. (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 central of the country (Andrade & Stigter, 2011), while the F concentration was found in an Italian study conducted on Monte Vulture volcano (Barbieri & 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 & 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.

1.5.5 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. in 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 2014, Merchán et al. 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. in the Italian study conducted on the Arborea plain's Quaternary aquifer in 2019. 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. in 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 in 2016 concerning the Jurassic aquifer located in the Turkish Edremit-Dalyan coastal wetland, where this process only affecting the coastal zone's water. In addition, the Italian study conducted in 2008 by Cucchi et al. 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).

1.6 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 was 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. Even the minimal and maximal values belong to Quaternary aquifers. 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. 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.

Chapter 2: The hydrogeochemical characteristics of groundwater in Abu Ali watershed

Chapter 2: The hydrogeochemical characteristics of groundwater in Abu Ali watershed (Northern Lebanon)

Rachad Al Haj[1, 2, *], Mohammad Merheb[1], Jalal Halwani[1], Baghdad Ouddane[2]

1 Lebanese University, Water & Environment Science Laboratory, FSP3, Tripoli, Lebanon

2 Université de Lille, LASIRE, UMR CNRS 8516, 59655 Villeneuve d'Ascq Cedex, France.

Rachad AL HAJ: https://orcid.org/0000-0002-4977-6876, mail: rachad.haj_1994@hotmail.com

Mohammad MERHEB: https://orcid.org/0000-0003-0233-9334, email: mohammad.merheb.1@ul.edu.lb

Jalal HALWANI: https://orcid.org/0000-0001-9049-2309, email: jhalwani@ul.edu.lb

Baghdad OUDDANE: https://orcid.org/0000-0002-3778-9696, email: baghdad.ouddane@univ-lille.fr

***Corresponding Author Email:** rachad.haj_1994@hotmail.com

Abstract

This study aims to analyze the hydrogeochemical characteristics of Abu Ali's groundwater (North Lebanon) and compare it to the Lebanese and Mediterranean aquifers. Sixty-five groundwater samples were collected between 2019-2020's wet and dry seasons. The following physicochemical parameters: Temperature, pH, total dissolved solids (TDS) and electrical conductivity (EC), were measured on the field. While the concentrations of 9 major ions, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-}, and PO_4^{3-} were measured via titration, colorimetric and potentiometric methods and Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). The data was analyzed using hydrogeochemical plots and multivariate analysis. Results show that Ca-HCO_3 with Ca-Mg-HCO_3 and rock-water interaction are the main hydrochemical facies and geochemical process respectively, while carbonate weathering is the main ions' source. Moreover, the cluster analysis and PCA divide the samples into 5 groups. The first group is characterized by high sulfate concentrations and higher gypsum saturation index, while the second group holds high values of physicochemical parameters and major ions due to the excessive use of fertilizers. In addition, the third group holds low physicochemical parameters and major ions values. In fact, the majority of its samples are springs located at high altitude, which result in a lower residence period. Moreover, the fourth group holds higher reverse ions exchange. Furthermore, the fifth group holds moderate chemical composition. Finally, The Lebanese comparison indicates that Abu Ali's study holds

both the lowest and highest ions concentrations, while it doesn't hold any extreme value when compared to the Mediterranean data.

Keywords:

Hydrogeochemistry, groundwater, Lebanon, water quality, geochemical processes, carbonate weathering

2.1 Introduction

Water is, without a doubt, one of the most important natural resources on our planet. However, with the huge population growth and the increasing needs for water, many problems emerge and threaten this valuable resource. For instance, climate change (Kløve et al., 2014), pollution (Mekonnen & Hoekstra, 2018) and seawater intrusion in coastal aquifers (Bear et al., 1999) put pressure on both the quantity and quality of water worldwide (Das et al., 2010).

The Mediterranean region is no exception. In fact, this region is characterized by a highly changing environment leading toward scarcity in water; which makes it a fragile natural resource (Iglesias et al., 2007). Moreover, the Mediterranean climate is characterized by a high inter and intra-annual variability of rainfall with a long dry summer. Hence, many Mediterranean countries depend heavily on groundwater as a stable water source to satisfy all domestic and economic activities (Ergil, 2000). This has led to the overexploitation of groundwater especially in densely populated coastal areas where seawater intrusion became a common problem (Daniele et al., 2013; Korfali & Jurdi, 2007; Tziritis et al., 2016). In addition to sea water intrusion, many aquifers around the Mediterranean are polluted (Fernandes et al., 2006; Giménez Forcada & Morell Evangelista, 2008; Manno et al., 2007; Merhabi et al., 2021), which put even more pressure on an already vulnerable resource. The intensive industrial activities, services and tourism of the developed countries could be the culprits leading to this problem (Daniele et al., 2013).

Like many other Mediterranean countries, groundwater in Lebanon is the main water source. The water authorities exploit many springs and public wells and many more illegal wells spread out all across the Lebanese territory, leading to a dramatic decrease in groundwater levels in the majority of the Lebanese aquifers (MoEW, 2014). In fact, this overexploitation affected by the population growth and hastened by the civil war between 1975 and 1992 (Acra & Ayoub, 2001) led to seawater intrusion (Halwani et al., 2001; Kalaoun et al., 2018; Samad et al., 2017) in many coastal areas. In addition, the groundwater in Lebanon faces many challenges. Indeed, climate change (Saadeh et al., 2012) and water pollution (Assaf & Saadeh, 2008; Bakalowicz, 2015; Fan et al., 2010; Koeniger et al., 2016) due to the presence of sewers and uncontrolled septic tanks, the existence of untreated household waste (M. A. Massoud et al., 2006) and the intensive agricultural

and domestic activities putting more and more strain on this valuable resource, inducing a quality problem and leading to scarcity in these resources (Baroudi et al., 2012).

Despite all these above-mentioned problems, groundwater hydrogeochemical studies in Lebanon remain scarce.

One under-studied area is the Abu Ali watershed, located in northern Lebanon. Previous studies focused on surface water quality (Houri & El Jeblawi, 2007; M. Massoud et al., 2004; Merhabi et al., 2019; Saba et al., 2016), while groundwater quality and hydrogeochemistry remain unknown.

The objective of this study is to reveal the hydrogeochemical characteristics of Abu Ali basin's groundwater and to compare it to the hydrogeochemical characteristics of the Lebanese and Mediterranean aquifers.

2.2 Study area

2.2.1 Description of the study area

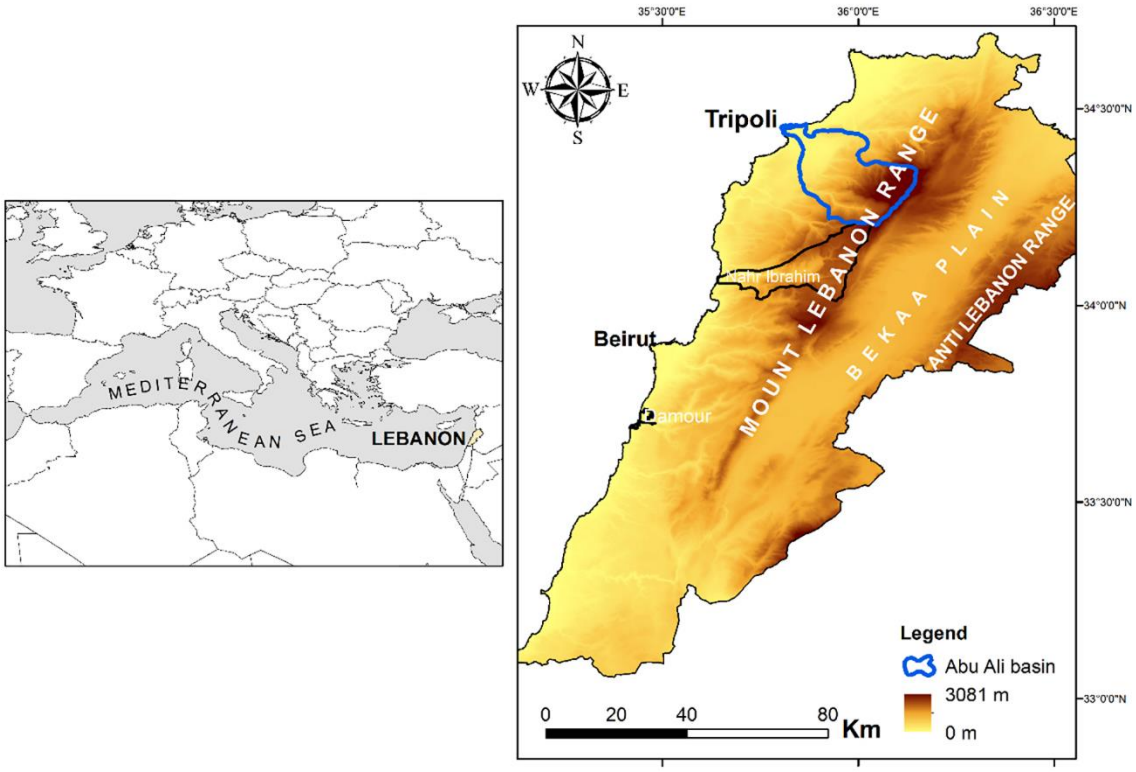


Figure 2.1 Location of Lebanon in the Mediterranean region and our study area in Lebanon.

Abu Ali watershed is located in the North Governorate of Lebanon to the east and southeast of Tripoli (Fig. 2.1). It covers a total area of approximately 489 Km^2 and reach an elevation of 3038 m, which is the highest elevation in Lebanon.

The study area has a typical Mediterranean climate with mild winters and moderately hot summers on the coast, but the increasing elevation inland result in colder winters and precipitation that is more abundant and occur mostly as snow on the highest peaks. Hence, snowmelt plays an active role as a source of water in Abu Ali watershed besides the precipitation (Merheb, 2015).

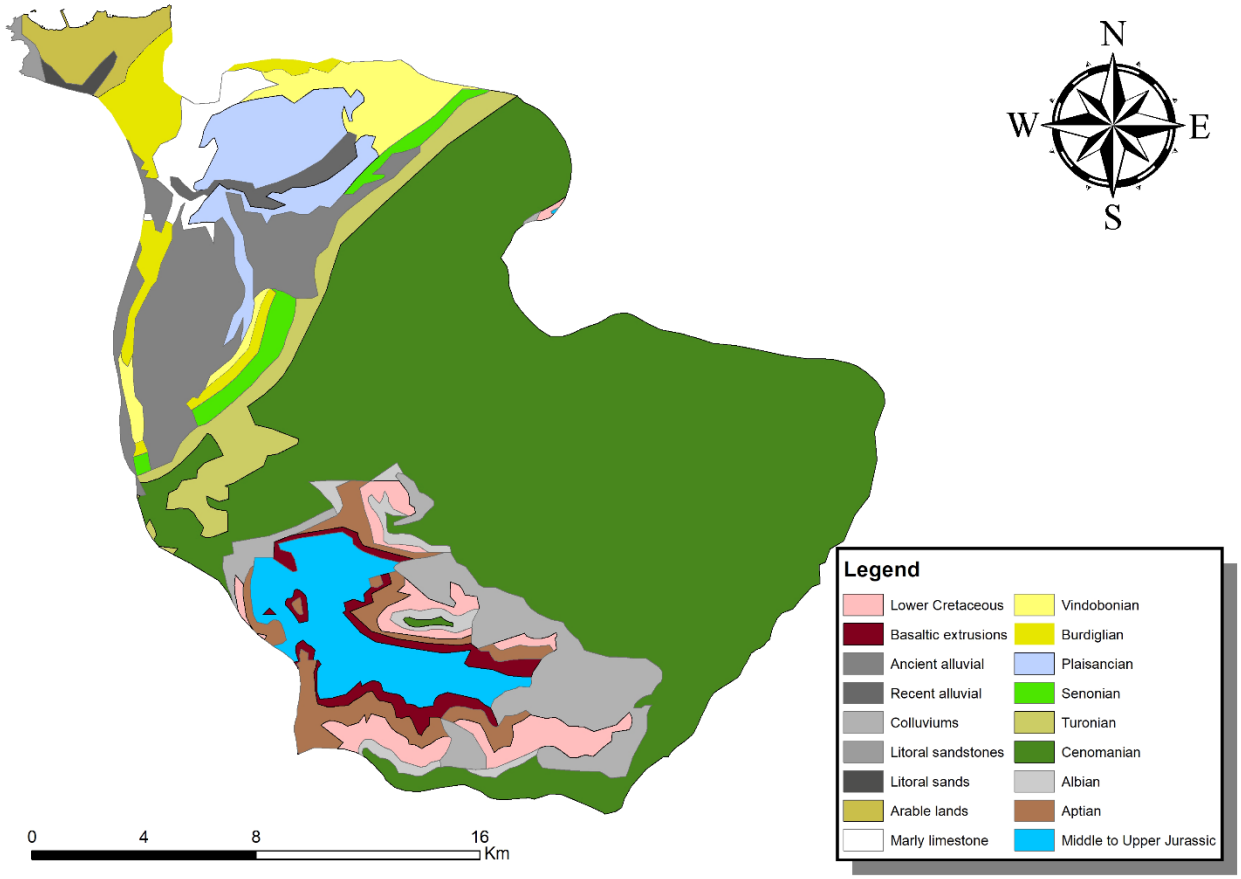


Figure 2.2 Geology of Abu Ali watershed (Dubertret L., 1955)**.**

2.2.2 Geology and hydrogeology

The outcropping stratigraphic sequence in the study area exposes rocks from the middle Jurassic to the Quaternary (Fig. 2.2). The main geological outcrops in the basin are from the Cenomanian-Turonian occupying 57% of the study area. This is also the main aquifer in the region and in the whole country; it can reach a thickness of 700 m of highly fractured and karstified limestone, dolomitic limestone and marly limestone. The second most important aquifer forming rocks in the

Abu Ali watershed are from the Miocene, it covers 11.2% of the total watershed surface area but it extends for another 16% of the study area beneath various forms of Quaternary deposits. The Miocene aquifer is made of massive limestone and has an average thickness of 200 – 250 m. The third aquifer in the basin is made of highly fractured and karstified dolomite and dolomitic limestone from the middle to upper Jurassic. These rocks can reach a thickness of 650 m. They cover around 5% of the basin area but extend for another 8% under basalt and Lower Cretaceous rocks.

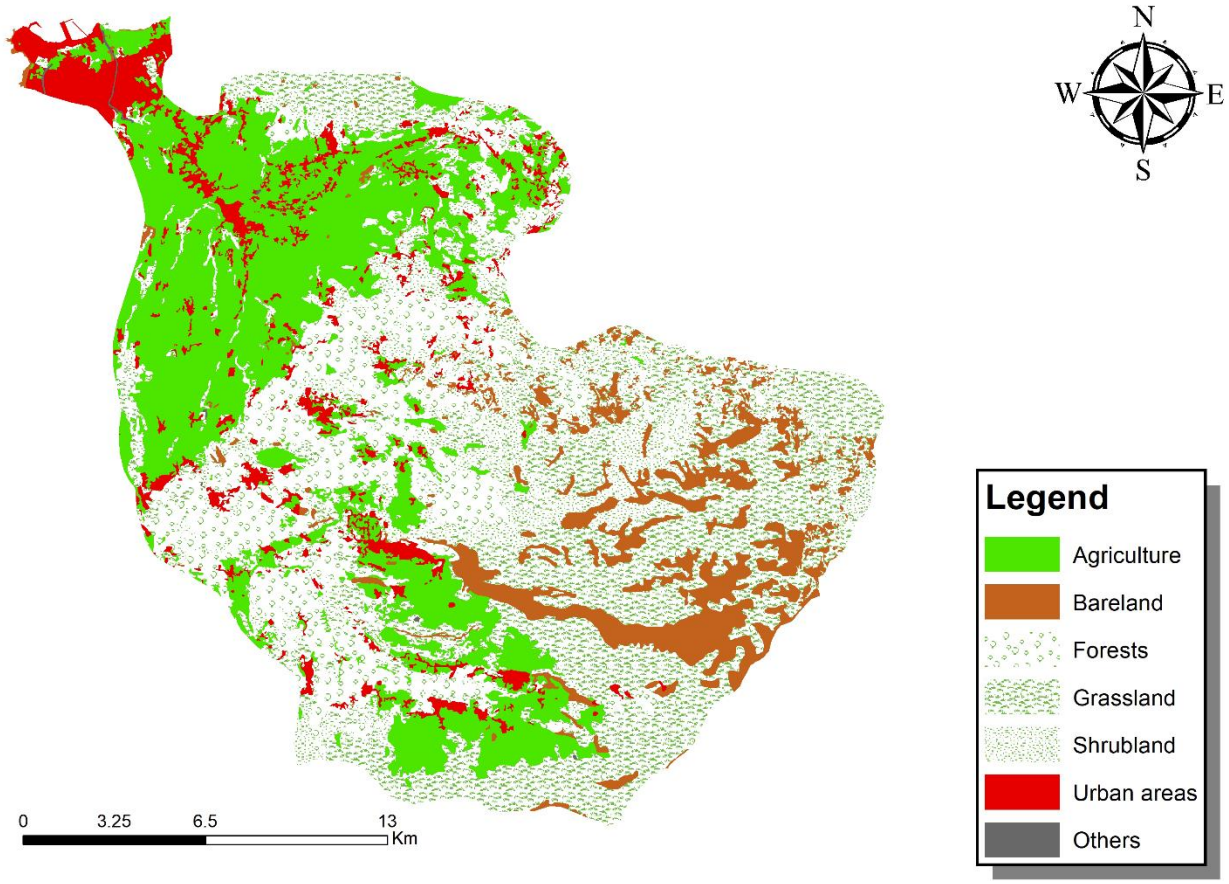


Figure 2.3 Land cover use of Abu Ali watershed (CNRS, 2010).

2.2.3 Land cover use

The land cover/use map of Abu Ali watershed (Fig. 2.3) (CNRS, 2010) shows that 6.8% of the total watershed area is made of urban areas, mainly on the coast around the city of Tripoli. Agricultural areas cover more than quarter (27.2%) of the total basin area. This highlights the importance of agriculture as a main economic activity in the region and as a main cause for groundwater exploitation and perhaps pollution. Around 65.9% of the basin area is covered by

natural areas: grassland (27.9%), forests (17.8%), shrubs (11.6%) and bare lands (8.6%). This is because more than 40 % of the Abu Ali area is above 1800 m in elevation. Such areas are usually covered with snow for more than 3 months per year and sustain no agriculture.

2.3 Materials and methods

2.3.1 Sampling

In total, sixty-five samples were collected. In fact, thirty-five samples were collected from the study area's groundwater and springs between 2019 and 2020 in the wet seasons, while thirty of them were collected again in the dry seasons of 2019 and 2020. Twenty of them were collected in May 2019 after the wet season. The same previous twenty samples were collected again after the dry season in September 2019. While other fifteen samples were collected in June 2020 after the wet season and the same sampling process was repeated after the dry season in September 2020. During these steps, temperature (T °C), pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured on the field, while 2 plastic bottles of 2 L and 500 mL in volume were filled and brought back to the laboratory for further chemical analysis.

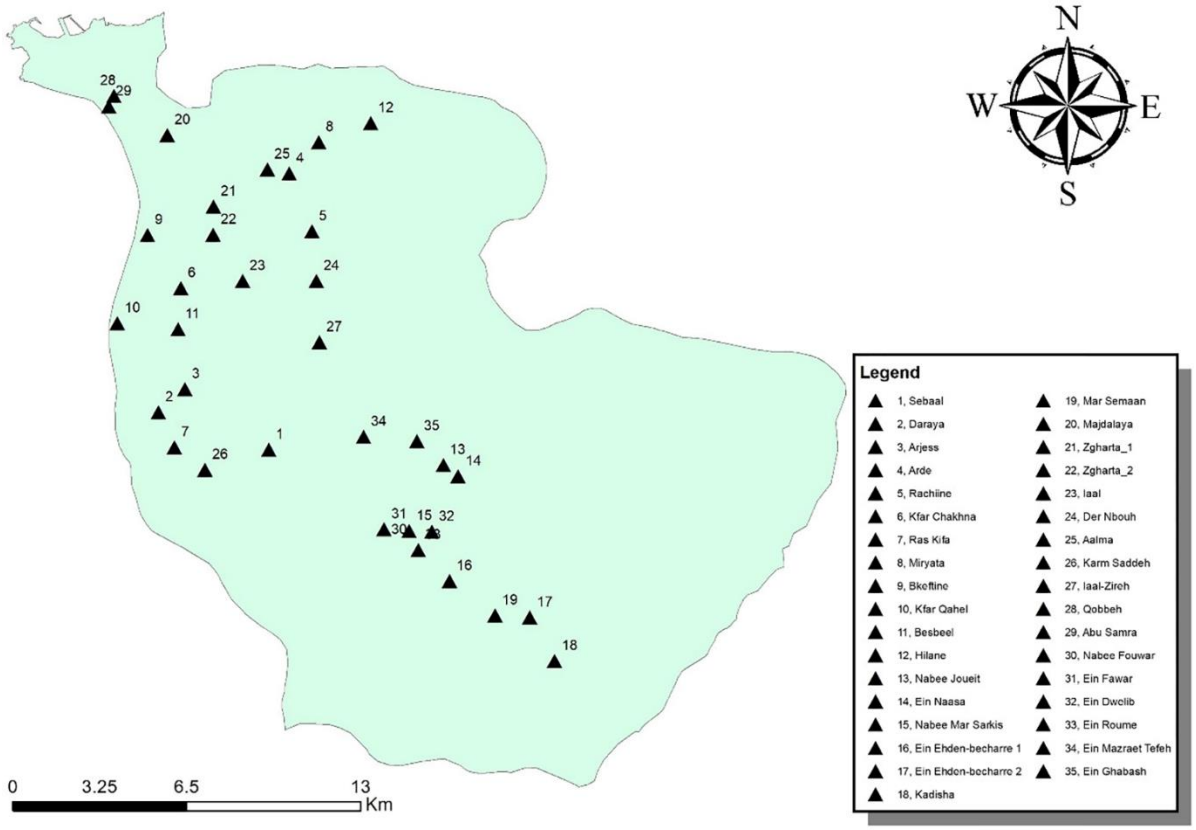


Figure 2.4 Map indicating the distribution of samples in Abu Ali's basin.

2.3.2 Laboratory work

In the laboratory, the concentrations of HCO_3^- and NO_3^- were measured via titration and colorimetric method respectively, while the concentrations of calcium, phosphate, magnesium, sulfate, sodium and potassium concentration were measured by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). The sampling date, points and coordinates, in addition to the values of physicochemical parameters and major ions was organized in a one data (Appendix 3).

2.3.3 Data analysis

In order to reveal the hydro-chemical facies, we used the Piper diagram (Piper, 1944) based on our concentrations. In fact, this diagram follows the fluctuation of major and minor ions' percentages in two different triangular plots, while the dots of the same samples were projected from the triangular parts into a central diamond-shaped part, where the different hydro-chemical facies are revealed.

Our physical and chemical parameters were analyzed via Gibbs plots (Gibbs, 1970) in order to identify the geochemical processes affecting our groundwater and its intensity. Moreover, they are represented by 2 plots: TDS vs $Na^+/(Na^++Ca^{2+})$ and TDS vs $Cl^-/(Cl^-+HCO_3^-)$ plots. In fact, the Gibbs plots indicate the main geochemical processes in shaping the groundwater chemistry. In addition, these plots focus on the following 3 different processes: evaporation, precipitation and rock-water interaction.

In addition, several scatter plots were observed in order to analyze different processes that may affect the groundwater's chemistry. For instance, the saturation index plots representing the variation of saturation index of calcite, dolomite and gypsum in function with TDS were used in order to reveal if our samples are over or under saturated. Furthermore, 4 plots representing HCO_3^- vs Ca^{2+}, HCO_3^- vs $Ca^{2+} + Mg^{2+}$, $HCO_3^- + SO_4^{2-}$ vs $Ca^{2+} + Mg^{2+}$ and SO_4^{2-} vs Ca^{2+} were used in order to unveil the weathering processes affecting the groundwater's chemistry. Moreover, in order to unveil the ions exchange reaction affecting Abu Ali's groundwater, the samples were plotted using the following two indexes: CAI-2 vs CAI-1. Finally, the evaporation process was assessed using 2 plots representing Na/Cl vs TDS and Na/Cl vs EC, while the pollution and anthropogenic impact were observed using the following 3 plot: NO_3^- vs SO_4^{2-}, SO_4^{2-} vs Cl^- and NO_3^- vs Cl^-.

2.3.4 Multivariate analysis

2.3.4.1 Hierarchical cluster analysis (HCA)

In order to observe the similarity in our data, the hierarchical cluster analysis was plotted. Using different approaches, this technic identifies the differences between samples and regroup them into several clusters based on their differences (Jiang et al., 2015). This method is considered as a classification data method and the popular one among the hydrogeochemical studies (Güler et al., 2002; Steinhorst & Williams, 1985). In fact, the dendrograms were plotted using the standardized data via RStudio software version 1.3.1093.

2.3.4.2 Principal component analysis (PCA)

In order to simplify our dataset (Cloutier et al., 2008) and reduce its dimensionality while maintaining its variability (Zhang et al., 2008) the PCA was plotted. The interesting aspect of this method is its capability in explaining the correlation between a big numbers of variables while reducing the loss in information (Shrestha & Kazama, 2007). In fact, it is designed to plot the principal components which are a whole new uncorrelated variables derived from the original ones as linear combinations (Shrestha & Kazama, 2007). Using RStudio software version 1.3.1093, the standardized data was plotted into 2 plots representing PC2 vs PC1 of the wet and dry samples. These samples were distributed based on the dendrograms groups, while the correlations between the 5 first PCs and the values of major ions and physicochemical parameters were measured using the same software.

2.3.5 Comparison with Lebanon and the Mediterranean data

On one hand, in order to observe the situation of Abu Ali's groundwater in Lebanon, 4 previous Lebanese studies' data were extracted and compared with this study. These 4 studies were conducted on the Bekaa (Awad, 2011), Anti-Lebanon (El Hakim, 2005), Nahr Ibrahim (Hanna et al., 2018) and Damour coastal aquifer (Khadra & Stuyfzand, 2014). In fact, the collected data includes the following 9 major ions and 4 physicochemical parameters: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, PO_4^{3-}, NO_3^{-}, T, pH, TDS and EC.

On the other hand, the Mediterranean comparison includes 32 studies, distributed equally between the "Jurassic & Cretaceous" and "Tertiary" aquifers. This data was collected in order to put into

perspective the situation of Abu Ali basin in comparison with the Mediterranean region (Al Haj et al., 2021). In fact, Abu Ali samples were distributed between the following 4 groups: Jurassic & Cretaceous wet, Jurassic & Cretaceous dry, Tertiary wet and Tertiary dry samples, based on their aquifer nature and seasons. In the following step we measured the mean of each group in order to compare them with other studies and analyze them via Piper diagrams and Gibbs plots. In fact, 7 major ions' concentrations were collected from the Mediterranean studies and the mean were calculated in order to compare the data, this group includes the following ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-}.

2.4 Results and discussion

2.4.1 General hydrogeochemistry

Firstly, the physicochemical data was analyzed. The temperature data vary between 9°C and 25°C in wet season, while its values range from 8°C to 29°C in the dry one, where the higher values belong to the dry season in comparison with the wet one with means equal to 19°C and 17°C respectively. In addition, the elevation of the sampling sites, ranges between 87 and 1782 m, affect the temperature values. In addition, the pH values vary from 6.52 to 8.45 and from 7.5 to 8.63 in the wet and dry season respectively, with the dry season mean equal to 8.0 higher than the wet season one equal to 7.1. Moreover, the TDS wet values range between 90 and 663 mg/L, while the dry ones vary from 98 to 509 mg/L. in addition, the EC values range between 195 and 1038 µS/cm in the wet season, while the dry season values vary from 200 to 1038 µS/cm. In fact, the TDS means in wet and dry seasons are equal to 267.5 and 267.6 mg/L respectively, while the EC means in wet and dry seasons are equal to 533.9 and 547.1 µS/cm respectively. Moreover, the medians show a bigger gap, for most of the parameters and ions, between the dry and wet data compared to the means.

Secondly, almost all of the major ions represent means higher in dry season except the bicarbonate and phosphate ions where the wet samples hold slightly higher means than the dry ones. In fact, the HCO_3^{-} data range between 103 and 370 mg/L in the wet season, while the dry season values range between 100 and 400 mg/L with means equal to 252.7 and 250.2 mg/L in wet and dry seasons respectively. In addition, the PO_4^{3-} wet data vary from 0.02 to 1.96 mg/L, while the dry values range from 0.02 to 1.62 mg/L, where the wet and dry means are equal to 0.9 and 0.2 mg/L respectively. The rest of the data including the following ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, NO_3^{-}

and Cl^- hold wet and dry samples with wet means equal to 45.7, 14.8, 9, 1.1, 17, 15.3 and 34.6 mg/L respectively and dry means equal to 57, 18.5, 12.1, 2.1, 15.9, 17.4 and 39 mg/L respectively. Moreover, the Ca^{2+} wet data range from 13.1 to 140.7 mg/L, while the dry ones fall between 19.7 and 124.6 mg/L. Furthermore, the Mg^{2+} wet data range from 3.4 to 56.9 mg/L while the dry values vary from 4 to 57.9 mg/L. In addition, Na^+ and K^+ wet values vary from 0.8 to 33.9 mg/L and from 0.07 to 6.87 mg/L respectively, while the dry values range from 0.9 to 70.9 mg/L and from 0.15 to 18.41 mg/L. In addition, the nitrate concentrations hold minimum and maximum values equal to 6.3 and 48 mg/L in the wet season, while the dry values fall between 6.3 and 85.7 mg/L. Finally, the SO_4^{2-} and Cl^- wet data range from 1.8 to 181.4 mg/L and from 8 to 79.3 mg/L respectively, while the dry values vary from 3.1 to 66.8 mg/L and from 8 to 138.2 mg/L respectively.

Ultimately, calcium and bicarbonate dominate Abu Ali's groundwater chemical composition as the major cation and anion respectively. In addition, the higher concentrations in the dry season compared to the wet one could be attributed to the fact that the precipitation is higher in the wet season, which lead to a higher infiltration and as results, more diluted groundwater.

2.4.2 Hydrochemical facies

The Piper diagrams (Fig. 2.5) indicate the dominance of Ca-HCO_3 and Ca-Mg-HCO_3 facies in the data, where 98.5% of the samples belong to these facies. In fact, 63.1% and 35.4% of the samples fall into Ca-HCO_3 and Ca-Mg-HCO_3 facies respectively. Some of these samples lean toward the mixed facies, while only 1 sample in the wet season (S09) belong to the mixed facies. In fact, this sample belong to a village dominated by a geological formation belonging to the Lower Miocene, where the main activity is the agriculture. In fact, the excess use of fertilizers especially potassium sulfate, since the concentration of these ions are high in this sample compared to the data, could explain the shift toward the mixed facies. In addition, the dry sample of the same village also lean toward the mixed facies. For the other 19 samples leaning toward the mixed facies, 16 samples were extracted during wet and dry seasons: S04, S08, S10, S11, S20, S21, S22 and S28, while the other 3 samples lean toward the mixed facies in either wet or dry season. For instance, only in the wet season S12 and S25 show this tendency, while S06 in the dry season also lean toward the facies mentioned previously. In addition, the main land cover/use varies from village to village between agriculture, urban area and grassland. In fact, the urban and agriculture zones dominate

the following samples: S04, S09 and S25, while S06, S08, S10, S11, S20, S21, S22 and S28 are dominated by urban areas. Finally, urban area and grassland are considered the main cover of S12.

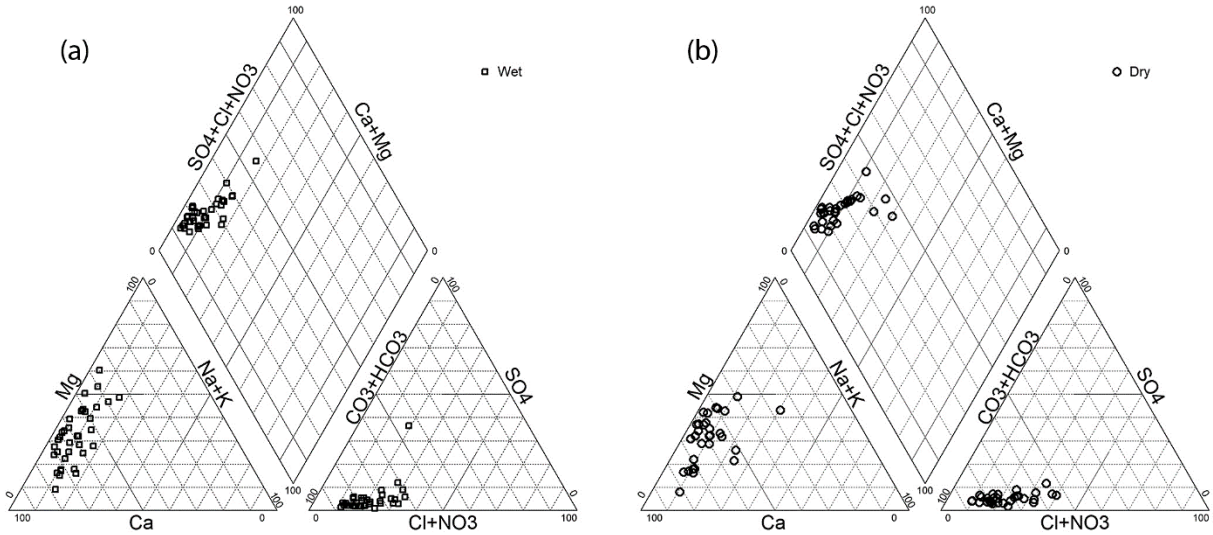


Figure 2.5 Piper diagrams of wet (a) and dry (b) samples.

2.4.3 Saturation index

The saturation index plots (Fig. 2.6) indicate that almost all of Abu Ali's samples hold positive calcite and dolomite saturation index during the dry season and a slightly negative values during the wet season. This difference could be attributed to the dilution of groundwater during the wet season due to the higher precipitation. Furthermore, the gypsum plot shows that all of the dots including the wet and dry season of all samples fall into the negative zone between -1 and -4. In fact, the previous findings indicate the high abundance of calcite and dolomite formation and the low abundance of gypsum formation in the aquifer. These results could also explain why the majority of the samples present a Ca-HCO_3 or Ca-Mg-HCO_3 facies. Indeed, it appears that calcite and dolomite weathering play an important role in modifying the groundwater chemistry in Abu Ali watershed aquifers. Despite the general aspect of dots in each plot some exceptions could be detected. For instance, despite that most of the samples fall from -1 to 1 in the calcite plot and from -2 to 2 in the dolomitic plot, only the S28D sample (Qobbeh) holds higher saturation indexes. In addition, S23W (Iaal) sample hold a S.I lower than -2 in the dolomite data. For the gypsum data, most of the samples hold saturation index between -1.5 and -4 except S09W (Bkeftine) holding a

value higher than -1.5, which could explain the mixed facies due to high sulfate concentration. In fact, the samples holding higher saturation indexes belong to the Tertiary formation located at lower altitude where the residence period is higher compared to the high altitude samples (El-Hakim & Bakalowicz, 2007; Guo et al., 2019).

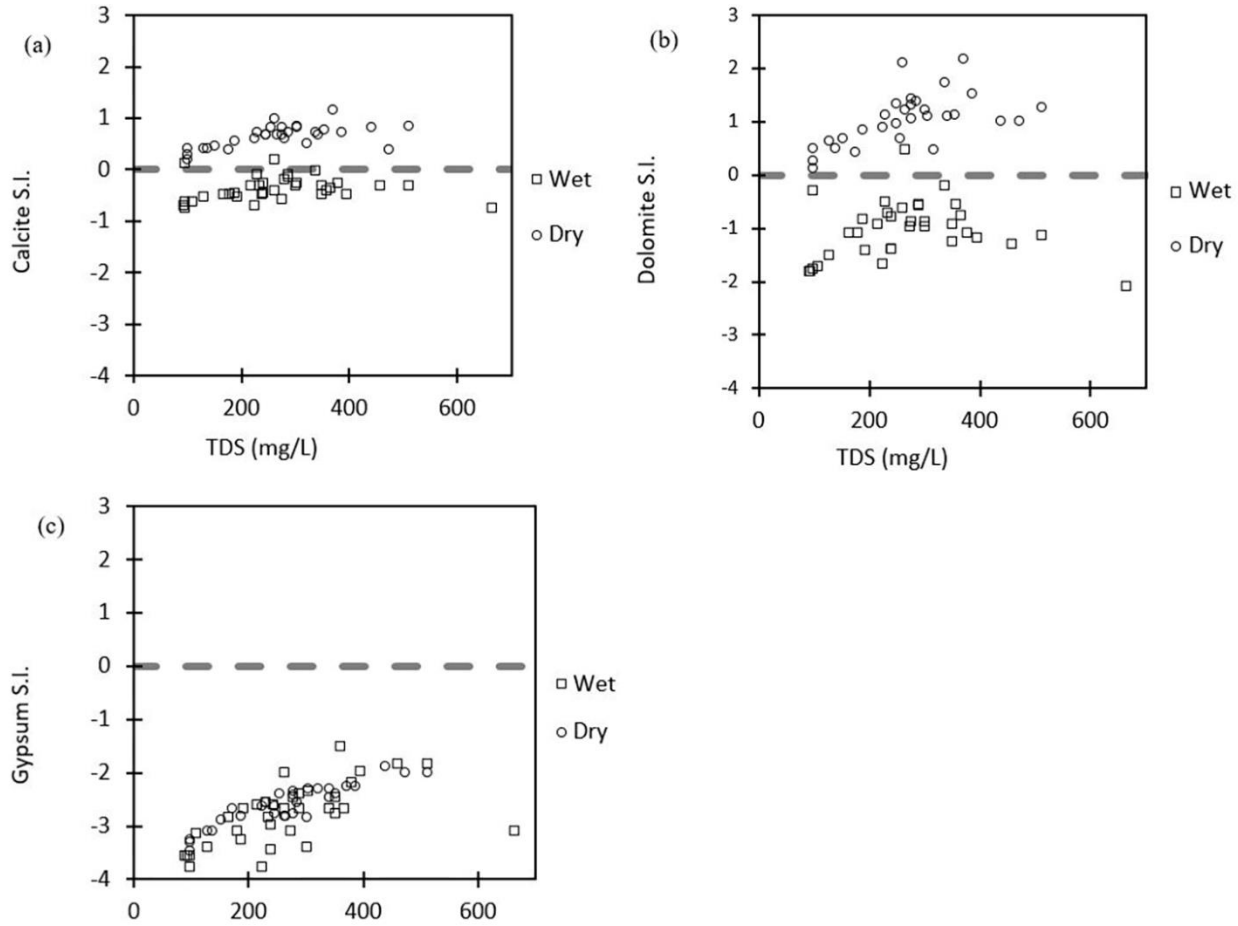


Figure 2.6 Saturation index vs TDS plots of calcite (a), dolomite (b) and gypsum (c).

2.4.4 Geochemical processes

The Gibbs plots (Fig. 2.7) indicate that almost all of samples are clustered in the rock-water interaction zone (98.5%), except the sample S23 falls slightly above this region. This observation indicate that this type of interaction is the main process in modifying the groundwater's chemistry in Abu Ali's basin. Despite the general aspect, some points hold lower TDS values in the rock-water zone. For instance, the samples S05 and S24 during the dry and wet season respectively while samples S13, S15, S17, S19 and S32 hold lower TDS values in both seasons. In fact, these 5 samples with S05 were extracted from springs. In fact, the results concerning the springs samples

located at high altitudes resemble to a Chinese study's results, conducted by Guo *et al.* in 2019 concerning a karstic spring system located in the north limb of Mountain Tai anticline, where the lower TDS values could be attributed to lower rock-water interaction's period, since Abu Ali's watershed is a karstic system characterized by low storage capacity and residence period leading to lower concentrations in general due to lower rock-water interaction (El-Hakim & Bakalowicz, 2007). Moreover, S24 was extracted during the wet season from a village where the main geological formation is the Cenomanian-Turonian formation characterized by high permeability (Hanini et al., 2021), which could lead to higher infiltration during the wet season and as a result higher dilution and lower TDS value. Moreover, only the S04 sample during the dry season fall near the evaporation zone in the Na^+/Na^++Ca^{2+} plot. In fact, the groundwater in this village may be shallow, which results in higher evaporation especially in the dry season.

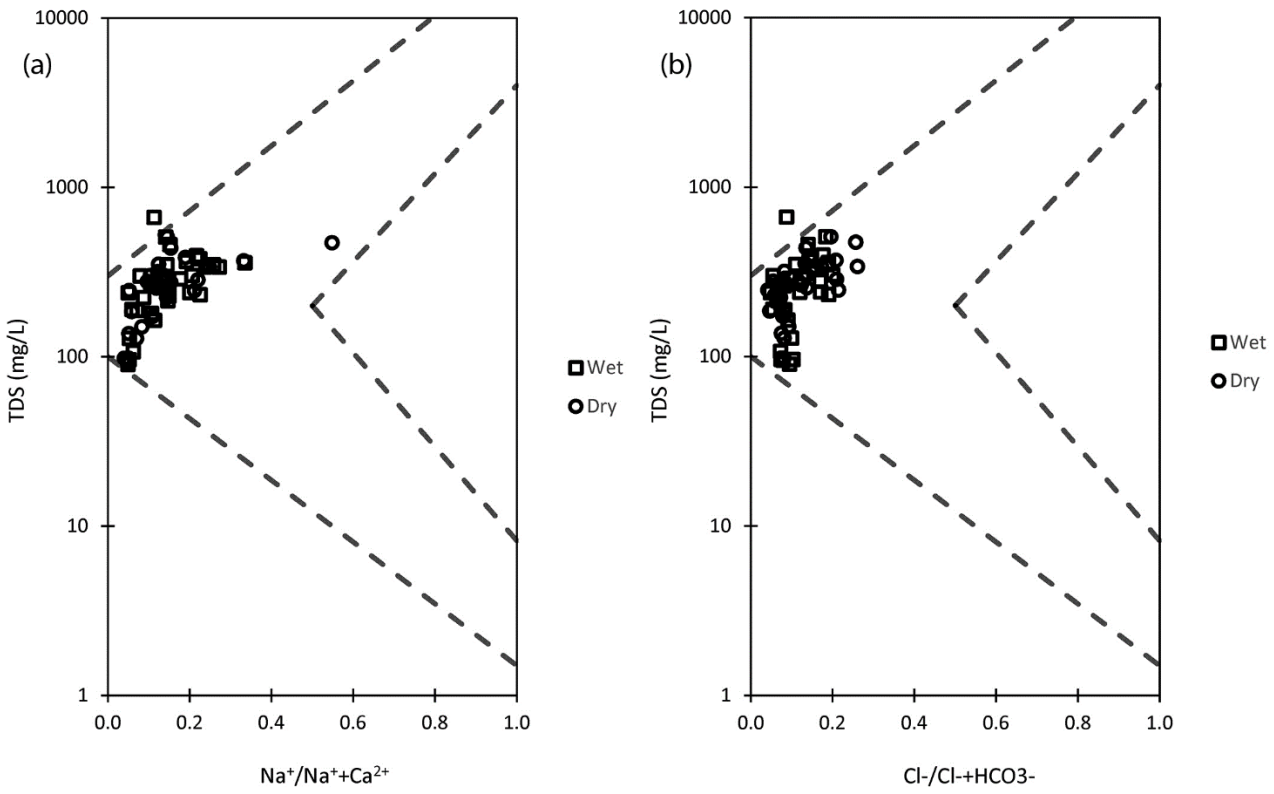


Figure 2.7 Gibbs plots representing the variation of TDS in comparison with the ratio (a) Na^+/Na^++Ca^{2+} and (b) $Cl^-/Cl^-+HCO_3^-$.

2.4.4.1 Carbonate weathering

First of all, the plot HCO_3^- vs Ca^{2+} (Fig. 2.8.a) indicates that almost all of our samples fall near the line 2:1. This observation indicates that calcite weathering is not the only source of bicarbonate. Moreover, the fact that almost all of the samples fall near the line 1:1 in the plot HCO_3^- vs Ca^{2+} + Mg^{2+} (Fig. 2.8.b) ensures the previous hypothesis, which imply that the dolomite weathering participates also in increasing the bicarbonate concentration. In fact, this conclusion reassures the previous findings in the saturation index part (Fig. 2.6), where Abu Ali's samples tend to have higher saturation indexes of calcite and dolomite compared to the gypsum values. Furthermore, by comparing the HCO_3^- vs Ca^{2+} + Mg^{2+}, (Fig. 2.8.b) and HCO_3^-+ SO_4^{2-} vs Ca^{2+} + Mg^{2+} (Fig. 2.8.c) plots, the impact of sulfate on the groundwater could be observed. In the Abu Ali's case, the difference between these two plots was minimal indicating the low concentration of sulfate due to the low impact of gypsum weathering in shaping the groundwater's chemistry. The previous finding could also explain the low saturation indexes of gypsum observed in the Figure 2.6. In fact, the low concentrations of sulfate could be observed in the 4th plot (Fig. 2.8.d), where almost all of the points hold low concentrations except for the wet season's sample S09 and the wet and dry samples of S04. In fact, the S09 dot falls slightly above the line 1:1. The higher concentration in S09 is a result of several sources. The first source may be the gypsum weathering, where the gypsum saturation index results display that S09 holds a higher value. In addition, S04 and S09 samples fall into the mixed facies zone in the Piper diagram (Fig. 2.5.a), and they are extracted from villages where the main activity is the agriculture. According to the previous observations, the agricultural anthropogenic impact could affect the groundwater's chemistry in these villages and could be considered as the second source of sulfate.

Furthermore, the data indicates that the chloride concentrations of these 3 samples are considered high with values trespassing 84.6% of the samples' values, which also could be considered as a sign of anthropogenic impact. Despite the general aspect, some samples are exceptional. For instance, in the plot representing HCO_3^- vs Ca^{2+} (Fig. 2.8.a), the following samples: S01W, S07W, S11W, S14W, S23W, S27W, S33W and S34W fall above the line 2:1, while only 4 samples belonging to 1 village (S21(W&D) and S22(W&D)) fall below the line 1:1. Moving to the plot highlighting HCO_3^- vs Ca^{2+} + Mg^{2+} (Fig. 2.8.b) some dots fall above and below the lines 2:1 and 1:1 respectively. In fact, S23W, S27W, S33W and S34W fall above 2:1, while S04D, S06D, S09W,

S11D, S21(W&D), S22(W&D), S23D and S25W fall below the line 1:1. In fact, most of the points falling above the line 2:1 are located in several areas covered by forest; which could explain the high HCO_3^- concentrations produced by carbonic acid due to the infiltration of rainfall in soil rich in organic matter (Saha et al., 2019), while the points falling below the line 1:1 indicate that, besides carbonate weathering, there is another process participating in increasing the concentrations of Ca and Mg. As a result, the next segment aims to investigate the ions exchange reaction and in particularly if the reverse ions exchange affects Abu Ali's samples, since this process could be the main culprit behind this increasing in Ca and Mg concentrations.

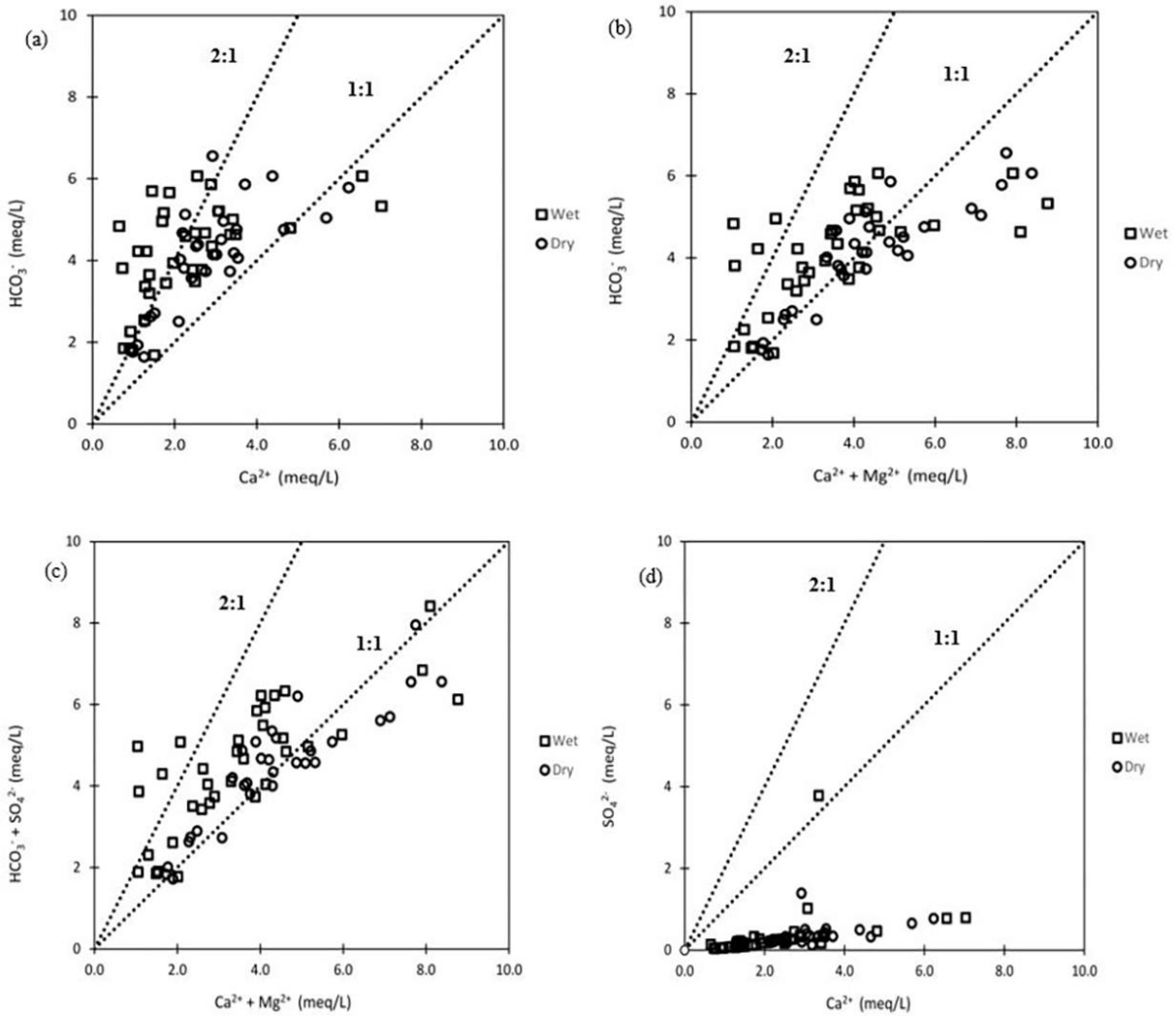


Figure 2.8 The carbonate weathering plots include the 4 following plots: HCO_3^- vs Ca^{2+} (a), HCO_3^- vs Ca^{2+} + Mg^{2+} (b), HCO_3^- + SO_4^{2-} vs Ca^{2+} + Mg^{2+} (c) and SO_4^{2-} vs Ca^{2+} (d).

2.4.4.2 Ions exchange

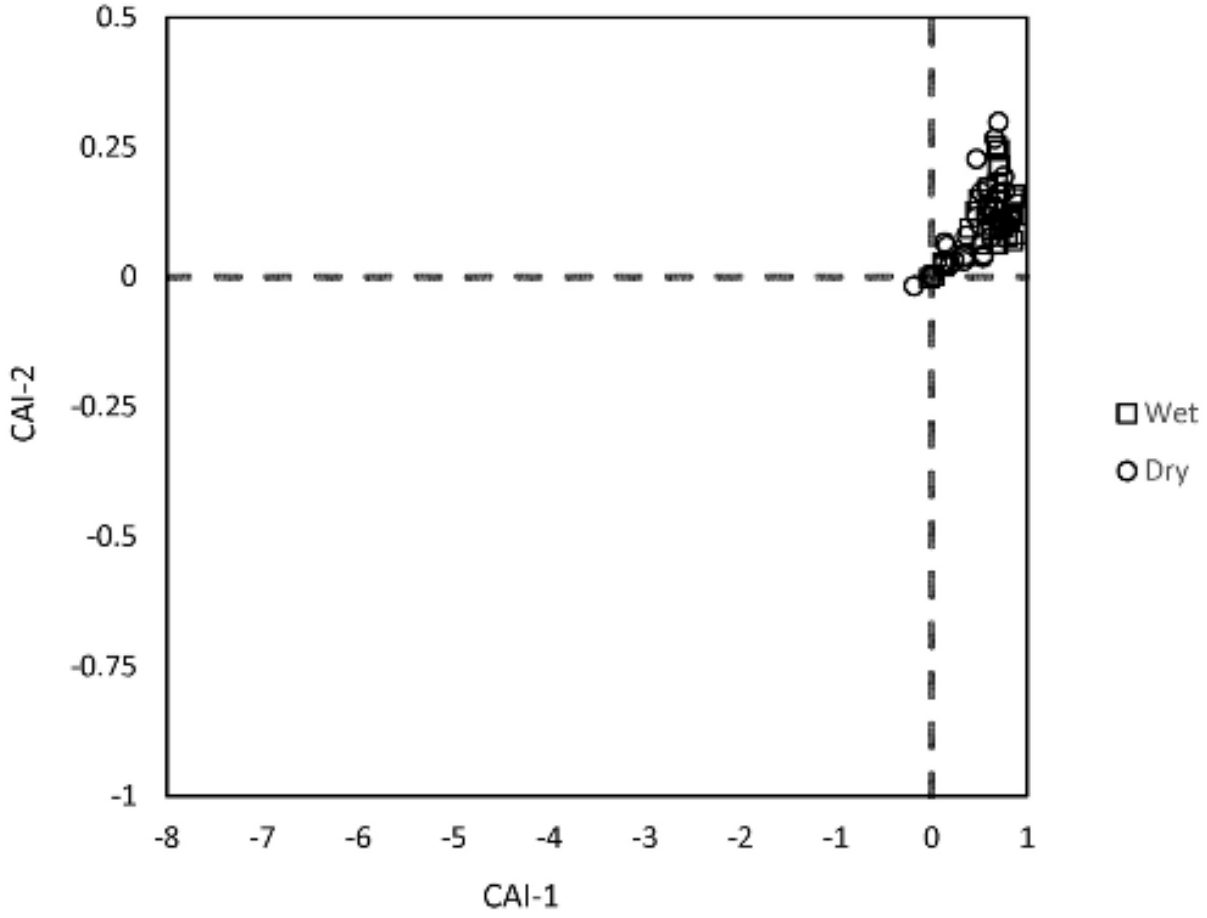


Figure 2.9 Ions exchange plot (CAI-2 vs CAI-1).

The ions exchange plot (Fig. 2.9) was used in order to reveal what kind of exchange affect Abu Ali's groundwater. This plot includes 2 Chloro-Alkaline indices "CAI-1 and CAI-2" (Schoeller, 1965) measured using the equations (1) and (2) respectively:

$$CAI - 1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \qquad (2.1)$$

$$CAI - 2 = \frac{Cl^- - (Na^+ + K^+)}{HCO_3^- + SO_4^{2-} + CO_3^{2-} + NO_3^-} \qquad (2.2)$$

In fact, the samples holding negative CAI-1 and CAI-2 are affected by ions exchange reaction where the soluble calcium in groundwater was exchanged with sodium in the rocks, while the samples holding positive CAI-1 and CAI-2 are affected by reverse ions exchange reaction, where

the soluble sodium in groundwater was exchanged with calcium in the rocks. Most of the samples hold slightly positive indices indicating the impact of reverse ions exchange on their chemistry, where a certain amount of sodium in groundwater was exchanged with the calcium in the aquifer rocks. However, some samples were more affected by this process. For instance, the following samples: S08W, S09D, S10W&D, S11W, S12W and S20W&D hold CAI-2 higher than 0.2. According to the Piper diagram (Fig. 2.5), Ca-Mg-HCO_3 facies dominates these samples, which are located at low altitude and most of the samples are extracted from wells, where the residence time is higher leading to a longer rock-water interaction period. Despite the high impact of reverse ions exchange on Abu Ali's watershed, the S30 sample extracted during the dry season fall into the negative area and was affected by ions exchange, while the other S30 wet sample and the S31 wet and dry samples fall near zero indicating that the ions exchange and the reverse reaction doesn't affect these samples.

2.4.5 Evaporation process

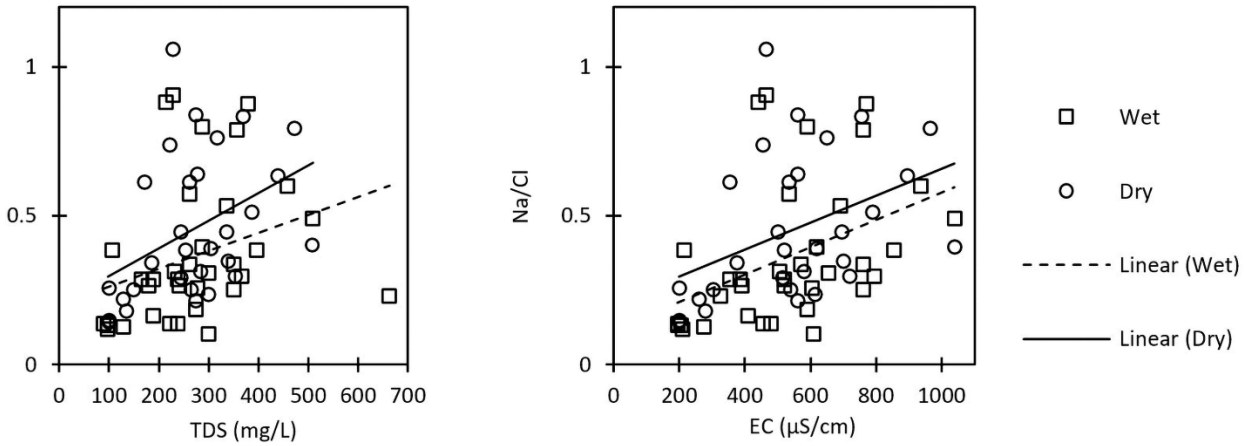


Figure 2.10 Evaporation plots: Na/Cl vs TDS (a) and Na/Cl vs EC (b)

The Na/Cl vs TDS and Na/Cl vs EC plots (Fig. 2.10) reveal that the ratio increase with the increasing of TDS and EC values in our data, which indicate the minimal effect of evaporation on Abu Ali's groundwater since the ratio is not constant independently of TDS and EC. In fact, these plots enforce the theory that the modification of groundwater's chemistry is mainly affected by rock-water interaction, where evaporation play a limited role in this regard. Despite the general aspect, some samples hold higher Na/Cl ratio. In fact, S04D, S09W, S23D, S25W, S28D, S29 (W&D), S30 (W&D) and S31 (W&D) belong to the group clustered above the Na/Cl ratio equal

to 0.7. In fact, according to the ions exchange plot the S30D was affected by ions exchange reaction which is responsible of increasing the sodium concentration in the sample due to the exchange between the soluble calcium and the sodium in the rocks; while the S30W and S31 (W&D) were not affected by neither ions exchange nor reverse ions exchange, and as a result the sodium concentration in the samples remain intact compared to the other samples affected by the reverse reaction. For the rest of the samples, they are located at lower altitude where the groundwater is considered shallow. These previous findings and observations could explain the higher Na/Cl ration observed in the evaporation plots.

2.4.6 Pollution and anthropogenic impact

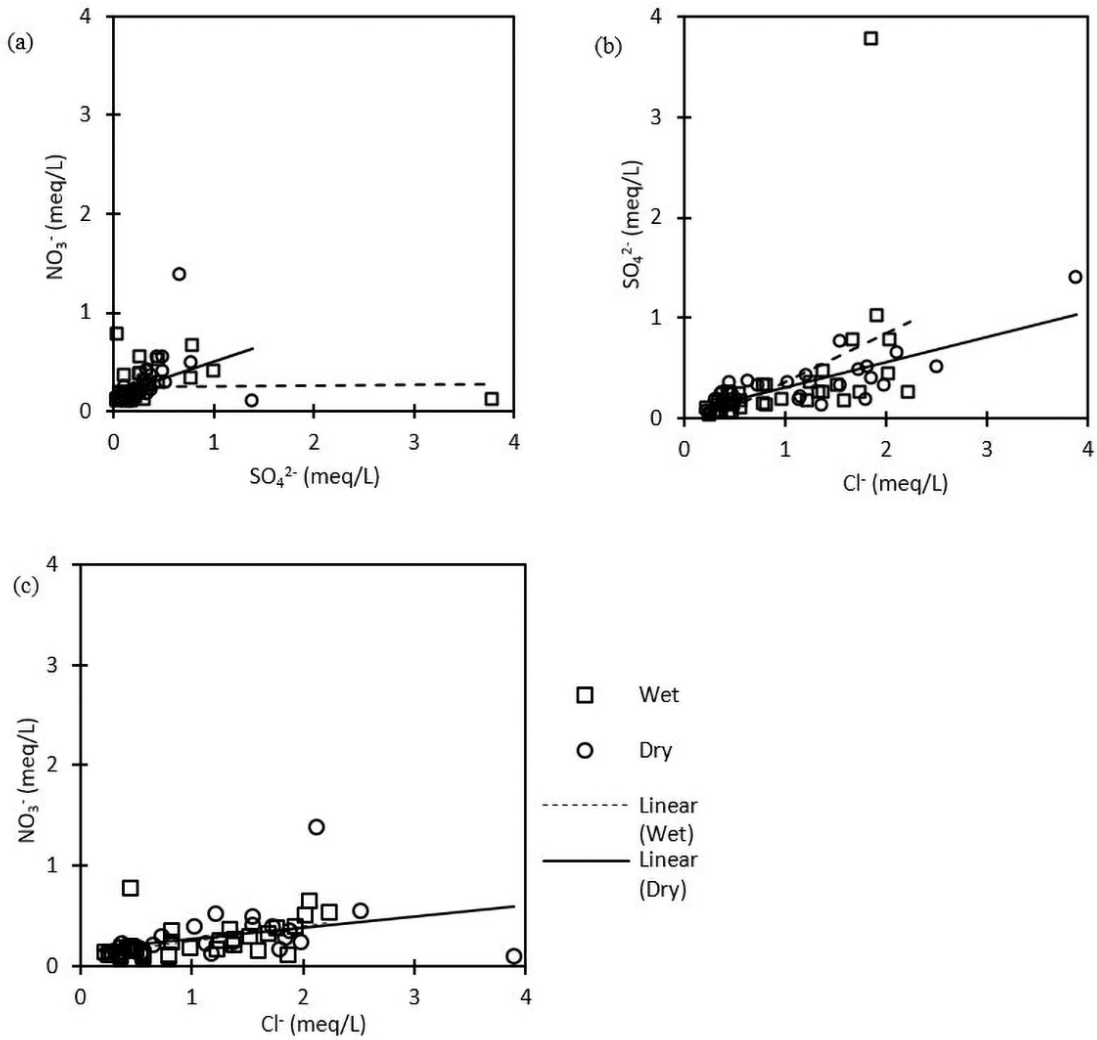


Figure 2.11 Three plots representing pollution and anthropogenic impact: NO_3^- vs SO_4^{2-} (a), SO_4^{2-} vs Cl^- (b) and NO_3^- vs Cl^- (c).

Most of dry and wet seasons' samples does not hold high concentrations of NO_3^-, SO_4^{2-} and Cl^-, where almost all of the values fall below 62, 48 and 71 mg/L respectively. In addition, the 3 plots represented in Fig. 2.11 indicate the low correlation between the 3 ions, therefore the origin of these 3 ions are not the same. Despite the general aspect, 2 samples represent high concentrations of SO_4^{2-} and Cl^-. For instance, S04D hold a Cl^- concentration equal to 138.2 mg/L, while a high concentration of SO_4^{2-} equal to 181.4 mg/L belong to S09W. In fact, following the Piper diagram (Fig. 2.5) S09W holds mixed facies indicating the importance of the sulfate in changing it chemistry. In fact, the source of this sulfate could be the anthropogenic impact, where S09W and S04D are located in villages characterized by the agriculture as their main activity. Moreover, the Gibbs diagrams (Fig. 2.7) indicated the active role played by the rock-water interaction in shaping the groundwater's chemistry except for the S04D sample which fall into the evaporation section. The high evaporation affecting this sample could explain the exceeding Cl^- concentration compared to the whole data.

2.4.7 Multivariate analysis

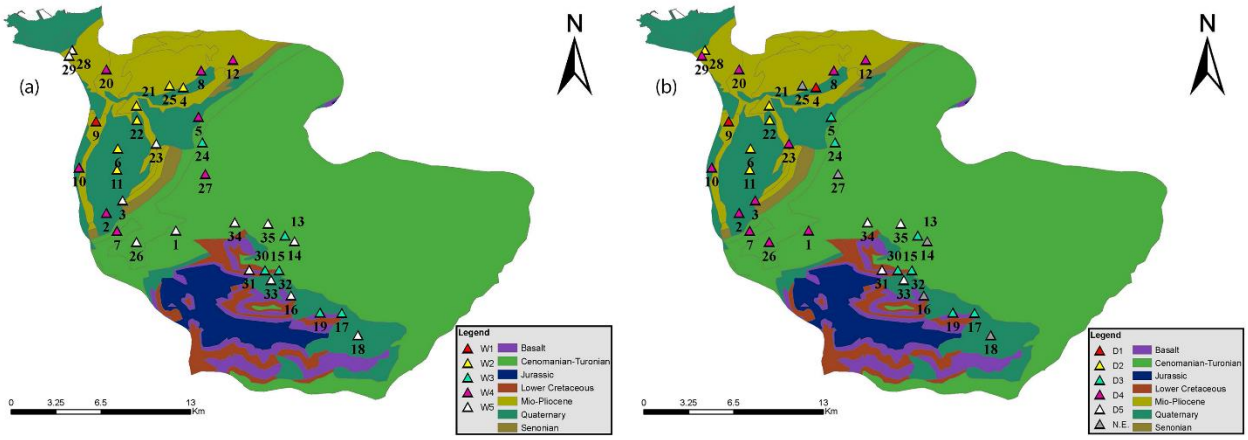


Figure 2.12 Geological maps representing the distribution of wet (a) and dry (b) samples based on the clusters' groups

First, the dendrograms of wet and dry samples were plotted using RStudio program version 1.3.1093. Furthermore, using ArcGIS version 10.4, all the samples were plotted in two geological maps based on the clustering distribution (Fig. 2.12). The observation of these maps indicate that each dendrogram holds 5 groups labelled W1 to W5 for the wet sample and D1 to D5 for the dry samples. In fact, the 5 wet groups from W1 to W5 hold a number of samples equal to 1, 6, 6, 9 and 13 samples respectively while 2, 5, 7, 11 and 5 samples belong to the 5 dry groups labelled from

D1 to D5 respectively. Moreover, a high number of Abu Ali's samples maintain the same dendrogram's distribution between the 2 seasons, while the following 9 samples switch groups between wet and dry season: S04 (W2 to D1), S05 (W4 to D3), S28 (W5 to D2), S31 (W4 to D5), S01, S03, S23, S26 and S29 (5 samples from W5 to D4). In addition, the maps reveal that almost all of the groups 3 and 5 samples (W3, W5, D3 and D5) are located south and south east of the study area; which indicate that the elevation plays certain role in the samples' clustering since this parameter increases from sea level at the north west to 3038 m at the south east of the study area. In addition, some groups show a tendency to cluster in certain geological formation. For instance, the second group labelled W2 and D2 is dominated by the Quaternary formation. Furthermore, the samples extracted from springs dominate most of the third group's samples (W3 and D3), where 11 out of 13 samples are springs samples.

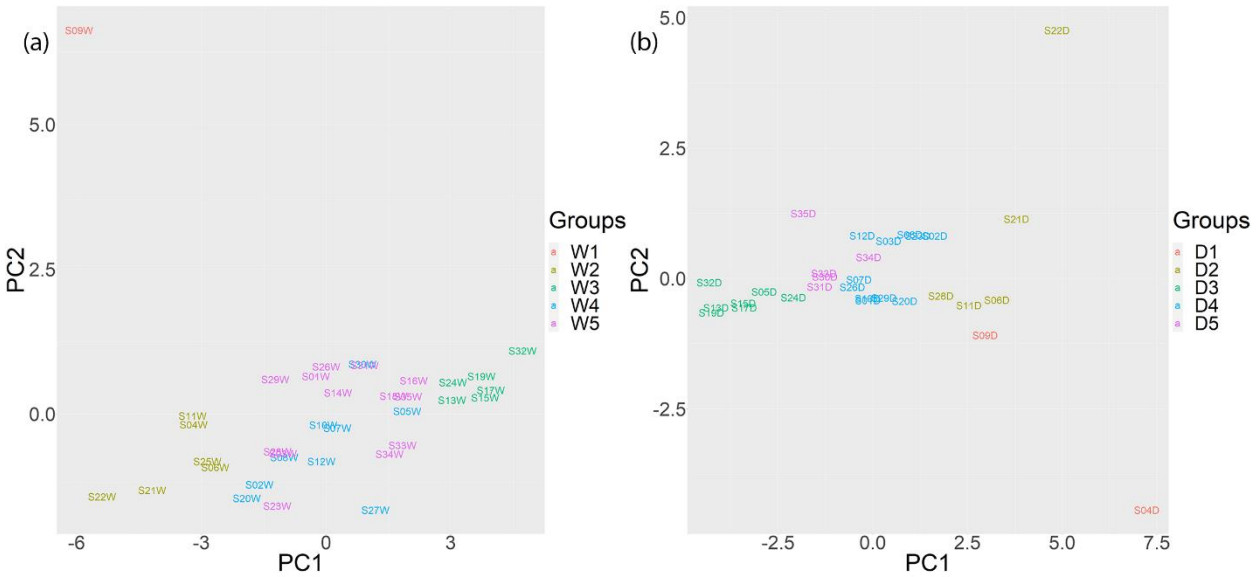


Figure 2.13 PCA of wet (a, percent variation of PC1=54% and PC2=15%) and dry (b, percent variation of PC1=59% and PC2=14%)

Table 2.1 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

The principal components analysis was realized based on the covariance matrix using RStudio program version 1.3.1093. The samples were distributed following the 5 dendrograms' groups, while the wet (Fig. 2.13.a) and dry (Fig. 2.13.b) samples were plotted into 2 different plots representing PC2 vs PC1. Based on scree plots, the first 4 PCs were chosen, where the variance contribution rates in wet season of PC1, PC2, PC3 and PC4 are equal to 54.1%, 15.1%, 9.6% and 5.5% respectively, while the dry data holds percentages equal to 59.6%, 13.9%, 8.2% and 6.8% respectively. In the next step, the correlations between the 4 PCs (from PC1 to PC4) and the variables (physicochemical parameters and major ions) were measured. For wet samples, the analysis indicates negative correlations between PC1 and the following variables: T, TDS, EC, Ca^{2+}, Na^{+}, HCO_3^{-} and Cl^{-}, a positive correlation between PC1 and pH and a positive correlation between PC2 and SO_4^{2-}. In addition, a positive correlation was observed between PC2 and sulfate from one hand and PC3 and phosphate from the other hand. While the dry season analysis represents positive correlation between PC1 and the following 8 variables: T, TDS, EC, Ca^{2+}, Na^{+}, SO_4^{2-}, HCO_3^{-} and Cl^{-} and a negative correlation between PC1 and pH. No other correlation was observed between the ions and the rest of PCs in the wet and dry data. By observing the 2 plots, a certain pattern could be identified. For instance, the 1st group holds only 3 samples S04D and S09(W&D), where S09W hold high PC2 which reveal the high sulfate concentration and ensure the saturation index result (Fig. 2.6) indicating the higher gypsum weathering in this sample in comparison with the whole data. In fact, this group is characterized by samples holding the highest sodium and chloride concentrations, which could be observed in the evaporation plots (Fig. 2.10) where S04 and S09 holds high ratio. In addition, S04D is the only sample falling into the

evaporation zone according to the Gibbs plots (Fig. 2.7) which could explain the high salinity. Moving to the 2nd group, the wet (W2) and dry (D2) samples hold negative and positive PC1 respectively, which indicate high values of T, TDS, EC, Ca^{2+}, Na^{+}, HCO_3^- and Cl^-. In fact, the geological distribution of the dendrograms groups (Fig. 2.12) indicate that the 2nd group samples were located at low altitude, in villages characterized by agriculture activities. In addition, these samples hold high SO_4^{2-} and NO_3^- concentrations and low pH values. The previous observations highlight that this group was influenced by anthropogenic impact due to agricultural activities. In fact, the ammonium sulfate is used in Lebanon as fertilizer especially in grapes crops (Darwish et al., 2011), which could result in increasing in sulfate and ammonium, then the ammonium reacts with the oxygen and transform into NO_3^- and H^+ (Bolan & Hedley, 2003; M. Fageria, 1989). In fact, these reactions cause the increasing in acidity and decreasing in pH (N. K. Fageria et al., 2010). Moreover, the samples of the 3rd groups labelled W3 and D3 were clustered toward the extreme positive PC1 in the wet season plot (W3) and the extreme negative PC1 in the dry season plot (D4). The previous observation indicates the low values of T, TDS, EC, Ca^{2+}, Na^{+}, HCO_3^- and Cl^- between the 3rd group's samples. This low concentrations and values in the 3rd group could be attributed to the high altitude and the fact that almost all of its samples are spring samples, where the groundwater's residence time is lower (El-Hakim & Bakalowicz, 2007; Guo et al., 2019). In addition, the Gibbs plots (Fig. 2.7) revealed a group of samples with lower TDS. These are indeed the samples of group 3 which are mainly high altitude springs samples. In such geological context, groundwater is expelled quickly leading to a limited interaction period with the bedrocks which could be observed easily in the Gibbs plots, where the samples hold lower TDS values. Moving to the 4th and 5th groups, most of the samples PC1 are around 0 since they hold a moderate concentration compared to the 2nd and 3rd groups. According to the ions exchange plots (Fig. 2.9), most of the samples holding slightly high CAI-2 belong to the 4th group, which could explain the 37% of its samples leaning toward the mixed facies. Finally, the 5th group, is in general characterized by its moderate chemical composition. However, most of them holds lower chloride samples compared to the whole data.

2.4.8 Lebanese and Mediterranean comparison

In order to observe the situation of Abu Ali's groundwater in Lebanon, 4 previous Lebanese studies' data were extracted and compared with this study. These 4 studies were conducted on the

Bekaa (Awad, 2011), Anti-Lebanon (El Hakim, 2005), Nahr Ibrahim (Hanna et al., 2018) and Damour coastal aquifer (Khadra & Stuyfzand, 2014). In fact, the collected data includes the following 9 major ions and 4 physicochemical parameters: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, T, pH, TDS and EC with means in Abu Ali's study equal to 58.3 mg/L, 15.5 mg/L, 10 mg/L, 1.7 mg/L, 258.3 mg/L, 30.8 mg/L, 17.5 mg/L, 0.6 mg/L, 16.5 mg/L, 17.5°C, 7.5, 317.7 mg/L and 495.5 µS/cm respectively. In fact, the comparison between Abu Ali and the 4 Lebanese study showcase that Abu Ali's study hold both the maximum and minimum values of Na^{+}, SO_4^{2-}, TDS and T, where the lowest values are equal to 0.8 mg/L, 1.8 mg/L, 90 mg/L and 8°C respectively and the highest values are equal to 70.9 mg/L, 181.4 mg/L, 663 mg/L and 29°C respectively. Moreover, Abu Ali's data hold the minimum values of $Ca^{2+}$and K^{+} equal to 13.1 and 0.07 mg/L respectively and the maximum values of Mg^{2+}, HCO_3^- and pH equal to 57.9 mg/L, 400 mg/L and 8.6 respectively. In addition, the Damour coastal aquifer (Khadra & Stuyfzand, 2014) holds the lowest HCO_3^- and NO_3^- values equal to 100 mg/L and 1.86 mg/L respectively and highest Ca^{2+}, Cl^- and EC values equal to 187 mg/L, 177 mg/L and 1094 µS/cm respectively. Furthermore, the study conducted in Bekaa (Awad, 2011) holds the lowest Mg^{2+}, pH and EC values equal to 0.84 mg/L, 5.4 and 195 µS/cm respectively and the highest K^{+} concentration equal to 32.4 mg/L. Finally, the two studies conducted on Nahr Ibrahim (Hanna et al., 2018) and Anti-Lebanon (El Hakim, 2005) hold the minimal value of Cl^- equal to 8.64 mg/L and the maximal value of NO_3^- equal to 112.5 mg/L respectively.

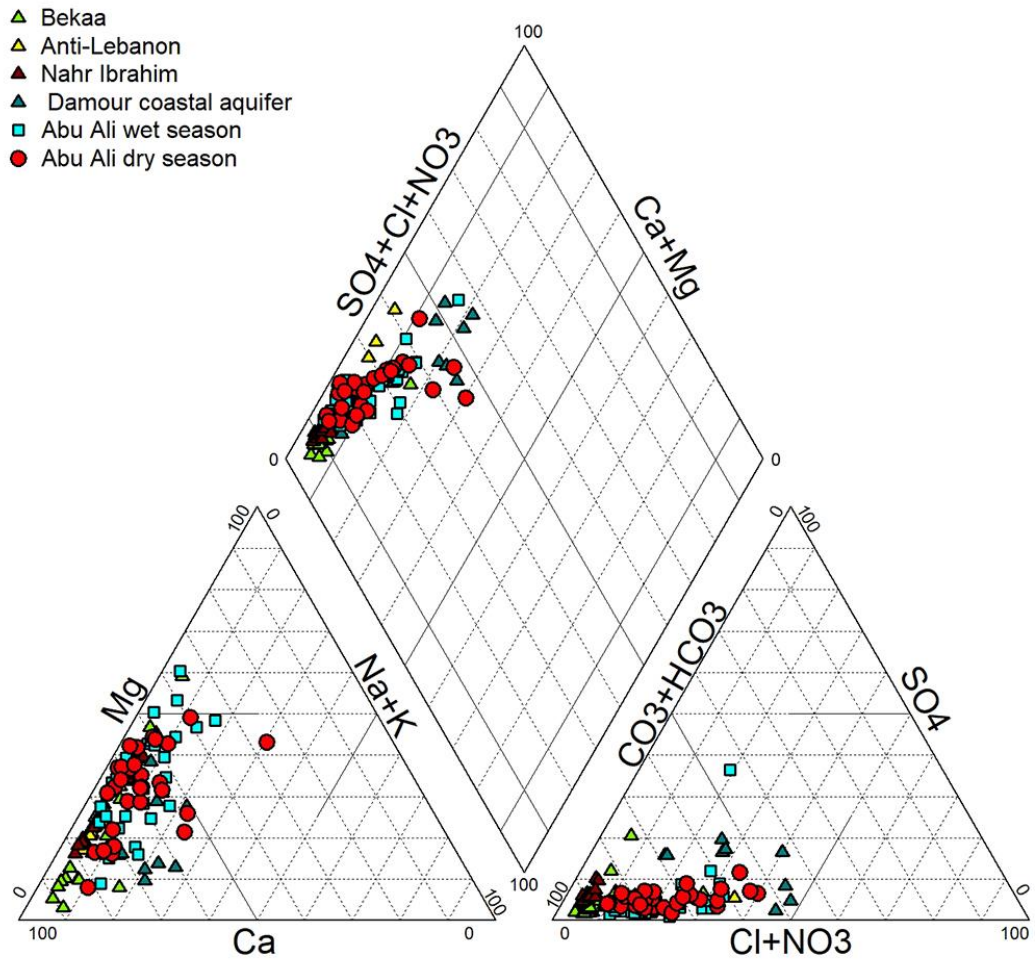


Figure 2.14 Lebanese Piper diagram.

The Piper diagram (Fig. 2.14) shows that most of Nahr Ibrahim (Hanna et al., 2018), Bekaa (Awad, 2011), and Abu Ali wet and dry samples fall into the Ca-HCO_3 and Ca-Mg-HCO_3 facies; which is normal considering the calcareous nature of Lebanon, while a few samples of Bekaa (Awad, 2011) and Abu Ali study and many of the Damour coastal study (Khadra & Stuyfzand, 2014) and Nahr Ibrahim (Hanna et al., 2018) samples fall into the mixed facies. This observation could be attributed to sea-spray process affecting the Nahr Ibrahim (Hanna et al., 2018) study, since those samples are located at the coastal zone and the seawater intrusion, due to overexploitation, occurs in the Damour coastal aquifer (Khadra & Stuyfzand, 2014). Furthermore, the main geochemical

processes affecting these samples were revealed using Gibbs plots (Fig. 2.15). In fact, the Abu Ali, Damour coastal aquifer (Khadra & Stuyfzand, 2014) and Nahr Ibrahim (Hanna et al., 2018) studies' samples are dominated by the rock-water interaction, while the samples of Bekaa (Awad, 2011) and Anti-Lebanon's studies (El Hakim, 2005) hold higher TDS values, and as result, fall slightly above the rock-water interaction area. In fact, these 2 regions are characterized by agricultural activity, which could explain the previous observation, where the samples hold higher TDS values.

Ultimately, Abu Ali's samples hold the lowest Ca^{2+}, Na^{+}, K^{+}, SO_4^{2-}, TDS and T values, in addition to the highest values of Mg^{2+}, Na^{+}, HCO_3^{-}, SO_4^{2-}, TDS, pH and T. In comparison with the other Lebanese studies, its main hydrochemical facies is similar, where the Ca-HCO_3 and Ca-Mg-HCO_3 facies dominate its samples, while the rock-water interaction is the main geochemical process in shaping Abu Ali's groundwater's chemistry, which also affect mainly the 4 other studies.

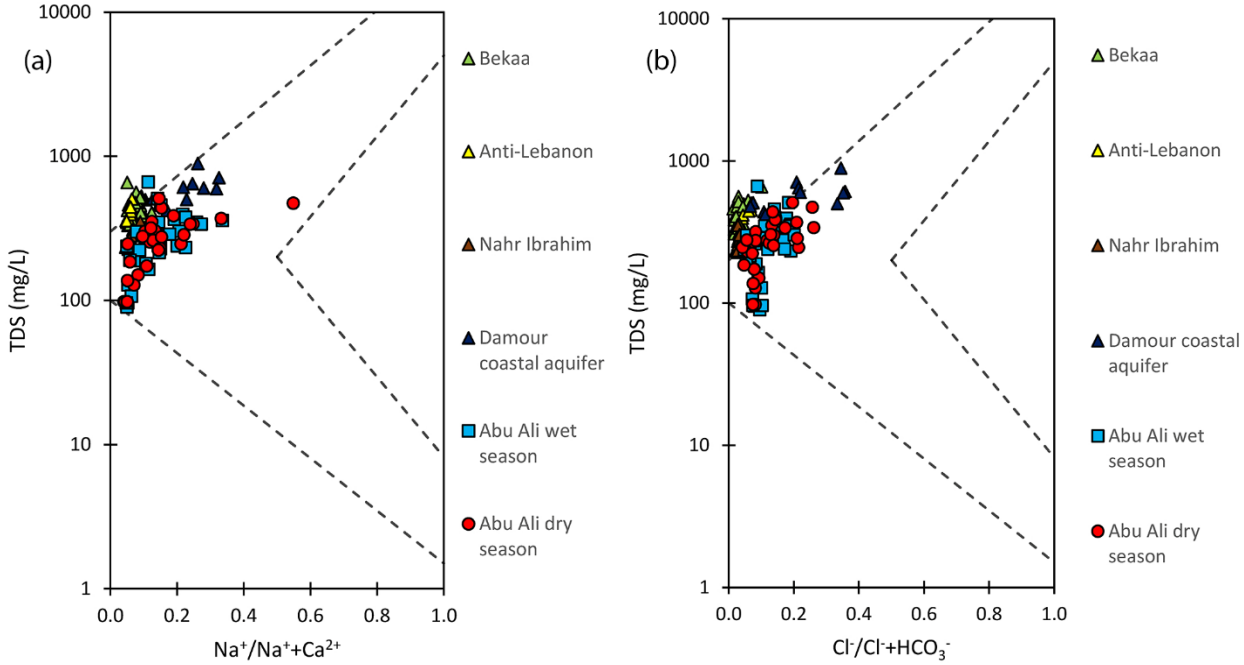


Figure 2.15 Gibbs plots of the Lebanese studies representing the variation of TDS in comparison with the ratios $Na^{+}/Na^{+} + Ca^{2+}$ (a) and $Cl^{-}/Cl^{-} + HCO_3^{-}$ (b).

From the Mediterranean perspective, the data of 23 studies, distributed equally between the "Jurassic & Cretaceous" and "Tertiary" aquifers, were collected in order to put into perspective the situation of Abu Ali basin in comparison with the Mediterranean region (Al Haj et al., 2021).

In fact, Abu Ali samples were distributed between the following 4 groups: Jurassic & Cretaceous wet, Jurassic & Cretaceous dry, Tertiary wet and Tertiary dry samples, based on their aquifer nature and seasons. In the following step, we measured the mean of each group in order to compare them with other studies and analyze them via Piper diagrams and Gibbs plots while avoiding the clustering of dots. In fact, 7 major ions' concentrations were collected from the Mediterranean studies and the mean were calculated in order to compare the data, this group includes the following ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-}. First, the data observation displays the moderate means of Abu Ali's mean in the 4 groups compared to the Jurassic & Cretaceous and Tertiary data, where its means do not represent nor the minimum nor the maximum values of the data. For the Jurassic & Cretaceous data, the wet season means of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-} in Abu Ali's basin are equal to 28.4, 12.6, 3.3, 0.7, 210.6, 17.3 and 6.4 mg/L respectively, while the dry season means are close with values equal to 40.8, 15.6, 4.4, 0.9, 205.2, 17, 8.7 mg/L respectively. By observing the whole data, Abu Ali's study does not hold nor the highest nor the lowest values of the 7 major ions. However, most of its ions tends to hold low values compared to the other Mediterranean studies. In addition, the closest means of ions to Abu Ali's study was observed in the Palestinian study conducted on a karstic aquifers located in the central West Bank (Jebreen et al., 2018), except for the Na+, K+ and Cl- means which are higher in the Palestinian study. These high values were attributed to the high agriculture contamination affecting the groundwater. Moreover, in 2018 Jebreen *et al.* proved that the Palestinian karstic aquifer was mainly influenced by water–rock interaction, followed by cation exchange and the carbonate minerals weathering, while Ca-Mg-HCO_3 was considered the dominate facies in this study. In fact, this study could be the closet one to Abu Ali's study due to the similarity in the geochemical process affecting the groundwater between them, in addition to the geographical location of the two countries and their similar weather.

For the Tertiary data, the wet season means of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-} in Abu Ali's basin are equal to 64, 17.1, 14.9, 1.5, 297.4, 53 and 28.1 mg/L respectively, while the dry season means are close with values equal to 71.2, 21.1, 18.7, 3.1, 289.5, 58.3 and 22.1 mg/L respectively. In fact, these values are considerate moderate, where all the ions values fall near the Tertiary medians. This observation is considerate different from the Jurassic & Cretaceous observations, where most of the ions' means are considered low. In addition, the closest values to

Abu Ali's values belong to a Lebanese study conducted on several Anti-Lebanon's aquifers (El Hakim, 2005). In fact, it was proven that Ca-HCO_3 and Ca-Mg-HCO_3 dominate several aquifers as a result of the high Ca^{2+} and HCO_3^- concentrations. In addition, the dissolution of carbonate minerals played an important role in shaping the groundwater's chemistry.

The Piper diagrams (Fig. 2.16) highlight the dominance of the Ca-HCO_3 and Ca-Mg-HCO_3 facies on the Abu Ali's study in both seasons and aquifers. The Jurassic & Cretaceous diagram (Fig. 2.16.a) indicate that only 2 studies, a Lebanese and a French one, fall near Abu Ali's study which implicate the dominance of the same facies. However, the other Mediterranean studies began to shift toward the Ca-Cl facies. For instance, all of the Grecian and Algerian studies in addition to a Palestinian, Lebanese, Turkish, Italian and 2 Tunisian studies fall into the mixed facies, while only 1 Italian and 1 Tunisian study fall into the Ca-Cl facies.

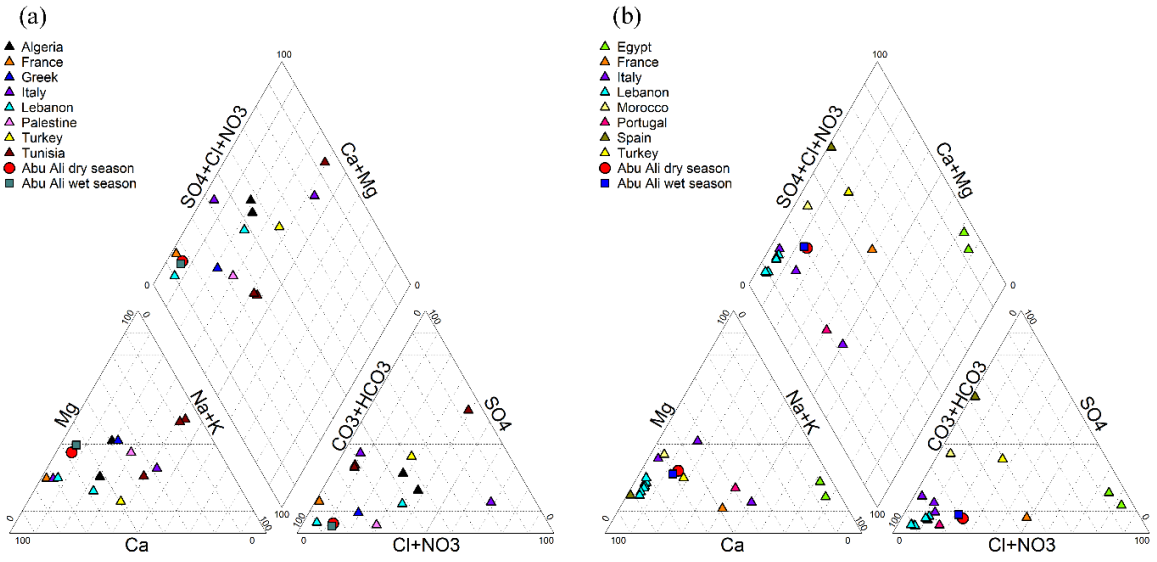


Figure 2.16 Mediterranean Piper diagrams representing: The Jurassic & Cretaceous aquifers (a) and the Tertiary aquifers (b).

For the Tertiary diagram (Fig. 2.16.b), a same aspect could be observed, where Abu Ali, 2 Lebanese and 2 Italian aquifers fall into the Ca-HCO_3 and Ca-Mg-HCO_3 facies, while most of the Italian and all of French, Moroccan and Spanish fall into the mixed facies. The main difference is the higher number of samples falling into the Na-Cl facies in the Tertiary diagram, where 2 Egyptian studies belong to this facies. Furthermore, 2 studies conducted in Italy and Portugal fall near the Na-HCO_3 zone. In addition, the Gibbs plots (Fig. 2.17) indicate that the dry and wet

samples' means of Abu Ali's Jurassic & Cretaceous aquifer holds lower TDS values compared to the Tertiary samples, while the majority the Mediterranean aquifers fall between rock-water interaction and evaporation zone. In fact, the Palestinian (Jebreen et al., 2018) and Lebanese (Awad, 2011) Jurassic and Cretaceous studies fall near Abu Ali's dots especially the Tertiary ones. This observation could be attributed to several similarities between Abu Ali's aquifer and these two aquifers such as: high abundance of karstic formation, the dissolution of the carbonate formations, similar geographical location and climate...etc. However, not all aquifers fall into the rock-water zone. In fact, 43.7% of the aquifers fall into the evaporation zone. Most of them are studies conducted in North Afrcia. In fact, 2 studies are Tunisian (Ben Cheikh et al., 2014; Houatmia et al., 2016), and 2 are Egyptian (Eissa et al., 2016, 2018). This distinctive pattern could be attributed to the high temperature and low precipitation due to arid and semi-arid climate, in addition in most of the cases these aquifers were affected at some degree by the dissolution of evaporates. Despite the high abundance of evaporation between the North African studies, most of Middle Eastern and European studies are clustered in the rock-water interaction zone which also includes Abu Ali's aquifers.

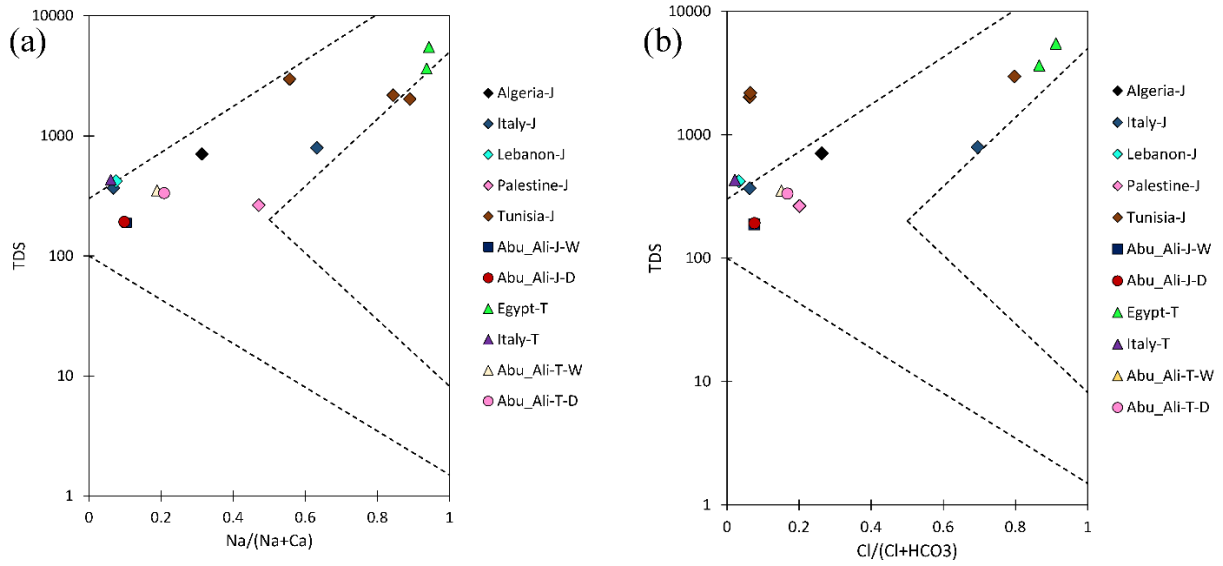


Figure 2.17 Gibbs plots of the Mediterranean studies representing the variation of TDS in comparison with the ratios $Na^+/Na^+ + Ca^{2+}$ (a) and $Cl^-/Cl^-+HCO_3^-$ (b). The data was divided based on the countries and the 2 main aquifers' types: Jurassic & Cretaceous and Tertiary. (Abbreviations in the legend: J "Jurassic & Cretaceous", T "Tertiary", W "Wet season", D "Dry season").

2.5 Conclusion

Ultimately, in this study, 65 samples were extracted and analyzed in laboratory via titration, colorimetric method and ICP-OES in order to reveal the major ions' concentrations. Furthermore, these samples were plotted into distinctive diagrams and plots. After analyzing these plots, the different processes affecting Abu Ali's groundwater were revealed. For instance, the dominant hydrochemical facies in Abu Ali's samples are Ca-HCO_3 and Ca-Mg-HCO_3 with only one exceptional sample falling into the mixed facies, while Gibbs plots showcase the importance of rock-water interaction process in modifying the groundwater's chemistry. In fact, the two previous plots in addition to the saturation index plots, insist on the importance of the weathering process in changing the groundwater chemistry, where the saturation index of calcite and dolomite was high compared to the gypsum saturation indexes; which hold extremely low values. These observations could explain the Ca-HCO_3 and Ca-Mg-HCO_3 dominance. The calcite and dolomite weathering dominate our study area, while the low sulfate concentrations in the plots reveal the low impact of gypsum weathering. Further investigations are needed in order to determine the importance and the impact of this process. Furthermore, the reverse cation exchange affects Abu Ali's groundwater, while the absence of evaporation was also proved. Moreover, the anthropogenic impact was minimal and most of the samples does not hold high concentrations of NO_3^-, SO_4^{2-} and Cl^-. For the multivariate analysis, the samples were plotted into cluster analysis and PCA using RStudio, after that the samples were plotted into maps using ArcGIS according to their distribution in dendrograms. By observing the maps, the importance of elevation in affecting the groundwater's chemistry is striking, where almost all of the groups 3 and 5 samples (W3, W5, D3 and D5) are located south and south east of the study area characterized by high altitude. Furthermore, the PCA plots revealed the processes affecting the 5 clusters' groups, where the 1st group is characterized by high sulfate concentrations and higher gypsum saturation index compared to the whole data, while the 2nd group holds high values of T, TDS, EC, Ca^{2+}, Na^+, HCO_3^-, SO_4^{2-}, NO_3^- and Cl^- and low pH values, which could be attributed to the usage of fertilizers during agriculture activities, especially ammonium sulfate. Furthermore, the 3rd group holds low T, TDS, EC, Ca^{2+}, Na^+, HCO_3^- and Cl^- values. In fact, the majority of its samples are springs located at high altitude, which result in a lower residence period and as a result lower ions and parameters values. Moreover, the 4th group holds higher CAI-2 values. Finally, the 5th group holds

moderate chemical composition without leaning toward the extremes except for chloride, where almost all of its values are considered low in this group.

The final step of our study was to compare Abu Ali's results with previous Lebanese and Mediterranean studies. In fact, the Lebanese comparison focus on 4 studies conducted on the Bekaa (Awad, 2011), Anti-Lebanon (El Hakim, 2005), Nahr Ibrahim (Hanna et al., 2018) and Damour coastal aquifer (Khadra & Stuyfzand, 2014). In fact, Abu Ali's study holds the maximal and minimal values of several ions and parameters, where the lowest concentrations of Ca^{2+}, Na^{+}, K^{+}, SO_4^{2-}, TDS and T and the highest concentrations of Mg^{2+}, Na^{+}, HCO_3^{-}, SO_4^{2-}, TDS, pH and T belong to this study. Moreover, the Ca-HCO_3 and Ca-Mg-HCO_3 facies dominate the Lebanese studies with the exception Nahr Ibrahim (Hanna et al., 2018) and Damour coastal study (Khadra & Stuyfzand, 2014) where most of their samples of fall into the mixed facies, since those samples are located at the coastal zone. In addition, the seawater intrusion, due to overexploitation, occurs in the Damour coastal aquifer. Furthermore, rock-water interaction is the main process affecting the Lebanese groundwater's chemistry.

From the Mediterranean perspective, the data of 23 studies, distributed equally between the "Jurassic & Cretaceous" and "Tertiary" aquifers, were collected in order to put into perspective the situation of Abu Ali basin in comparison with the Mediterranean region. By comparing Abu Ali's Tertiary means and Cretaceous & Jurassic means with the previous Mediterranean studies, it became clear that Abu Ali's study doesn't hold nor maximal nor minimal values of the major ions. In addition, the Piper diagram indicates that Abu Ali's samples and most of the studies in both types of aquifer are dominated by the Ca-HCO_3 and Ca-Mg-HCO_3, with some Mediterranean studies leaning toward the Ca-Cl facies. Finally, the Gibbs plots indicate that Abu Ali's "Jurassic & Cretaceous" and "Tertiary" aquifers, like most of the Mediterranean studies, fall into the rock-water interaction zone during the wet and dry season, while the Jurassic aquifer of Abu Ali in both seasons holds lower TDS values. In addition, the closest means of ions to Abu Ali's Jurassic & Cretaceous aquifer was observed in the Palestinian study conducted on a karstic aquifers located in the central West Bank (Jebreen et al., 2018), which was mainly influenced by water–rock interaction, followed by cation exchange and the carbonate minerals weathering, while Ca-Mg-HCO_3 was considered the dominate facies in this study. In addition, Palestinian (Jebreen et al., 2018) and Lebanese (Awad, 2011) Jurassic and Cretaceous studies fall near Abu Ali's dots

especially the Tertiary one. Due to several similarities between Abu Ali's aquifer and these two aquifers such as: high abundance of karstic formation, the dissolution of the carbonate formations, similar geographical location and climate...etc. Finally, the North African studies conducted in Tunisia (Ben Cheikh et al., 2014; Houatmia et al., 2016) and Egypt (Eissa et al., 2016, 2018) fall into the evaporation zone far from Abu Ali's dots. This distinctive observation could be attributed to the high temperature and low precipitation due to arid and semi-arid climate, in addition to the dissolution of evaporate.

Chapter 3: Water quality assessment of groundwater in Abu Ali basin, Northern Lebanon

Chapter 3: Water quality assessment of groundwater in Abu Ali basin, Northern Lebanon

Rachad Al Haj[1, 2, *], Mohammad Merheb[1], Jalal Halwani[1], Baghdad Ouddane[2]

1 Lebanese University, Water & Environment Science Laboratory, FSP3, Tripoli, Lebanon

2 Université de Lille, LASIRE, UMR CNRS 8516, 59655 Villeneuve d'Ascq Cedex, France.

Rachad AL HAJ: https://orcid.org/0000-0002-4977-6876, mail: rachad.haj_1994@hotmail.com
Mohammad MERHEB: https://orcid.org/0000-0003-0233-9334, email: mohammad.merheb.1@ul.edu.lb
Jalal HALWANI: https://orcid.org/0000-0001-9049-2309, email: jhalwani@ul.edu.lb
Baghdad OUDDANE: https://orcid.org/0000-0002-3778-9696, email: baghdad.ouddane@univ-lille.fr

***Corresponding Author Email:** rachad.haj_1994@hotmail.com

Abstract

World widely, the groundwater is an important natural resource, where several pollutants decreasing its quantity or quality. In fact, the Mediterranean aquifers in general and Lebanese groundwater are also impacted by several pollutants. Therefore, this study focuses on assessing the quality of Abu Ali's groundwater. This Lebanese aquifer is an understudied one located north of the country. First, 65 samples were extracted and physicochemical parameters, major and minor ions' values were measured during the field and laboratory work. Furthermore, different indexes, ratios and plots were computed and constructed. For the domestic usage quality assessment, 1, 1, 2, 8, 13 and 30 samples fall above the limits of TDS, nitrate, arsenic, antimony, thallium and lead respectively. The irrigation quality of Abu Ali's groundwater was assessed after computing the following 7 parameters: RSC, %Na, SAR, PI, total concentrations, KR and MR. According to RSC, 6.2% of the samples were considered unsuitable, due to the infiltration during wet season. Meanwhile, according to sodium percentages, only 3 samples are considered just good and not excellent. The Wilcox diagram indicates that 13 samples, located at low to mid altitude, were considered good to permissible. The same 13 samples hold high salinity hazard according to USSL

diagram, while 8 and 44 samples hold low and medium level respectively. In addition, no sodium hazard was observed. According to Doneen Plot, 10 samples were identified as unsuitable. Furthermore, all samples are safe according to Kelly's ratios. Finally, only 7 samples hold high magnesium ratio. Ultimately, most of the ions, except lead, fall below the thresholds. Meanwhile, following the 7 parameters and several plots, a high number of samples were considered suitable for irrigation

Keywords:

Water quality, groundwater, Lebanon, domestic use, irrigation quality

3.1 Introduction

Water is, without a doubt, one of the most important natural resources on our planet. In fact, groundwater in several countries are considered as indispensable source of life for fauna and flora (Singh et al., 2020), where they rely heavily, even solely, on groundwater as the main source of water (Salifu et al., 2017). This valuable resource could be jeopardized by several problems affecting it quality or quantity. In fact, the increasing needs to cover the demand for irrigation affect this natural resource (Bhat et al., 2018). Meanwhile, the usage of fertilizers, pesticides, and other chemical compounds during the agricultural practices affect its quality (Nag & Lahiri, 2012; Singh et al., 2020). The Mediterranean region is no exception. In fact, this region is characterized by a highly changing environment leading toward scarcity in water; which makes it a fragile natural resource (Iglesias et al., 2007). In addition, many Mediterranean countries depend heavily on groundwater as a stable water source to satisfy all domestic and economic activities (Ergil, 2000). Moreover, many pollutants affect the Mediterranean groundwater (Fernandes et al., 2006; Giménez Forcada & Morell Evangelista, 2008; Manno et al., 2007; Merhabi et al., 2021). Similar to other parts in the Mediterranean, many Lebanese aquifers were affected by several anthropogenic activities. For instance, multiple previous studies proved that seawater intrusion is a serious problem in coastal aquifers (Halwani et al., 2001; Kalaoun et al., 2018; Samad et al., 2017) due to overexploitation of springs and public wells in addition to the illegal wells spread-out all over the country (MoEW, 2014). In addition, the intensive agricultural and domestic activities puts more strain on this valuable resource (Baroudi et al., 2012). Furthermore, in urban areas, wastewater intrusion or sewer pipes crossing could be a source of groundwater contamination (Kjellen, 2000; Korfali & Jurdi, 2007; Saghir et al., 2000). All these problems affecting the groundwater increase the incertitude in the quality of these water supplies. As a result, the quality assessment studies became an important tool in increasing the knowledge concerning the safeness of aquifers' groundwater usage in domestic and agricultural practices. In fact, Abu Ali is a basin located north of Lebanon, where several villags use its groundwater in domestic and agricultural activities. However, this aquifer is considered as an understudied one. The aim of this work is to assess Abu Ali's groundwater quality in order to inspect its viability in domestic and agricultural practices.

3.2 Study area description

3.2.1 Description of the study area

Abu Ali watershed (Fig. 3.1) is located in the North Governorate of Lebanon to the east and southeast of Tripoli. It covers a total area of approximately 489 Km^2 and reach an elevation of 3083 m, which is the highest elevation in Lebanon.

Abu Ali's climate is a Mediterranean one characterized by mild winters and moderately hot summers on the coast. Meanwhile, the precipitation is more abundant in the inland regions, due to colder winters. This precipitation occurs mostly as snow on the highest peaks, and consequently snowmelt plays an active role as a source of water in Abu Ali watershed besides the precipitation (Merheb, 2015).

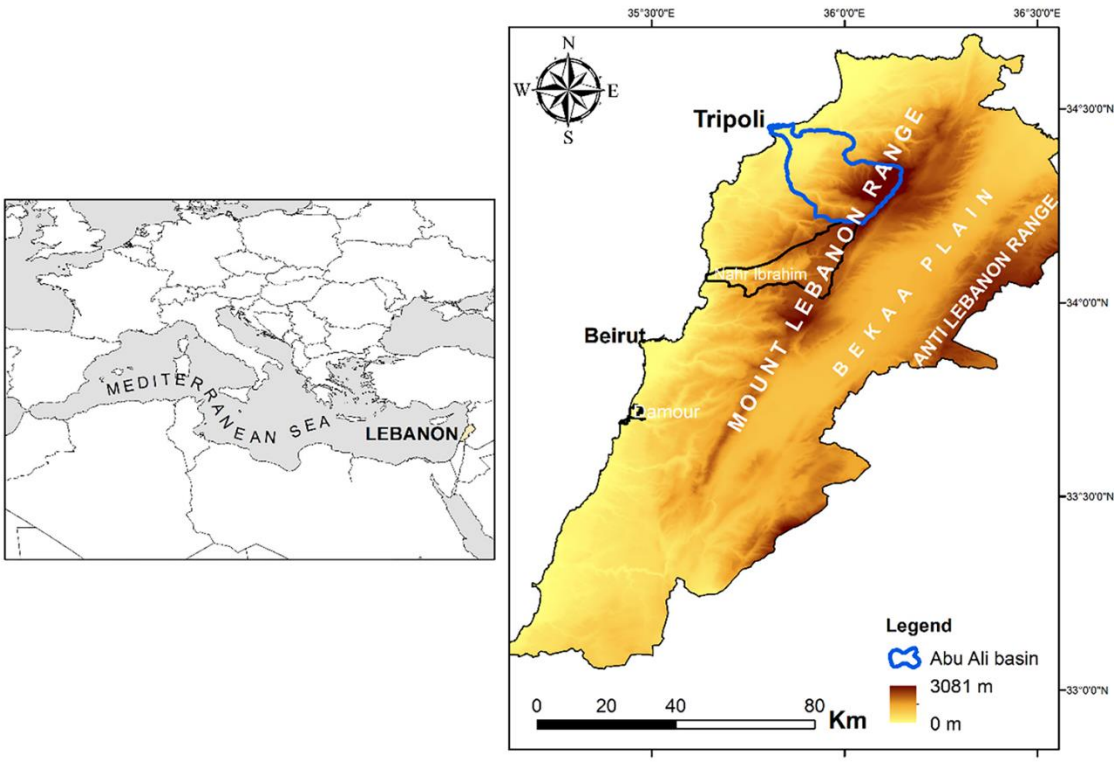


Figure 3.1 Location of Lebanon in the Mediterranean region and our study area in Lebanon

3.2.2 Geology and hydrogeology

The outcropping stratigraphic sequence in the study area exposes rocks from the middle Jurassic to the Quaternary. The main geological outcrops in the basin are from the Cenomanian-Turonian

occupying 57% of the study area. This is also the main aquifer in the region and in the whole country; it can reach a thickness of 700 m of highly fractured and karstified limestone, dolomitic limestone and marly limestone. 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). The second most important aquifer forming rocks in the Abu Ali watershed are from the Miocene, it covers 11.2% of the total watershed surface area but it extends for another 16% of the study area beneath various forms of Quaternary deposits. The Miocene aquifer is made of massive limestone and has an average thickness of 200 – 250 m. The third aquifer in the basin is made of highly fractured and karstified dolomite and dolomitic limestone from the middle to upper Jurassic. These rocks can reach a thickness of 650 m. They cover around 5% of the basin area but extend for another 8% under basalt and Lower Cretaceous rocks.

3.3 Materials and methods

3.3.1 Sampling step and field work

During 2 year, between 2019 and 2020, sixty-five groundwater and springs samples were collected from the study area. In fact, thirty-five samples, distributed randomly, were collected during the wet seasons, while thirty samples were collected during the dry seasons. Twenty of them were collected in May 2019 after the wet season. The same previous twenty samples were collected again after the dry season in September 2019. While other fifteen samples were collected in June 2020 after the wet season and the same sampling process was repeated after the dry season in September 2020. The distribution of samples is presented in figure 3.2. During the sampling process, electrical conductivity (EC) and total dissolved solids (TDS) were measured on the field, while 2 plastic bottles of 2 L and 500 mL in volume were filled and brought back to the laboratory for further chemical analysis.

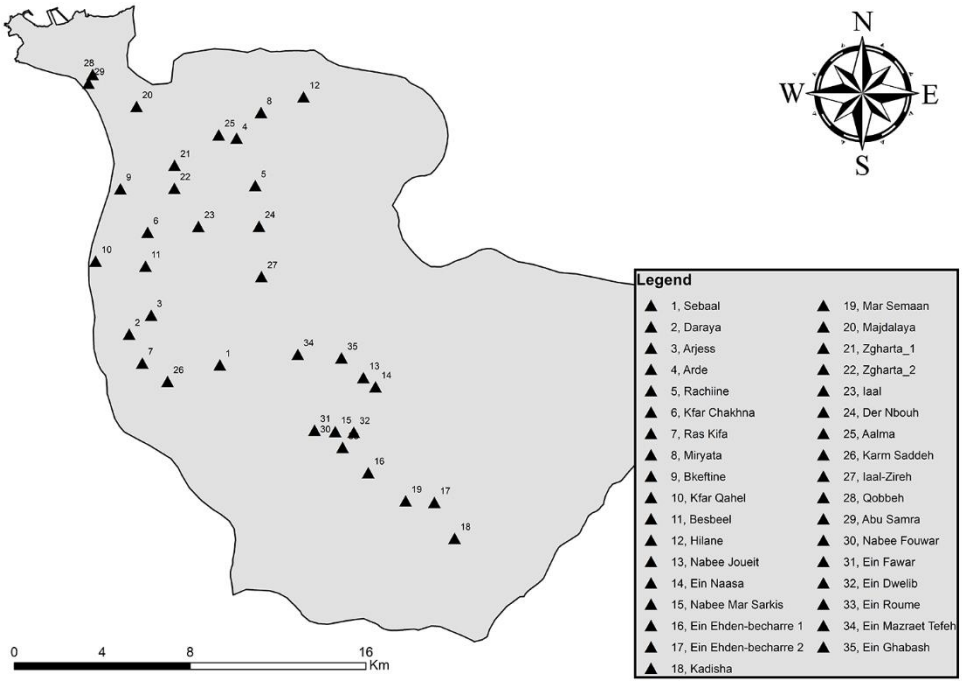


Figure 3.2 Distribution of Abu Ali's samples.

3.3.2 Laboratory work

In the laboratory, the concentrations of bicarbonate and nitrate were measured via titration and colorimetric method respectively. Meanwhile, the concentrations of the following major ions: “calcium, phosphate, magnesium, sulfate, sodium and potassium” and the following 24 minor ions: “aluminium, arsenic, boron, barium, beryllium, bismuth, cadmium, cobalt, chromium, copper, iron, lithium, manganese, molybdenum, nickel, phosphorus, lead, antimony, selenium, strontium, titanium, thallium, vanadium and zinc” were measured by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

3.3.3 Data analysis

In order to assess the quality of Abu Ali’s groundwater several plots and indexes were analyzed. First of all, our data was organized into a statistical table. This data includes total dissolved solids (TDS), 7 major ions, nitrate and 24 minor ions values. Then, the concentrations were compared to the thresholds put by WHO and EPA (EPA, 2018; WHO, 2017) in order to assess the groundwater’s quality in domestic use. For the irrigation quality, the following 7 indexes were computed: percentage sodium (%Na), sodium adsorption ratio (SAR), permeability index (PI),

residual sodium carbonate (RSC), Kelly's ratio (KR), magnesium ratio (MR) and total concentration (T.conc.). Then Wilcox diagram, USSL diagram and Doneen plot were plotted.

3.3.3.1 Residual sodium carbonate (RSC)

The residual sodium carbonate is a parameter measured to inspect the safeness of the water in agricultural practices (Eaton, 1950). The following equation was used in order to reveal the RSC for each sample, where all concentrations were represented in meq/L (Raghunath, 1987):

$$RSC = (HCO_3^- + CO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (3.1)$$

3.3.3.2 Sodium Percentages (%Na)

Sodium is one of the most influential ions in water quality assessment for agriculture (Wilcox, 1948). In fact, the soil permeability is affected heavily by high sodium amount (Jeevanandam et al., 2012). In addition, it can affect the growth of plant (Ameur et al., 2016). %Na were measured using the following equation (Wilcox, 1948), where all the concentrations are expressed in meq/l:

$$\%Na = \frac{Na^+ + K^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \times 100 \quad (3.2)$$

3.3.3.3 Sodium absorption ratio (SAR)

The sodium absorption ratio (SAR) were measured in order to inspect the level of sodium absorption by the soils (Belkhiri & Mouni, 2012). The following equation was used (Richards, 1954), where all concentrations are in meq/L:

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \quad (3.3)$$

3.3.3.4 Permeability index (PI)

The soil permeability could be sensitive to water's chemical composition, where calcium, magnesium, sodium and bicarbonate could affect it (Raghunath, 1987). As a result, the utilization of this water consistently could harm the soil (Madhav et al., 2018). Therefore, the permeability index (PI) was measured. All concentrations were presented in meq/L and the following equation was used (Doneen, 1964):

$$PI = \frac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+} \times 100 \quad (3.4)$$

3.3.3.5 Kelly's ratio (KR)

Kelly's ratio is a formula of Na^+ against Ca^{2+} and Mg^{2+}. In fact, the ratio exceeding 1 indicates an excess level of Na^+ in groundwater which can be considered harmful in irrigation uses. Meanwhile, if the ratio is below 1, the water is considered suitable for irrigation (Kelley, 1951). All concentrations were represented in meq/L and KR was computed following the equation:

$$KR = \frac{Na^+}{Ca^{2+}+Na^+} \quad (3.5)$$

3.3.3.6 Magnesium ratio (MR)

Normally, calcium and magnesium ions maintain an equilibrium in groundwater (Janardhana Raju et al., 2011). In fact, plant growth and soil productivity are affected by the magnesium quantity (Ameur et al., 2016). According to Szabolcs (1964), it plays a vital role if the ratio is below 50%, while a ratio above 50% is considered hazardous. Magnesium ratio (MR) is measured using the following equation, where all concentrations are represented in meq/L (Szabolcs, 1964):

$$MR = \frac{Mg^{2+}}{Mg^{2+}+Ca^{2+}} \times 100 \quad (3.6)$$

3.3.3.7 Wilcox diagram

The Wilcox diagram represents the variation of sodium percentages (%Na) in duction with electrical conductivity (EC). This diagram was used in order to organize and categorize Abu Ali's samples in the following 5 groups: excellent to good, good to permissible, permissible to doubtful, doubtful to unsuitable and unsuitable. Based on this classification, the degree of samples' suitability for agricultural was determined.

3.3.3.8 US Salinity Laboratory's (USSL) diagram

The USSL diagram is a plot representing the variation of sodium adsorption ratio (SAR) in function with electrical conductivity (EC). The SAR represents the sodium hazard, while the electrical conductivity represents the salinity hazard (Wilcox, 1948). The sodium hazard zones are: S1: Low, S2: Medium, S3: High and S4: Very High. Meanwhile, the salinity hazard zones were distributed in the following order: C1: Low (0-249 µS/cm), C2: Medium (250-749 µS/cm), C3: High (750-2249 µS/cm) and C4: Very High (2250-5000 µS/cm).

3.3.3.9 Doneen plot

Doneen plot represents the variation of total concentrations of cations following the permeability index. This plot was divided into 3 parts, which determine the suitability of groundwater's samples for irrigation. The first class is class-1 which is suitable for irrigation and doesn't affect the soil. Meanwhile, class-2 samples are still considered suitable despite that the soil will lose 25% of its permeability due to the utilization of this water consistently during irrigation. However, class-3 samples are considered unsuitable, where the soil's maximum permeability will drop to 25% with constant irrigation.

3.4 Results and discussion

3.4.1 Domestic use

The statistical table (Table 3.1) includes the minimum, mean and maximum values of the total dissolved solids (TDS), 7 major ions, nitrate and 24 minor ions. In addition, the concentrations were compared to the thresholds put by WHO and EPA (EPA, 2018; WHO, 2017). First, the TDS and major ions thresholds are taste thresholds, as result the samples trespassing these limits does not impose serious health problems on consumers. Almost TDS concentrations fall below the threshold equal to 600 mg/L (WHO, 2017), except for 1 sample (S23W) holding a concentration slightly higher than the limit equal to 663 mg/L. In addition, all of sodium, chloride and sulfate concentrations fall below the thresholds equal to 200 mg/L (EPA, 2018), 250 mg/L (WHO, 2017) and 250 mg/L (EPA, 2018) respectively. For calcium, magnesium, potassium and bicarbonate no threshold was assigned by WHO or EPA since they are not of health concern at levels found in drinking-water. For nitrate concentrations, only 1 sample (S22D) falls above the threshold equal to 50 mg/L (WHO, 2017). This sample presents a serious health risk especially on the newborn and infants, since drinking the water can lead to methaemoglobinaemia.

For the minor ions, no WHO or EPA thresholds were found for the following ions: bismuth, cobalt, lithium, phosphorus, strontium, titanium and vanadium. According to WHO, most of the time iron, molybdenum and zinc concentrations are safe in the water, therefore no thresholds were enforced. Moreover, all of Abu Ali's samples fall below the thresholds of aluminium, boron, barium, beryllium, cadmium, chromium, copper, manganese, nickel and selenium. For arsenic, only 2 samples (S04W and S30D) fall above the threshold equal to 10 µg/L (WHO, 2017). In fact, the arsenic is a strong carcinogenic agent. The ingestion of this compound through food or water,

especially untreated well-water, could cause chronic arsenicism. Severe symptoms and implications are observed in the patient such as: dermal lesions (hyperpigmentation and hypopigmentation), peripheral neuropathy, peripheral vascular disease, and skin, bladder and lung cancers. For antimony, 8 samples (S02D, S04W, S08D, S09 (W&D), S13W, S16W and S19W) fall above WHO threshold equal to 20 µg/L. Normally raw water does not includes antimony. The most common source of this ion is the dissolution from metal plumbing and fittings (WHO, 2017). Moreover, 13 samples fall above the EPA threshold of thallium equal to 2 µg/L. Finally, the lead concentrations showcase the most worrying data in this study. In fact, 30 samples, which represents 46.2% of the data, fall above the threshold equal to 10 µg/L (WHO, 2017). The long exposure to this compound could cause several neurodevelopmental effects, cardiovascular diseases leading to mortality, impaired renal function, hypertension, impaired fertility and adverse pregnancy outcomes (WHO, 2017).

Table 3.1 Statistical table represents the major and minor ions and their thresholds according to WHO (World Health Organization, 2017) and EPA (Environmental Protection Agency, 2018). (D.L.: Detection Limit, N.D.: Not determined, below the detection limit, N.A.: not available).

		Min	Mean	Max	D.L.	Thresholds	Sample numbers exceeding the thresholds	References
mg/L	TDS	90.0	267.6 ± 115.8	663.0	N.A.	600 mg/L	1	WHO 2017
	Ca	13.1	50.9 ± 28	140.7	0.00003	N.A.	N.A.	N.A.
	Mg	3.4	16.5 ± 11.4	57.9	0.0001	N.A.	N.A.	N.A.
	Na	0.8	10.4 ± 11.1	70.9	0.001	200 mg/L	0	EPA 2018
	K	0.1	1.5 ± 2.7	18.4	0.01	N.A.	N.A.	N.A.
	HCO3	100.0	251.5 ± 76.6	400.0	N.A.	N.A.	N.A.	N.A.
	Cl	8.0	36.7 ± 26.2	138.2	N.A.	250 mg/L	0	WHO 2017
	SO4	1.8	16.4 ± 23.8	181.4	0.02	250 mg/L	0	EPA 2018
	NO3	6.3	16.3 ± 12.7	85.7	N.A.	50 mg/L	1	WHO 2017
µg/L	Al	3.0	5.5 ± 3.8	17.0	1.5	200 µg/L	0	EPA 2018
	As	14.0	18 ± 3.5	20.0	12	10 µg/L	2	WHO 2017
	B	95.0	102 ± 9.9	109.0	1.5	2400 µg/L	0	WHO 2017
	Ba	1.0	21.4 ± 30.4	134.9	0.07	1300 µg/L	0	WHO 2017
	Be	N.D.	N.D.	N.D.	0.2	4 µg/L	0	EPA 2018
	Bi	N.D.	N.D.	N.D.	12	N.A.	N.A.	N.A.

		Min	Mean	Max	D.L.	Thresholds	Sample numbers exceeding the thresholds	References
	Cd	N.D.	N.D.	N.D.	1.5	3 µg/L	0	WHO 2017
	Co	N.D.	N.D.	N.D.	5	N.A.	N.A.	N.A.
	Cr	N.D.	N.D.	N.D.	4	50 µg/L	0	WHO 2017
	Cu	3.0	3.3 ± 0.6	4.0	2	2000 µg/L	0	WHO 2017
	Fe	N.D.	N.D.	N.D.	1.5	No risk	N.A.	WHO 2017
	Li	16.0	73 ± 80.6	130.0	0.6	N.A.	N.A.	N.A.
	Mn	0.8	2.5 ± 4.7	21.1	0.3	400 µg/L	0	WHO 2017
	Mo	N.D.	N.D.	N.D.	4	No risk	N.A.	WHO 2017
	Ni	7.0	11 ± 3.6	14.0	5.5	70 µg/L	0	WHO 2017
	P	23.0	50.3 ± 43.1	100.0	18	N.A.	N.A.	N.A.
	Pb	22.0	65.1 ± 24.9	107.0	14	10 µg/L	30	WHO 2017
	Sb	20.0	25.9 ± 4.3	33.0	18	20 µg/L	8	WHO 2017
	Se	N.D.	N.D.	N.D.	37	40 µg/L	0	WHO 2017
	Sr	20.3	339.5 ± 1325	10640.0	0.02	N.A.	N.A.	N.A.
	Ti	N.D.	N.D.	N.D.	0.6	N.A.	N.A.	N.A.
	Tl	18.0	109.4 ± 92.1	314.0	16	2 µg/L	13	EPA 2018
	V	3.0	4.6 ± 1.4	10.0	2	N.A.	N.A.	N.A.
	Zn	0.9	52.8 ± 163	800.2	0.9	No risk	N.A.	WHO 2017

3.4.2 Irrigation water quality

In order to assess the irrigation usage of Abu Ali's groundwater, EC for the 65 samples were measured on the field and the following 7 parameters where computed: percentage sodium (%Na), sodium adsorption ratio (SAR), permeability index (PI), residual sodium carbonate (RSC), Kelly's ratio (KR), magnesium ratio (MR) and total concentration (T.conc.). In addition, this data was organized in 1 table (Appendix 4).

3.4.2.1 Residual sodium carbonate (RSC)

In fact, RSC mean was equal to 0.2, while its data hold a minimum -3.5 equal to and a maximum equal to 3.8. According to table 3.2, 86.1% of Abu Ali's samples are considered harmless. However, 7.7% and 6.2% of the samples are marginally suitable and unsuitable respectively. Moreover, all of these samples above 1.25 were extracted during the wet season, which could be

the main culprit behind the increase in RSC values. In fact, the infiltration of rainfall during this season could cause higher rock-water interaction leading to higher bicarbonate dissolution in Abu Ali's groundwater. In fact, this observation became more obvious after comparing the RSC means of wet and dry seasons equal to 0.6 and -0.3 respectively.

Table 3.2 Residual sodium carbonate (RSC) of Abu Ali's samples.

RSC	Quality	number of samples	"Marginally Suitable" or "Unsuitable" samples
<1.25	**Safe**	56	
1.25-2.5	**Marginally Suitable**	5	S02W, S06W, S07W, S11W and S14W
>2.5	**Unsuitable**	4	S23W, S27W, S33W and S34W

3.4.2.2 Sodium percentage (%Na)

Table 3.3 Sodium percentages of Abu Ali's samples.

%Na	Quality	No. of samples
<20	**Excellent**	62
20-40	**Good**	3
40-60	**Permissible**	0
60-80	**Doubtful**	0
>80	**Unsuitable**	0
Total		65

After obtaining the sodium percentages, the groundwater's samples were assessed based on it. According to table 3.3, almost all of Abu Ali's samples are excellent with sodium percentages below 20%. Meanwhile only 3 samples hold percentages between 20% and 40% and as a result are considered good. In fact, S04D, S09D and S28D are the 3 samples trespassing 20%. In fact, these higher percentages could be attributed to several processes. Based on the previous hydrogeochemical study of Abu Ali's groundwater (Al Haj et al., 2021), the samples S04D and S28D were slightly more affected by evaporation process compared to the majority of samples, while reverse ions exchange reaction plays an important role in shaping S09D chemistry. In order to categorized the groundwater's samples, according to sodium percentages and EC, Wilcox (1984) diagram was used (Fig. 3.3).

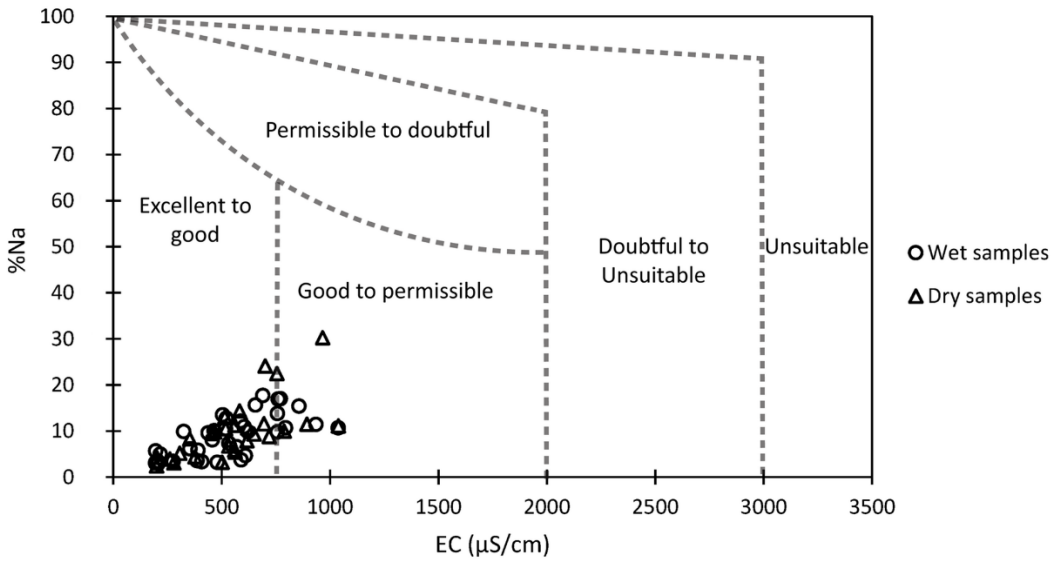


Figure 3.3 Wilcox diagram for classification of Abu Ali's samples.

By observing the diagram, it became clear that most of Abu Ali's samples follow a similar pattern, where 80% of the dots are clustered in the "Excellent to good" zone. Meanwhile, the following 13 samples: S02W, S04 (W&D), S06 (W&D), S09W, S11W, S21 (W&D), S22 (W&D), S25W and S28D are considered good to permissible. All those samples are located at low to mid altitude, which could explain this distribution. In fact, the residence time is generally higher in low altitude groundwater leading to higher total dissolved solids and electrical conductivity (El-Hakim & Bakalowicz, 2007; Guo et al., 2019).

3.4.2.3 Sodium absorption ratio (SAR)

The US Salinity Laboratory's diagram was plotted, in which Abu Ali's samples are classified based on the variation of SAR following electrical conductivity (Richards, 1954). According to figure 3.4, all of Abu Ali's samples fall into the S1 zone, which ensure that the samples are not sodium hazardou**s.** Meanwhile, these samples are spreading between 3 salinity hazard groups, from low (C1) to high (C3). The table 3.4 represents the number of samples in each group. In fact, most of Abu Ali's samples hold medium salinity hazardous effect on the soils, with 67.7% of the samples falling into this territory. Meanwhile, only 8 samples belong to the group C1, where the salinity hazard is considered low. Finally, the high salinity hazard group (C3) includes the same 13 samples considered good to permissible according to Wilcox diagram (Fig. 3.3).

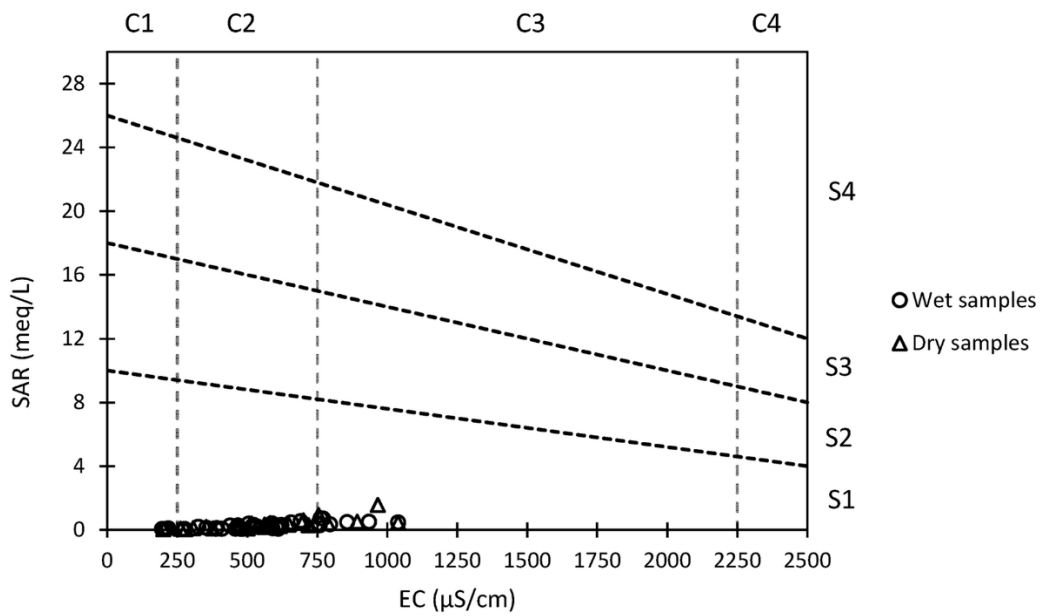


Figure 3.4 USSL diagram for classification of Abu Ali's irrigation groundwater (Sodium Hazard: S1 low, S2, medium, S3 high and S4 very high, Salinity Hazard: C1 low, C2 medium, C3 high and C4 very high).

Table 3.4 Salinity Hazard of Abu Ali's samples.

Classes	Salinity Hazard	number of samples	"Low" and "High" Salinity Hazard samples
<250 µS/cm (C1)	**Low**	8	S13D, S15W, S17W, S19 (W&D), S24W and S32 (W&D)
250-750 µS/cm (C2)	**Medium**	44	
750-2250 µS/cm (C3)	**High**	13	S02W, S04 (W&D), S06 (W&D), S09W, S11W, S21 (W&D), S22 (W&D), S25W and S28D
>2250 µS/cm (C4)	**Very High**	0	----------

3.4.2.4 Permeability Index

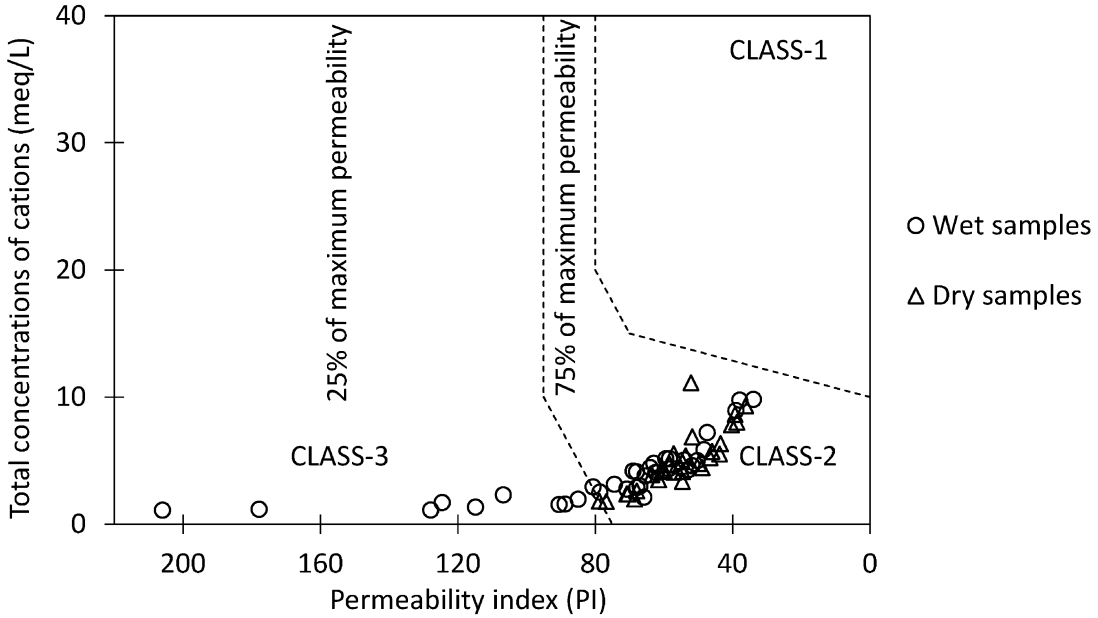


Figure 3.5 Doneen Plot of Permeability Index for Abu Ali's groundwater.

The samples were plotted into Doneen plot (Fig. 3.5). In fact, most of the samples are observed in the class-2 zone, where 84.6% of the samples fall into this area. Therefore, those samples are considered as good for agricultural practices, where the soil maintain its permeability for about 75% of its full capacity. Meanwhile, the following 10 samples: S13 (W&D), S15W, S17W, S19W, S23W, S27W, S32W, S33W and S34W were located in villages dominated by agricultural activities. These samples belong to the class-3. Therefore, they are considered as unsuitable for agriculture and irrigation since they affect the soil greatly, where its permeability could drop to 25% of its maximum permeability. This observation was accompanied by the fact that 9 out of 10 samples falling in class-3 zone were extracted during the wet season. In fact, these findings could lead to a conclusion that only the sodium and bicarbonate concentrations increased in these samples in wet season, while the calcium, magnesium concentrations remain constant or even decreased, which led to higher permeability index in the wet season samples. The most probable cause of this increasing could be the poor agricultural practices due to a misuse of certain fertilizers or pesticides such as sodium bicarbonate, accompanied with the infiltration of rainfall and precipitation in wet season.

3.4.2.5 Kelly's ratio (KR)

Kelly's ratio is a formula of Na^+ against Ca^{2+} and Mg^{2+}. In fact, the ratio exceeding 1 indicates an excess level of Na^+ in groundwater which can be considered harmful in irrigation uses. Meanwhile, if the ratio is below 1, the water is considered suitable for irrigation (Kelley, 1951). All of Abu Ali's samples hold Kelly's ratios falling below 1, and as result they are considered suitable for irrigation.

3.4.2.6 Magnesium ratio (MR)

Table 3.5 Magnesium ratio of Abu Ali's samples

Magnesium ratio	Quality	number of samples	Unsuitable samples
<50%	**Suitable**	58	
>50%	**Unsuitable**	7	S01W, S04D, S09W, S11 (W&D), S14W and S18W

In fact, 89.2%, of Abu Ali's samples are considered safe for use, where the magnesium ratios were below 50%. However, 7 samples hold higher ratios trespassing 50%. As a result, 10.8% of Abu Ali's samples are considered unsuitable for irrigation and may be harmful to soil and plants.

3.5 Conclusion

Ultimately, in this study, 65 samples were extracted and TDS and EC were measured during the field work. Then these samples were analyzed in laboratory via titration, colorimetric method and ICP-OES in order to reveal the nitrate, 7 major and 24 minor ions' concentrations. In order to analyze the groundwater quality for irrigation, different indexes and ratios were computed and several diagrams were plotted. After analyzing these samples from different perspective, the groundwater quality of Abu Ali's samples was assessed. From one hand, in order to assess the domestic use quality, the samples concentrations were compared by the thresholds put by WHO or EPA. Only 1 sample falls above the thresholds of TDS and nitrate, while 2, 8 and 13 samples trespass the limits of arsenic, antimony and thallium respectively. However, the most alarming observation in the statistical analysis was the lead, where 30 samples fall above the limit. In fact, lead is highly carcinogenic compound. The rest of ions fall below the detection limit or the quality limit put by WHO or EPA. From the other hand, the irrigation quality of Abu Ali's groundwater

was assessed after computing 7 different parameters. First, the residual sodium carbonate (RSC) data holds a mean equal to 0.2, while its values fluctuate between -3.5 and 3.8. in Fact, 86.1% of Abu Ali's samples were considered harmless. However, 7.7% and 6.2% of the samples were considered marginally suitable and unsuitable respectively, with the unsuitable ones extracted during the wet season. Meanwhile, according to sodium percentages (%Na), almost all of Abu Ali's samples are excellent and only 3 samples are considered just good. The Wilcox diagram indicates that 80% of the samples were considered excellent to good. Meanwhile, 13 samples, located at low to mid altitude, were considered good to permissible, which could explain this distribution, due to higher residence time leading to higher TDS and EC. For sodium absorption ratio (SAR), the samples show several levels of salinity hazard, where most of the samples hold medium level and only 8 samples hold low level. In addition, the high salinity hazard group (C3) includes the same 13 samples considered good to permissible according to Wilcox diagram. According to Doneen Plot of Permeability Index, almost all samples belong to class-2 and were considered good for agricultural practices. Meanwhile, 10 unsuitable samples, belong to class-3, located in villages dominated by agricultural activities. In addition, the majority was extracted during the wet season. Furthermore, all of Abu Ali's samples hold Kelly's ratios falling below 1, and as result they are considered suitable for irrigation. Finally, for magnesium ratio, 89.2%, of Abu Ali's samples are considered safe for use, while 7 samples of Abu Ali's samples are considered unsuitable for irrigation and may be harmful to soil and plants. To summarize the analysis, most of major and minor ions values, except for lead, fall below the WHO or EPA thresholds. Furthermore, according to the computed ratios and indexes, a high number of Abu Ali's samples are considered suitable for irrigation, while some samples are considered permissible or doubtful. In fact, rarely Abu Ali's samples are considered completely unsuitable for agricultural practices.

General Conclusion

General Conclusion

This thesis aimed at analyzing the hydrogeochemical characteristics of groundwater Abu Ali's basin, located north of Lebanon, and compare it the Mediterranean region aquifers. In addition, the domestic and irrigation quality of Abu Ali's groundwater was inspected and assessed. For this purpose, the first chapter focuses of the Mediterranean region, where 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 considered the geographical location of the studies with a focus on 3 main geographical regions: Europe, North Africa and the Middle East. Meanwhile, second chapter focuses on the hydrogeochemical characteristics of Abu Ali's groundwater. During the field work, 65 samples were extracted and the physicochemical parameters were measured. During the laboratory work, each sample was analyzed via titration, colorimetric method and ICP-OES in order to reveal the major ions' concentrations. Furthermore, the data was analyzed using classical geochemical diagrams and multivariate analysis. After analyzing these plots, the different processes affecting Abu Ali's groundwater were revealed. After obtaining the hydrogeochemical knowledge of the Lebanese basin, the comparison between Abu Ali's groundwater and the Mediterranean data was executed. For the third chapter, Abu Ali's groundwater quality was assessed. In order to achieve this goal, the 65 samples were analyzed in laboratory via ICP-OES in order to reveal the concentrations of 24 minor ions. Then the minor ions concentrations were organized along with the previously measured values of TDS, nitrate, and 7 major ions. Furthermore, using this data, different indexes and ratios were computed and several diagrams were plotted. After analyzing these samples from different perspective, the groundwater quality of Abu Ali's samples was assessed.

The first chapter concerning the hydrogeochemical characteristics of the Mediterranean region, tackles a qualitative and quantitative analysis. From 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. From 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: 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 addition, 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. Finally, 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. Even the minimal and maximal values belong to Quaternary aquifers. 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‰.

The second chapter of the thesis focuses on revealing the hydrogeochemical characteristics of Abu Ali's groundwater and compare it to the previously discussed characteristics of the Mediterranean region. First, the dominant hydrochemical facies in Abu Ali's samples are Ca-HCO_3 and Ca-Mg-HCO_3 with only one exceptional sample falling into the mixed facies, while Gibbs plots showcase the importance of rock-water interaction process in modifying the groundwater's chemistry. In fact, the two previous plots in addition to the saturation index plots, insist on the importance of the weathering process in changing the groundwater chemistry, where the saturation index of calcite and dolomite was high compared to the gypsum saturation indexes; which hold extremely low values. These observations could explain the Ca-HCO_3 and Ca-Mg-HCO_3 dominance. The calcite and dolomite weathering dominate our study area, while the low sulfate concentrations in the plots reveal the low impact of gypsum weathering. Further investigations are needed in order to determine the importance and the impact of this process. Furthermore, the reverse cation exchange affects Abu Ali's groundwater, while the absence of evaporation was also proved. Moreover, the anthropogenic impact was minimal and most of the samples does not hold high concentrations of NO3-, SO42- and Cl-. For the multivariate analysis, the samples were plotted into cluster analysis and PCA using RStudio, after that the samples were plotted into maps using ArcGIS according to their distribution in dendrograms. According to the cluster analysis, our samples was distributed between 5 groups in the wet (from left to right: W1, W2, W3, W4 and W5) and dry (from left to right: D1, D2, D3, D4 and D5) dendrograms. By observing the maps, the importance of elevation in affecting the groundwater's chemistry is striking, where almost all of the groups 3 and 5 samples (W3, W5, D3 and D5) are located south and south east of the study area characterized by high altitude. Furthermore, the PCA plots revealed the processes affecting the 5 clusters' groups, where the 1st group is characterized by high sulfate concentrations and higher gypsum saturation index compared to the whole data, while the 2nd group holds high values of T, TDS, EC, Ca2+, Na+, HCO3-, SO42-, NO3- and Cl- and low pH values, which could be attributed to the usage of

fertilizers during agriculture activities, especially ammonium sulfate. Furthermore, the 3rd group holds low T, TDS, EC, Ca2+, Na+, HCO3- and Cl- values. In fact, the majority of its samples are springs located at high altitude, which result in a lower residence period and as a result lower ions and parameters values. Moreover, the 4th group holds higher CAI-2 values. This observation indicates that this group was more affected by reverse ions exchange. Finally, the 5th group holds moderate chemical composition without leaning toward the extremes except for chloride, where almost all of its values are considered low in this group.

The final step of our study was to compare Abu Ali's results with previous Lebanese and Mediterranean studies. In fact, the Lebanese comparison focus on 4 studies conducted on the Bekaa (Awad 2011), Anti-Lebanon (El Hakim 2005), Nahr Ibrahim (Hanna et al. 2018) and Damour coastal aquifer (Khadra and Stuyfzand 2014). In fact, Abu Ali's study holds the maximal and minimal values of several ions and parameters, where the lowest concentrations of Ca2+, Na+, K+, SO42-, TDS and T and the highest concentrations of Mg2+, Na+, HCO3-, SO42-, TDS, pH and T belong to this study. Moreover, the Ca-HCO_3 and Ca-Mg-HCO_3 facies dominate the Lebanese studies with the exception Nahr Ibrahim (Hanna et al. 2018) and Damour coastal study (Khadra and Stuyfzand 2014) where most of their samples of fall into the mixed facies, since those samples are located at the coastal zone. In addition, the seawater intrusion, due to overexploitation, occurs in the Damour coastal aquifer. Furthermore, rock-water interaction is the main process affecting the Lebanese groundwater's chemistry.

From the Mediterranean perspective, the data of 23 studies, distributed equally between the "Jurassic & Cretaceous" and "Tertiary" aquifers, were collected in order to put into perspective the situation of Abu Ali basin in comparison with the Mediterranean region. By comparing Abu Ali's Tertiary means and Cretaceous & Jurassic means with the previous Mediterranean studies, it became clear that Abu Ali's study doesn't hold nor maximal nor minimal values of the major ions. In addition, the Piper diagram indicates that Abu Ali's samples and most of the studies in both types of aquifer are dominated by the Ca-HCO_3 and Ca-Mg-HCO_3, with some Mediterranean studies leaning toward the Ca-Cl facies. Finally, the Gibbs plots indicate that Abu Ali's "Jurassic & Cretaceous" and "Tertiary" aquifers, like most of the Mediterranean studies, fall into the rock-water interaction zone during the wet and dry season, while the Jurassic aquifer of Abu Ali in both seasons holds lower TDS values. In addition, the closest means of ions to Abu Ali's Jurassic &

Cretaceous aquifer was observed in the Palestinian study conducted on a karstic aquifer located in the central West Bank (Jebreen et al. 2018), which was mainly influenced by water–rock interaction, followed by cation exchange and the carbonate minerals weathering, while Ca-Mg-HCO_3 was considered the dominate facies in this study. In addition, Palestinian (Jebreen et al. 2018) and Lebanese (Awad 2011) Jurassic and Cretaceous studies fall near Abu Ali's dots especially the Tertiary one. Due to several similarities between Abu Ali's aquifer and these two aquifers such as: high abundance of karstic formation, the dissolution of the carbonate formations, similar geographical location and climate...etc. Finally, the North African studies conducted in Tunisia (Ben Cheikh et al. 2014; Houatmia et al. 2016) and Egypt (Eissa et al. 2016, 2018) fall into the evaporation zone far from Abu Ali's dots. This distinctive observation could be attributed to the high temperature and low precipitation due to arid and semi-arid climate, in addition to the dissolution of evaporate.

The third chapter focuses on the water quality assessment of Abu Ali's groundwater. In this part, the domestic use and irrigation quality were analyzed. From one hand, in order to assess the domestic use quality, the samples concentrations were compared by the thresholds put by WHO or EPA. Only 1 sample falls above the thresholds of TDS and nitrate, while 2, 8 and 13 samples trespass the limits of arsenic, antimony and thallium respectively. However, the most alarming observation in the statistical analysis was the lead, where 30 samples fall above the limit. In fact, lead is highly carcinogenic compound. The rest of ions fall below the detection limit or the quality limit put by WHO or EPA. From the other hand, the irrigation quality of Abu Ali's groundwater was assessed after computing 7 different parameters. First, the residual sodium carbonate (RSC) data holds a mean equal to 0.2, while its values fluctuate between -3.5 and 3.8. in Fact, 86.1% of Abu Ali's samples were considered harmless. However, 7.7% and 6.2% of the samples were considered marginally suitable and unsuitable respectively, with the unsuitable ones extracted during the wet season. Meanwhile, according to sodium percentages (%Na), almost all of Abu Ali's samples are excellent and only 3 samples are considered just good. The Wilcox diagram indicates that 80% of the samples were considered excellent to good. Meanwhile, 13 samples, located at low to mid altitude, were considered good to permissible, which could explain this distribution, due to higher residence time leading to higher TDS and EC. For sodium absorption ratio (SAR), the samples show several levels of salinity hazard, where most of the samples hold

medium level and only 8 samples hold low level. In addition, the high salinity hazard group (C3) includes the same 13 samples considered good to permissible according to Wilcox diagram. According to Doneen Plot of Permeability Index, almost all samples belong to class-2 and were considered good for agricultural practices. Meanwhile, 10 unsuitable samples, belong to class-3, located in villages dominated by agricultural activities. In addition, the majority was extracted during the wet season. Furthermore, all of Abu Ali's samples hold Kelly's ratios falling below 1, and as result they are considered suitable for irrigation. Finally, for magnesium ratio, 89.2%, of Abu Ali's samples are considered safe for use, while 7 samples of Abu Ali's samples are considered unsuitable for irrigation and may be harmful to soil and plants. To summarize this part, most of major and minor ions values, except for lead, fall below the WHO or EPA thresholds. Furthermore, according to the computed ratios and indexes, a high number of Abu Ali's samples are considered suitable for irrigation, while some samples are considered permissible or doubtful. In fact, rarely Abu Ali's samples are considered completely unsuitable for agricultural practices.

In the end, the first chapter 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. 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. Moreover, specific problems that are more common in the Mediterranean region should be studied more thoroughly such as sea water intrusion in coastal areas especially since areas are heavily populated in the Mediterranean and depend to large extent on groundwater. In addition, this work only focused on the inorganic aspect of groundwater chemistry, organic pollutant and emerging pollutants in general should be accounted for in the Mediterranean in future studies. Furthermore, our work did not take into account seasonal variability of groundwater hydrogeochemical characteristics. This should certainly be studied in more details especially for shallow quaternary aquifers. Finally, the Mediterranean meta-analysis presented in this thesis only focuses on one aspect of groundwater quality, while groundwater quantity is also a major concern in the Mediterranean region. A concern that should be addressed in similar comparative studies.

The second chapter of this thesis is a hydrogeochemical study focusing on Abu Ali's aquifer. Despite the focusing on Abu Ali's groundwater, this study only takes into consideration the general hydrogeochemical characteristics of groundwater in this basin, while a number of knowledge remains understudied. One can mention, the water origin, residence time, water fluxes groundwater-surface water interaction, etc. So in order to increase the border of investigation, an isotopic study concerning Abu Ali's groundwater is needed. Moreover, in this study, and due to technical and financial issues, it was not possible to measure the potentiometric level of groundwater in Abu Ali's aquifers. This is certainly one major shortcoming of this work that limited our ability to model groundwater chemistry and water flow in the studied aquifers. This limitation should certainly be addressed in future studies. Moreover, this work only focused on field measurements and data analysis, perhaps the use of this data in future studies for the groundwater modeling in the aquifers of the basin will provide more insights on the chemical evolution of groundwater in this study area.

Finally, the third chapter focuses on Abu Ali's groundwater quality for domestic and irrigation use. Despite analyzing a relatively big data, including TDS, nitrate, 7 major ions and 24 minor ions values of 65 samples, this study focuses only on the chemical aspect of this groundwater, therefore even if the chemical composition of groundwater was safe according to the analysis, the drinkability state of this groundwater remains unclear. Therefore, microbiological studies for this aquifer are needed in order to reveal the extent of bacterial and viral contamination in Abu Ali's groundwater. Moreover, and as mentioned for the first chapter, this work only dealt with the inorganic aspect of groundwater chemistry. More work is certainly needed to assess the organic and emergent pollutant in the basin.

Finally, this work was also limited in space and time. It only focuses on one basin in Lebanon and the data were collected during only two years. Long term studies for groundwater monitoring in various part of the country and in all the Mediterranean region are certainly a most. One would certainly recommend to undertake annual survey of the studied wells and springs in order to study the temporal evolution of the groundwater chemistry.

At the end, all of these perspectives and recommendations are certainly limited by the available technical and financial capacities that are unfortunately decreasing in the Lebanon especially after the unprecedented ongoing economic crisis ravaging the country since October 2019. Hence, the

prospects for water quality in general and groundwater quality in particular over the Lebanese territories do not look good at all.

References

Abo, R. K., & Merkel, B. J. (2015). Comparative estimation of the potential groundwater recharge in Al Zerba catchment of Aleppo basin, Syria. *Arabian Journal of Geosciences*, *8*(3), 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). *Environmental Earth Sciences*, *75*(15), 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. *Science of The Total Environment*, *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). *Geologica Acta: An International Earth Science Journal*, *11*(4), 389–407.

Acra, A., & Ayoub, G. M. (2001). Indicators of coastal groundwater quality changes induced by seawater infiltration. *International Journal of Environmental Studies*, *58*(6), 761–769. https://doi.org/10.1080/00207230108711367

Al Haj, R., Merheb, M., Halwani, J., & Ouddane, B. (2021). The hydrogeochemical characteristics of groundwater in Abu Ali watershed (Northern Lebanon). *Submitted in Groundwater Journal*.

Al-Agha, M. R. (2005). Hydrogeochemistry and carbonate saturation model of groundwater, Khanyounis Governorate—Gaza Strip, Palestine. *Environmental Geology*, *47*(7), 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. *Journal of Hydrology*, *359*(1–2), 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. *Environmental Earth Sciences*, *75*(12), 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. *Journal of Hydrology: Regional Studies*, *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). *Journal of Geochemical Exploration*, *185*, 105–115. https://doi.org/10.1016/j.gexplo.2017.11.004

Ameur, M., Hamzaoui-Azaza, F., & Gueddari, M. (2016). Suitability for human consumption and agriculture purposes of Sminja aquifer groundwater in Zaghouan (north-east of Tunisia) using GIS and geochemistry techniques. *Environmental Geochemistry and Health*, *38*(5), 1147–1167. https://doi.org/10.1007/s10653-015-9780-2

Andrade, A. I. A. S. S., & Stigter, T. Y. (2011). Hydrogeochemical controls on shallow alluvial groundwater under agricultural land: Case study in central Portugal. *Environmental Earth Sciences*, *63*(4), 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). *Journal of African Earth Sciences*, *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. *Science of The Total Environment*, *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). *Environmental Earth Sciences*, *72*(8), 3205–3225. https://doi.org/10.1007/s12665-014-3226-5

Assaf, H., & Saadeh, M. (2008). Assessing water quality management options in the Upper Litani Basin, Lebanon, using an integrated GIS-based decision support system. *Environmental Modelling & Software*, *23*(10), 1327–1337. https://doi.org/10.1016/j.envsoft.2008.03.006

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 Resources Management*, *23*(4), 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]. https://doi.org/10/1/ASSAKER.pdf

Aureli, A., Ganoulis, J., & Margat, J. (2008). Groundwater resources in the Mediterranean region: Importance, uses and sharing. *Water in the Mediterranean, Med*.

Awad, S. (2011). Hydrochimie et faciès géochimiques des eaux souterraines, Plaine de Bekaa. *Hydrological Sciences Journal*, *56*(2), 334–348. https://doi.org/10.1080/02626667.2011.559331

Bakalowicz, M. (2014). Karst at depth below the sea level around the Mediterranean due to the Messinian crisis of salinity. Hydrogeological consequences and issues. *Geologica Belgica*. https://popups.uliege.be/1374-8505/index.php?id=4435

Bakalowicz, M. (2015). Karst and karst groundwater resources in the Mediterranean. *Environmental Earth Sciences*, *74*(1), 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*(7), 258. https://doi.org/10.3390/geosciences8070258

Bakalowicz, M., El Hakim, M., & El-Hajj, A. (2008). Karst groundwater resources in the countries of eastern Mediterranean: The example of Lebanon. *Environmental Geology*, *54*(3), 597–604. https://doi.org/10.1007/s00254-007-0854-z

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.

Barbieri, M., & Morotti, M. (2003). Hydrogeochemistry and strontium isotopes of spring and mineral waters from Monte Vulture volcano, Italy. *Applied Geochemistry*, *18*(1), 117–125. https://doi.org/10.1016/S0883-2927(02)00069-0

Baroudi, M., Bakkour, H., Halwani, J., Taha, S., EL-OSMANI, R., & Mouneimne, A. (2012). Determination of pesticides, nitrates and nitrites level in groundwater of Akkar plain in Northen Lebanon. *Journal of Applied Sciences Research*, *8*, 4663–4667.

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. *Environmental Earth Sciences*, *73*(6), 2881–2894. https://doi.org/10.1007/s12665-014-3297-3

Bear, J., Cheng, A. H.-D., Sorek, S., Ouazar, D., & Herrera, I. (1999). *Seawater Intrusion in Coastal Aquifers: Concepts, Methods and Practices*. Springer Science & Business Media.

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. *Applied Water Science*, *7*(3), 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. *Applied Water Science*, *2*(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*(1), 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 and Evaporites*, *29*(2), 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 Procedia*, *119*, 318–324. https://doi.org/10.1016/j.egypro.2017.07.115

Bhat, M., Wani, S., Singh, V., Sahoo, J., Tomar, D., & Prakash, R. (2018). *An Overview of the Assessment of Groundwater Quality for Irrigation*. *9*, 1000209.

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 B. Andreo, F. Carrasco, J. J. Durán, & J. W. LaMoreaux (Eds.), *Advances in Research in Karst Media* (pp. 157–162). Springer Berlin Heidelberg. 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. *Science of The Total Environment*, *647*, 1121–1136. https://doi.org/10.1016/j.scitotenv.2018.08.007

Bolan, N. S., & Hedley, M. J. (2003). Role of Carbon, Nitrogen, and Sulfur Cycles in Soil Acidification. In *Handbook of Soil Acidity*. CRC Press.

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). *Chemical Geology*, *55*(1–2), 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. *Environmental Earth Sciences*, *76*(21), 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 Geophysica*, *64*(3), 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. *Science of The Total Environment*, *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). *Journal of Contaminant Hydrology*, *15*(1–2), 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 and Evaporites*, *26*(3), 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). *Journal of Hydrology*, *253*(1–4), 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. *Hydrogeology Journal*, *19*(1), 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. *Applied Geochemistry*, *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. *Journal of Environmental Radioactivity*, *110*, 30–37. https://doi.org/10.1016/j.jenvrad.2012.01.022

CEPF, (Critical Ecosystem Partnership Fund). (2017, July). *Mediterranean Basin Biodiversity Hotspot*. https://www.cepf.net/sites/default/files/mediterranean-basin-2017-ecosystem-profile-summary-english.pdf

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). *Journal of African Earth Sciences*, *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). *Hydrogeology Journal*, *17*(7), 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. *Environmental Science and Pollution Research*, *25*(15), 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. *Environmental Earth Sciences*, *74*(1), 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. *Applied Geochemistry*, *16*(7–8), 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*(3), 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. *Journal of Hydrology*, *353*(3), 294–313. https://doi.org/10.1016/j.jhydrol.2008.02.015

CNRS. (2010). Lebanese land cover use map (ArcMap). *National Center for Remote Sensing, National Council for Scientific Research (CNRS), Beirut, Lebanon.*

Corniello, A., & Ducci, D. (2014). Hydrogeochemical characterization of the main aquifer of the “Litorale Domizio-Agro Aversano NIPS” (Campania—Southern Italy). *Journal of Geochemical Exploration*, *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). *Environmental Earth Sciences*, *74*(1), 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. *Environmental Geology*, *55*(5), 985–999. https://doi.org/10.1007/s00254-007-1048-4

Da’as, A., & Walraevens, K. (2013). Hydrogeochemical investigation of groundwater in Jericho area in the Jordan Valley, West Bank, Palestine. *Journal of African Earth Sciences*, *82*, 15–32. https://doi.org/10.1016/j.jafrearsci.2013.01.010

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). *Applied Geochemistry*, *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. *Journal of Applied Sciences Research*, *9*(4), 2777–2787.

Darwish, T., Atallah, T., Francis, R., Saab, C., Jomaa, I., Shaaban, A., Sakka, H., & Zdruli, P. (2011). Observations on soil and groundwater contamination with nitrate: A case study from Lebanon-East Mediterranean. *Agricultural Water Management*, *99*(1), 74–84. https://doi.org/10.1016/j.agwat.2011.07.016

Das, M., Kumar, A., Mohapatra, M., & Muduli, S. D. (2010). Evaluation of drinking quality of groundwater through multivariate techniques in urban area. *Environmental Monitoring and Assessment*, *166*(1), 149–157. https://doi.org/10.1007/s10661-009-0991-9

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). *Environmental Geology*, *31*(3–4), 133–141. https://doi.org/10.1007/s002540050172

De Caro, M., Crosta, G. B., & Frattini, P. (2017). Hydrogeochemical characterization and Natural Background Levels in urbanized areas: Milan Metropolitan area (Northern Italy). *Journal of Hydrology*, *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. *Engineering Geology*, *99*(3–4), 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). *Applied Geochemistry*, *23*(8), 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). *Environmental Geology*, *49*(3), 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*(3), 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. *Hydrological Sciences Journal*, *58*(8), 1760–1778. https://doi.org/10.1080/02626667.2013.826358

Doneen, L. D. (1964). *Notes on water quality in agriculture*. Department of Water Science and Engineering, University of California, Davis.

Dubertret L. (1955). *Carte géologique du Liban au 1/200.000*. Institut Géographique National, Paris & Ministère des Travaux Publiques, Beyrouth.

Eaton, F. M. (1950). SIGNIFICANCE OF CARBONATES IN IRRIGATION WATERS. *Soil Science*, *69*(2), 123–134.

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

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. *Journal of African Earth Sciences*, *121*, 365–381. https://doi.org/10.1016/j.jafrearsci.2016.05.031

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, Montpellier 2]. https://www.theses.fr/2005MON20190

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 Resources Management*, *20*(2), 161–180. https://doi.org/10.1007/s11269-006-7376-4

El-Hakim, M., & Bakalowicz, M. (2007). Significance and origin of very large regulating power of some karst aquifers in the Middle East. Implication on karst aquifer classification. *Journal of Hydrology*, *333*(2), 329–339. https://doi.org/10.1016/j.jhydrol.2006.09.003

EPA. (2018). *2018 Edition of the drinking water standards and health advisories tables*. USEPA Office of Water.

Ergil, M. E. (2000). The salination problem of the Guzelyurt aquifer, Cyprus. *Water Research*, *34*(4), 1201–1214. https://doi.org/10.1016/S0043-1354(99)00253-5

European Union. (n.d.). *The Mediterranean Region*. Retrieved March 18, 2021, from https://ec.europa.eu/environment/nature/natura2000/biogeog_regions/mediterranean/index_en.htm

Fageria, M. (1989). Tropical soils and physiological aspects of crop production. *Brasilia: EMBRAPA-DPU, Brasilia, EMBRAPA-CNPAF. Document*, *18*, 425.

Fageria, N. K., dos Santos, A. B., & Moraes, M. F. (2010). Influence of Urea and Ammonium Sulfate on Soil Acidity Indices in Lowland Rice Production. *Communications in Soil Science and Plant Analysis*, *41*(13), 1565–1575. https://doi.org/10.1080/00103624.2010.485237

Fan, X., Cui, B., Zhao, H., Zhang, Z., & Zhang, H. (2010). Assessment of river water quality in Pearl River Delta using multivariate statistical techniques. *Procedia Environmental Sciences*, *2*, 1220–1234. https://doi.org/10.1016/j.proenv.2010.10.133

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. *Environmental Earth Sciences*, *68*(5), 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. *Environmental Geology*, *58*(7), 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. *Mathematical Geology*, *38*(6), 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. *Bulletin of the Geological Society of Greece*, *50*(2), 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. *Environmental Earth Sciences*, *78*(5), 140. https://doi.org/10.1007/s12665-019-8167-6

Gat, J. R. (1996). OXYGEN AND HYDROGEN ISOTOPES IN THE HYDROLOGIC CYCLE. *Annual Review of Earth and Planetary Sciences*, *24*(1), 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 International*, *23*(4), 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. *Hydrogeology Journal*, *17*(2), 447–466. https://doi.org/10.1007/s10040-008-0369-z

Gibbs, R. J. (1970). Mechanisms Controlling World Water Chemistry. *Science*, *170*(3962), 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. *Hydrogeology Journal*, *16*(3), 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). *Environmental Geochemistry and Health*, *32*(3), 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 Journal of Geosciences*, *9*(6), 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). *Journal of Iberian Geology*, *32*(1), 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). *Environmental Earth Sciences*, *67*(3), 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. *Hydrogeology Journal*, *10*(4), 455–474.

Guo, Y., Qin, D., Li, L., Sun, J., Li, F., & Huang, J. (2019). A Complicated Karst Spring System: Identified by Karst Springs Using Water Level, Hydrogeochemical, and Isotopic Data in Jinan, China. *Water*, *11*(5), 947. https://doi.org/10.3390/w11050947

Halwani, J., Ouddane, B., Crampon, N., & Wartel, M. (2001). Contamination saline dans les eaux souterraines de la plaine d'Akkar au Liban. *Journal européen d'hydrologie*, *32*(1), 93–108. https://doi.org/10.1051/water/20013201093

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. *Journal of African Earth Sciences*, *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. *Journal of African Earth Sciences*, *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. *Environmental Monitoring and Assessment*, *174*(1–4), 283–298. https://doi.org/10.1007/s10661-010-1457-9

Hanini, A., Houla, Y., Djaiz, F., Chairat, I., Boughdiri, M., Maamri, R., & Zagrarni, M. F. (2021). Characterization of Cenomanian-Turonian oxic facies in Tunisia: Sequence stratigraphy and correlation of recorded bioevents. *Arabian Journal of Geosciences*, *14*(11), 954. https://doi.org/10.1007/s12517-021-07286-x

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). *Aquatic Geochemistry*, *24*(5), 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). *Environmental Earth Sciences*, *61*(1), 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*(3–4), 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. *Environmental Earth Sciences*, *75*(9), 746. https://doi.org/10.1007/s12665-016-5441-8

Houri, A., & El Jeblawi, S. W. (2007). Water quality assessment of Lebanese coastal rivers during dry season and pollution load into the Mediterranean Sea. *Journal of Water and Health*, *5*(4), 615–623. https://doi.org/10.2166/wh.2007.047

Huneau, F., & Blavoux, B. (2000). Isotopic hydrogeology within the Miocene basin of Carpentras-Valreas (southeastern France). *Tracers and Modelling in Hydrogeology. Proceedings of TraM'2000, the International Conference on Tracers and Modelling in Hydrogeology Held at Liège, Belgium, May 2000*, 433–438.

Iglesias, A., Garrote, L., Flores, F., & Moneo, M. (2007). Challenges to Manage the Risk of Water Scarcity and Climate Change in the Mediterranean. *Water Resources Management*, *21*(5), 775–788. https://doi.org/10.1007/s11269-006-9111-6

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 Journal of Geosciences*, *8*(4), 2203–2215. https://doi.org/10.1007/s12517-014-1346-6

Janardhana Raju, N., Shukla, U. K., & Ram, P. (2011). Hydrogeochemistry for the assessment of groundwater quality in Varanasi: A fast-urbanizing center in Uttar Pradesh, India. *Environmental Monitoring and Assessment*, *173*(1), 279–300. https://doi.org/10.1007/s10661-010-1387-6

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. *Environmental Earth Sciences*, *77*(6), 261. https://doi.org/10.1007/s12665-018-7440-4

Jeevanandam, M., Nagarajan, R., Manikandan, M., Senthilkumar, M., Srinivasalu, S., & Prasanna, M. V. (2012). Hydrogeochemistry and microbial contamination of groundwater from Lower Ponnaiyar Basin, Cuddalore District, Tamil Nadu, India. *Environmental Earth Sciences*, *67*(3), 867–887. https://doi.org/10.1007/s12665-012-1534-1

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*(2), 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*(3), 104. https://doi.org/10.3390/w8030104

Kalaoun, O., Jazar, M., & Al Bitar, A. (2018). Assessing the Contribution of Demographic Growth, Climate Change, and the Refugee Crisis on Seawater Intrusion in the Tripoli Aquifer. *Water*, *10*(8), 973. https://doi.org/10.3390/w10080973

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. *Science of The Total Environment*, *609*, 1140–1151. https://doi.org/10.1016/j.scitotenv.2017.07.199

Kelepertsis, A. (2000). *Applied geochemistry (in Greek)*.

Kelley, W. P. (1951). *Alkali soils; their formation, properties, and reclamation*.

Khadra, W. M., & Stuyfzand, P. J. (2014). Separating baseline conditions from anthropogenic impacts: Example of the Damour coastal aquifer (Lebanon). *Hydrological Sciences Journal*, *59*(10), 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). *Hydrogeology Journal*, *26*(6), 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. *Applied Geochemistry*, *79*, 36–51. https://doi.org/10.1016/j.apgeochem.2017.02.005

Kjellen, M. (2000). Complementary Water Systems in Dar es Salaam, Tanzania: The Case of Water Vending. *International Journal of Water Resources Development*, *16*(1), 143–154. https://doi.org/10.1080/07900620048626

Kløve, B., Ala-Aho, P., Bertrand, G., Gurdak, J. J., Kupfersberger, H., Kværner, J., Muotka, T., Mykrä, H., Preda, E., Rossi, P., Uvo, C. B., Velasco, E., & Pulido-Velazquez, M. (2014). Climate change impacts on groundwater and dependent ecosystems. *Journal of Hydrology*, *518*, 250–266. https://doi.org/10.1016/j.jhydrol.2013.06.037

Koeniger, P., Toll, M., & Himmelsbach, T. (2016). Stable isotopes of precipitation and spring waters reveal an altitude effect in the Anti-Lebanon Mountains, Syria. *Hydrological Processes*, *30*(16), 2851–2860. https://doi.org/10.1002/hyp.10822

Korfali, S. I., & Jurdi, M. (2007). Assessment of domestic water quality: Case study, Beirut, Lebanon. *Environmental Monitoring and Assessment*, *135*(1), 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. *International Journal of Environmental Studies*, *30*(2–3), 203–208. https://doi.org/10.1080/00207238708710394

Leduc, C., Pulido-Bosch, A., & Remini, B. (2017). Anthropization of groundwater resources in the Mediterranean region: Processes and challenges. *Hydrogeology Journal*, *25*(6), 1529–1547. https://doi.org/10.1007/s10040-017-1572-6

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

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). *Environmental Geology*, *58*(8), 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. *Applied Geochemistry*, *16*(9–10), 1179–1192. https://doi.org/10.1016/S0883-2927(01)00012-9

Madhav, S., Ahamad, A., Kumar, A., Kushawaha, J., Singh, P., & Mishra, P. K. (2018). Geochemical assessment of groundwater quality for its suitability for drinking and irrigation purpose in rural areas of Sant Ravidas Nagar (Bhadohi), Uttar Pradesh. *Geology, Ecology, and Landscapes*, *2*(2), 127–136. https://doi.org/10.1080/24749508.2018.1452485

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, and Soil Pollution*, *178*(1), 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. *Hydrogeology Journal*, *22*(1), 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

Massoud, M. A., El-Fadel, M., Scrimshaw, M. D., & Lester, J. N. (2006). Factors influencing development of management strategies for the Abou Ali River in Lebanon: I: Spatial variation and land use. *Science of The Total Environment*, *362*(1), 15–30. https://doi.org/10.1016/j.scitotenv.2005.09.079

Massoud, M., El-Fadel, M., Scrimshaw, M., & Lester, J. (2004). *Land Use Impact on the Spatial and Seasonal Variation of the Contaminant Loads to Abou Ali River and Its Coastal Zone in North Lebanon*. https://ecommons.cornell.edu/handle/1813/10404

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). *Journal of African Earth Sciences*, *147*, 511–522. https://doi.org/10.1016/j.jafrearsci.2018.07.009

Mekonnen, M. M., & Hoekstra, A. Y. (2018). Global Anthropogenic Phosphorus Loads to Freshwater and Associated Grey Water Footprints and Water Pollution Levels: A High-Resolution Global Study. *Water Resources Research*, *54*(1), 345–358. https://doi.org/10.1002/2017WR020448

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. *Science of The Total Environment*, *502*, 330–343. https://doi.org/10.1016/j.scitotenv.2014.09.041

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. *Agriculture, Ecosystems & Environment*, *195*, 127–138. https://doi.org/10.1016/j.agee.2014.05.011

Merhabi, F., Amine, H., & Halwani, J. (2019). Evaluation de la qualité des eaux de surface de la rivière Kadicha. *Journal Scientifique Libanais*, *20*(1), 10–34.

Merhabi, F., Gomez, E., Amine, H., Rosain, D., Halwani, J., & Fenet, H. (2021). *Occurrence, Distribution, and Ecological Risk Assessment of Emerging and Legacy Contaminants in the Kadicha River in Lebanon*.

Merheb, M. (2015). *Hydrology of Lebanese catchments in the Mediterranean context* [Phdthesis, AgroParisTech]. https://tel.archives-ouvertes.fr/tel-01262314

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. *Hydrological Sciences Journal*, *61*(14), 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. *International Journal of Water Resources Development*, *20*(4), 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). *Journal of Hydrology*, *399*(1–2), 29–47. https://doi.org/10.1016/j.jhydrol.2010.12.032

MoEW, U. (2014). Assessment of groundwater resources of Lebanon. *Ministry of Energy and Water, Lebanon, Beirut*.

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). *Hydrogeology Journal*, *22*(5), 1115–1129. https://doi.org/10.1007/s10040-014-1113-5

Mongelli, G., Argyraki, A., Lorenzo, M. L. G., Shammout, M. W., Paternoster, M., & Simeone, V. (2019). Groundwater Quality in the Mediterranean Region. *Geofluids*, *2019*, 1–4. https://doi.org/10.1155/2019/7269304

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. *Hydrology and Earth System Sciences*, *17*(7), 2917–2928. https://doi.org/10.5194/hess-17-2917-2013

Moores, E. M., & Fairbridge, R. W. (1997). *Encyclopedia of European and Asian regional geology*. Chapman & Hall. https://scholar.google.com/scholar_lookup?title=Encyclopedia+of+European+and+Asian+regional+geology&author=Moores%2C+Eldridge+M.&publication_year=1997

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). *Journal of African Earth Sciences*, *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 Research and Management*, *26*(1), 1–14. https://doi.org/10.1080/15324982.2011.631688

Nag, S. K., & Lahiri, A. (2012). Hydrochemical Characteristics of Groundwater for Domestic and Irrigation Purposes in Dwarakeswar Watershed Area, India. *American Journal of Climate Change*, *01*(04), 217. https://doi.org/10.4236/ajcc.2012.14019

Navarro, A., & Carbonell, M. (2007). Evaluation of groundwater contamination beneath an urban environment: The Besòs river basin (Barcelona, Spain). *Journal of Environmental Management*, *85*(2), 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. *Hydrology and Earth System Sciences*, *6*(5), 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*(6), 914–928. https://doi.org/10.1029/TR025i006p00914

Plan Bleu. (2006). Faire face aux crises et pénuries d'eau en Méditerranée. *Les Notes Du Plan Bleu: Environnement et Développement Durable En Méditerranée (4)*.

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 Management*, *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). *Environmental Geology*, *26*(4), 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). *Hydrogeology Journal*, *14*(5), 713–728. https://doi.org/10.1007/s10040-005-003-2

Raghunath, H. (1987). Groundwater Wiley Eastern Ltd. *New Delhi, India*.

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). *Applied Geochemistry*, *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

Richards, L. A. (1954). Diagnosis and Improvement of Saline and Alkali Soils. *Soil Science*, *78*(2), 154.

Rouchy, J.-M., Suc, J.-P., Ferrandini, J., & Ferrandini, M. (2006). *The Messinian Salinity Crisis Revisited. Sedimentary Geology, 188/189.* ELSEVIER. https://hal.archives-ouvertes.fr/hal-00164184

Saadeh, M., Semerjian, L., & Amacha, N. (2012). Physicochemical Evaluation of the Upper Litani River Watershed, Lebanon. *The Scientific World Journal*, *2012*, e462467. https://doi.org/10.1100/2012/462467

Saba, M., Iaaly, A., Carlier, E., & Georges, N. (2016). Assessing Water Quality Using GIS: The Case of Northern Lebanon Miocene Aquifer. *International Journal of Environmental and Ecological Engineering*, *10*(2), 147–155.

Sadeg, S., & Karahanoðlu, N. (2001). Numerical assessment of seawater intrusion in the Tripoli region, Libya. *Environmental Geology*, *40*(9), 1151–1168. https://doi.org/10.1007/s002540100317

Saghir, J., Schiffler, M., & Woldu, M. (2000). *Urban water and sanitation in the Middle East and North Africa Region: The way forward*. World Bank, Middle East and North Africa Region, Infrastructure Development ….

Saha, S., Reza, A. H. M. S., & Roy, M. K. (2019). Hydrochemical evaluation of groundwater quality of the Tista floodplain, Rangpur, Bangladesh. *Applied Water Science*, *9*(8), 198. https://doi.org/10.1007/s13201-019-1085-7

Salem, Z. E., Elsaiedy, G., & ElNahrawy, A. (2017). Hydrogeochemistry and Quality Assessment of Groundwater Under Some Central Nile Delta Villages, Egypt. In A. M. Negm (Ed.), *Groundwater in the Nile Delta* (Vol. 73, pp. 625–645). Springer International Publishing. https://doi.org/10.1007/698_2017_111

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. *Environmental Science and Pollution Research*, *24*(4), 3675–3704. https://doi.org/10.1007/s11356-016-8056-4

Salifu, M., Aidoo, F., Hayford, M. S., Adomako, D., & Asare, E. (2017). Evaluating the suitability of groundwater for irrigational purposes in some selected districts of the Upper West region of Ghana. *Applied Water Science*, *7*(2), 653–662. https://doi.org/10.1007/s13201-015-0277-z

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. *Environmental Earth Sciences*, *76*(4), 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. *Science of The Total Environment*, *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). *Science of The Total Environment*, *573*, 233–246. https://doi.org/10.1016/j.scitotenv.2016.08.087

Schoeller, H. (1965). Qualitative evaluation of groundwater resources. *Methods and Techniques of Groundwater Investigations and Development. UNESCO, 5483*.

Selenica, A. (n.d.). *The Mediterranean region: An Hydrological Overview*. Retrieved March 18, 2021, from http://medhycos.mpl.ird.fr/en/t1.resi&gn=res.inc&menu=fresimf.inc.html

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*, *22*(4), 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. *Hydrology and Earth System Sciences*, *14*(10), 1863–1880. https://doi.org/10.5194/hess-14-1863-2010

Siegel, F. R. (2002). *Environmental geochemistry of potentially toxic metals*. Springer.

Singh, K. K., Tewari, G., & Kumar, S. (2020). Evaluation of Groundwater Quality for Suitability of Irrigation Purposes: A Case Study in the Udham Singh Nagar, Uttarakhand. *Journal of Chemistry*, *2020*, e6924026. https://doi.org/10.1155/2020/6924026

Skordas, K., Papastergios, G., Tziantziou, L., Neofitou, N., & Neofitou, C. (2013). Groundwater hydrogeochemistry of Trikala municipality, central Greece. *Environmental Monitoring and Assessment*, *185*(1), 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. *Journal of African Earth Sciences*, *123*, 29–38. https://doi.org/10.1016/j.jafrearsci.2016.07.003

Stamatis, G., Voudouris, K., & Karefilakis, F. (2001). Groundwater Pollution by Heavy Metals in Historical Mining Area of Lavrio, Attica, Greece. *Water, Air, and Soil Pollution*, *128*(1), 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 Resources Research*, *21*(8), 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*.

Szabolcs I. (1964). The influence of irrigation water of high Sodium Carbonate content on soils. *Agrokémia és talajtan*, *13*(sup), 237–246.

Tayfur, G., Kirer, T., & Baba, A. (2008). Groundwater quality and hydrogeochemical properties of Torbalı Region, Izmir, Turkey. *Environmental Monitoring and Assessment*, *146*(1–3), 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. *Physics and Chemistry of the 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. *Physics and Chemistry of the 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. *Journal of Hydrology*, *343*(1–2), 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. *Regional Environmental Change*, *20*(3), 83, s10113-020-01665-y. https://doi.org/10.1007/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 and Water Treatment*, *57*(25), 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). *Journal of Geochemical Exploration*, *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. *Applied Geochemistry*, *21*(4), 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. *Journal of Water and Health*, wh2018003. https://doi.org/10.2166/wh.2018.003

Vlachogianni, T., Vogrin, M., & Scoullos, M. (2012). *Biodiversity in the Mediterranean region*. MIO-ECSDE.

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. *Journal of Geochemical Exploration*, *159*, 79–92. https://doi.org/10.1016/j.gexplo.2015.08.007

Ward, J. H. (1963). Hierarchical Grouping to Optimize an Objective Function. *Journal of the American Statistical Association*, *58*(301), 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. *Journal of Environmental Quality*, *19*(3), 441–448. https://doi.org/10.2134/jeq1990.00472425001900030015x

WHO. (2017). *Guidelines for drinking-water quality: First addendum to the fourth edition*.

Wilcox, L. V. (Ed.). (1948). *The Quality of Water for Irrigation Use*. https://doi.org/10.22004/ag.econ.170282

Youssef, L., Younes, G., Kouzayha, A., & Jaber, F. (2015). Occurrence and levels of pesticides in South Lebanon water. *Chemical Speciation & Bioavailability*, *27*(2), 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). *Journal of African Earth Sciences*, *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. *Environmental Monitoring and Assessment*, *152*(1), 123. https://doi.org/10.1007/s10661-008-0301-y

Appendixes

Appendixes

Appendix 1 The studied articles references, Country, study area, sampling dates and data availability. Y refers to data availability, N for missing data. The availability of Isotopes data is indicated by (**) in the reference. The # refers to the code of the article used later on in the classification.

Reference	#	Country	Study area	Sampling dates	Ions		Reference	#	Country	Study area	Sampling dates	Ions	
					Major	Minor						Major	Minor
(Aouidane & Belhamra, 2017)	Al1	Algeria	Remila aquifer	10 -> 12/2013 - 05->06/2014	Y	Y	(Koeniger et al., 2016)	Lb25	Lebanon	the Anti-Lebanon Mountains	2011 - 2012	N	N
(Belfar et al., 2017)	Al2	Algeria	Tezbent plateau	----------	Y	N	(Bakalowicz, 2014)	Lb26	Lebanon	Chekka karst system	----------	N	N
(Bouderbala et al., 2016)	Al3	Algeria	Coastal Aquifer of Nador	04/2013 - 09/2013	Y	N	(Youssef et al., 2015)	Lb27	Lebanon	South Litani region	2012	N	N
(Bouderbala & Gharbi, 2017)	Al4	Algeria	Upper Cheliff plain	9/1/2014	Y	N	(Bakalowicz, 2015)	Lb28	Lebanon	Mediterranean	----------	N	N
(Fehdi et al., 2009)	Al5	Algeria	Morsott-El Aouinet aquifer	----------	Y	Y	(Ghannam et al., 1998)	Lb29	Lebanon	Lebanon	----------	N	N
(Belkhiri & Mouni, 2012)	Al6	Algeria	Ain Azel area	Mar-08	Y	Y	(Metni et al., 2004)	Lb30	Lebanon	Lebanon	----------	N	N
(Chemseddine et al., 2015)	Al7	Algeria	Tezbent Plateau	2012 - 2013	Y	N	(Lababidi et al., 1987)	Lb31	Lebanon	coastal strip in Beirut	Apr-85	N	N
(Belkhiri & Mouni, 2014)	Al8	Algeria	El Eulma aquifer	----------	N	N	(Sadeg & Karahanoðlu, 2001)	Li1	Libya	Tripoli	1/8/1994	Y	N
(Bettahar et al., 2017)	Al9	Algeria	the Wadi Righ Valley	----------	N	N	(Alfarrah et al., 2016)	Li2	Libya	oases of Al Wahat	2016	N	N
(Terzić et al., 2007)	Cr1	Croatia	island of Dugi Otok	----------	N	N	(Mountadar et al., 2018)	Mo1	Morocco	aquifer Sidi Abed-Ouled Ghanem	2011 - 2012 - 2013	Y	N
(Neal & Shand, 2002)	Cy1	Cyprus	Cyprus ophiolites	May-85	Y	Y	(Karroum et al., 2017)**	Mo2	Morocco	Bahira plain	01/2008 - 04/2011	Y	Y
(Milnes, 2011)	Cy2	Cyprus	Akrotiri aquifer	----------	N	N	(Re et al., 2013)	Mo3	Morocco	Bou-Areg coastal aquifer	11/2009 - 06/2010	Y	Y

Reference	#	Country	Study area	Sampling dates	Ions		Reference	#	Country	Study area	Sampling dates	Ions	
					Major	Minor						Major	Minor
(Z. E.-S. Salem & Osman, 2017)	Eg1	Egypt	West Nile Delta	Jul-12	Y	N	(De Jong et al., 2008)	Mo4	Morocco	mountainous karst areas	----------	Y	Y
(Gomaah et al., 2016)	Eg2	Egypt	Ismailia and El Kassara canals	03/2013 - 06/2013.	Y	Y	(Chafouq et al., 2018)	Mo5	Morocco	Ghis-Nekor plain	1/5/2015	Y	N
(Z. E. Salem et al., 2017)	Eg3	Egypt	Central Nile Delta Villages	2016	Y	Y	(Re et al., 2014)	Mo6	Morocco	Bou-Areg region	06/2010 - 11/2010	N	N
(Eissa et al., 2016)**	Eg4	Egypt	Bagoush area	42064	Y	N	(Da'as & Walraevens, 2013)	Pa1	Palestine	The West Bank	1971 - 2004	Y	Y
(Eissa et al., 2018)	Eg5	Egypt	aquifer at Ras El-Hekma	Mar-13	Y	N	(Abu-alnaeem et al., 2018)	Pa2	Palestine	coastal aquifer	----------	Y	Y
(Charmoille et al., 2009)	Fr1	France	Coaraze spring	----------	Y	Y	(Al-Agha, 2005)	Pa3	Palestine	Khanyounis Governorate	Apr-02	Y	Y
(Santoni et al., 2016)**	Fr2	France	aquifer of Bonifacio	Nov-14	Y	Y	(Jabal et al., 2015)	Pa4	Palestine	Khan Younis City	12/2011 -> 06/2012.	Y	Y
(De Montety et al., 2008)**	Fr3	France	Rhône delta	05/2005 -> 05/2006 -11/2006.	N	Y	(Jebreen et al., 2018)	Pa5	Palestine	Central West Bank	08/2016 - 03/2017	Y	Y
(Maréchal et al., 2014)**	Fr4	France	La Salvetat	2010 - 2011	N	Y	(Qahman & Larabi, 2006)	Pa6	Palestine	Gaza coastal aquifer	----------	N	N
(Bosch et al., 1986)	Fr5	France	LES MALINES (GARD, FRANCE)	Nov-79	N	N	(Aliewi & Al-Khatib, 2015)	Pa7	Palestine	Salfit District	----------	N	N
(Bourg & Richard-Raymond, 1994)	Fr6	France	Drac and Isère rivers	12/1988 - 01/1990.	N	N	(Fernandes et al., 2006)	Po1	Portugal	Sines Coastal Aquifer	1999 -> 2002	Y	Y
(Bicalho et al., 2010)	Fr7	France	The Lez spring	Mar-06	N	N	(Carreira et al., 2011)	Po2	Portugal	Serra da Estrela Mountain area	09/2003 -> 09/2007	Y	Y
(Huneau & Blavoux, 2000)	Fr8	France	Carpentras-Valreas	1997	N	N	(Andrade & Stigter, 2011)	Po3	Portugal	central Portugal	03-04-09/2001 - 01-03-09/2002	Y	Y

Reference	#	Country	Study area	Sampling dates	Ions		Reference	#	Country	Study area	Sampling dates	Ions	
					Major	Minor						Major	Minor
(Skordas et al., 2013)	Gr1	Greece	basin of Pinios river	07/2006 - 10/2006 - 01/2007 - 04/2007	Y	Y	(Van der Weijden & Pacheco, 2006)	Po4	Portugal	The basin of the Rio Vouga	----------	N	N
(Tziritis et al., 2016)	Gr2	Greece	southern of Greek	wet: 11/2011 - > 12/2011) dry: 07/2012 - > 08/2012	Y	Y	(Carreira et al., 2017)	Po5	Portugal	Lisbon Volcanic Complex	2016	N	N
(Filippidis et al., 2016)	Gr3	Greece	island of andros	Sep-14	Y	Y	(Marques et al., 2017)	Po6	Portugal	Cabeço de Vide	----------	N	N
(Voutsis et al., 2015)	Gr4	Greece	central Euboea	dry in 2005 - 2006	Y	Y	(Freitas et al., 2019)	Po7	Portugal	Porto	----------	N	N
(Biddau et al., 2019)**	It1	Italy	The Arborea plain	02/2013 - 02/2014.	Y	Y	(Barroso et al., 2015)	Po8	Portugal	peri-urban area	----------	N	N
(Manno et al., 2007)**	It2	Italy	Biviere di Gela	07/2003 - 04/2004 - 11/2004.	Y	Y	(González-Ramón et al., 2012)	Sp1	Spain	Real-Pegalajar aquifer	10/2002 - 05/2003	Y	Y
(Allocca et al., 2018)	It3	Italy	Phlegraean Fields	----------	Y	Y	(Merchán et al., 2015)	Sp2	Spain	The Lerma Basin	10/02/2011 - 27/07/2011 - 10/01/2012 - 31/07/2012	Y	N
(De Caro et al., 2017)	It4	Italy	Milan Metropolitan area	period 1980–2014	Y	Y	(Merchán et al., 2014)**	Sp3	Spain	Lerma Basin	27/07/2011 - 10/01/2012	Y	Y
(Capaccioni et al., 2001)	It5	Italy	Mt Catria-Mt Nerone ridge	01 -> 06/1998	Y	N	(Navarro & Carbonell, 2007)	Sp4	Spain	The Besos river basin	2002 - 2003	Y	Y
(Ghiglieri et al., 2009)**	It6	Italy	Nurra Region	12/2004 - 06/2005	Y	Y	(Lentini et al., 2009)	Sp5	Spain	coastal Velez River aquifer	1994 (dry) & 1996 (wet)	Y	N
(Barbieri & Morotti, 2003)	It7	Italy	Mt. Vulture (Italy)	2003	Y	Y	(Pulido-Bosch et al., 1995)	Sp6	Spain	Crevillente Aquifer	Jul-90	Y	Y

Reference	#	Country	Study area	Sampling dates	Ions		Reference	#	Country	Study area	Sampling dates	Ions	
					Major	Minor						Major	Minor
(Critelli et al., 2015)	It8	Italy	Lago (Southern Italy)	09 & 10/2013	Y	Y	(Daniele et al., 2013)	Sp7	Spain	Aguadulce	37043	Y	N
(Cucchi et al., 2008)**	It9	Italy	Friuli Venezia Giulia aquifers	1995 -> 2007	Y	Y	(Molina-Navarro et al., 2014)	Sp8	Spain	the Pareja basin	4 seasons in 2008 - summer 2011.	Y	Y
(Corniello & Ducci, 2014)	It10	Italy	Campania — southern Italy	2003 -> 2006	Y	Y	(Giménez Forcada & Morell Evangelista, 2008)	Sp9	Spain	aquifer of Castellón Plain	Jul-03	Y	Y
(Preziosi et al., 2019)	It11	Italy	Central Italy	beginning 2016	Y	Y	(Gómez et al., 2006)	Sp10	Spain	Hesperian Massif (Spain)	2001->2003	N	Y
(Giménez-Forcada et al., 2010)	It12	Italy	Elba Island	12/1/1996	Y	N	(Acero et al., 2013)	Sp11	Spain	Ebro Valley	01/2011 -> 01/2012	Y	N
(Pierotti et al., 2013)	It13	Italy	Magra Valley aquifers	05->06/2002	N	N	(López-Chicano et al., 2001)	Sp12	Spain	Cabra-Alcaide aquifer	10/1995 -> 04/1997	Y	Y
(Brozzo et al., 2011)	It14	Italy	Lower Magra Basin	05->06/2004 - 10->11/2005	N	N	(Hidalgo et al., 2010)	Sp13	Spain	mining district of La Carolina	2003	N	Y
(Busico et al., 2018)	It15	Italy	Campania Plain	----------	N	N	(Vallejos et al., 2015)	Sp14	Spain	Sierra de Gádor	Jul-09	N	N
(Awad, 2011)	Lb1	Lebanon	Bekaa	----------	Y	Y	(Argamasilla et al., 2017)**	Sp15	Spain	TheMarbella-Estepona aquifers	2013 and 2014	Y	Y
(Khadra & Stuyfzand, 2014)**	Lb2	Lebanon	Damour coastal aquifer	2011/12	Y	Y	(Abo & Merkel, 2015)	Sy1	Syria	Al Qweek & Al Zerba	2001 - 2005	Y	Y
(El Hakim, 2005)	Lb3->Lb9	Lebanon	ANTI-LIBAN	2003 - 2004	Y	N	(Abou Zakhem, 2016)	Sy2	Syria	Damascus Basin	2006–2007 and 2007–2008	N	N
(Hanna et al., 2018)**	Lb10	Lebanon	Nahr Ibrahim, Lebanon	03/2014 - 08/2016.	Y	N	(Tayfur et al., 2008)	Tr1	Turkey	Torbalı Region, Izmir	2001-2002	Y	N

Reference	#	Country	Study area	Sampling dates	Ions		Reference	#	Country	Study area	Sampling dates	Ions	
					Major	Minor						Major	Minor
(Assaker, 2016)	Lb11	Lebanon	Ibrahim watershed	06/2012 -> 05/2013	N	N	(Demirel & Güler, 2006)	Tr2	Turkey	Mersin-Erdemli basi	May and August 2002	Y	N
(Daou et al., 2013)	Lb12	Lebanon	Ibrahim And El-Kalb Rivers	12/2007 - 07/2008	N	N	(Varol & Şekerci, 2018)	Tr3	Turkey	Korkuteli district center	Dry: 11/2016 Wet: 05/2017	Y	Y
(Khadra et al., 2017)	Lb13	Lebanon	Lebanon	2011/12	N	N	(Somay, 2016)**	Tr4	Turkey	Edremit-Dalyan coastal wetland	Apr-13	Y	Y
(Korfali & Jurdi, 2007)	Lb14	Lebanon	Ras-Beirut	2007	Y	Y	(Hamzaoui-Azaza et al., 2011)	Tu1	Tunisia	The aquifer of Zeuss–Koutine	2005	Y	N
(Acra & Ayoub, 2001)	Lb15	Lebanon	Beirut	1978	Y	N	(Telahigue et al., 2018)	Tu2	Tunisia	coastal aquifer	1/10/2011	Y	N
(Kalaoun et al., 2016)	Lb16	Lebanon	Tripoli	----------	N	N	(Hamed & Dhahri, 2013)	Tu3	Tunisia	Northwestern Tunisia	07 -> 08/2001	Y	Y
(Saadeh et al., 2012)	Lb17	Lebanon	Litani River	2005 -> 2012	N	N	(Mejri et al., 2018)**	Tu4	Tunisia	Sminja aquifer	May-15	Y	N
(Bakalowicz et al., 2007)	Lb18	Lebanon	the Levantine coast	----------	N	N	(Zghibi et al., 2014)	Tu5	Tunisia	aquifer of Cap-Bon	Jun-05	Y	N
(Bakalowicz et al., 2008)	Lb19	Lebanon	Several Karst groundwater	----------	N	N	(Farid et al., 2013)	Tu6	Tunisia	Central Tunisia	2009 - 2010.	Y	Y
(Assaf & Saadeh, 2008)	Lb20	Lebanon	the Upper Litani Basin	02/2005 - 06/2005	N	N	(Houatmia et al., 2016)	Tu7 & Tu8	Tunisia	Kairouan aquifer system	May-14	Y	N
(Khadra & Stuyfzand, 2018)	Lb21	Lebanon	The Damour coastal aquifer	2012 -> 2015	N	N	(Hamdi et al., 2018)	Tu9	Tunisia	SANS aquifer	42125	Y	N
(El Moujabber et al., 2006)	Lb22	Lebanon	Choueifat-Rmeyle region	1999 -> 2002	N	N	(Ben Cheikh et al., 2014)**	Tu10	Tunisia	south-eastern Tunisia	Jan-08	Y	N
(Samad et al., 2017)	Lb23	Lebanon	south of Beirut	2016	N	N	(Moussa et al., 2012)	Tu11	Tunisia	part of the Cap Bon peninsula	Mar-08	Y	Y
(Chaza et al., 2018)	Lb24	Lebanon	Akkar groundwater	May-15	N	N							

Appendix 2 Statistical summary of physicochemical parameters and major ions. T and EC are expressed in °C and µS/cm respectively. All ions and TDS are in mg/L.

	Quaternary			Jurassic & Cretaceous			Tertiary		
	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
pH	6.8	7.6 ± 0.4	9	6.9	7.6 ± 0.4	8	7.4	7.6 ± 0.2	7.8
T	15.1	20 ± 2.7	24.1	10.8	18.8 ± 5.7	25.1	18.5	20.1 ± 2.2	21.7
EC	3.6	1996.4 ± 1494.4	5093.1	349.2	1396.1 ± 1161.1	3796.2	471.5	3996 ± 3807.6	8126.3
TDS	80.6	1434.2 ± 925	3710.7	264.7	1215.9 ± 1024.9	2970	430.7	3188.5 ± 2561.8	5494
Ca^{2+}	2.9	150.5 ± 130.7	849.4	7.3	88.1 ± 73.6	319.2	19	91.8 ± 60.1	293.5
Mg^{2+}	0.6	70 ± 49.1	248.8	4.6	53.7 ± 61.5	191.7	12	41.8 ± 60.3	259.4
Na^{+}	4.6	276.8 ± 241.8	1131.1	1.8	96.4 ± 127.9	400.8	2.5	168.4 ± 400.8	1501.1
K^{+}	0.1	11.8 ± 13.7	60.8	0.3	5.7 ± 7.2	21.9	0.7	8 ± 15.5	60.6
HCO_3^{-}	5.3	291.8 ± 106.8	509.8	6.2	342.3 ± 348.9	1199.7	115.9	264.6 ± 78	448.5
Cl^{-}	5.3	466.4 ± 466.1	2516.2	2.5	134.3 ± 188.9	665.3	5.3	275.3 ± 706.4	2862.1
SO_4^{2-}	2.4	292.5 ± 307.2	1728	3.9	183.5 ± 332.1	1272.5	8.1	135.6 ± 209.2	645.7

Appendix 3 The data of 65 samples extracted during the wet and dry seasons of 2019 and 2020. The data represents the samples' coordinates, 4 physicochemical parameters (T: Temperature in °C, TDS: Total dissolved solids in mg/L, EC: electrical conductivity in µS/cm and pH) and 9 major ions (All concentrations are in mg/L).

Sample	Sampling date	Sampling point	X	Y	T	TDS	EC	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	PO_4^{3-}	NO_3^{-}	HCO_3^{-}	Cl^{-}
S01W	May-19	Sebaal_Wet	35.91500	34.31500	18	261	570	7.06	34.7	28.0	6.1	0.8	15.6	1.6	7.4	315.0	28.0
S02W	May-19	Daraya_Wet	35.86972	34.32639	22	349	758	6.83	57.8	13.6	9.7	0.5	17.0	0.0	16.1	357.5	44.3
S03W	May-19	Arjess_Wet	35.88028	34.33444	23	288	621	7.00	68.4	13.6	11.1	0.5	8.3	1.0	10.6	305.0	43.6
S04W	May-19	Arde_Wet	35.91972	34.40806	19	395	857	6.71	61.5	15.3	17.0	2.0	48.8	1.5	24.8	317.5	68.2
S05W	May-19	Rachiine_Wet	35.92972	34.38889	15	180	391	7.27	25.8	13.0	3.1	0.5	6.8	0.1	11.1	205.0	18.0
S06W	May-19	Kfar Chakhna_Wet	35.87722	34.36833	23	366	795	6.79	51.0	24.6	12.1	0.9	12.7	1.0	23.7	370.0	62.4
S07W	May-19	Ras Kifa_Wet	35.87667	34.31472	23	239	518	7.12	26.3	15.7	6.6	0.8	9.7	0.0	11.6	257.5	35.1
S08W	May-19	Miryata_Wet	35.93139	34.41889	24	278	604	7.02	58.1	8.4	9.1	1.7	15.5	0.0	19.0	265.0	54.1
S09W	May-19	Bkeftine_Wet	35.86306	34.38583	23	358	761	6.83	67.2	56.9	33.9	6.9	181.4	1.1	7.2	282.5	66.3
S10W	May-19	Kfar Qahel_Wet	35.85194	34.35583	21	232	505	7.14	39.4	15.9	11.5	0.6	8.6	0.0	9.8	240.0	56.5
S11W	May-19	Besbeel_Wet	35.87667	34.35444	22	349	758	6.83	37.5	26.9	13.1	3.5	12.7	1.4	33.1	345.0	79.3
S12W	May-19	Hilane_Wet	35.95222	34.42583	21	240	522	7.12	48.9	3.4	8.2	1.7	12.9	0.0	23.3	230.0	47.4
S13W	May-19	Nabee Joueit_Wet	35.98611	34.31167	10	128	277	7.41	25.4	7.4	1.4	0.2	3.1	1.2	10.1	155.0	17.2
S14W	May-19	Ein Naasa_Wet	35.99222	34.30806	11	274	590	7.04	29.0	29.6	3.4	0.2	7.0	1.2	6.3	347.5	28.4
S15W	May-19	Nabee Mar Sarkis_Wet	35.97306	34.28917	9	95	205	7.50	18.6	4.5	1.0	0.1	2.5	0.2	7.3	137.5	11.8
S16W	May-19	Ein Ehden-Bcharre1_Wet	35.99000	34.27278	12	164	354	7.32	27.7	14.5	3.6	0.5	10.9	1.0	8.5	195.0	19.5
S17W	May-19	Ein Ehden-Bcharre2_Wet	36.02306	34.26139	9	90	195.3	7.51	19.4	6.2	1.0	0.1	2.3	0.0	7.4	110.0	11.5
S18W	May-19	Kadisha road_Wet	36.03361	34.24694	16	188	409	7.25	27.7	18.2	2.1	0.3	4.3	1.2	7.6	222.5	20.2

Sample	Sampling date	Sampling point	X	Y	T	TDS	EC	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	PO_4^{3-}	NO_3^{-}	HCO_3^{-}	Cl^{-}
S19W	May-19	Mar Semaan_Wet	36.00889	34.26167	9	96	208	7.49	18.2	7.5	1.0	0.1	2.6	1.3	6.4	112.5	12.9
S20W	May-19	Majdalaya_Wet	35.86972	34.41972	24	302	656	6.96	54.8	8.8	14.2	0.9	21.5	0.2	31.7	285.0	71.6
S21W	May-20	Zgharta_1_Wet	35.88944	34.39611	19	458	935	6.52	131.2	16.2	23.4	0.1	37.2	1.3	20.0	370.0	60.1
S22W	May-20	Zgharta_2_Wet	35.88972	34.38667	21	509	1038	6.55	140.7	20.8	23.1	1.7	38.1	1.2	40.7	325.0	73.1
S23W	May-20	Iaal_Wet	35.90222	34.37139	22	663	325	6.63	34.0	4.5	4.3	1.5	5.7	1.9	21.8	302.5	29.0
S24W	May-20	Der_Nbouh_Wet	35.93222	34.37222	15	107	217.4	7.37	30.2	6.1	2.0	0.7	4.4	1.6	9.3	102.5	8.0
S25W	May-20	Aalma_Wet	35.91083	34.40917	22	378	771	6.73	96.3	13.9	28.0	0.3	22.2	1.1	17.0	292.5	49.1
S26W	May-20	Karm_Saddeh_Wet	35.88944	34.30750	23	262	534	7.49	50.1	25.5	7.4	1.7	8.2	0.9	6.7	285.0	20.0
S27W	May-20	Iaal_Zireh_Wet	35.93417	34.35167	16	223	457	7.26	14.6	4.1	1.4	1.3	2.3	0.1	48.0	232.5	16.0
S28W	May-20	Qobbeh_Wet	35.84750	34.43222	25	338	690	7.27	45.4	14.0	17.0	0.1	12.3	1.2	13.3	280.0	49.1
S29W	May-20	Abu_Samra_Wet	35.84556	34.42861	19	288	588	7.06	69.7	20.0	15.0	2.2	16.1	2.0	15.5	282.5	29.0
S30W	May-20	Nabee_Fouwar_Wet	35.96278	34.28944	13	228	466	7.37	53.2	17.7	9.4	2.1	12.8	0.2	12.1	230.0	16.0
S31W	May-20	Ein_Fawar_Wet	35.96278	34.28944	13	214	438	7.22	50.0	16.6	8.6	1.5	12.0	1.9	11.3	212.5	15.0
S32W	May-20	Ein_Dwelib_Wet	35.98222	34.28917	9	96	196.2	8.45	15.4	3.4	0.8	1.1	1.8	0.2	7.1	112.5	9.0
S33W	May-20	Ein_Roume_Wet	35.97694	34.28278	13	238	480	7.27	22.4	6.2	1.2	0.1	3.4	1.1	11.7	257.5	13.0
S34W	May-20	Ein_Mazraet_Tefeh_Wet	35.95333	34.32028	15	299	610	7.6	13.1	4.7	1.1	0.1	6.4	1.4	11.7	295.0	17.0
S35W	May-20	Ein_Ghabash_Wet	35.97500	34.31944	11	190	387	7.14	35.8	11.9	2.2	0.2	6.4	2.0	6.9	210.0	12.0
S01D	Sep-19	Sebaal_Dry	35.91500	34.31500	18	275	560	8.02	45.2	24.4	5.7	0.7	10.5	0.2	8.5	312.5	41.6
S02D	Sep-19	Daraya_Dry	35.86972	34.32639	21	352	719	7.83	74.2	14.3	10.5	0.7	16.3	0.1	25.9	357.5	54.7
S03D	Sep-19	Arjess_Dry	35.88028	34.33444	27	301	616	7.95	63.8	8.4	7.4	0.4	6.0	0.2	15.1	302.5	48.5
S04D	Sep-19	Arde_Dry	35.91972	34.40806	21	472	966	7.53	58.5	57.9	70.9	10.8	66.8	0.2	6.3	400.0	138.2

Sample	Sampling date	Sampling point	X	Y	T	TDS	EC	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	PO_4^{3-}	NO_3^{-}	HCO_3^{-}	Cl^{-}
S05D	Sep-19	Rachiine_Dry	35.92972	34.38889	12	150	307	8.32	30.3	11.6	2.7	0.6	8.8	0.3	11.2	165.0	16.9
S06D	Sep-19	Kfar Chakhna_Dry	35.87722	34.36833	21	386	788	7.75	87.6	48.0	20.5	1.5	23.7	0.1	24.8	370.0	61.4
S07D	Sep-19	Ras Kifa_Dry	35.87667	34.31472	20	264	539	8.05	43.9	16.4	6.6	0.9	9.5	0.2	13.8	285.0	40.2
S08D	Sep-19	Miryata_Dry	35.93139	34.41889	22	304	620	7.95	70.2	10.5	10.9	2.0	20.4	0.1	32.9	290.0	43.0
S09D	Sep-19	Bkeftine_Dry	35.86306	34.38583	29	339	701	7.85	60.3	14.3	19.9	18.4	24.1	0.2	34.0	252.5	89.2
S10D	Sep-19	Kfar Qahel_Dry	35.85194	34.35583	26	246	515	8.07	44.6	16.7	12.0	0.8	9.7	0.2	11.1	232.5	63.6
S11D	Sep-19	Besbeel_Dry	35.87667	34.35444	28	338	695	7.86	61.1	46.1	19.2	2.6	19.1	0.4	22.1	317.5	66.5
S12D	Sep-19	Hilane_Dry	35.95222	34.42583	21	254	518	8.07	66.9	4.0	9.0	1.6	16.3	0.2	24.7	227.5	36.2
S13D	Sep-19	Nabee Joueit_Dry	35.97306	34.28917	9	98	200.2	8.45	21.9	8.1	0.9	0.2	3.9	0.1	7.9	117.5	9.9
S15D	Sep-19	Nabee Mar Sarkis_Dry	35.98611	34.31167	8	137	279.5	8.36	28.4	10.7	1.5	0.3	5.6	0.1	8.5	160.0	13.0
S17D	Sep-19	Ein Ehden-Bcharre2_Dry	36.02306	34.26139	11	128	261.5	8.38	25.6	12.0	1.9	0.4	6.2	0.1	7.7	152.5	13.6
S19D	Sep-19	Mar Semaan_Dry	36.00889	34.26167	8	98	199.6	8.45	19.7	9.1	0.9	0.1	3.1	0.1	8.0	107.5	9.5
S20D	Sep-19	Majdalaya_Dry	35.86972	34.41972	27	285	582	7.99	50.5	17.9	14.3	2.1	15.8	0.2	15.4	265.0	70.4
S21D	Sep-20	Zgharta_1_Dry	35.88944	34.39611	21	438	893	7.66	124.6	16.9	22.6	0.3	37.0	0.0	30.6	352.5	55.1
S22D	Sep-20	Zgharta_2_Dry	35.88972	34.38667	24	509	1038	7.82	113.8	17.3	19.4	1.9	31.3	1.6	85.7	307.5	75.1
S23D	Sep-20	Iaal_Dry	35.90222	34.37139	19	318	649	7.59	93.2	12.9	12.9	1.3	15.6	0.1	18.4	290.0	26.0
S24D	Sep-20	Der_Nbouh_Dry	35.93222	34.37222	15	173	353	8.09	42.1	11.7	5.2	2.1	10.9	0.0	13.9	152.5	13.0
S26D	Sep-20	Karm_Saddeh_Dry	35.88944	34.30750	25	261	533	8.30	51.4	27.7	7.6	0.9	8.8	0.3	7.7	267.5	19.0
S28D	Sep-20	Qobbeh_Dry	35.84750	34.43222	27	369	755	8.34	70.8	21.5	35.2	0.6	24.9	0.3	17.5	247.5	65.1
S29D	Sep-20	Abu_Samra_Dry	35.84556	34.42861	22	275	561	8.04	68.9	19.7	12.5	4.0	18.2	0.0	13.6	255.0	23.0
S30D	Sep-20	Nabee_Fouwar_Dry	35.96278	34.28944	12	229	467	8.21	55.2	18.5	9.6	1.9	12.8	0.5	10.5	227.5	14.0

Sample	Sampling date	Sampling point	X	Y	T	TDS	EC	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	PO_4^{3-}	NO_3^{-}	HCO_3^{-}	Cl^{-}
S31D	Sep-20	Ein_Fawar_Dry	35.96278	34.28944	13	223	456	8.13	48.4	16.0	8.2	1.5	11.5	0.2	11.0	217.5	17.0
S32D	Sep-20	Ein_Dwelib_Dry	35.98222	34.28917	9	98	200.1	8.63	25.1	7.7	1.3	1.1	3.8	0.6	7.3	100.0	8.0
S33D	Sep-20	Ein_Roume_Dry	35.97694	34.28278	12	246	502	8.08	58.7	16.5	3.2	0.2	9.6	0.1	9.6	252.5	11.0
S34D	Sep-20	Ein_Mazraet_Tefeh_Dry	35.95333	34.32028	15	278	562	7.93	62.7	25.1	6.7	0.4	16.8	0.6	11.0	275.0	16.0
S35D	Sep-20	Ein_Ghabash_Dry	35.97500	34.31944	12	185	377	8.13	42.7	14.4	2.7	1.5	8.7	1.5	6.9	245.0	12.0

Appendix 4 Irrigation quality assessment parameters of wet and dry seasons samples. (EC: electrical conductivity in µS/cm, %Na: percentage sodium, SAR: sodium adsorption ratio, PI: permeability index, RSC: residual sodium carbonate, KR: Kelly's ratio, MR: magnesium ratio, T.conc.: total concentration)

Samples	EC	%Na	SAR	PI	RSC	KR	MR	T.conc.
S01W	570	6.6	0.2	58.6	1.1	0.1	57.3	4.4
S02W	758	9.8	0.3	64.0	1.8	0.1	28.2	4.5
S03W	621	9.8	0.3	54.0	0.4	0.1	24.9	5.1
S04W	857	15.4	0.5	59.4	0.9	0.2	29.2	5.1
S05W	391	5.8	0.1	78.6	1.0	0.1	45.6	2.5
S06W	795	10.7	0.3	58.3	1.5	0.1	44.6	5.1
S07W	518	10.5	0.2	80.6	1.6	0.1	49.9	2.9
S08W	604	10.9	0.3	62.1	0.7	0.1	19.3	4.0
S09W	761	16.9	0.7	37.9	-3.5	0.2	58.6	9.7
S10W	505	13.5	0.4	65.4	0.6	0.2	40.3	3.8
S11W	758	13.8	0.4	62.9	1.5	0.1	54.5	4.8
S12W	522	12.8	0.3	74.4	1.0	0.1	10.5	3.1
S13W	277	3.4	0.1	84.9	0.7	0.0	32.8	2.0
S14W	590	3.7	0.1	62.3	1.8	0.0	63.0	4.1
S15W	205	3.4	0.1	114.8	1.0	0.0	28.5	1.3
S16W	354	6.1	0.1	70.8	0.6	0.1	46.5	2.8
S17W	195.3	3.1	0.1	90.5	0.3	0.0	34.8	1.5
S18W	409	3.3	0.1	66.9	0.7	0.0	52.2	3.0
S19W	208	2.9	0.0	88.7	0.3	0.0	40.9	1.6
S20W	656	15.6	0.5	67.9	1.2	0.2	21.2	4.1
S21W	935	11.4	0.5	39.0	-1.8	0.1	17.1	8.9
S22W	1038	10.7	0.5	33.9	-3.4	0.1	19.8	9.8
S23W	325	9.9	0.2	106.7	2.9	0.1	18.0	2.3
S24W	217.4	4.9	0.1	65.8	-0.3	0.0	25.2	2.1
S25W	771	17.0	0.7	47.4	-1.2	0.2	19.4	7.2
S26W	534	7.3	0.2	50.2	0.0	0.1	45.9	5.0

Samples	EC	%Na	SAR	PI	RSC	KR	MR	T.conc.
S27W	457	8.1	0.1	177.8	2.7	0.1	31.9	1.2
S28W	690	17.7	0.6	68.9	1.1	0.2	34.0	4.2
S29W	588	12.1	0.4	48.3	-0.5	0.1	32.4	5.9
S30W	466	10.0	0.3	51.7	-0.4	0.1	35.7	4.6
S31W	438	9.6	0.3	52.7	-0.4	0.1	35.6	4.3
S32W	196.2	5.7	0.0	127.8	0.8	0.0	26.9	1.1
S33W	480	3.2	0.1	124.5	2.6	0.0	31.6	1.7
S34W	610	4.7	0.1	205.9	3.8	0.0	37.4	1.1
S35W	387	3.6	0.1	67.8	0.7	0.0	35.7	2.9
S01D	560	5.9	0.2	55.4	0.8	0.1	47.3	4.6
S02D	719	8.8	0.3	53.7	1.0	0.1	24.3	5.4
S03D	616	7.9	0.2	60.5	1.1	0.1	18.1	4.2
S04D	966	30.2	1.6	52.1	-1.2	0.4	62.3	11.1
S05D	307	5.2	0.1	67.8	0.2	0.0	38.9	2.6
S06D	788	10.0	0.4	36.2	-2.3	0.1	47.7	9.3
S07D	539	8.0	0.2	63.5	1.1	0.1	38.4	3.9
S08D	620	10.7	0.3	54.6	0.4	0.1	20.0	4.9
S09D	701	24.1	0.6	57.1	-0.1	0.2	28.4	5.5
S10D	515	13.0	0.4	59.8	0.2	0.1	38.4	4.2
S11D	695	11.6	0.4	40.3	-1.7	0.1	55.7	7.8
S12D	518	10.5	0.3	57.0	0.0	0.1	9.1	4.1
S13D	200.2	2.4	0.0	78.8	0.2	0.0	38.1	1.8
S15D	279.5	3.1	0.1	70.8	0.3	0.0	38.6	2.4
S17D	261.5	3.9	0.1	70.4	0.2	0.0	43.8	2.4
S19D	199.6	2.4	0.0	76.8	0.0	0.0	43.4	1.8
S20D	582	14.4	0.4	58.3	0.3	0.2	37.2	4.7
S21D	893	11.5	0.5	39.3	-1.9	0.1	18.4	8.6
S22D	1038	11.1	0.4	38.7	-2.1	0.1	20.2	8.0

Samples	EC	%Na	SAR	PI	RSC	KR	MR	T.conc.
S23D	649	9.4	0.3	43.5	-1.0	0.1	18.8	6.3
S24D	353	8.3	0.2	54.6	-0.6	0.1	31.7	3.4
S26D	533	6.7	0.2	46.6	-0.5	0.1	47.3	5.2
S28D	755	22.5	0.9	51.7	-1.3	0.3	33.6	6.9
S29D	561	11.3	0.3	46.0	-0.9	0.1	32.3	5.7
S30D	467	9.8	0.3	49.8	-0.6	0.1	35.9	4.8
S31D	456	9.5	0.3	54.6	-0.2	0.1	35.6	4.1
S32D	200.1	4.3	0.1	68.5	-0.3	0.0	33.7	2.0
S33D	502	3.2	0.1	48.8	-0.2	0.0	31.9	4.5
S34D	562	5.4	0.2	43.8	-0.7	0.1	40.0	5.5
S35D	377	4.4	0.1	61.5	0.7	0.0	35.9	3.5