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GROUNDWATER IN URBAN COASTAL AREAS: HYDROGEOCHEMICAL BASED APPROACH FOR MANAGING THE TRANSITION AREAS.
The example of the lagoon of Nador (Morocco).

PhD Candidate: **Viviana Re**
955409

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Programme coordinator:
Prof. **Giovanni Maria Zuppi**

Advisor:
Prof. **Giovanni Maria Zuppi**

Co-Advisors:
Dr. **Alice Aureli**
Dr. **Andrea Merla**

…we made from water every living thing.
[Al-Qur'aan 21:30]

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Abstract

The urgent need for integrated approaches to water resources management in coastal regions implies performing studies on the relations between the drainage basin (catchment area) and the aquifer throughout the near coastal zone, and to develop adequate science based policies oriented to achieve sustainability goals. The Mediterranean basin is a good example of such needs, since a strong public and scientific effort promoted the application of a holistic approach for achieving the sustainable exploitation of water resources and the adoption of best management practices. This area has been object of several studies and conventions; however, discrepancies, still exist between the European rim countries and the Middle East and North Africa (MENA) region ones, especially related to environmental protection. Moreover, even for areas where increasing attention is paid to coastal environments, transition zones, and lagoon system protection, so far most of the interest was focused on the ecological functions of these areas and the possible development for aquaculture activities.

Based on these premises, the Strategic Action Plan for Large Marine Ecosystems, the first project bringing together some of the main partners working in the Mediterranean for joint implementation of actions, was created with the goal of protecting the natural Mediterranean environment and to improve the quality of the life in rim countries. Within this framework, the lagoon of Nador (Morocco) represents the pilot case study for the UNESCO IHP sub component (Management of Coastal Aquifers and Groundwater).

The investigation on the Bou-Areg aquifer and the lagoon of Nador was therefore aimed at (i) applying hydrogeochemical tools for supporting coastal aquifers management, with a specific focus on urban coastal areas in semi-arid climates, and (ii) at unravelling the role of groundwater in sustaining coastal lagoons and wetlands, including their habitats and ecosystems, around the Mediterranean shores, concentrating on the Nador Lagoon in Morocco.

The geochemical and isotopic ($\delta^{2}H$, $\delta^{18}O$, $\delta^{13}C$, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$) characterization of the Bou Areg aquifer based on samples collected during two surveys in November 2009 and June 2010, allowed for the identification of runoff from the mountain regions and agricultural return flows as the main sources of aquifer recharge. The high salinization of the aquifer is not only due to the intensive agricultural activities but it is also associated to the natural characteristics of the catchment. The isotopic signal of dissolved nitrates allowed for the identification of two main sources of nitrogen in the system: (i) fertilizers and (ii) manure and septic effluent. The multivariate statistical analysis supported the geochemical evidences and confirmed the need for deeper investigation on the irrigation channel and rivers network in order to identify adequate end members for mixing processes studies.

Riassunto

Gli approcci integrati per la gestione di zone costiere richiedono una approfondita conoscenza delle relazioni tra acque superficiali, sotterranee e la zona litorale circostante, poiché gli obiettivi di sostenibilità possono essere raggiunti soltanto attraverso politiche basate su adeguati dati scientifici.

Il bacino del Mediterraneo è un buon esempio del tentativo di applicare un approccio olistico alla gestione delle risorse idriche. Sebbene tale area sia da molti anni oggetto di svariati progetti e convenzioni, il divario esistente tra i paesi Europei e quelli del litorale sud (la cosiddetta regione MENA) è ancora piuttosto ampio, soprattutto per quanto riguarda la protezione ambientale. Inoltre, a scala di bacino, anche laddove siano presenti studi di gestione di ambienti costieri, zone di transizione e lagune, che rappresentano le risorse più fragili, l'attenzione è quasi sempre focalizzata sulle loro funzioni ecologiche ed il loro possibile utilizzo per fini commerciali (in particolare pesca ed acquacoltura).

Sulla base di queste premesse è stata creata la *Strategic Action Plan for Large Marine Ecosystem*, (Partenariato strategico per i grandi ecosistemi marini) che rappresenta il primo progetto a cui afferiscono tutti i principali attori che lavorano nel Mediterraneo, con l'obiettivo di preservarne il suo ambiente naturale ed allo stesso tempo, migliorare la qualità della vita nei paesi che su di esso si affacciano.

Nell'ambito del progetto SAP MED, la laguna di Nador è stata scelta per rappresentare il caso di studio del Marocco per la sottocomponente gestita da UNESCO-IHP. L'analisi dell'acquifero di Bou-Areg e della laguna di Nador ha due obiettivi principali: (i) applicare strumenti di analisi idrogeochimici a supporto dei progetti di gestione degli acquiferi costieri e (ii) chiarire lo stato di qualità delle acque sotterranee ed il loro impatto sulla qualità delle acque lagunari.

L'analisi geochimica ed isotopica ($\delta^{2}H$, $\delta^{18}O$, $\delta^{13}C$, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$) dei dati raccolti durante due campagne (Novembre 2009 e Giugno 2010) ha permesso di identificare le acque di ruscellamento ed i flussi di ritorno dall'attività agricola come le due principali fonti di ricarica dell'acquifero. L'elevata urbanizzazione e le attività agricole rappresentano invece le principali cause di alterazione della normale salinità dell'acquifero. Lo studio idrochimico, supportato dall'analisi statistica multivariata, non ha evidenziato presenza di processi di intrusione salina dalla laguna verso l'acquifero.

L'analisi isotopica dei nitrati disciolti ha infine permesso di individuare due principali fonti di azoto nelle acque sotterranee: (i) fertilizzanti sintetici e (ii) effluenti di fosse settiche e letame.

I dati ottenuti in questo studio, opportunamente integrati con quelli ottenuti nelle due campagne successive previste dall'intero progetto, verranno presentati alle autorità competenti del Marocco ed utilizzati a supporto di adeguate politiche di gestione delle risorse idriche nella regione di Nador.

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PART ONE

Introduction

I. Towards a holistic approach and the need for integration: Integrated Water Resources Management (IWRM) and Integrated Coastal Zone Management (ICZM)

Water is a fundamental resource for human development and wellbeing, nevertheless its use for urban, industrial and agricultural needs has severe impacts on the ecological, environmental, social, economical and political spheres.

The above interactions, given the integrated nature of the water cycle, further complexify water resource management.

Therefore, over the years both scientists and politicians acknowledged that an integrated approach is the only way for properly managing water resources.

The necessary integration has to be performed avoiding the study of each component of the water cycle in an isolated way. It has to be applied both at hydrological and ecological levels, i.e. studying the catchment basin in its whole complexity, and considering its impact on fauna and flora. Hence, “integration” must be translated into a holistic approach, where hydrogeology, social and economical sciences acts in a synergic way, and global/climatic changes are taken into account in water use categories.

Following the uncertainty related to climate changes, population growth (especially in urban areas), and the consequent need to address emerging water scarcity and human induced pollution, the integrated approach is seen to be the only possible way for finding adequate solutions to water issues.

There are several models proposing integrated approach to deal with water sustainability at different levels.

The most used one, an operative framework for achieving sustainability goals, is the so-called Integrated Water Resource Management (IWRM), whose features and evolution over the years are presented in the following section. The focus of the second part of this chapter is than on another specific application of IWRM, the Integrated Coastal Zone Management (ICZM). This approach considers the relevance and vulnerability of coastal systems, another important issue for the proposed research project.

To conclude, a combination of IWRM and ICZM, is presented: the Integrated Coastal Area and River Basin Management (ICARM).

Tackling all the aspects of the above-mentioned approaches is beyond the scope of the manuscript, nevertheless some introductory notes are presented in order to facilitate the reader and introduce the main purposes of the research.

I.I. Integrated Water Resource Management (IWRM)

The concept of Integrated Water Resource Management, that become a mainstream idea after the 1977 United Water Conference in Mar de la Plata (McDonnell, 2008), has been discussed for more than 30 years (Braga, 2001).

Initially the innovation, in the framework of water management, was the inclusion of the term “integration”. As McDonnell (2008) pointed out, since the very beginning integration meant “to include the natural hydrological environment in engineering and economic driven solutions”. More recently new considerations have been added to the IWRM concept, therefore it is now perceived as a new paradigm that can lead to long term solutions to water problems. From a practical point of view, there is a shift from a top-down (supply-led) approach, towards a more holistic approach, based on local ideas and demand management (McDonnell, 2008).

These evolutions allowed to pass from single purpose projects to multidisciplinary ones (GWP 2003; Braga and Lotufo, 2008), more coherent with the intrinsic nature of water resources and the features of the planning process.

According to the level chosen for the analysis and implementation, IWRM can be a powerful tool to solve upstream-downstream conflicts (for a river) or transboundary controversies (in particular in cases of shared groundwater resources) considering the whole basin (catchment) scale (GWP, 2009).

In fact, management plans taking into account all the component of a problem are more likely to lead to sustainable water use, although the main problem is related to the concrete implementation of those practices.

Indeed, even if many attempts have been done to put those concepts into practice, not many changes have occurred at global level. During the World Summit on Sustainable Development (WSSD) held in Johannesburg in 2002, the international community made an important step towards more sustainable patterns of water management by including in the Plan of Implementation (POI) as a call for all countries to "develop integrated water resource management and water efficiency plans by 2005“ (Jønch-Clausen, 2004). However, a scarce response so far has been given to key commitment from the national and international governments, possibly for lack of replicable examples.

This is why Molle (2008) defined IWRM as a good example of the so-called Nirvana Concepts, i.e. a “vision”, an “image of what the world should tend to”.

In order to achieve the IWRM goals, many efforts are required by the involved agents. If the scientists have to avoid performing a pure “conceptual and academic exercise”, the other stakeholders have not to consider it as a “ticked box on the way to securing funding for a project or program” (McDonnell, 2008).

As already mentioned, the ideas of good governance through integrated water resources management are predicated on bringing together our understanding of water from many domains, thus the supply of knowledge and information is an important part of any enabling environment (McDonnell, 2008).

A robust basis for good policy choices (through the incorporation of IWRM in national policies; GWP, 2009) needs adequate information on hydrological, ecological, social and economical characteristics of the catchment area. Once the baseline conditions are defined the focus should than move to the analysis of human impacts (or alteration of the baseline conditions). This will allow the prediction of the responses of the catchment system to factors such as effluent discharges, diffuse pollution, changes in agricultural or other land use practices and the building of water retaining structures (Edmunds and Shand, 2008; McDonnell, 2008).

I.II. Integrated Coastal Zone Management (ICZM)

Under the need for integration in water management, another holistic approach has been developed over the years: the Integrated Coastal Zone Management (ICZM) aimed to consider all the aspect of a coastal zone, including geographical and political boundaries, in the attempt to achieve sustainability.

This concept was developed for the fist time in 1992 during the Earth Summit of Rio de Janeiro, and the related policy was defined in the chapter 17 of the proceedings of the summit within Agenda 21 (UN, 1992).

From that moment on several scientists and inter-governmental associations proposed their definition of ICZM (Vallega, 2003). Despite some differences, all the definitions have in common the most relevant features and the stress on the holistic approach.

A quite exhaustive definition is the one given by the European Commission (2000):

> [ICZM is] *a dynamic, multidisciplinary and iterative process to promote sustainable management of coastal zones. It covers the full cycle of information collection, planning (in its broadest sense), decision making, management and monitoring of implementation. ICZM uses the informed participation and cooperation of all stakeholders to assess the societal goals in a given coastal area, and to take actions towards meeting these objectives. ICZM seeks, over the long-term, to balance environmental, economic, social, cultural and recreational objectives, all within the limits set by natural dynamics. 'Integrated' in ICZM refers to the integration of objectives and also to the integration of the many instruments needed to meet these objectives. It means integration of all relevant policy areas, sectors, and levels of administration. It means integration of the terrestrial and marine components of the target territory, in both time and space.*

In the same way the Protocol on Integrated Coastal Zone Management in the Mediterranean (UNEP, 2008) was settled down defining the main objectives for a correct management.

The core points are the following:

a) facilitate the sustainable development of coastal zones taking into account the environment and landscapes protection together with economic, social and cultural development;
b) preserve coastal zones for the benefit of present and future generations;
c) ensure the sustainable use of natural resources, particularly with regard to water use;
d) ensure preservation of the integrity of coastal ecosystems, landscapes and geomorphology;
e) prevent and/or reduce the effects of natural hazards and in particular of climate change, which can be induced by natural or human activities;

f) achieve coherence between public and private initiatives, and between all decisions by the public authorities, at the national, regional and local levels, which affect the use of the coastal zone.

Form this brief description the strong connection between IWRM and ICZM emerges, as well as the necessity to consider both the approaches for a correct management at catchment level in coastal areas.

I.III. Integrated Coastal Area and River Basin Management (ICARM)

As discussed before, river basins and coastal areas are linked through their physical and ecological structures and components. They both provide space and natural resources, and they host valuable recreational and economic activities. Therefore, their interconnections are translated in links and exchanges among the different compartments. For example economic activities in downstream areas benefit from upland resources, such as water; coastal resources are often threatened due to the pollution generated in upstream areas, while they provide space for settlement, industrial activity and tourist developments that have a positive advantages for the broader river basin area.

In this framework, another good example of implementation is the so called Integrated Coastal Area and River Basin Management (ICARM), providing a key for the integrated development of natural and socio-economic environments within river basins and coastal areas.

The concept of ICARM is reflected in the UNEP-ICARM approach, in the European Water Framework Directive and partly in LOICZ (Land-Ocean Interactions in the Coastal Zone). In each case there is the recognition of the need for an approach to manage both river basins and coastal areas in an integrated manner, on the basis of their hydrological, ecological and geochemical relationship, as well as based on a need for a more effective socio-economic development of the two management units.

It must be underlined that the ICARM approach constitutes a supplement to traditional ICZM rather than a replacement. Objectives are to raise awareness as well as to promote and to ensure a sustainable integrated coastal water – river management (Schernewski *et al*., 2005).

Therefore, the focus is involving all the stakeholders, linking broad scale management to local level intervention, and regulating of conflicting uses (Coccossis *et al*, 1999; PAP/RAC, 2000).

Integration creates room for a more rationale use of water resources and a more effective environmental protection, and it is in this direction that the all the project and policies should work.

All these concepts are nowadays implemented (in some cases just attempts) at both scientific and political level, and increasing attention has been paid over the years to the protection and sustainable management of vulnerable coastal areas/basins.

A good example is the Mediterranean basin, where the social, environmental and economical actors involved in the management of water resources belonging to twenty-one countries spread over three continents.

II. The Mediterranean Basin

The Mediterranean basin covers portion of three continents (Europe, Asia and Africa) with twenty-one rim countries (Figure I) and a coastline of 46,000 km, 42% of which (i.e., 19,000 km) belong to several islands. The latter represents an invaluable asset not only because of the relevance of its ecosystems and its cultural heritage, but also for its social and economic functions (Coudert, 2007).

Source : Gaussen & De Philippis - FAO

Figure I. The Mediterranean rim countries and the Mediterranean catchment Basin (Plan Bleu.org).

With the resources shared by all the rim countries, the Mediterranean is constantly exposed to human pressure on its general environment, and consequently victim of conflicts over natural resources, both at regional and international level. This is mainly due to increasing urbanization, agricultural activities along the coast, industrial sites, tourism and maritime circulation.

The main consequence is therefore the degradation of the *milieu* with often irreversible losses of biodiversity and alteration of the ecosystem functions.

According to the Blue Plan report (Coudert, 2007) the land-based contamination represents 80% of total pollution affecting coastal waters (the remaining 20% is due to off shore activities).

According to the same source, the main pollution spots in the Mediterranean are due to:

- Eutrophication (nitrogen and phosphorous nutrients stimulating the aquatic primary production), mainly originated from diffuse agricultural discharges;
- Chemical contaminations due to industrial draining;
- Organic and microbiological pollutions, caused by untreated domestic sewages and industrial wastewaters.

-Solid and dangerous wastes, which are the by-products of coastal districts (e.g. discharges from households, tourism and landfills generate between 30 and 40 million tons of solid waste per year).

In addition to these sources, another cause of habitats' degradation and loss of biodiversity is the coastal erosion affecting a significant portion of the Mediterranean coastline. The phenomenon has been strongly exacerbated by anthropogenic action, with watershed development (solid inflows to the sea reduced by 90% over the past 50 years), sand extraction, construction of sea embankments and restructuring of the coasts.

Despiite their differences all those processes are all side effects of coastal overdevelopment (i.e. concentration of people and activities on the coastal zone) in the Mediterranean area, which has been ongoing for several decades, leading to inevitable consequences on the natural environment.

While half of the world population is in process of becoming urban, in the Mediterranean rim countries two out of three inhabitants are already city-dwellers. By 2030, three quarters of the Mediterranean population will be urban (Laria, 2007), with severe environmental and social consequences (e.g. youth unemployment, lack of adequate infrastructures and services, pollution, domestic waste, increase in water demand).

The Mediterranean urban population (i.e. the population living in agglomeration of over 10,000 inhabitants) passed from 94 million in 1950 to 274 million in 2000. The reason of this increase, in particular for Southern and Eastern rim countries, has to be found in endogenous driving forces; despite the fertility rate is decreasing over the time, the urban population is growing thanks to internal redistribution and migration (inter-urban and rural to rural). However, countries like Tunisia and Egypt are experiencing a decreasing urbanization, while in countries like Morocco, Syria and Turkey migrations are still quite important. In the same way, Northern Mediterranean countries, which experienced a steady growth in past, nowadays show quite moderate growth rates (0.7% over the period 1970-2000) that are likely to continue in future.

According to the urbanization scenario for the Mediterranean region, by 2025, urban population would pass from 145 million inhabitants in 2000 to over 243 million in Southern and Eastern countries and from 129 million to about 135 million in the countries of the European rim. A third of this growth would take place in the Mediterranean coastal regions (Laria, 2007).

Particular attention should be paid to the features of urbanization in terms of city expansion. While the Northern shore is experiencing a general spreading of cities further and further away, in the Southern and Eastern shore this process is substituted by increase of informal settlements in the peripheral areas, as many people migrating from the countryside cannot afford houses in cities.

Informal settlements in urban outskirts are often lacking basic sanitation facilities and are more vulnerable to natural hazards, such as earthquakes, floods, landslides, with often catastrophic consequences.

All these factors should be taken into account while dealing with environmental management plans and, if on the one hand a more sustainable city development has to be promoted (e.g. more strict application of Agenda 21, endorsement of green transports, increase of projects of regeneration and renewal), environmental protection and natural resource preservation should be the first goal.

Based on this brief description, it emerges that despite sharing common catchment basin, Mediterranean rim countries are experiencing dissimilar situations, which have to be managed according to different strategies, but according to a common general framework and involving a reinforcement of coastal policies.

Several projects and agreements have been carried out with this aim, and in all the numerous sectors of integrated management, both at regional-local and national-international level.

At the same time numerous conventions has been signed in order to protect the Mediterranean Sea and its precious resources.

All those conventions put the Mediterranean Sea ahead of all other seas in terms of management and environmental protection.

For example, at regional level, the riparian countries and the European Community signed in 1976 a common legal framework, the **Barcelona Convention** for the Protection of the Sea against pollution (and its Protocol for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources, signed in Athens on May 1980), which entered in force in 1978. This protocol was then revised in 1995 as the Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean, though it is not yet in force.

The adoption by the Parties in the Barcelona Convention of a Protocol on Sustainable Management of Mediterranean Coastal Areas, in process of drafting, will provide a clear signal of the direction of new management approach, and it could help countries to develop or strengthen their policies (Coudert, 2007).

Other examples of adopted protocols on the protection of the Mediterranean basin are the following ones: (UNEP 2009):

- The Protocol for the Prevention and Elimination of Pollution of the Mediterranean Sea by Dumping from Ships and Aircraft (**Dumping Protocol**); adopted in Barcelona (Spain) in 1976 (in force in 1978). This protocol was revised in 1995 as the Protocol for the Prevention and Elimination of Pollution of the Mediterranean Sea by Dumping from Ships and Aircraft or Incineration at Sea;
- The Protocol Concerning Cooperation in Combating Pollution of the Mediterranean Sea by Oil and other Harmful Substances in Cases of Emergency (**Emergency Protocol**); adopted in Barcelona (Spain) in 1976, in force since 1978;
- Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources (**LBS Protocol**); adopted in Athens (Greece) in 1980, and in force since 1983, this protocol was amended in Syracuse (Italy) in 1996 as the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources and Activities;
- The Protocol Concerning Mediterranean Specially Protected Areas (**SPA Protocol**); adopted in Geneva (Switzerland) in 1982 (in force 1986), and revised in Barcelona (Spain) in 1995 as the Protocol Concerning Specially Protected Areas and Biological Diversity in the Mediterranean (SPA and Biodiversity Protocol);
- The Protocol for the Protection of the Mediterranean Sea against Pollution Resulting from Exploration and Exploitation of the Continental Shelf and the Seabed and its Subsoil (**Offshore Protocol**), adopted in Madrid (Spain) in 1994;

- The Protocol on the Prevention of Pollution of the Mediterranean Sea by Transboundary Movements of Hazardous Wastes and their Disposal (**Hazardous Wastes Protocol**); adopted in Izmir (Turkey) in 1996, but not yet in force.

More recently, but only at European level, the **European Water Framework Directive (EWFD; Directive 2000/60/EC)**, came into force in 2000 to commit European Union member states to achieve good qualitative and quantitative status of all water bodies (including marine waters) by 2015. The purpose of the *directive is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater* in a broader sense and in order to promote sustainable water use and long-term protection of waters within Europe (European Commission, 2010).

In addition to the EWF, the **Marine Strategy Framework Directive**, adopted in June 2008**,** was designed to effectively manage the marine environment across Europe, thus including the Mediterranean sea and its coastal environments.

Moreover, in order to combat land-based pollution, as part of the implementation of the specific protocol of the Barcelona Convention, a Strategic Action Plan was adopted in 1997, and included in National Action Plans, setting ambitious objectives regarding pollution reduction up to 2025 (e.g. wastewater treatment of all coastal cities, reduction of industrial pollutants and of dangerous wastes). However, significant implementation difficulties persist in a context of increasing disparity of response capacity among the EU member countries or future members, and the other riparian countries (Coudert, 2007).

Despite the increasing attention and the amount of protocols signed to protect the Mediterranean basin ample room for progress still exists especially regarding the setting up of regulatory and institutional tools. In 2004, only five countries (Algeria, France, Greece, Lebanon and Spain) already had a frame-law on the coastal zone, and three countries (Algeria, France and Tunisia) had coastal dedicated agencies (Coudert, 2007). Furthermore, it has to be underlined that if the implementation of adequate policies under the guidance of the European Union (Northern shore) is long and complex, the situation is even more difficult in the countries belonging to the so called Middle East and North African (MENA) region, occupying the Southern shore.

II.I. The Middle East and North Africa (MENA) region

According to the World Bank (as no unique definition/grouping exists) the acronym MENA (Middle East and North Africa region) groups the following African and Asian Countries: Algeria, Bahrain, Djibouti, Egypt, Iran, Iraq, Israel, Jordan, Kuwait, Lebanon, Libya, Morocco, Oman, Palestinian territories (the West Bank and Gaza Strip), Qatar, Saudi Arabia, Syria, Tunisia, United Arab Emirates and Yemen, with nine countries bordered by the Mediterranean Sea (Figure II).

The region as a whole accounts for about the 5% of world’s population (313 Million people in 2007; World Bank, 2009a). Less than 2% of MENA’s population lives on less than $1 a day while about 20% of the regional population lives on less than $2 a day (World Bank-MENA, 2009).

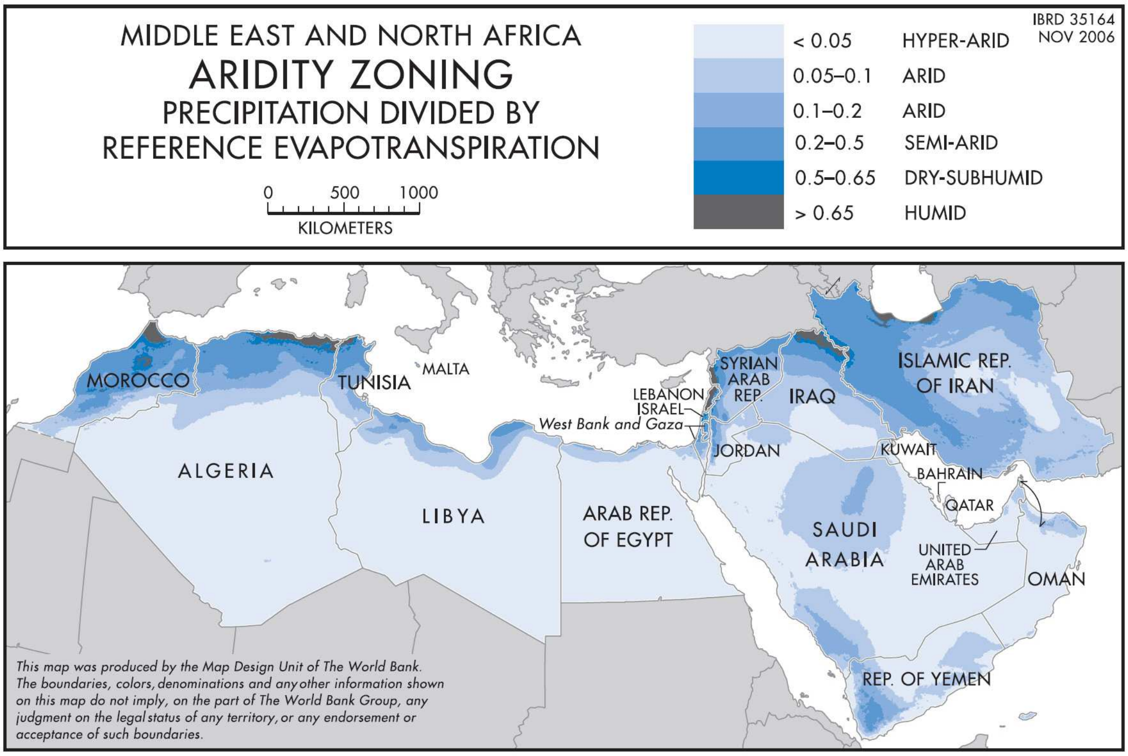
As a general feature, the majority of these countries is either in arid or hyper-arid zone (Figure II), they depend on seasonal rainfall, they have very few rivers (some of which carry runoff from other countries) and they often rely on fragile (and sometimes non renewable) aquifers.

Moreover, this region is one of the most vulnerable to climate changes; therefore the issue of water scarcity (the highest in the world) is of particular relevance for its social and economic consequences. The dependence on climate-sensitive agriculture, the concentration of population and economic activity in flood-prone urban coastal zones, make this area particularly vulnerable to climate-induced problems, which can eventually escalate in violence and political turmoil, even beyond the region's boundaries (World Bank, 2007a). This could be even worse in areas lacking of strong political and economic stability.

This is why in such a context it is of primary and vital importance to create integrated policies for water resource management.

As previously mentioned, since ancient times MENA region had to cope with difficult water conditions: aridity, high variability, and high dependence on waters crossing international borders (e.g. Northern Sahara Aquifer System, shared among Algeria, Tunisia and Libya). Within this context a rational water management matters even more than it does elsewhere (World Bank, 2007b).

The combined action of population growth and foreseen climate changes will reduce the per capita water availability (50% by 2050) and both droughts and floods will be more frequent (IPCC, 2008).



This map was produced by the Map Design Unit of The World Bank. The boundaries, colors, denominations and any other information shown on this map do not imply, on the part of The World Bank Group, any judgment on the legal status of any territory, or any endorsement or acceptance of such boundaries.

Figure II. Countries of the MENA region and the associated aridity index (World Bank, 2007b).

Moreover, in such situation each region obviously has to take advantage of new technologies to answer both the increasing water demand due to population growth and the natural water scarcity. This in most of the cases leads to incapacity of regulators to effectively manage the natural resources (World Bank, 2007b).

In a context of poor water availability, high government expenditure on water infrastructures and inefficient water use, MENA countries are exhausting non renewable water resources (e.g. tapping groundwater for human consumption), polluting water bodies, damaging ecosystems and allowing infrastructures to deteriorate through lack of maintenance (World Bank, 2007b). The consequences of these processes span at not only environmental level, but also affect the socio-economic sphere.

Over the years, MENA region has achieved significant improvements to cope with these problems and to accomplish a more sustainable water management. Nevertheless the process is still too slow (World Bank, 2009b), due to factors covering various sectors (e.g. not all the stakeholders have been involved in the decision processes, water reforms have been too impalpable and the accountability on the public has been to weak (World Bank, 2007a).

However, if on the one hand the process is slow, on the other hand MENA region has all the possibilities to meet its management water challenge. The best way to achieve these goals is to go over the classic sector-based approach, and consider the combined actions of all the factors contributing to the water question.

This means that the best way to tackle this problem is to use an integrated approach, and to start its application to the more vulnerable zone: the transition coastal systems (and in particular the lagoons).

III. The African shore and its lagoons

Several transition zones, wetlands and lagoons characterize the Mediterranean basin, representing a precious ecological heritage (Dakki, 2003).

The shallow shore and the abundance of rivers allow for the formation of several lagoons in both the European and the African littorals, whose classification is quite complex to handle.

This is mainly due to the absence of a univocal definition, and the relatively high number of wetlands in the Mediterranean basin.

Phleger (1967) defined costal lagoons as "*shallow marine inland waters, usually oriented parallel to the coast, separated from the ocean by a barrier, and connected to the ocean by one or more restricted inlet*".

Kjerfve (1994) released a more practical definition, adding some details to the previous one: [a coastal lagoon is a] "*shallow coastal water body separated from the ocean by a barrier, connected at least intermittently to the ocean by one or more restricted inlets, and usually oriented shore parallel*".

According to the climatic conditions, the presence of estuaries and other freshwater inputs, lagoons show different salinity ranges, spanning from completely freshwater to brackish or hypersaline waters (Kjerfve, 1994). Therefore, one can also classify lagoons according to other characteristics as salinity, estuarine nature, primary productivity, morphology or numbers of inlets.

For the purpose of the study, the adopted classification of coastal lagoons is the one proposed by Nichols and Allen (1981), which divides coastal lagoons into four categories:

1) Estuarine lagoons: areas where the intensity of the tide flows are more or less equal to the river flows;
2) Open lagoons: characterized by a high tidal range, that allows the natural opening of the inlet, and a permanent alimentation by seawaters;
3) Semi-closed lagoons, as the opposite of the open ones: the tidal range is not so strong to brush the sediments brought into the lagoon at the inlet level. Therefore, in most of the case there is the need for human intervention to maintain the inlet open;

4) Closed lagoons: ponds separated to the sea by a littoral spit and characterized by absence of seawater flows.

If we consider the Southern (i.e. African) shore several lagoons are present (Figure III), that have been mainly investigated considering their ecological and economic functions, with a general focus on aquaculture and fisheries activities (Vanden Bossche and Bernacsek, 1991).

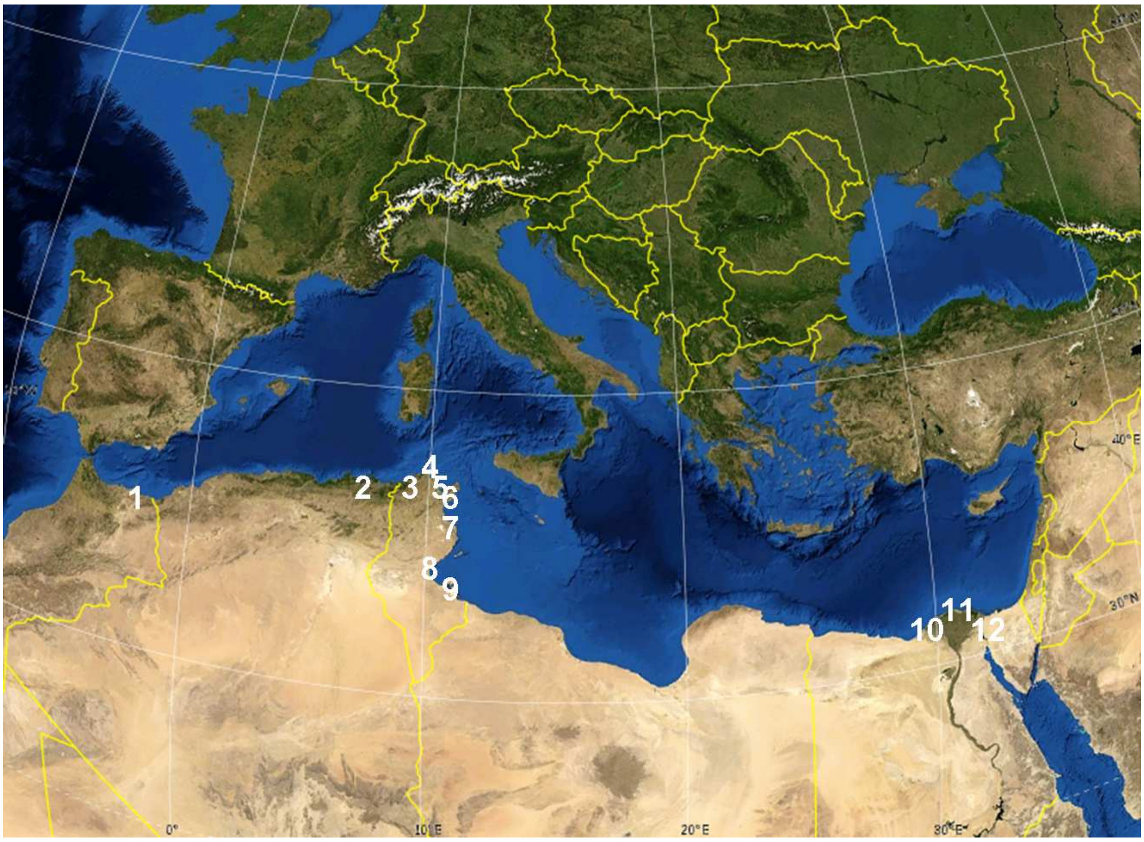


Figure III. Location of the lagoons in the Southern Mediterranean shore. 1) Lagoon of Nador (or Sebkha Bou-Areg); 2) lake of El-Mellah; 3) Ichkeul Lagoon; 4) Bizerte Lagoon; 5) Ghar El Melh Lagoon; 6) Tunis lagoon; 7) Khenis Lagoon; 8) Bou Grara Lagoon; 9) Bahiret el Bibane Lagoon; 10) Burullus; 11) Manzalah; 12) Bardawil (Modif. Google Earth).

Divided county by country one can find the following lagoons (Figure III):

Morocco: the lagoon of Nador (or Sebkha Bou-Areg), as the only one in the Mediterranean side;

Algeria: a small lagoon in the extreme east of the country: lake of El-Mellah:

Tunisia: seven important coastal lagoons with a combined surface area of 550 km^2 (e.g. Bahiret el Bibane Lagoon, Bizerte Lagoon, Ghar El Melh Lagoon, Ichkeul Lagoon, Khenis Lagoon, Tunis Lagoon and Bou Grara Lagoon);

Libya has no real inland lagoon of significant size. Farwa Lagoon, described in Lemoalle (1987), is widely open to the sea (salinity over 40‰) and therefore it cannot be included in the inland waters;

Egypt has an extensive surface area of coastal lagoons (2500 Km^2) and the most characteristic are located in the deltaic zone of the Nile River (Figure IV).

The largest are Manzalah (900 km2), Bardawil (726 km^2), and Burullus (560 km^2).

The others are Port Fouad, Edku, Mariut, Um El Rish, Nozha Hydrodrome, Alamain and Matrooh.

Than there are the Great Bitter Lake and Small Bitter Lake and the Timsah Lake.

Figure IV. Location of the Egyptian lagoons located in the deltaic zone of the Nile River (Modif. Google Earth).

The strong morphological variety of these lagoons is associated to a biological richness, representing an important resource for the ecological value *per se* and in second instance for the attributed economic value. The mixing of seawater and freshwater creates, under particular climatic conditions, unique environments and rare ecosystems. The resulting high biodiversity makes these region particularly exposed to human settlements and exploitation.

Consequently, urbanization, agriculture, industrialization and tourism are threatening these singular and weak ecosystems. Moreover, in several cases all these effects are exacerbated by arid climate, and long dry seasons.

This is why Mediterranean lagoons must be protected and the ecosystems preserved from excessive exploitation and human induced contamination. In addition to that, impact of climate changes and the possible environmental scenarios have to be taken into account, and studied in order to avoid abrupt loss of biodiversity and magnification of water scarcity problems.

Under the need for a correct and integrated management, a series of agreement have been stipulated at international level, focused on wetlands protection.

Among the others, the most important is the **Ramsar convention** (from the name of the Iranian city where the convention was signed in 1971). This Convention on Wetlands is an intergovernmental treaty providing the framework “for national action and international cooperation for the conservation and wise use of wetlands and their resources” (Ramsar, 2009). There are presently 159 Contracting Parties to the Convention, with 1847 wetland sites, totalling 181 million hectares, designated for inclusion in the Ramsar List of Wetlands of International Importance. The mission statement is “*the conservation and wise use of all wetlands through local and national actions and international cooperation, as a contribution towards achieving sustainable development throughout the world*".

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem (SP-MED-LME)

As previously mentioned in 1975, 16 Mediterranean countries and the European Community signed the Mediterranean Action Plan (MAP), and the Barcelona Convention to protect the Mediterranean Sea from Pollution. The Mediterranean Action Plan was the first-ever plan adopted as a Regional Seas Programme under the UNEP umbrella (UNEP-MAP, 2010).

The main objectives of the MAP were: "*to assist the Mediterranean countries to assess and control marine pollution, to formulate their national environment policies, to improve the ability of governments to identify better options for alternative patterns of development, and to optimize the choices for allocation of resources"* (UNEP-MAP, 2010).

In the early stages of the Plan, the focus was controlling marine pollution in the Mediterranean Basin. However, as environmental problems are often a side effect of socio-economic trends combined with inadequate management and development planning, Integrated Costal Zone Management and Planning were rapidly included as key issues of the Action.

In 2005 the Action Plan for the Protection of the Marine Environment and the Sustainable Development of the Coastal Areas of the Mediterranean (MAP Phase II) was designed, taking into account the achievements and shortcomings of the MAP in the context of recent developments (UNEP-MAP, 2010).

In the framework of Mediterranean Action Plan, Mediterranean rim countries, the World Bank, regional and international organizations and non-governmental organizations (NGOs) created a Strategic Partnership for the Mediterranean Large Marine Ecosystem (LME).

This Partnership represents the first project bringing together some of the main partners working in the Mediterranean for joint implementation of actions (UNEP-MAP, 2010), as well as the main international technical assistance and investment at Mediterranean level.

Its goals are to enable "*a coordinated and strategic approach to catalyze the policy, legal and institutional reforms, and the investments necessary to reverse the degradation trends affecting this unique large marine ecosystem, including its coastal habitats and biodiversity*" (UNEP-MAP-LME, 2010).

UNEP/MAP is the regional institution supporting and coordinating the implementation of the Barcelona Convention and Protocols adopted by all Mediterranean riparian countries to protect the marine and coastal environment. Global Environment Facility (GEF) and other partners, including the EU and all participating countries, financially support the implementation of the project, as a contribution to the sustainable development objectives of the Union for the Mediterranean.

The Project is implemented in 13 GEF eligible countries: Albania, Algeria, Bosnia and Herzegovina, Croatia, Egypt, Lebanon, Libya, Morocco, Montenegro, Syria, Tunisia and Turkey. The Palestinian Authority also participates.

A preliminary action, the Transboundary Diagnostic Analysis (TDA), identified the 101 hot spots of environmental concern (Figure V) and provided a foundation for interventions at the national and regional level with expected outcomes both at local and at basin's scale (UNEP, 2005).

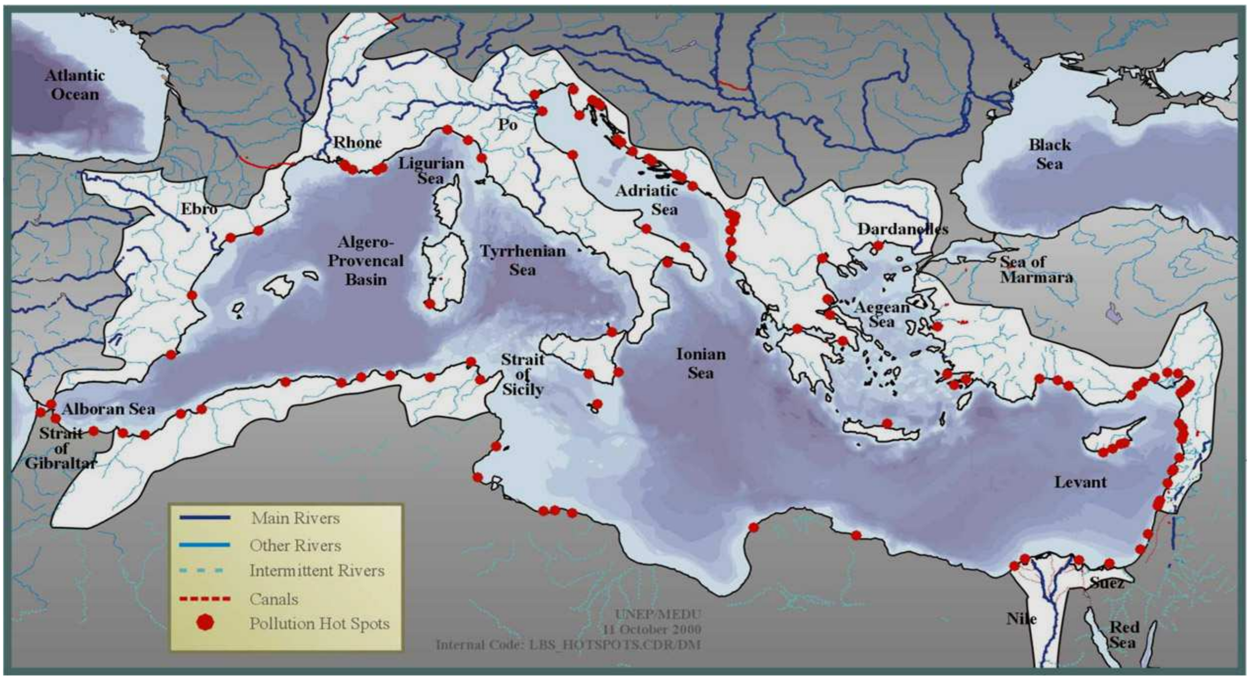


Figure V. Mediterranean pollution hotspots (in Appelgren 2007).

As a second step, the actions for hot spots' pollution remediation were identified and agreed in two Strategic Action Programs (SAPs):

- Strategic Action Programme for the Conservation of Mediterranean Marine and Coastal Biological Diversity (SAP-BIO), aiming at protecting biodiversity, living resources and their habitats;
- Strategic Action Programme to address pollution from land-based activities (SAP-MED) aimed at reducing land-based sources of marine pollution (UNEP, 2010).

Today SAP-MED involves 21 rim countries (and 13 recipient countries) "*determined to meet the challenges of environmental degradation in the sea, coastal areas and inland, and to link sustainable resource management with development, in order to protect the Mediterranean region and contribute to an improved Mediterranean quality of life*" (UNEP, 2010).

The two SAPs identify the major problems, indicate possible remedial measures and their cost, and set concrete targets and deadlines for their implementation.

Figure VI, summarizes the main aspects of the Strategic Partnership.

Following the activities of all the involved partners, the main outcomes of the Strategic Partnership are planned to be (UNEP-MAP, 2010):

- a long term partnership for joint planning and financing in the Mediterranean basin;
- the improvement of environmental conditions in 15% of the hotspots and sensitive areas of national priority;
- more sustainable use of coastal resources through the implementation of Integrated Water Resource Management (IWRM), Integrated Coastal Zone Management (ICZM) and aquifer management;
- the reduction of pollution from land based sources through the demonstration and adoption of environmentally sound technology;
- more sustainable use of fisheries resources through the adoption of an ecosystem based approach to fisheries, and improved protection of critical biodiversity through the management of a coherent network of Marine Protected Areas; and
- the replication and scaling up of investment projects and demonstrations during the 5 year lifespan of the project.

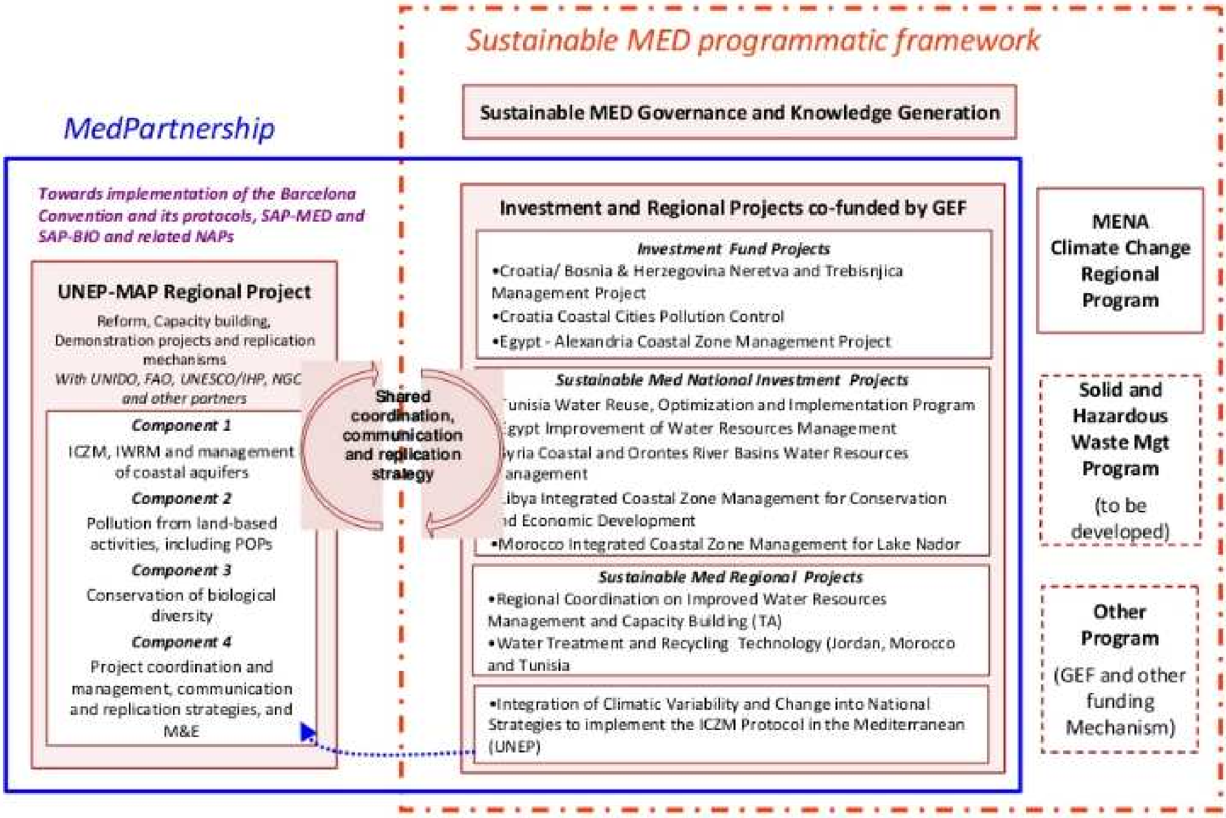


Figure VI. Schematic representation of the ME-LME strategic Partnership (MED Partnership website).

UNESCO IHP is one of the executive partners for the development of regional projects within the Component 1 (Integrated approaches for the implementation of the SAPs and National Action Plans: ICZM, IWRM and management of coastal aquifer).

The main objectives of this action are to "*reverse the trends in over-extraction and degradation in the quality of coastal aquifers thorough policy interactions for providing appropriate capacity and technology for groundwater management and fill the* existing *knowledge gaps*" (UNESCO-IHP, 2010).

In practical terms, its main activities are:

1. Assessing the risks to coastal aquifers and associated uncertainties;
2. preparation of a regional action plan, demonstrations in collaboration with ICZM and IWRM;
3. develop legislative, policy and institutional reforms;
4. monitoring and crosscutting activity (UNESCO-IHP, 2010).

Within the sub-component 1.1 (Management of Coastal Aquifers and Groundwater) executed by UNESCO-IHP, and under the activity "Assessment of risk and uncertainty related to Mediterranean coastal aquifers" a case study in the Nador Lagoon (North-East Morocco) was initiated in collaboration with the University of Venice, Department of Environmental Sciences (UNEP, 2010). The study is aimed at assessing the quality of the groundwater discharging to the lagoon, identifying human impacts on the groundwater quality and examining the possible occurrence of submarine discharge of polluted groundwater into the marine environment. Activities started at the end of 2009 and included:

(i) field trip, evaluation mission and scoping meeting with partners and national authorities in Rabat (Morocco);

(ii) exploration missions to Nador and identification of Moroccan Partners;

(iii) three hydrogeochemical sampling campaign undertaken in November 2009, June 2010, and November 2010, jointly performed with experts from Morocco (Faculté Pluridisciplinaire of Nador-University Mohammed I of Oujda, and Laboratoire des Sciences de l'Environnement et Développement Faculté des Sciences et Techniques, University of Settat).

The activities for the Nador case study constitute author's doctoral research, focused on water quality, pollution and salinization hazards in both the lagoon and the near coastal aquifer, and have been performed accordingly to the research outlines and strategies described in the following section.

All the outcomes and results obtained so far are presented in this manuscript.

It must be underlined that the main innovative aspect of this work concerns the inclusion of coastal aquifers in coastal zone management studies, together with the investigation on the role of groundwater in sustaining coastal lagoon and wetlands.

Research outlines and strategies

Under the premise of the need for an integrated approach it is fundamental to take into account the relations between drainage basins (catchment areas) and aquifers through the near coastal zone, and to develop adequate science based policies oriented to achieve sustainable water management.
Furthermore, urban and agricultural settlements must be condidered, as their interactions change the natural systems through engineering structures, resource withdraw and waste discharge.
When human are present some other factors have also to be added to the ecological dimension. Health and economic well-being, hazards and vulnerability dynamics, legal and cultural rights, ownership and management structures, spiritual, investment needs and cost-recovery therefore make the processes of understanding and consequently decision making extremely complex (McDonnell, 2008).
To be effective a correct policy should consider these factors, and has to be based on robust and accountable data on both the baseline aquifer conditions and the origin and distribution of the human impacts (e.g. pollution, saline water intrusion etc.).

From a first literature review it appears that in the Mediterranean area relatively scarce attention has been paid to the role of the aquifers in the lagoon circulations (and the interaction between fresh groundwater and saline or brackish lagoon waters) if compared to surface circulation or biodiversity studies.
The reason of the general reduced attention to groundwater can be seen in its underground nature and the associated problems in having reliable data, and the difficulties of physically visualize the interactions with surface waters and the lagoon itself.

According to those assumptions, the proposed research project aims to deal with the complex issue of groundwater management in urban coastal areas in arid zones, in the big framework of the provision of safe and equitable water for human consumption and trying to consider all the gaps existing in the previous studies.
Hence specific objectives of the Nador case study in the framework of the UNESCO-IHP sub component of the SAP/MED are the following:

1. definition of the hydrochemical interaction between the lagoon and the aquifer;
2. identification of the principal geochemical units, to relate these to the geology and establish relations between units;
3. determination of the baseline conditions and the natural water quality;

4. identification and quantification of the impact of the human activities on the catchment area;
5. establishment of the suitability of the water for the domestic, agricultural and industrial use;
6. provision of advices for sound integrated coastal aquifer management.

Finally, the work aims at providing recommendations for the sustainable management of the groundwater resources of the Bou-Areg plain within the context of integrated coastal zone management and protection of coastal wetlands, lagoons and humid zones in the South shores of the Mediterranean.

There are therefore two purposes for this research in the case study area:
one is more strictly scientific related to the understanding of the hydrogeochemical model of the Bou-Areg plain and its interactions with the lagoon of Nador; the second directed to support the translation of the scientific findings into sustainable coastal zone management policies in Nador area, and more broadly along the Southern Mediterranean shore.

To tackle these objectives a multitracer geochemical approach was applied, with the main goal to identify the sources of salinization and to define the origin and fate of pollution impacts due to human activities.
Concerning the *in situ* measurements and sampling campaign for obtaining the data of the present work, a preparatory mission was performed in November 2009, allowing for the identification of the potential sampling sites and the definition of the main objectives of the following field investigation.
Then, the Spring 2010 and Fall 2010 fieldworks were more effectively focused on collection of groundwater samples in the Bou-Areg Plain and surface water in the Nador Lagoon, *oued* Selouane and the irrigation channel.
A fourth field work is scheduled for spring 2011 wich will allow for obtaining information on the seasonal variations within the studied system, and afeterwards all the data will be presented to the Moroccan institution, compared with the existing ones, and used to promote sustainable management practices in the area.

A detailed description of the *in situ* measurements and analytical procedures can be found in Chapter 3.

PART TWO

1. The study area: the lagoon of Nador and the Bou-Areg coastal aquifer

1.1. Physical geography

The areas proposed as pilot case study are the lagoon of Nador and the Bou-Areg coastal plain (Figure 1.1), located in the Mediterranean coast of Morocco, administrative region Oriental, province of Nador. The region is also locally known as Grand Nador.

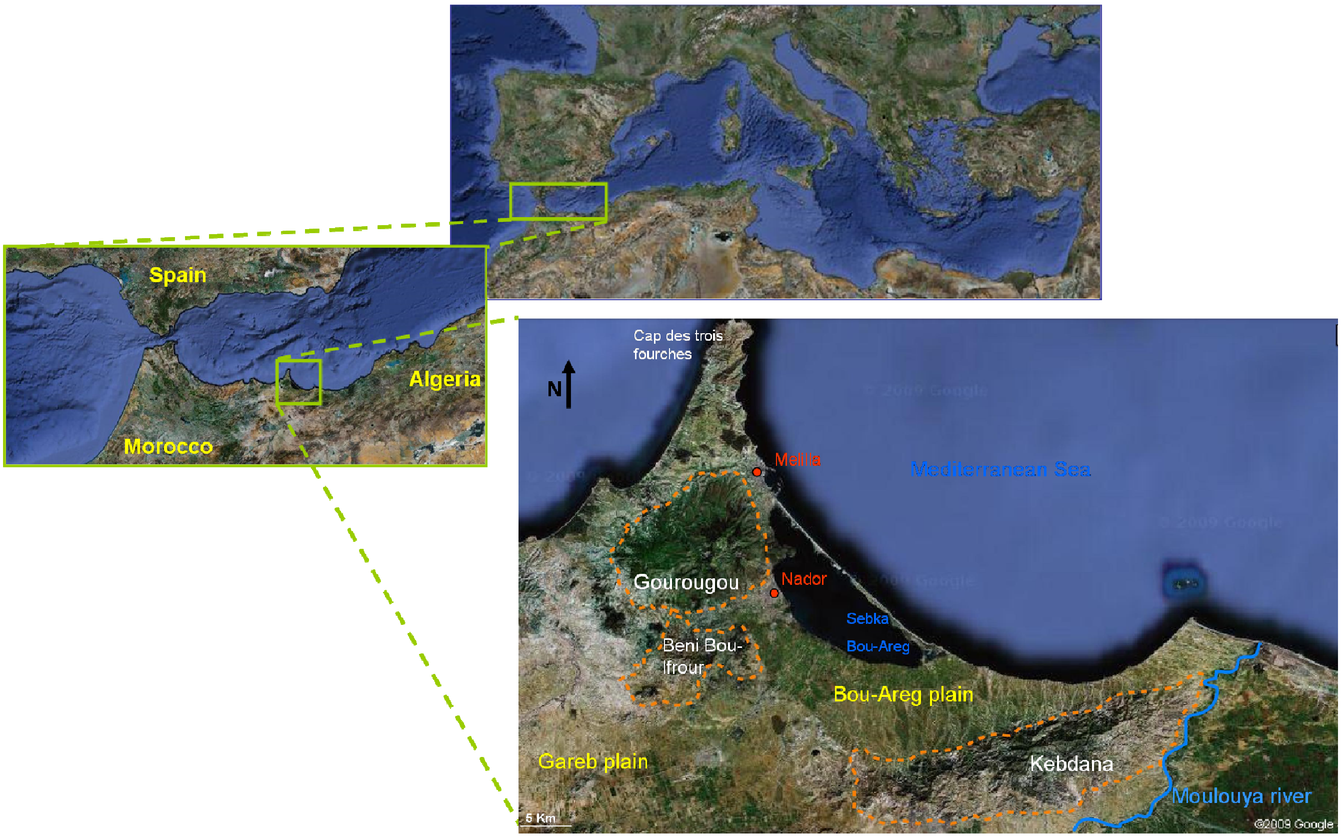


Figure 1. 1. Location of the lagoon of Nador (coordinates 35°9'14.48"N, 2°51'4.19"O) and the Bou-Areg plain (Modif. Google Earth).

1.1.1. Morphology

Three main morphological units compose the area:

i) **The Bou-Areg plain**. Covering 190 Km^2, it is a synclinal depression bounded to the North-West and West by the Gourougou and Beni Bou Ifrour massifs, to the South by the corridor of Selouane (linking the plain to the one of Gareb) and to the East by the Kebdana ranges (Chaouni Alia *et al*., 1997). The northern part of the plain coincides with the arched shape of the lagoon. The plain is characterized by the presence of salt marshes, intermittent streams (*oued*), some of which often serve as sewage outflow for urban areas upstream (Gonzales *et al*., 2007).

ii) The **lagoon of Nador** (also called Sebkha Bou-Areg or Mar Chica) is the only lagoon on the Mediterranean coast of Morocco. With a surface of 115 Km^2 (Figure 1.1), a length of 24 km and a width of 7.5 km it is the second largest lagoon on the Mediterranean southern shore. The lagoon has an oval shape, NW-SE extension, and a depth not exceeding 8 m (Umgiesser *et al*., 2005; Figure 1.2A). The lagoon of Nador is characterized by semidiurnal tide and it has micro tidal regime as the water levels range from about 0.1 m at neap tide to about 0.5 m at spring tide (Brethes and Tesson, 1977; Umgiesser *et al*., 2005). The salinity varies from 39.5 to 43.5 psu over the year (Umgiesser *et al*., 2005).

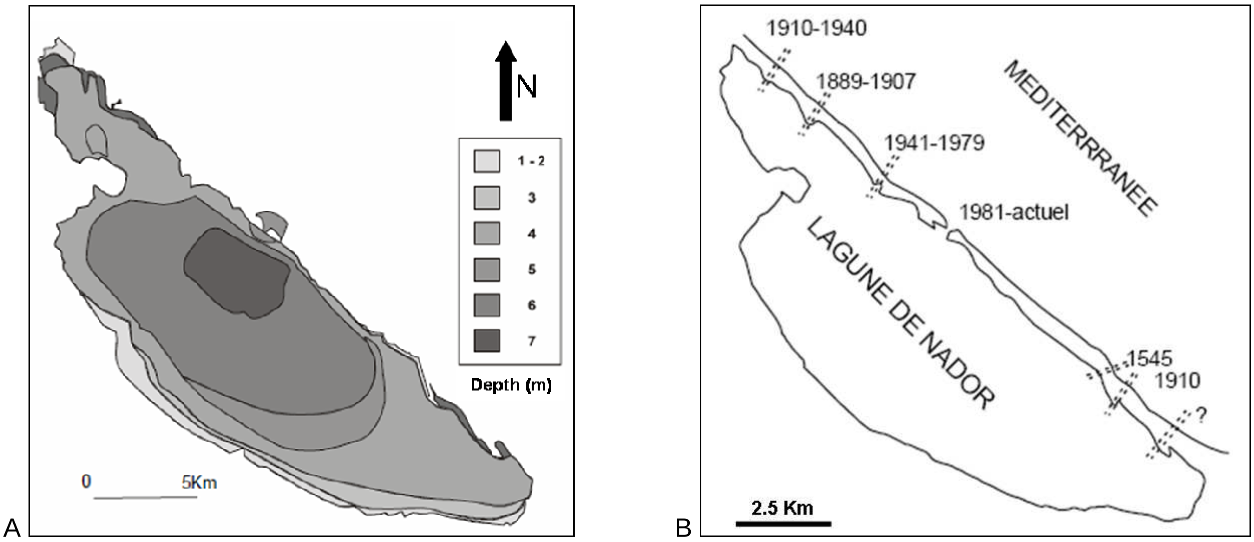


Figure 1. 2. A. Bathymetric chart of the lagoon of Nador (Dakki, 2003) and B Evolution of the inlet over the time (Modif. Dakki, 2003).

iii) **The coastal barrier** oriented NW-SE with a length of about 25 Km and a width of 300-400 m (only the southernmost part reaches the maximal width of 2 Km) and characterized by the presence of a single inlet. During the past fifty year the cross section of the lido has changed several times (Figure 1.2B) and the inlet was often absent, as a result of wave action and littoral drift (Guelorget *et al*., 1987).

From 1987 the *bokhana* (or the actual position opened in 1981, after having been shut for two years) was progressively filled by sediments, until its closure in 1993 (Inani, 1995).

Dams, safeguarding the communication between the sea and the lagoon (Dakki, 2003), ensure the current position of the inlet. According to the new eco-touristic project involving the lagoon of Nador and the surrounding area, launched by His Majesty, the King of Morocco, in June-July 2009, another inlet will be added to the current one 1.5 Km northward. The new inlet will be deeper (6 m instead of 3) and wider (300 m instead of 250) in order to increase water exchange rate between the sea and the lagoon (CAP Nador Action Plan, 2009).

1.1.2. Hydroclimatology

The climate of the region is mainly semi-arid and characterized by two pronounced seasons: the summer period from May to October, with average temperature of 20 ℃ and the winter season from November to April, with average temperatures of 12 ℃. The coldest month is January, with minimum temperature values that could reach 5 or 7 ℃ (Figure 1.3 A).

However, seasonal variations are usually moderate, with a general high level of humidity (50-80%) due to the proximity to the sea (Figure 1.3 C).

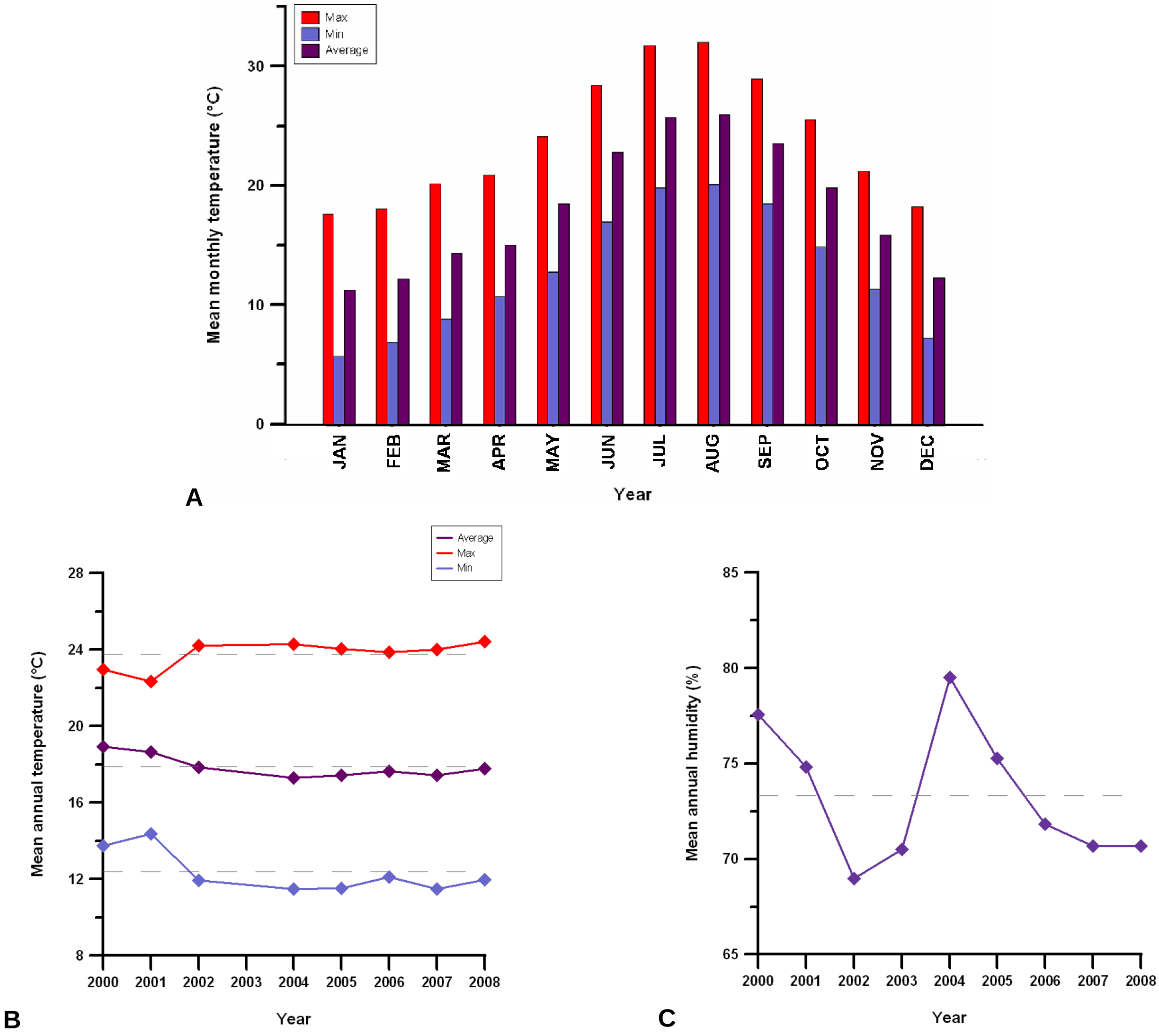


Figure 1. 3. Meteorological data for the period 2000-2008. (A). Mean monthly temperature; (B): Mean Annual temperature; (C): Mean annual humidity (Unpublished data for the Meteo station WMO SYNOP DATA 60340: Nador, Latitude: 35-09N , Longitude: 002-55W, Altitude: 3m).

The dominant winds have W-SW direction from November to May and E-NE direction from May to October (Tesson, 1977). There is no regular rain season, and the precipitation varies from 150 to 450mmyear^{-1}, with an average of 346mm (El Yaouti *et al*., 2009).

Regional precipitations are mainly related to Atlantic (Açores) perturbations, which are the primary source of humid masses in the Rif, and Mediterranean perturbations associated to cold air coming from the North. The latter are less frequent but more humid.

Moreover the region is affected by the influence of Saharan regime, originating the east or southeast desert winds of Chergui (or *Sharqi*) and Scirocco.

Climatic data are particularly abundant, but they mainly concern precipitations over the lagoon. Dakki (2003) provided a good analysis of the precipitations over 10 years (1992-2002), giving a main idea of the climate and its effects on the lagoon (Figure 1.4 A). There is a strong inter-annual variation of the precipitations, with a main trend of reduction of rains (the driest year is the 1998, with 131-168 mm).

In general, precipitations are more abundant in February-March and November-December (Figure 1.4 B). The driest months are July and August with scarce or even absent rain episodes.

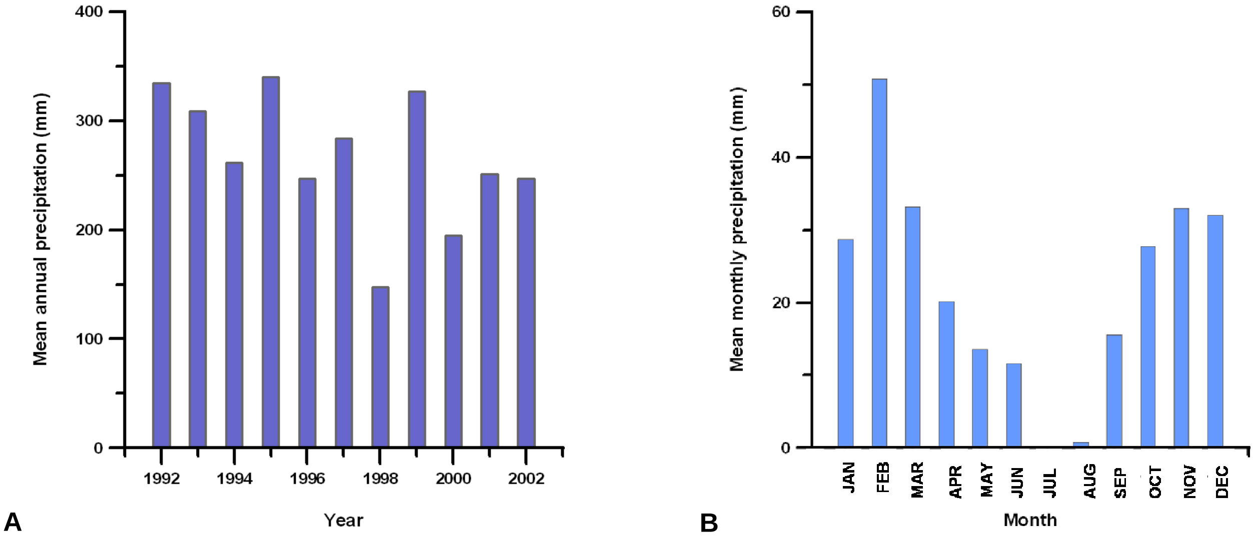


Figure 1. 4. Mean of total monthly (A) and annual (B) precipitations over 10 years (1002-2002; Modif. Dakki, 2003).

1.2. Geological settings

The lagoon of Nador is located in the Neogene basin of Meilla-Nador. This catchment area is characterized by three main structural domains: the **Gourougou volcanic massif** (NW), the **Beni-Bou-Iffrour volcanic** massif and the **Bou-Areg coastal plain** (W-SW), and the **Kebdana** range (SE). These structures represent the limits of the lagoon as well as its source of sediments (Figure 1.5).

The **Gourougou** volcanic massif is the highest mountain overhanging the cities of Nador and Mellila, with a height of 887 m a.s.l. and a diameter of 15 km along the N-S axis (Bloundi, 2005).

This is a strato-volcano resulting from three different processes occurred between the Messinian and the Plio-Quaternary (Morel, 1985). El Yaouti *et al*. (2008) discuss the three types of eruptions as follow:

calco-alkaline (potassic trend), intermediate (shoshonites, trachytes and latites) and alkaline (basalts to sodium tendency).

This massif extends up to North through the massif of Trois Fourches, formed by a metamorphic Palaeozoic basement (Bloundi, 2005).

The **Beni-Bou-Iffrour volcanic** massif (699 m a.s.l. and oriented SSN-NNE) formed of Jurassic (limestone, limestone-sandstone and marls) and Cretaceous deposits (schisto-sandstone and volcano-sedimentary). The complex is covered by Miocene molasse (El Yaouti et. al., 2008). A part of the massif is crossed by several micro-grandorite veins, associated to a hydrothermal mineralization (El Bakkali, 1995) that could explain the richness of iron ore in the region (Ouchxane *jebel*).

The **Kebdana** range extends over 973 m a.s.l. and its deposits consists of Jusassic formations (marls and marly-limestones, sandstones, limestones and dolomites) locally overlain by Miocene formations (limestones and marls) (Bloundi, 2005).

Towards the Bou-Areg plain, the Kebdana range is made up of Villafranchian and recent Quaternary rocks (limestone, conglomerates, gravels, and pink silts) while he Neogene post-nappe unit is comprised of marls, beds of sand and conglomerate levels (Barathon, 1989; El Yaouti *et al.*, 2009).

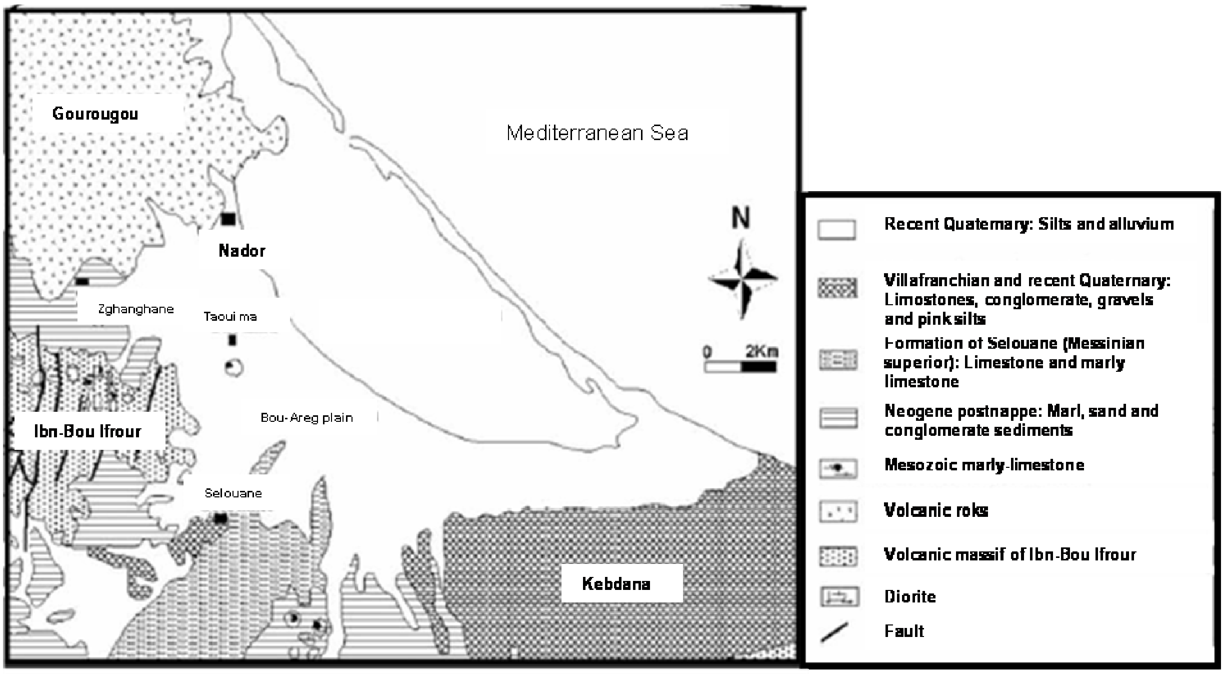


Figure 1. 5. Geologic framework of the coastal Bou-Areg palin (El Yaouti *et al*. 2009).

The **Bou-Areg coastal plan** has a surface of 190 Km^2 and its northern part coincides with the curved shape of the lagoon of Nador, while the southern limit is represented by the Selouane passage that connects it to the Gareb plain (El Yaouti *et al*., 2009). It belongs to the subsiding basin Gareb-Bou-Areg and its history, stated during the Neocene, is particularly related to more recent activities (as most of the sediments covering the plan are dated Plio-Quaternary). This plain represents the border between the African plates and the Alboran Sea.

The Gareb-Bou-Areg basin appears to result from lithospheric flections under the charge caused by the thickening of the crust in correspondence to the collision area between the two plates (Bloundi, 2005).

The **Selouane** formation (Figure 1.5), attributed to the upper Messinian, is mainly composed by marls and intercalations of marly-limestones (El Yaouti *et al*., 2009), with occasional intercalations of lagoon sediments.

The Bou-Areg depression forms part of the Melilla-Nador Basin, one of the Mediterranean areas affected during the Late Miocene by the rapid and dramatic palaeoenvironmental change known as the Messinian Salinity Crisis (Hsü *et al*., 1973). Between 5.96 Ma and 5.33 Ma, isolation of the Mediterranean Sea from the Atlantic Ocean resulted in an initial sea-level drop of about 1500 m (Hsü *et al*., 1973; Clauzon *et al*., 1996; Loget *et al*., 2005). This event induced strong incision of the continental surface by rivers and was characterized by the deposition of thick evaporite materials in both peripheral and deep basins (El Yaouti *et al*., 2009).

Moreover, the Bou-Areg plain is characterized by deformations like faults, syncline and anticlines folds (Figure 1.6); the subsidence associated to these deformations give origin to recent stream terraces covering older formations.

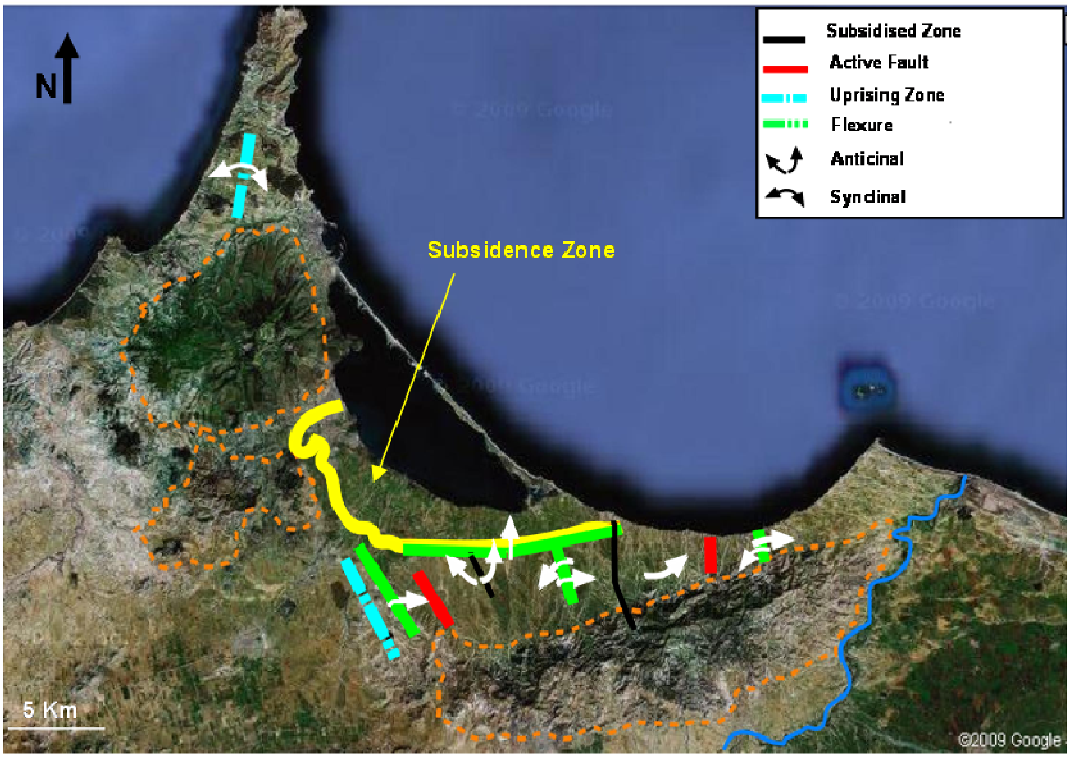


Figure 1. 6. Recent tectonic of the region in the Bou-Areg basin (Modif. Dakki, 2003).

According to the geologic evolution of the area, the processes that gave origin to the **lagoon** can be summarized as follow (Bloundi, 2005).

After the formation of the two massifs of Kebdana and Beni-Bou-Iffrour during the Jurassic, in the middle Miocene the lateral overlap of the African Plate on the Alboran Plate generated a crustal thickening in the Bou-Areg plain followed by a subsidence. The plain was than flooded during the Tortonian transgression that also caused the deposition of green marls.

Thus, the collision of the two plates provoked a volcanic activity during the lower Messinian, and the consequent formation of the Gourougou massif. This represents the main Miocene episode in the Rif, and its major effect is the uprising of the Rif range. This uprising caused the definitive regression of the sea in the Miocene (Morel, 1985).

Moreover, lava effusion followed the formation of the massif on the Bou-Areg plain, whose charge generated a subsidence and subsequent transgression in the late Messinian (characterized by a deposition of grey marls).

The deposition of conglomerates during the Quaternary caused a severe change on the basin. This charge led to a new subsidence followed by a transgression-regression cycle that finally gave birth to the lagoon.

The genesis of the Nador lagoon is therefore related to tectonic activities, volcanism of the Gourougou and subsidence of the Bou-Areg plain (Guillemin and Houzay, 1982).

Thus, laguno-lacustrine regime and continental sedimentation characterize the region (El Yaouti *et al.*, 2009). In particular, tectonic episodes during Quaternary distributed the sediments (clay, marls, silts, lacustrine limestone) in the area, originating the current stratigraphy.

As concern the sandbar (lido), its central part is aged Pleistocene and is mainly composed sandstone (Guelorget *et al.*, 1987). A massif of a maximum height of 20m now dominates this part, corresponding to the old dune zone.

On the Mediterranean side, coarse sand deposits, blown by the wind and forming dunes sometimes fixed by weak vegetation, characterize the lido. On the the lagoon side of the lido, sediments are generally thinner and sometimes muddy (Guelorget *et al.*, 1987).

1.3. Hydrological settings

From a hydrological point of view, the dominant features of the Grand Nador are the permanent and semi permanent streams of the Bou-Areg plain, the lagoon of Nador, and the Mediterranean Sea (namely the Alboran Sea).

Due to the ecologic, economic, and social relevance of all these components, it is fundamental to recognize and to quantify their interactions, as well as to identify their associated hydrodynamics. For example if we consider the lagoon, it is possible to assume that internal hydrodynamics principally depends on two kinds of inputs: terrestrial and marine. On the other hand, the external hydrodynamics depend on tidal regime, littoral drift currents and the prevailing waves (Ruiz *et al.*, 2006).

1.3.1. Terrestrial inputs

Terrestrial inputs (as the total fresh water contributions) are estimated to range between $50 \cdot 10^6$ and $150 \cdot 10^6$ $m^3 year^{-1}$ (Tesson, 1977). These have two main components: surface water (including sewage and urban wastewaters), and groundwater.

Due to the arid climate and the geomorphological behaviour of the mountain area, most of the strams of the region have a temporary regime (Dakki, 2003). Moreover, the topography of the catchment area draining in the lagoon, i.e. a large plain surrounded by low mountains, does not allow for the creation of a hierarchical hydrographical network, which is than composed by several fragmented water courses (Figure 1.7).

Therefore, because of their permanent regime only three streams could be assumed to significantly contribute to the lagoon water budget (Bloundi, 2005), and they represent the natural surface water contribution to the lagoon. From N-W to S-E of the lagoon, we can distinguish (Figure 1.7):

- ***Oued* Bouaroug**. Its mouth is located at the South of Nador city. The main inputs of this stream to the lagoon are associated on the one hand to anthropic contribution (e.g. untreated waters from Zeghanghane municipality) and on the other to the natural supply of residual material deriving from leaching processes of Gourougou strato-volcano lithology.
- ***Oued* Selouane** (Figure 1.8). This river represents the most important water course in the area. Its contribution to the lagoon is both natural (residuals from the river erosion e.g. marls, limestones and limos from the Bou-Areg plain) and anthropogenic (industrial and agricultural)
- ***Oued* Afelioun**. Located in the southern part of the lagoon it mainly brings sewages and wastewaters from the city of Kariat-Arekman and debris from Kebdana range.

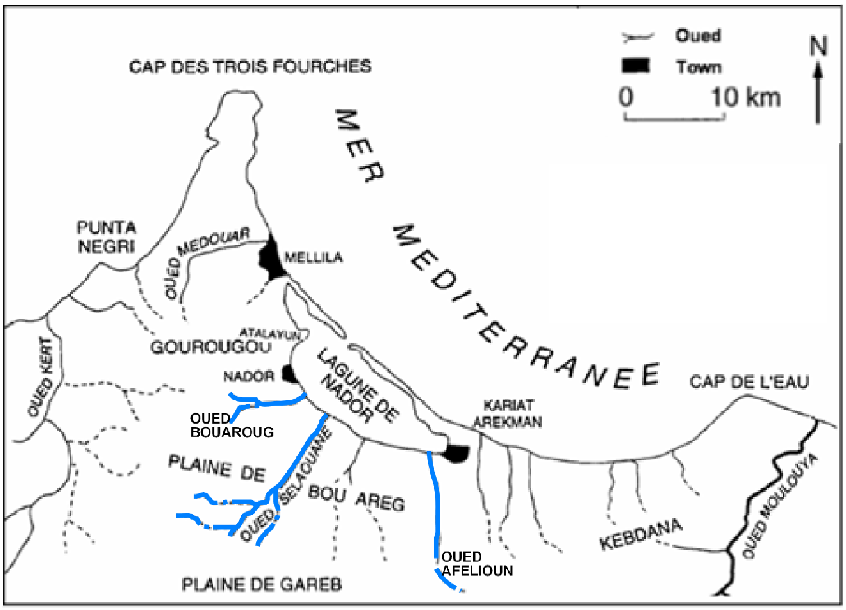


Figure 1. 7. Hydrographic network of the Nador lagoon (Modif. El Alami *et al.*, 1998), and location of terrestrial inputs (permanent water courses are highlighted in light blue).

In addition to surface water contribution, sewage and wastewaters inputs are also present (Figure 1.9), and are mainly associated to the urban and suburban areas at the borders of the lagoon (SE: Kariat Arekman; NW: Beni-Enzar).

The city of Nador has a Public Treatment Station (STEP, or *Station d'Epuration* in French), discharging in the lagoon only byproducts of the tertiary phase of the process (Figure 1.10). Due to the pollutant load associated to these inputs the National Office for Drinking Water (ONEP, *Office National Eau Potable*) is currently planning to increase the number of treatment stations in the region, and to add a third level treatment of activated sludge (ONEP, 2009).

Figure 1. 8. *Oued* Selouane (A) the upper part of the *oued*, at the limit of the Bou-Areg plain and (B) the lower part, close to the mouth discharging into the lagoon (November 2010).

Figure 1. 9. Channell discharging directly in the lagoon of Nador: (A) mouth of the (November 2010)and (B) Mouth of a channel in Beni Insar (June 2010).

The Bou-Areg and Gareb aquifer, rising at the southeastern limit of the lagoon, represents its underground inputs. Groundwater contributions are the main component of terrestrial inputs feeding the lagoon, with values estimated to be $45\cdot10^{6}$ $m^{3}year^{-1}$. Due to their relevance for the aim of the study, these contributions will be object of a detailed description in paragraph 1.4.

Figure 1. 10. Lagoon pools of the old STEP (June 2010).

1.3.2. Marine inputs

According to some authors (Guelorget *et al*. 1987; Dakki 2003; Ruiz *et al*., 2006), marine inputs are the dominant contribution for the lagoon hydrodynamic.

Seawaters mainly enter in the lagoon through the inlet, in direction S-E, creating a circle pushing the water of the lagoon in direction N-W, and leaving the central zone more stable (Bloundi, 2005; Figure 1.11).

Nevertheless, flows of water across the sandbar might occur (Guelorget *et al*., 1987).

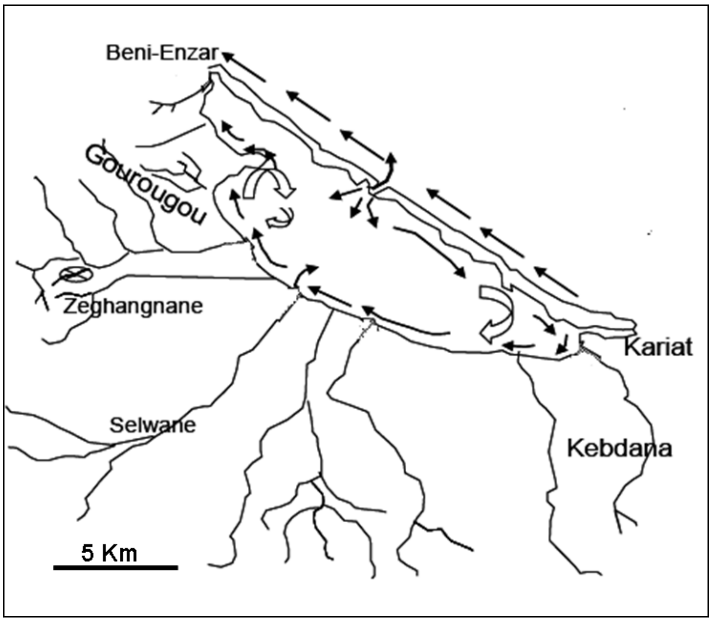


Figure 1. 11. Water circulation in the lagoon of Nador (Modif. Bloundi, 2005).

1.4. Hydrogeological settings

From a hydrogeological point of view, the Lagoon of Nador represents the main outlet of the Bou-Areg aquifer (Figure 1.12).

The Bou-Areg aquifer covers a surface of about 190 Km^2 (Dakki, 2003) and consists in two sedimentary formations of Plio-Quaternary age. The upper layer is made of fine silts and the lower one is made of coarse silts with sand and gravels (El Yaouti *et al*., 2009). The thickness of the aquifer ranges from environs 40 m at Kebdana to 1 m next to the shore (Figure 1.13). Moreover, several springs are present at the continental border of the lagoon, close to the city of Kariate Arkmane, and next to the artificial drains (Dakki, 2003).

As can be seen in Figure 1.13, the Bou-Areg aquifer communicates with the one of Gareb. The latter covers a surface of 290Km^2, and indirectly influences the hydrology of the lagoon of Nador.

Therefore the aquifer alimentation is given by groundwater from the Gareb aquifer, rainwater, freshwater from the Selouane River (as the main surface drainage), and irrigation waters (El Yaouti *et al*., 2009). Furthermore seawater contribution are widely recognized (Dakki, 2003), as Bou-Areg groundwater are not diffusely used for agricultural purposes due to the high salinity (2 to 10 gL^{-1}). If on the one hand the salinity can be related to the soil nature, on the other the increase in salt content (14-10 gL^{-1} in the area close to the City of Nador) could be associated to a local saline water intrusion.

Several authors have studied the hydrogeology of the Bou-Areg system (Carlier, 1971; Tesson, 1977; Brethes and Tesson, 1978; Tesson and Gensous, 1981) providing the basis for all the recent studies, and allowing for the identification of the main features of the aquifer.

The presence of nearly thirty boreholes spread over the plain, allowed for the study and the identification of the sedimentary structure deriving by the various processes occurred between the late Pliocene and early Quaternary (Chaouni Alia *et al*., 1997).

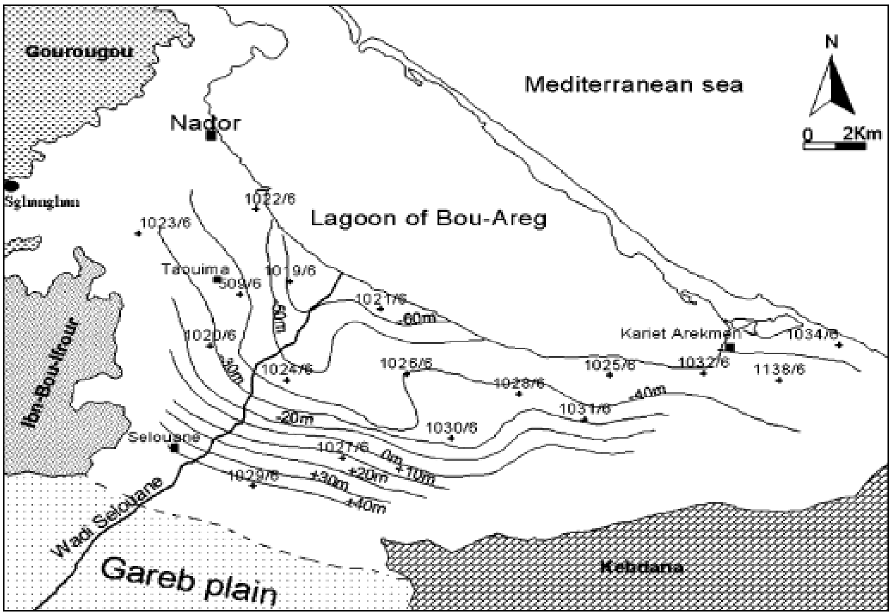


Figure 1. 12. Substratum map of the uncinfined aquifer of Bou-Areg (El Mandour, 2008).

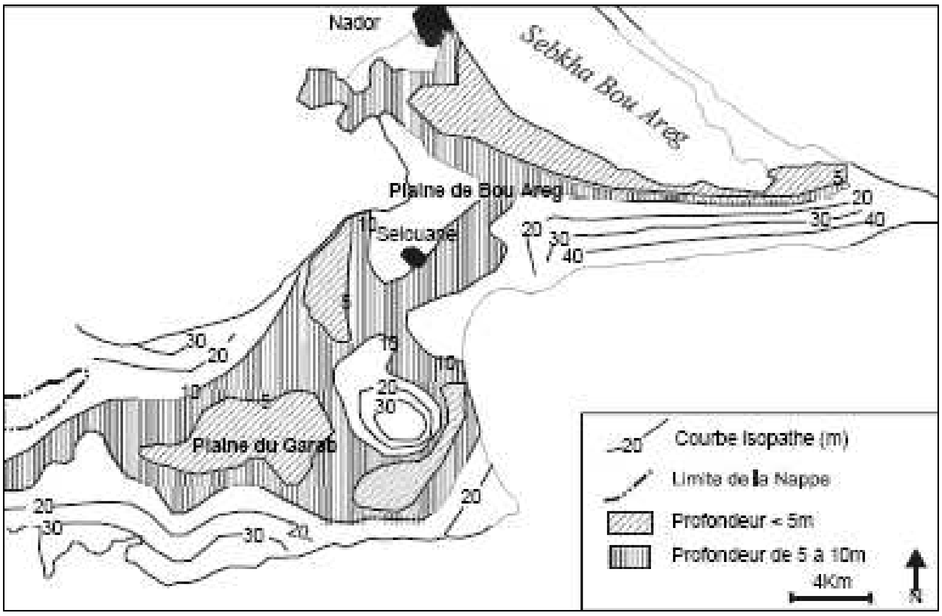


Figure 1. 13. The Bou-Areg aquifer plain (Carlier, 1971).

In particular, it is possible to define four main formations, grouping different layers with the same hydrological behaviour (Figure 1.14).

- **Formation I** corresponds to the upper layer, and is constituted by thin materials with low permeability, including silts, clayey silts, encrusted limestone and marl-calcareous tufa that may contain gravels. These deposits have a thickness ranging between 0 and 44 m, with permeability of the order of 10^{-5} ms^{-1}.
- **Formation II** is the bottom of the aquifer reservoir, grouping coarser elements with high permeability (10^{-4} ms^{-1}), like pebbles, gravels of volcanic or sedimentary origin, and sands. The depth of this formation varies from 8 to 74 m.
- **Formation III** has a composition quite similar to Formation I, made by fine sediments with permeability of 10^{-5} ms^{-1} and contains gypsiferous marls of Pliocene age. This formation represents the impervious bed to the upper Quaternary aquifer dipping towards the lagoon. Thus, the Plio-Quaternary formations of Bou-Areg basin form an unconfined aquifer limited on the bottom by the Pliocene substratum of gypsiferous marls. (El Yaouti *et al*. 2009). The presence of these gypsiferous materials could be seen as a result of the Messinian Salinity Crisis.
- **Formation IV**, reached only by the deeper boreholes, is nearly impermeable and clays and pure marls form it (Chaouni Alia *et al*., 1997).

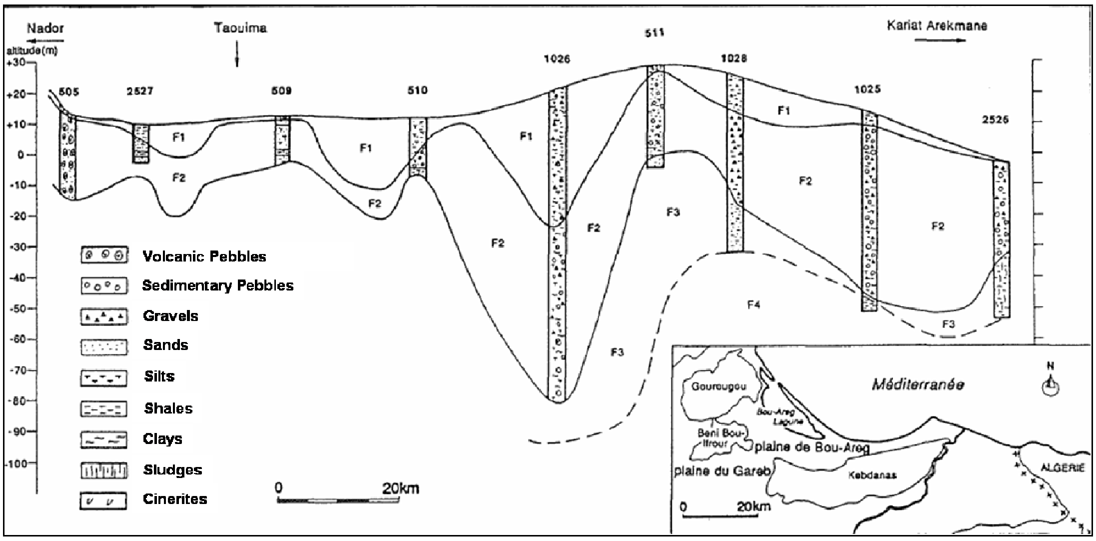


Figure 1. 14. Hydrogeologic profileof the transet Nador-Taouima-Kariat Arekmane; (Modif. ChaouniAlia *et al*., 1997).

Therefore, the aquifer in Formation II is framed on the top and the bottom by two less permeable layers, Formation I and Formation III respectively. Formation IV (thickness of 56-66m), could be assumed as the impermeable substratum (Chaouni Alia *et al*., 1997).

The geometry of Formation II (Figure 1.14) shows a series of “valleys”, oriented perpendicularly to the lagoon shore. The maximum depth of these valleys is found in the central part of the plain (East of the *oued* Selouane) and in the valley of Kariat Arekmane.

During the so-called Messinian salinity crisis, the sea level was approximately 1500 m lower than current one (Figure 1.15), inducing the formation of deep canyons and at the same time developing deeply fractured media (Loget *et al*., 2005; Garcia-Castellanos *et al*., 2009). Consequently, these incisions can represent paleo valleys or canyons excavated by rivers flowing to the empty sea during the Messinian stage.

As general features, many authors (El Mandour *et al*., 2008; El Yaouti *et al*., 2009) conclude that the aquifer has good hydrodynamic characteristics, mainly associated to high permeability (reaching 7·10-4 ms^{-1} in the vicinity of the lagoon and in the western zone, while the lowest values are found at the borders of the Kebdana massif).

Transmissivity varies continuously from upstream to the coastal zone, ranging from $9{\cdot}10^{-4}$ to $2{\cdot}10^{-2}$ m^{2}s^{-1}. The highest values are found in the west (north of the plain), whereas the lowest are measured at the borders of the Kebdana massif, probably due to the accumulation of marls. All along the coast, the transmissivity varies around $2{\cdot}10^{-2}$ m^{2}s-^{1} (El Yaouti *et al*., 2009).

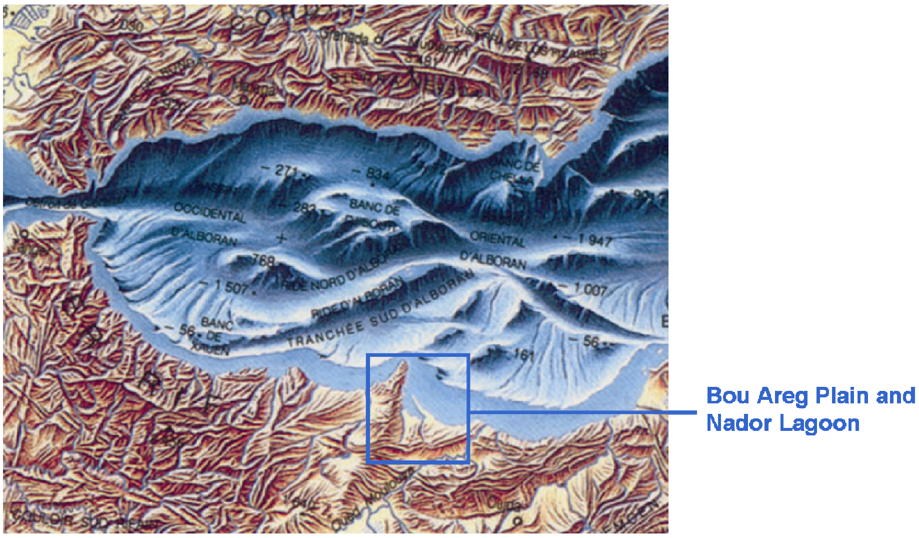


Figure 1. 15. Detali of the bathimetric map of the Alboran sea shoving the canyons and the depressions associated to the incisions resulting from the Messinian Salinity Crisis.

1.4. Human geography

Five administrative entities spread along the Lagoon of Nador: the three rural districts of Bouareg, Kariat Arekmane and Iheddadène, and two municipalities: Beni Ensar and Nador, with a total of environ 225 000 inhabitants (Table 1.1). The population growth rate for the area is 0.65% (CAP Nador Action Plan, 2009).

The area hosts two Sites of Biological and Ecological Interest (SIBE): part of Jbel Gourougou and the Nador Lagoon, also classified as RAMSAR site (Ramsar, 2009).

Municipality	Inhabitants
Nador	124 915
Beni Ansar	31 800
Kariat Arekmane	18 960
Bouareg	23 111
Ihaddadène	25 480
Total	224 266

Table 1.1. Population in the area surrounding the lagoon of Nador (CAP Nador Action Plan, 2009).

The main economic activities in the region are (Khattabi *et al*., 2007):

- **Agriculture**, limited by water availability for irrigation and mainly focused on the production of cereals, fruits, olives and market garden products.
- **Livestock farming** (ovines, bovines and goats).
- **Fisheries**, mainly performed in the lagoon with small boats. Despite the small scale of fishery activities and the use of traditional tools, this activity is particularly important due to the high values of the fish species. These are mainly migrant fishes with high market value as sea breams, seawolf, eels, octopus, anchovies, whose trade (mainly related to local consumption) contributes to the economic development of the region (Khattabi *et al*., 2007).

It must be underlined that until 2006 aquaculture was a common practice in the lagoon, covering an important productive sector.

- **Industry**, with about 53 factories distributed along the whole coast of the province of Nador, but quite few in the area around the lagoon. The industrial sector is quite diversified in kind of production spanning from food industry, textile, cement and production of construction material, as well as pottery and craft industry.
- **Mining**: essentially based on iron, bentonite, lead, salt and gypsum extraction. This sector is not really known at international level, but its relevance at national level is fundamental.
- **Commerce**, representing the main economic activity and it is mainly related to the presence of harbours in the area.
- **Tourism** mainly associated to the coastal zone and the lagoon of Nador.

In this framework it must be underlined the great project, launched in June-July 2009, is involving the lagoon of Nador. According to this new management programme several project will be carried out (starting in late 2009), with the common goal of creating a new touristic and economic area in the lagoon of Nador (CAP Nador, 2009). The construction of a new harbour, a new energy plant (production, conditioning and storage of hydrocarbon), an integrated industrial platform, a touristic harbour, are just the main examples of the facilities that will be created in the area.

According to the government, all these activities are aimed to increase the socio-economic potential of the region, in order to create new employments and trades. Moreover, every activity in the area will be performed paying particular attention to the natural environment, as another main goal is the safeguard of the local biodiversity, coastal system and freshwater resources. This is why the project will involve use of local raw materials and recycled ones, where possible.

Despite the wide number of activities, the main driver for economic growth is seen in the commercial (and industrial) development of the area. If on the one hand a positive consequence is the improvement in wellbeing, on the other, negative impact have been exerted on the environment. These negative externalities of the economic activities in the region are not only related to depletion of natural resources and by-products release in the environment, but also to the increase in urbanization often associated to lack in adequate sanitation infrastructures. Therefore uncontrolled waste deposal and sewage discharge in the lagoon have been the main sources of pollution for both the lagoon of Nador and the Bou-Areg plan.

Over the years the situation have been improved with the construction of the public treatment station (TSN) of Nador, built in 1980 and enlarged for a population of 100,000 households in 1990 (Ruiz *et al*., 2006). The station originally provided only partial biological treatment, without any additional physicochemical purification, microbiological control or disinfection. For this reason, in order to reduce the impacts on the lagoon, and therefore on human health, a tertiary treatment plant is under construction under the supervision of the ONEP (Le Matin.ma, 2009).

Moreover, as other towns and villages, like Beni Enzar and Kariet Arkmane, also drains their sewages and waste waters directly into the lagoon (Ruiz *et al*., 2006) other treatment plants are planned to be constructed.

Private households discharge and industries pouring wastewaters directly in the rivers (especially in the Selouane industrial area) or in the lagoon (Ruiz *et al*., 2006), are not the only sources of pollution. In fact, irrigation channels and other *oueds* drain the southern border of the lagoon, carrying the liquid/solid residues of a broad area occupied by small farming exploitations (Ruiz *et al*., 2004).

Figure 1. 16. Panoramic view of the lagoon of Nador and the rim urban areas of Melilla, Beni Insar and Nador (June 2010).

The real impact of all these activities, associated to the one deriving by the new tourist development, on both the aquifer and the lagoon system is still not really quantified.

Several consequences are expected, associated to the increase in water (especially groundwater) extraction, e.g. possible increase in urban and industrial pollution load, impacts on local flora and fauna communities and change in the lagoon hydrodynamic (following the change of the inlet). These are just some possible effects that will be considered in the present work as foreseen changes

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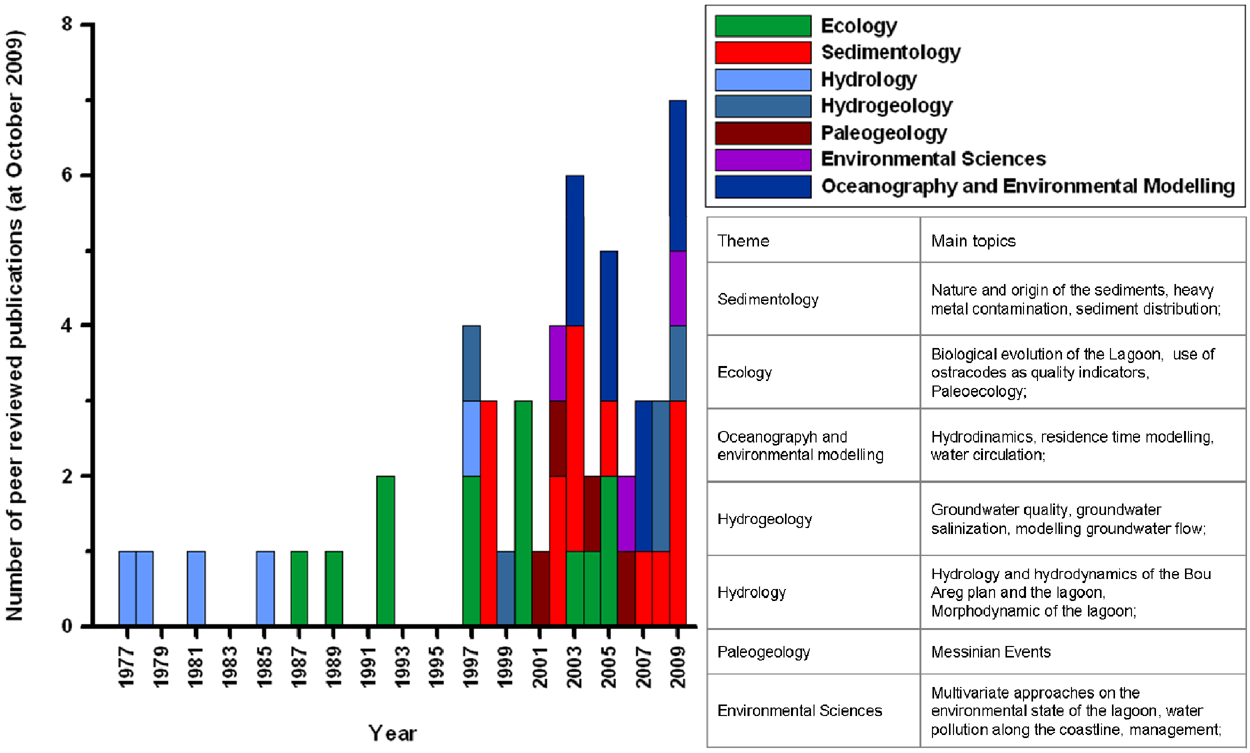
2. The study area: literature review

In past decades increasing attention has been paid to the investigation of the lagoon of Nador and its environment (Figure 2.1).



Theme	Main topics
Sedimentology	Nature and origin of the sediments, heavy metal contamination, sediment distribution;
Ecology	Biological evolution of the Lagoon, use of ostracodes as quality indicators, Paleoecology;
Oceanograpyh and environmental modelling	Hydrodinamics, residence time modelling, water circulation;
Hydrogeology	Groundwater quality, groundwater salinization, modelling groundwater flow;
Hydrology	Hydrology and hydrodynamics of the Bou Areg plan and the lagoon, Morphodynamic of the lagoon;
Paleogeology	Messinian Events
Environmental Sciences	Multivariate approaches on the environmental state of the lagoon, water pollution along the coastline, management;

Figure 2. 1. Number of peer reviewed publications focused on the lagoon of Nador and/or the Bou-Areg plain. 52 papers have been found using scientific web search engines (ISI web, Science Direct and Scirus before 10/30/2009). Thesis manuscripts, regional and national reports are not listed, but considered in the detailed analysis. It must be underlined that the lack of peer reviewed articles on the geological features of the Bou-Areg plain does not correspond to a real lack of knowledge. In fact most of the works belong to National and Regional reports. The same applies to most of the aquaculture reposts that have been published either by the national authority or by the FAO.

Works focused on the geomorphologic, geological and hydrological aspects have been deeply discussed in the previous section. **Therefore, this chapter aims to present a brief review on the existing literature concerning the Grand Nador area.**

Some authors focused their work on the **general ecology of the lagoon** and the use of molluscs and macroalgae spatial distribution, to study their biological evolution and the quality of lagoon waters (Guelorget *et al*., 1987; Clanzig, 1989; Zine and Menioui, 1992; Lefebvre *et al*., 1997; Zine *et al*., 1997;

Guelorget *et al*., 2000; Bouchereau *et al*., 2000; Boussalwa *et al*., 2000; Ruiz *et al*., 2004; González-Regalado *et al*., 2005; Ruiz *et al*., 2005). Others have applied Ostracodes and diatoms community analysis to define the present environmental scenarios, and characterise and reconstruct paleoenvironments (Andreu, 1992; Saint Martin *et al*., 2003)

These papers, as other more recent studies and projects (described in the next section), allowed for a clear definition of the natural lagoon ecosystem, and presented an excellent biophysical analysis of the coastal system of Nador.

The biological, ecological, economical and landscape relevance of the lagoon has already been underlined. This area, classified as RAMSAR wetland of international relevance (Ramsar, 2009), and as SIBE (*Site Interet Biologique et Ecoloquique*) according to the Moroccan environmental authorities, presents a high level of biodiversity for both flora and fauna. However, the impact of human activities, related to urbanization and industrialization, is endangering this fragile ecosystem. (CAP-Nador Action Plan, 2009).

Other works have focused on the **sedimentology** of the lagoon.

Tesson and Gensous (1981), El Alami *et al* (1998), Mahjoubi *et al*., (2003), Bloundi *et al*. (2008a) and Piazza *et al*. (2009) have evaluated the distribution of clay minerals and organic matter in the sediments of the Nador lagoon. Several investigations were performed to quantify the occurrence of trace elements and their distributions in sediments (Inani, 1995; Bellucci *et al*., 2003; Bloundi, 2005; Mahjoubi, 2005; Gonzalez *et al*., 2007; Bloundi *et al*. 2008b; Flower, 2009), emphasizing that sediment quality and quantity have strong influences on lagoon ecosystem functions and sedimentation plays a relevant role in the lagoon hydromorphology, with consequences in water quality.

Moreover as Bloundi *et al*. (2008a) pointed out, other studies were aimed to evaluate the influence of anthropogenic pressures leading, in some zones of the lagoon, to morphological abnormalities in living organisms, e.g. nanism in foraminifera and Oostracods (Irzi, 1987; Irzi 2002; Ruiz *et al*., 2004).

In more recent years several authors applied **hydrodynamic** and **ecological models** to the lagoon (Umgiesser *et al*., 2003; Hilmi *et al*., 2007, Umgiesser *et al*., 2005; Ruiz *et al*., 2006). Among the others Idrissi *et al*. (2005) developed and validated a model for the lagoon of Nador, that permits to forecast the cycles of surface water temperature as well as other water quality parameters (dissolved oxygen and phytoplankton biomass) by using meteorological information and physicochemical data obtained from *in situ* measurements

Finally, a series of studies were performed to assess **groundwater quality** and **pollutants distribution** (using several geochemical techniques) in the Bou-Areg Aquifer (Chaouni Alia *et al*., 1997; Chaouni Alia *et al*., 1999; El Yaouti *et al*.,2008, El Mandour *et al*., 2008; El Yaouti *et al*., 2009). All these studies confirm the occurrence of salinization processes in several parts of the aquifer (i.e. downstream, close to the lagoon and upstream from the plain). Waters with low to medium salinity, located in the western and eastern zone, show a high concentration of nitrate, often exceeding the Moroccan drinking standards (40 mgL^{-1}). In the eastern part agricultural activities are intense, while the western zone is characterised by a high population density (the town of Nador), therefore, these nitrates are assumed to be of anthropogenic origin, such as the leakage of domestic and industrial wastewater and the use of chemical fertilizers (El Yaouti *et al*., 2009). An aggravating factor is represented by the fact that only the city of Nador is provided by a wastewater treatment plant (Dakki *et al*., 2000; El Mandour *et al*., 2007), while other urban areas discharge wastewater directly into the *oued* Selouane, or in other semi-permanent rivers, that cross the Bou-Areg plain and flow directly into the lagoon. Moreover according to the National Action Plan for the Mediterranean part of Morocco (Khattabi *et al*., 2007) and following a multidisciplinary analysis based on impact matrices, sewage, waste waters and solid wastes are identified as the main environmental concerns for the Province of Nador. Considering these results the other considered environmental factors that have to be tackled are: heavy metals (resulting from industrial activities), pesticides, Biogeochemical Oxygen Demand (BOD_5 of industrial origin) and PCB.

Besides, if we consider the new development project of the lagoon of Nador, the area will experience several externalities on the local environment, whose impact is still unknown and might be worsened by conjoint action of climate changes.

As emerges from this brief review, there is a good number of works on the Grand Nador area, but data are really unevenly distributed among all the different disciplines (Figure 2.1).

Literature accounts for a wide variety of works focused on the general environment at regional scale, while hydrological and hydrogeological data regarding the catchment area are scarce. Moreover, a study deeply focused on integrated analysis on both the aquifer and the lagoon is missing.

In order to consider all the possible future scenarios, and to promote the best practices for sustainable development, it is fundamental to have a complete knowledge of the present state of the environment. Thus, on the one hand, homogenization and reorganization of all the previous studies must be done, and on the other, new studies more oriented to cover the knowledge gap (but avoiding overlaps to gain in efficiency and effectiveness) and more oriented on integrated approach (e.g. hydrological and hydrochemical studies on the whole catchment) must be performed.

2.1. Previous Projects

To conclude the review of works focused on the Nador lagoon and its catchment basin, it must be underlined that several project at national and international level have been developed (Table 2.1).

A common feature among the projects is the acknowledgement of the crucial role of wetlands and transition zones in the Mediterranean Basin, as well as the urgent need to preserve the lagoon from further anthropogenically induced damages. Several aspects are considered in each project, but the main investigation is always performed focusing on the ecological functions of the lagoon.

Nevertheless, the projects recognise the need for integration, stakeholders' involvement, training activities to raise awareness and disseminations of the results, to share knowledges and actios at national and Mediterranean level. The issues of Integrated coastal Zone Management (ICZM) and Climate Changes (CC) adaptation are particularly present in recent projects, though, again, scarce attention is paved at the catchment basin in its complexity.

Project Title	**Period**	**Organizations-parthners**	**Project goals description**
Sustainability of Mediteranean Coastal Lagoon Ecosystems Under Semi Arid (**COLASU**)	July 2002 -July 2005	National Institute for Fisheries Research, Morocco Université Mohammed V, Agdal, Morocco	Understand the natural variations in lagoon ecosystem functioning; define the parameters inducing alterations due to anthropogenic activity; contribute to the safeguarding of their environmental cleanliness; contribute to the development of sustainable long-term management strategies at a regional scale.
Monitoring and Modelling Coastal Lagoons: Making Management Tools for Aquatic Resources in North Africa (**MELMARINA**)	November 2002-2005	University College London (UCL), UK DHI - Water and Environment (DHIWE) Institut Scientifique, Rabat – ISRABATm Morocco); Joint Research Centre (JRC-European Commisison) Ispra,) University of Ulster, UK	Development of early warning tools and decision support systems that examine with the environmental equilibria between the aquatic resources of specific coastal and inland lagoonal areas; establish and evaluate long-term research on monitoring, measuring and modelling sustainable development in the coastal lagoonal areas; assess and model the impact of human activities on water availability, distribution and quality; promote communality in research methodology through information exchange and by instigating training programmes for young scientists within North African partner institutions in specialist areas of aquatic resource monitoring and modelling forge active links with other international and national bodies concerned with management of aquatic resources
Coastal Action Plan for Nador-Reducing conflicts of coastal natural resources in the Nador area of Morocco (**CAP-Nador**)	January 2006 – 2009	EUCC The Costal Union ENFI (Ecole Nationale Forestière d'Ingénieurs), Sale, Morocco Commune Rurale De Boudinar, Morocco FUED (Forum of Urbanism, Environment and Development), Morocco	Contribute to stop the decline of Nador´s coastal natural wealth and secure the livelihood of its population through the establishment of an Integrated Coastal Zone Management (ICZM) Plan of Action with full stakeholders' participation.
MED WET COAST MAROC Conservation of coastal zones in the Mediterranean Basin	December 2006-ongoing	Fonds de l'Environnement Mondial (FEM) Fonds Français pour l'Environnement Mondial (FFEM)	Ecosystem rehabilitation and biodiversity conservation; Stakeholders involvements in order to increase the attention on environmental issues and promote more effective national policies; legal reinforcement and promote the introduction of new laws on wetlands; promote the coordination at Mediterranean level and environmental education at national level.
Adaptation to Climate Changes to Morocco (**ACCMA**)	2008- ongoing	Direction de la Météorologie Nationale (DMN), Casablanca, Morocco Interdisciplinary Centre for Environmental Research (CIRSA), University of Bologna, Italy National School of Forestry Engineering (ENFI), Sale, Morocco (COORDINATION) Potsdam Institute for Climate Impact Research (PIK), Potsdam, Germany Université de Moncton, Faculté des Sciences de l'Education, Canada Université Mohamed V (UM5), Rabat, Morocco EUCC The Coastal Union, Leiden, The Netherlands	Increase knowledge and awareness about climate change and improve capacity to assess climate change vulnerability in different sectors in Morocco (Coastal zones of the provinces of Berkane and Nador); develop research, to improve stakeholders' adaptive capacities to climate change, to improve interaction capacities in the decision making process.

Table 2.1. List of the main project focused on the region of Nador and the Bou-Areg Pla. References, project websites).

3. Materials and Methods

Based on the research outlines previously described, the main steps of the present work are:

i. **Assessment of the natural groundwater quality**, as baseline criteria are a fundamental reference to quantitatively and qualitatively gauge whether anomalous concentrations are natural, or anthropogenic contamination is occurring. The natural baseline of groundwater may show a range of concentrations depending on aquifer mineralogy, facies changes, flow paths and residence time (Edmunds *et al*., 2003; Edmunds and Shand, 2008). Therefore, in order to understand pollution trends and impacts on an aquifer, it is essential to know its intrinsic characteristics so that imposed environmental changes can be measured with an acceptable degree of confidence.

ii. **Evaluation and quantification of deviations from the natural conditions**: i.e. evaluation of pollution sources and trends, and quantification of saline water encroachment in the aquifer.

iii. **Assessment and quantification of aquifer/lagoon interactions**, evaluation of groundwater quality discharging in the lagoon, and identification of the possible occurrence of Submarine Groundwater Discharge.

Major and trace element geochemistry was applied to groundwater samples collected in different period of the year, and analysis of some environmental isotopes was preformed in order to investigate the sources of pollution affecting groundwater quality.

Conservative tracers, which remain unchanged in content over short timescale, or for which a change in composition indicates a new input source of groundwater (e.g. Cl, Br, $\delta^{18}O$, $\delta^{2}H$), were used to track contributions from the atmosphere, land surface and soils to the groundwater system (Edmunds and Shand, 2008). Reactive tracers, on the other hand, include H^+, cations deriving from weathering and other reactions along flow lines (e.g. B, Li, Sr, Si) and isotopes like $\delta^{13}C$. Those tracers were applied to study water-rock interaction processes.

As literature accounts for an increase of nitrogen concentration in groundwater, mainly associated to human activities, it apperared fundamental to discriminate the contribution of different loads in drainage waters. The basis for the identification of NO_3^- is the use of natural abundance of ^{15}N. The $\delta^{18}O$ composition of nitrate added more information allowing for a clear distinction between synthetic and natural fertilizers (Clark and Fritz, 1998). Moreover, the analysis of nitrogen isotope pattern was used to highlight the occurrence of contamination by septic effluents apart from agricultural sources. In addition, the use of ^{13}C in DIC (Dissolved Inorganic Carbon) was analysed to trace carbon sources in groundwater.

3.1. Water sampling and instrumentation

A total of 94 water samples were collected during three surveys between November 2009 and November 2010.

Samplings were carried out in fall and spring over two years, in order to have information about the seasonal effect and possible local recharge in the area.

The preliminary survey (November 2009) allowed for the identification of potential sampling sites and for the definition of the main characteristics of the Bou-Areg plain (limited by the irrigation channel represented by the dotted line in Figure 3.1). A sample (P 10) was collected in the confining Gareb Plain in order to obtain a reference point for evaluating possible of groundwater mixing professes.

A second and more detailed investigation was performed in June 2010, with a special focus on the agricultural area of the plain (Figure 3.2). In addition, 20 surface water samples have been collected in the Lagoon of Nador (including two fresh water springs, L2 and L19 in Figure 3.2).

In the third campaign (November 2010), the investigation was extended to the whole Bou-Areg aquifer. Some wells, previously sampled in November 2009 and June 2010, were sampled again to obtain seasonality information. Others, as too narrow or redundant were substituted to get a more homegeneous spatial distribution of sites over the plain. Again, one sample (P 31) was collected in the Gareb plain. The spatial distribution of the samples collected in November 2010 is reported in Figure 3.3.

In the third campaign three river water samples (*oued* Selouane) together with one in the irrigation channel were also collected in order to better define recharge and pollution end-members in the area (Figure 3.3). Table 3.1 summarizes the main goals of the three field works:

Activity	Main goals
• Collection of groundwater samples in the Bou-Areg Plain and surface water in the Nador Lagoon, *oued* Selouane and irrigation channel for chemical and isotopic analyses (see last paragraph)	• Application of major and trace elements geochemistry in order to define the geological origin of nutrients and salinity, and to provide evidence of groundwater pollution due to human impacts • Identification of possible occurrence of Submarine Groundwater Discharge
• *In situ* measurements of pH, Eh, Conductivity, Temperature, Salinity and Dissolved Oxygen (DO)	• Definition of the environmental conditions and of the main physicochemical parameters
• Preparation of water samples and storage for analysis	• Application of general chemistry and isotope geochemistry to identify and quantify the main drivers of pollution
• Collection of phytoplankton samples	• Identification of the species; definition of bio indicatior for the quality of the lagoon of Nador (not object of the present study)

Table 3. 1. Summary of the main activities and goals of the sampling campaigns.

Site characterization and fieldwork during the first two missions were performed in cooperation with the Faculté Pluridisciplinaire de Nador, Université de Oujda (Morocco), which also provided the geological map of Annex I.

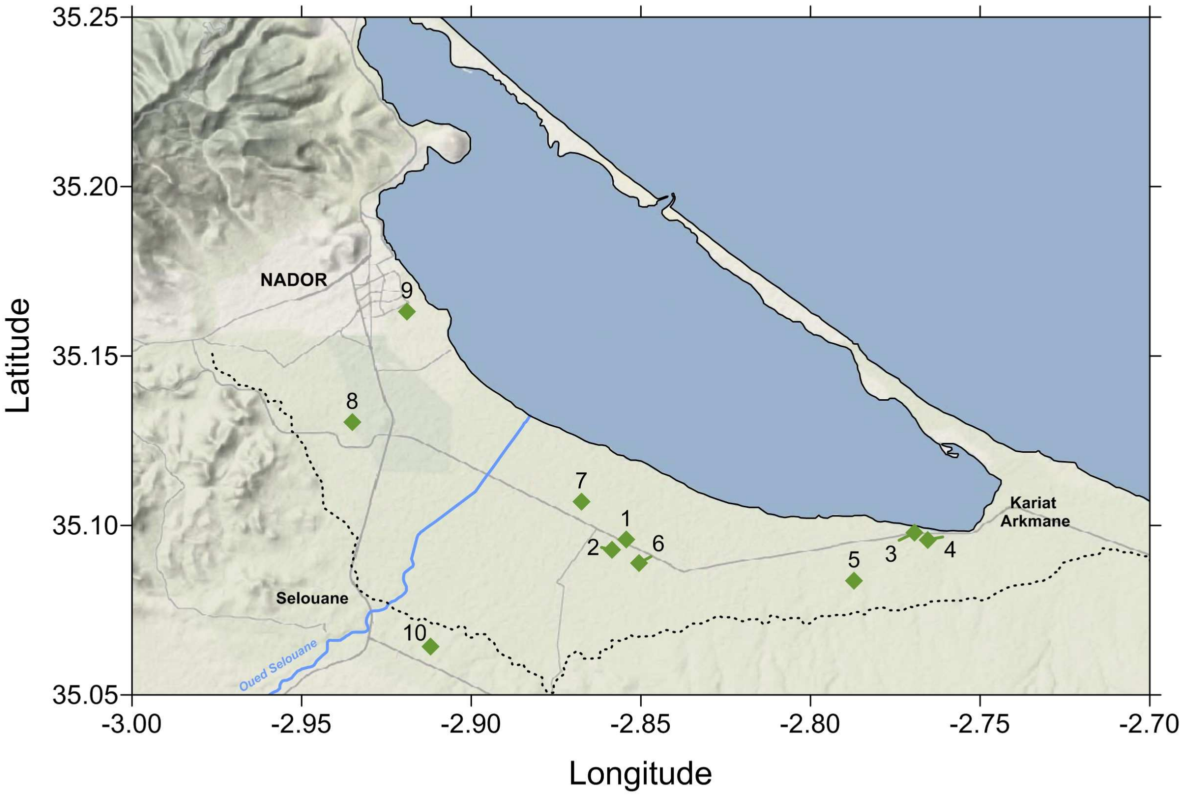


Figure 3. 1. Location of the sampling points of wells in the Bou-Areg Plain (November 2009). Dotted line represent the irrigation channel, as well as the limit of the coastal plain.

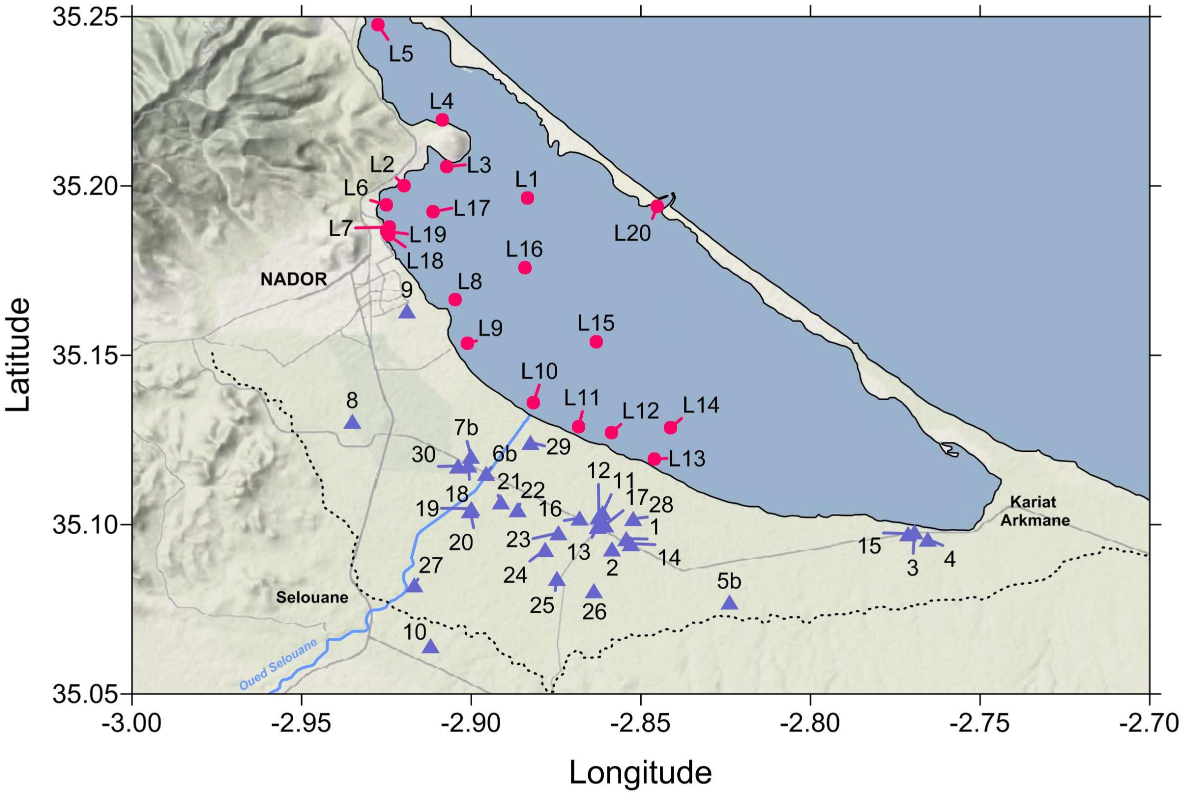


Figure 3. 2. Location of the sampling points of wells in the Bou-Areg Plain and surface water in the Lagoon of Nador (L-) (June 2010).

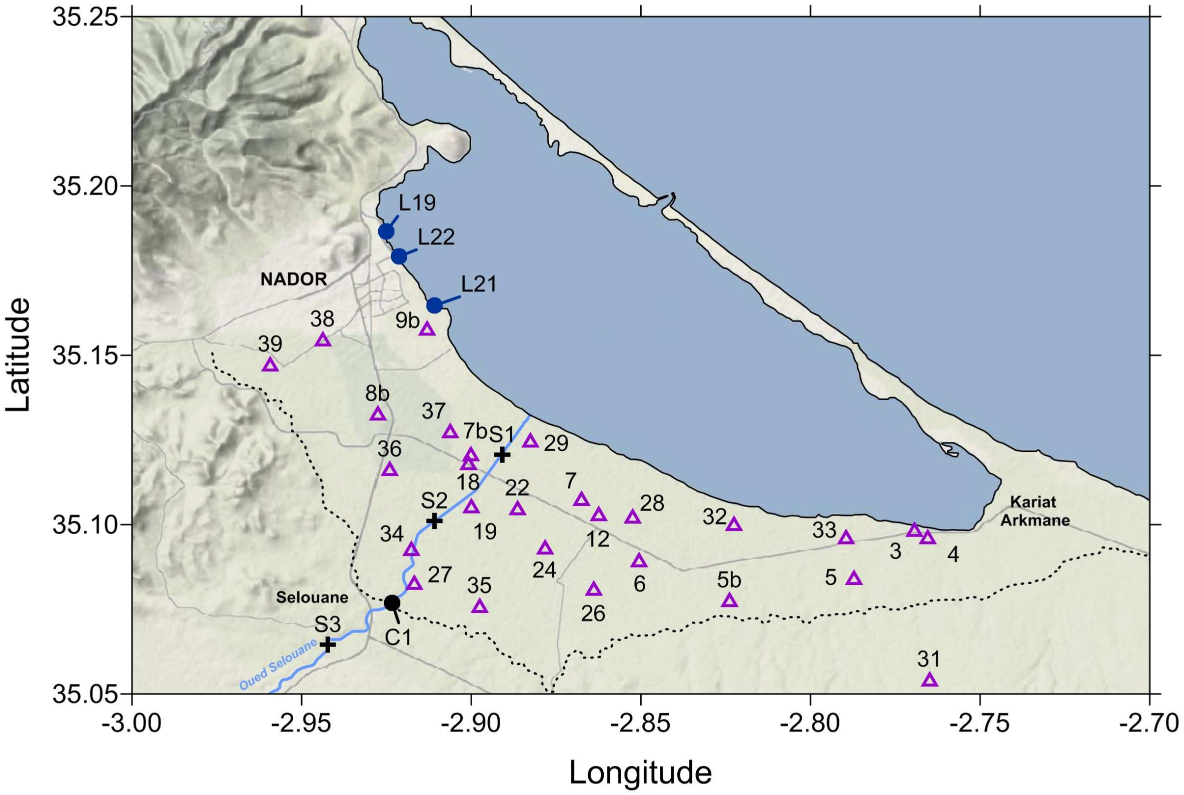


Figure 3. 3. Location of the sampling points of wells in the Bou-Areg Plain, surface water of the *oued* Selouane (S-) in the Irrigation channel (C1), and the Lagoon of Nador (November 2010).

3.1.1. Groundwater sampling

Water level has been measured using an acoustic phreatimeter (Figure 3.3 A). Some wells were equipped with active pumping system, therefore pumping until EC stabilization was performed before sampling collection. For all the others piezometric level was measured in a static level. To be sure that the collection of groundwater samples could be considered representative of the aquifer, only the most used wells in households and private properties where included in the survey.

During the sampling phase the following chemical-physical parameters were collected (Figure 3.3 B): temperature, pH, conductivity and Eh (measured using a pH-meter pH/cond 340/SET, WTW) Measures of air temperature and altitude were taken using an altimeter (OREGON EB 833).

Alkalinity (total mgL^{-1} of methyl orange alkalinity as calcium carbonate, $CaCO_3$) was determined after sampling by titration, in order to prevent precipitation or degassing processes, using an alkalinity test kit (HACH 5-400 mgL^{-1}, AL-AP MG-L; Figure 3.3 C).

Samples for major ion analysis were stored in polyethylene bottles and filtered in laboratory through 0.45 µm cellulose membrane (Figure 4.4 D). Samples for cation analysis were preserved with addition of 5NHNO^{3} just after filtration. Samples for stable isotope analysis were collected according to the procedures described by Clark and Fritz (1997). Water samples were preserved after acidification to pH 2 with HCl, to prevent anty biological activity. Samples for carbon-13 analyses were kept at dark and cold until analyzed.

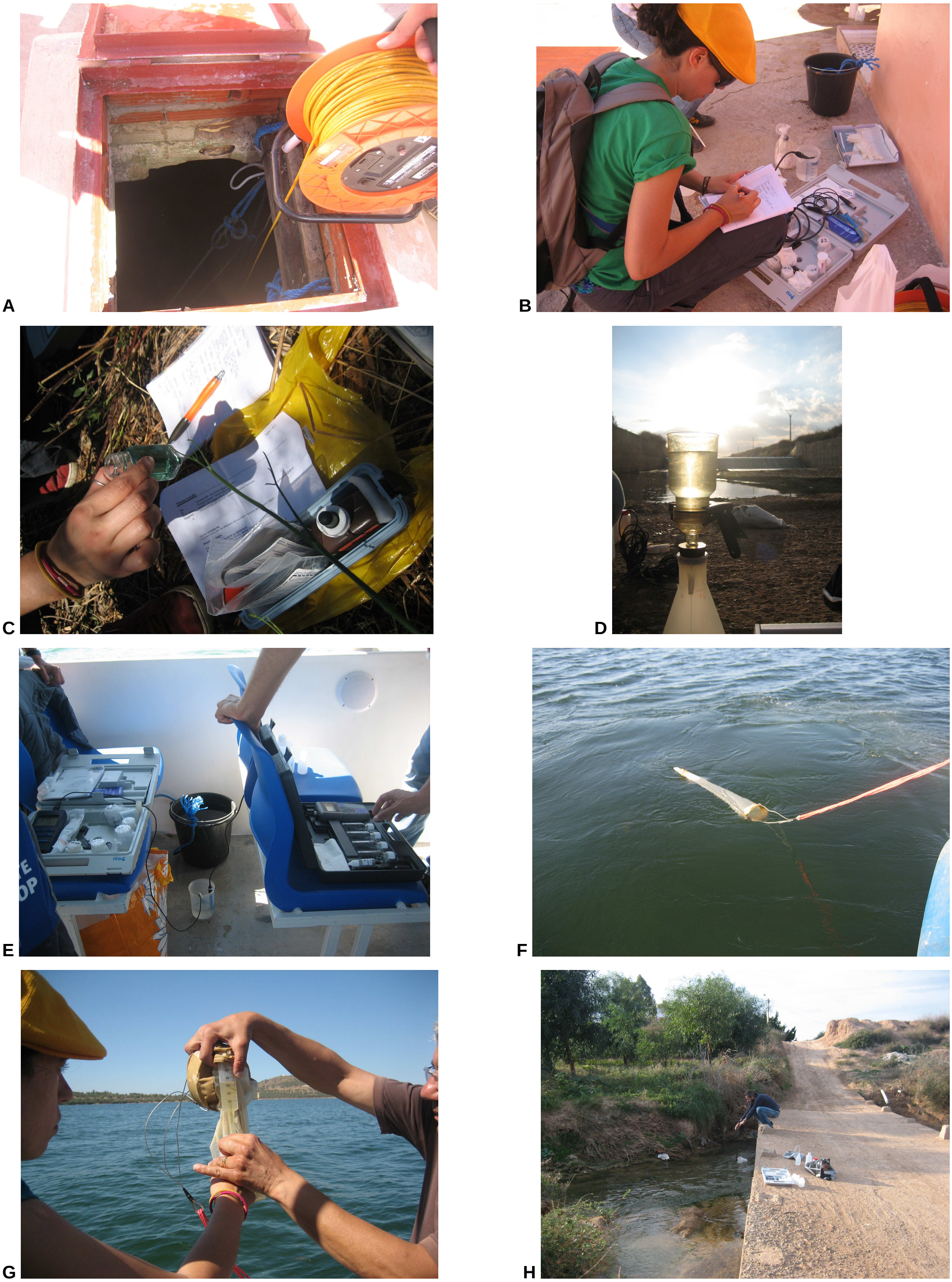


Figure 3. 4. Steps of the in situ measurement and sampling.during the June 2010 (A, B, C, E, F, G) and November 2010 (D and H) fieldworks.

3.1.2. Lagoon and river water sampling

The choice of the lagoon sampling sites (Figure 3.2) has been done considering the potential presence of pollution sources (e.g. *oueds* mouths and wastewater treatment station), and the possible occurrence of freshwater discharging in the lagoon and the inlet.

The same *in situ* measurement described in the previous section were carried out. Moreover, Dissolved Oxygen had been measured using a Ecoscan Eutech DO6+ electrode (Figure 3.2 D).

For each station nearly one 1.5 L of bulk water has been collected, applying the procedures previously described for sampling preservation; Moreover in every station samples for biological analysis waere collected using a phytoplancton net with 20 μm mesh. The net was lowered slowly to the desire depth, and then is pulled up more quickly, allowing for the concentration of phytoplankton in the attached sample jar (Figure 3.2.F and G). Collected samples have been stored in glass bottles and preserved by addition of formalin. The biological analysis is not object of the present study.

In the same way, surface water samples of *oued* Selouane [Figure 1.6. (A) site S2 and (B) S1; Figure 3.4 H], the only natural river with permanent regime, were collected in November 2010 and prepared for storage according to the same procedure used for groundwater samples.

3.2. Analytical methods

Both lagoon and groundwater samples were analysed according to the analytical procedures summarized in Table 3.2. Isotopes were analyzed referring to the standards shown in Table 3.3.

Element	Laboratory	
Ca , Mg, Na' K, Cl, SO_4, NO_3^-, F, PO_4 (of the November 2009 sampling campaign)	CNR-IGAG (Montelibretti, Italy)	Ionic Chromatography
Ca , Mg, Na' K, Cl, SO_4, NO_3^-, of the June 2010 sampling campaign	Earth Sciences Department of the Pavia University (Pavia, Italy)	Ionic Chromatography
Br	Geosciences and Earth Resources Institute, National Research Council (IGG -CNR), Pisa, Italy	Ionic Chromatography
B, Li, Sr, Si	Earth Sciences Department of the Pavia University (Pavia, Italy)	ICP-AES
$\delta^{18}O$, δ^2H, $\delta^{13}C$, $\delta^{15}N_{\_NO3}$, $\delta^{18}O_{\_NO3}$	ISO4 snc (Torino, Italy)	Mass spectrometry

Table 3. 2. Resume of the analytical procedures and laboratories that performed the analysis.

Element	Isotopic ratio	Standard
$\delta^{18}O$ water	$^{18}O/^{16}O$	V-SMOW (Vienna Standard Mean Ocean Water)
, δ^2H water	$^2H/^1H$	V-SMOW (Vienna Standard Mean Ocean Water)
$\delta^{13}C$	$^{13}C/^{12}C$	V-PDB (Vienna Pee Dee Belemnite)
$\delta^{15}N_{\_NO3}$	$^{15}N/^{14}N$	AIR N_2
,$\delta^{18}O_{\_NO3}$	$^{18}O/^{16}O$	V-SMOW (Vienna Standard Mean Ocean Water)

Table 3. 3. Reference standards and isotopic ratios of the investigated environmental isotopes.

3.2.2. General chemistry and trace elements

The hydrochemistry of minor elements, (i.e. B, Br, Li, Sr) associated to the major-ion chemistry (chloride, sodium and calcium) has been studied to restrict the sources and the processes of salinisation occurring in the aquifer.

Sampled waters were analysed in order to determine the major ionic contents and verify the opportunity to proceed with isotopic determinations.

Chemical analyses of water samples (November 2009) were performed at the hydrochemical laboratory of CNR-IGAG (Montelibretti, Italy). Mayor anions (Cl-, NO_3^- and SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) concentrations were analysed in filtered samples using ionic chromatography. Chemical analyses of water samples for the June 2010 campaign were conducted, according to the same procedures, at the hydrochemistry laboratory of the Earth Sciences Department of the Pavia University (Pavia, Italy). Trace elements analyses (B, Li, Sr) were performed at the Earth Sciences Department of the Pavia University (Italy), using an ICP-AES Jobyn Yvon 24. Br analyses were performed at the IGG-CNR (Pisa) using ionic chromatography (Dionex 100) with an accuracy of 3%.

Data quality was further assessed using the charge balance errors (%CBE). Charge balance error, based on the concept that the sum of positive charges should equal the sum of the negative charges in a solution, is calculated as (Freeze and Cherry, 1979):

$$CBE = \left(\frac{\sum^{+} - \sum^{-}}{\sum^{+} + \sum^{-}} \right) \cdot 100 \;;$$

Where Σ^+ is the sum of the measured, positively charged equivalents, and Σ^- is the sum of the measured, negatively charged equivalents.

3.2.2. Environmental isotopes

Isotopic analyses were performed by the private laboratory ISO4 s.s. Turin, Italy, after sampling preparation held in the Pavia ISO4 laboratory, as stable isotopes of water samples are measured using gas mass spectrometry, which requires a specific preparation in relation to the considered isotope.

Hydrogen isotope composition was measured by water reduction over metallic zinc (Coleman *et al*., 1982), while $\delta^{18}O$ was analyzed by water-CO_2 equilibration at 25 °C (Epstein and Mayeda, 1953); both results are expressed in V-SMOW (Gonfiantini, 1978; Gonfiantini *et al*., 1995). The analytical errors are ±1 and ±0.1 ‰ respectively. The $\delta^{13}C$ of DIC was analysed by direct acidification of the water sample with phosphoric acid (Kroopnick, 1974) and the released CO_2 recuperated in vacuum line for further analysis through the dual inlet of the mass spectrometer. Results are expressed in ‰ V-PDB (Gonfiantini, 1978; Gonfiantini *et al*., 1995). Analytical errors are ±0.3. $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ of dissolved nitrate were analysed following the procedures described by Kendall and Grim (1990) and by Silva *et al*., (2000) and refer to V-AIR (Gonfiantini *et al*., 1995). The analytical error is ±0.5‰ and ±1‰ respectively. All gases were analysed on a Finnigan MAT 250 Mass Spectrometer at ISO4 s.s. (Pavia, Italy).

Annex 2 presents a more detailed description of the use of isotopes in hydrogeology.

3.3. Data treatment

3.3.1. Hydrochemistry

In order to define the hydrogeochemical regime of the Bou-Areg aquifer, and to better illustrate different water types, chemical data have been plotted on Piper-Hill trilinear diagram (Piper, 1954). This qualitative representation is useful for visualising chemical relationships among groundwater samples. The diagram is composed by two triangles, one for anions and one for cations, which are combined to show a single point in a diamond shaped field, from which inference is drawn on the basis of the hydrogeochemical facies concept (Ravikumar *et al*., 2010).

Pourbaix diagrams, or pH- Eh diagrams, were used to or to represent the stability limits of different species. Diagrams are built using logarithmic expressions of redox equilibrium for different species. Therefore, for each Eh-ph value stable phases of an aqueous system could be highlighted (Sigg *et al*., 1999).

Another graphical representation, useful to classify water samples based on their chemical composition is the Langelier-Ludwig (or LL) diagram (Langelier and Ludwig, 1944). This is a square plot diagram, where the position of a sample in the plot is obtained by first calculating the sum of main anions, (Σ_{an}), and of main cations (Σ_{cat}), by means of the following equations:

$\Sigma_{an} = [Cl^-] + [SO_4^{2-}] + [HCO_3^-]$

$\Sigma_{cat} = [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+]$,

where [X] refer to the concentration of each component in eq/l or meq/l.

Within the plot each axis ranges from 0 to 50 meq%, and, as a general rule, the sum of selected cations is plotted on the y-axis, against the percentage of each selected anion (Baneschi, 2007).

To better understand the processes controlling salinity evolution and solute content the following molar ratios were studied:

i. Na/Cl, B/Cl and Br/Cl ratios, used to identify seawater mixing (Edmunds, 1996a; Edmunds and Smedley, 1999;) and anthropogenic contamination or vegetation/soil adsorption processes (Sanchez-Martos *et al*., 2002; Vengosh, 2003; Panno *et al*., 2006);

ii. Mg/Ca, Ca/Na, and Ca+Mg/SO_4+HCO_3 ratios, used to determine mineral weathering, dissolution/precipitation of minerals and evaporation of surface and lake water (Green *et al*., 2005; Baneschi, 2007).

iii. Trace elements (e.g. Li, Sr, B and Br) to discriminate different sources of groundwater origin (Edmunds *et al*., 1987; Edmunds *et al*., 2003; Bouchaou *et al*., 2008).

Moreover plots of chloride concentration (or Electrical Conductivity) versus the isotopic signal of water molecule (Figure 3.3) were used to point out the origin of groundwater salinization and discriminate among evaporation, seawater mixing and dissolution.

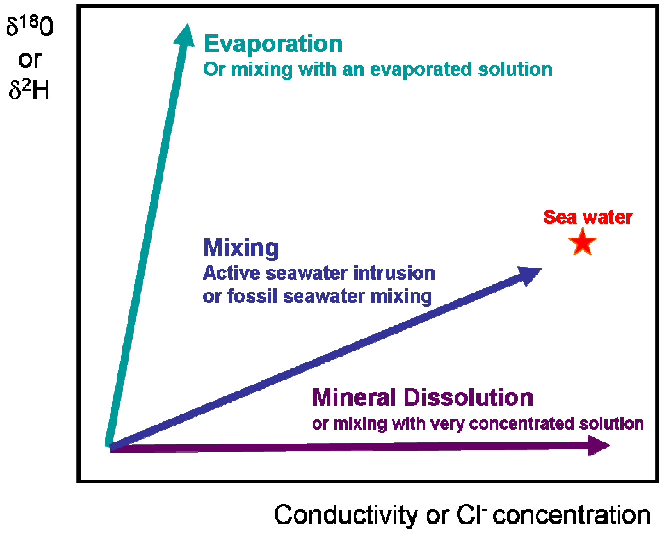


Figure 3. 3. Schematic representation of a preliminary approach to the study of groundwater salinization based on environmental tracers end isotopes of water molecule (Modif. Michelot, 2010).

By combining this analysis to the one of major and trace elements (e.g. B, Br, Li and Sr) and/or other isotopes it is also possible:

- to better understand if real evaporation (or mixing with an evaporated solution) is occurring, and which kind of mixing is dominant (e.g. advective or diffusive);
- if the so called “mixing” is actually an active seawater mixing, possibly induced by excessive exploitation), or mixing with fossil seawaters;
- if groundwater are dissolving with freshwater or with concentrated solutions;

However, despite the number of tracers and tools, tracing the origin of salinity is not easy, particularly if multiple non-point, saline sources are present within the basin (Vengosh, 2003).

The same tools were applied to define lagoon geochemical processes.

To conclude Saturation Indices for Calcite, Dolomite, Gypsum and Aragonite were calculated to obtain more evidences of mineralization processes in both the aquifer and the lagoon.

The Saturation Index (SI) is a coefficient reflecting the saturation of waters with respect to a specific mineral, hence showing if water has tendency to dissolve or precipitate a particular mineral (Hem, 1985).

The SI Is calculated as follow:

$$SI = \log(IAP / K_s),$$

where: IAP is the ion activity product, or the chemical activity of the dissolved ions of the mineral and K_S is the solubility product.

Waters are in equilibrium with a mineral if SI is zero (i.e. IAP= K_S), they are supersaturated when SI>0, meaning that the mineral precipitated, and undersaturated when the mineral is dissolved (SI<0).

In this work SI have been calculated usingthe progamme PhreeqC, included in the Diagramme 4.0 Software developed by the Hydrology group of the University of Avignone (France).

As concerns data presentation, hydrochemical results are generally shown using three units: mgL^{-1} (or ppm), $mmolL^{-1}$ and $meqL^{-1}$. Despite the defect in coherence, in this work all the units are used.

Data are presented in mgL^{-1} when dealing with pollution issues and in accordance with the main regulation (e.g. WHO) and sanitation reports. In all the other cases $mmolL^{-1}$ or $meqL^{-}$ are used.

3.3.2. Principal Component Analysis

The assessment of groundwater geochemical processes is a multivariate problem by nature. In fact, when many correlated variables are investigated using univariate methods, they may show conflicting signals that are not easily interpretable, or over emphasize the relevance of the certain geochemical processes. A multivariate approach allows instead for the simultaneous examination of the ways in which numerous variables vary in relation to each other, with the goal of shed some light on the nature of the processes underlying natural systems.

Among other multivariate techniques used to explore datasets structure, Principal Component Analysis (PCA; Chatfield and Collins, 1980) is a mathematical procedure that transforms a number of (possibly) correlated variables into a (smaller) number of uncorrelated variables, called factors or principal components (PCs).

The Principal Components emerge from a modelling of the observed data and represent a linear combination of the original variables. A new set of independent variables is thus identified with the aim of providing an integrated picture of the observations and of the communalities/discrepancies between the groups of variables, highlighting the common structures present in all or some of these sets.

PCA's outcomes are necessarily more hypothetical and tentative, since they represent a "transformation" of the original space of variables to an idealized and less complex one. Therefore, results given by the analysis have to be discussed and verified together with theories and further direct observation in order to determine if the relationships discovered are significant.

For the purpose of this study, PCA was used to support the hydrochemical interpretation and to infer the main processes affecting the composition of both the lagoon and the aquifer system.

The analysis was applied on the June 2010 dataset, and using for calculation the statistical package SPSS 15.0 for Windows® (SPSS, Inc., Chicago, IL, USA, 2004).

The values of p different hydrochemical variables for both lagoon and ground water samples, denoted x_1; x_2...x_p each with N observations (see Tables in paragraph 4.2), were normalized prior to the multivariate analyses. One must note that, variables describing the same observations may largely vary from one to the other and so normalization is required to equally weight all variables to the same statistical parameters (zero mean and unit standard deviation) and avoid that the structure of PCs would be dominated by those with the largest variance.

The normalized values, Z_{ij}, are hence computed from the N observations of the *i*th variable as:

$$Z_{ij} = \frac{X_{ij} - \mu_i}{\sigma_i},$$

where $X_{i,j}$ is measured value of the *j*th observation for the *i*th variable with i = 1, 2,…p and j = 1., 2,…N, and μ_i and σ_i are respectively the mean and standard deviation of the *i*th hydrochemical variable.

The reduction of dimensionality of the data table was obtained through the diagonalization of the correlation coefficients matrix and, subsequently, by transforming the normalized chemical and isotopic data in into an equal number of uncorrelated, orthogonal principal components (Menció and Mas-Pla, 2008).

Furthermore, the correlation coefficient matrix measures how well the variance of each constituent can be explained by relationships with each of the others (El Yaouti *et al.*, 2009). The eigenvalues of each principal component are a measure of their associated variance, the participation of the original variables in the principal components is given by the loadings, and the individual transformed observations are called scores.

The Kaiser criterion was applied (Kaiser, 1958) when choosing the PCs to be retained in the analysis, which states that we only interpret factors with Eigenvalues greater than 1.

After the application of the PCA, orthogonal rotation was done with Kaiser's varimax scheme (Kaiser, 1958), allowing for a cleaning up of the Principal Components, by increasing the participation of the variables with a higher contribution, and at the same time reducing the participation of the variables with a lower contribution (Menció and Mas-Pla, 2008).

Principal Components scores are computed for each sample by a matrix multiplication of the PC's score coefficient with the standardized data. The value of each score represents the importance of a given PC at the sample site. A PC's score >+1 indicates intense influence by the process. Very negative values (<-1) reflect areas virtually unaffected by the process while near-zero scores reflect areas with only a moderate effect of the process. The spatial distribution of the Principal Components (and hence the hydrochemical process represented by them) can be assessed by a contour of the scores representing each PC.

3.3.3. Clustering Analysis

Cluster analysis is a technique allowing for a classification of the data into categories according to their intrinsic nature and behaviour. The grouping is done without making any a priori assumption about the data, and the latter are merged according to their nearness or similarity (Menció and Mas-Pla, 2008).

In the hierarchical cluster analysis the distance between samples is used as a measure of similarity.

In the present work, the agglomerative technique is the Ward's method which uses the squared Euclidean distances as a measure of similarity.

The statistical package SPSS 15.0 for Windows® (SPSS, Inc., Chicago, IL, USA, 2004), was used for calculation, and the analysis was performed using the Principal Components obtained in the PCA as classification variables.

3.3.4. Thematic Cartography

Graphic representations and thematic cartography are generally powerful tools for results dissemination and support to decisional processes.

By applying mathematical algorithms, it is possible to generalize a geochemical data, transforming punctual information into more general ones, which provide information about the spatial distribution of the variables (De Vivo *et al*., 2004).

Therefore, to translate the punctual information (in geochemistry, for example the chemical or isotopic composition of water sampled in a specific well) into a map, interpolation is required.

Beside the well known problem related to the extremely high heterogeneity of the geochemical data, the reconstruction of spatial patterns allows one to obtain a first, although rough, description of the occurrence of gradients and/or hotspots as derived from the experimental data.

Such an analysis, combined with the pollution sources identification, might be efficiently used to identify potential vulnerable areas in order to specifically address future monitoring efforts toward critical areas.

In the present work, physicochemical properties of groundwater samples were investigated in their spatial characteristics trough a state of the art method, namely the Kriging interpolation algorithm (Cressie, 1991) as implemented in the GIS-Surfer™ software.

Kriging is a complex stochastic statistical method, based on the theory of the so-called regionalized variables (Krige, 1966; Matheron, 1971). Kriging belongs to the family of linear least squares estimation algorithms. As all the interpolation algorithms, this method estimates the value at a given location as a weighted sum of data values at surrounding locations (Bohling, 2005).

Of course, the denser is the spatial distribution of the data, the more accurate is the estimation, regardless the interpolation algorithm (Bohling, 2005).

For the maps presented in this work, the default interpolation provided by the Surfer™ software was accepted.

4. Results

4.1. Preliminary campaign: November 2009

4.1.1 The Bou-Areg Aquifer

Water temperature varies between 15.4 °C and 22.3 ° C, with an average of 20.6 °C, these values are typical of cold-hypothermal waters (Table 4.1). pH has a mean of 7.7, with values ranging between 7.4 (P9) and 8.3 (P5), showing neutral or slightly alkaline nature.

Electrical conductivity suggests the presence of exceedingly mineralized waters, with an average of 4,780 μScm^{-1}, and a maximum of 8,120 μScm^{-1}in well 4 (while well 5 is the least mineralized).

Salinity ranges between 0.64 and 3.10 gL^{-1}. Dominant major ions (Table 4.3) are sodium-chloride. The abundance of major ions, especially of nitrate, chloride and sulphate suggest an elevated undesirable evolution of physical-chemical properties of fresh water resources, and thus an increased risk for public health.

In particular, for some wells the content of nitrate is quite high and sometimes (wells 1, 8 and 9) exceeding the WHO regulatory limit of 50 mgL^{-1} (WHO, 2006). The same drinking water limits are exceeded also for fluoride; in fact wells 1, 3, 5 and 8 are quite above the limit of 1.5 mgL^{-1}, while wells 4 and 7 are slightly below, suggesting the presence of agricultural induced pollution.

Among the analyzed trace elements, lithium is the least abundant, with concentrations ranging between 0.006 and 0.2 mgL^{-1}.

Boron and bromine have average values of 2.9 mgL^{-1} and 1.4 mgL^{-1} respectively.

The $\delta^{15}N_{-NO3}$ values (Table 4.2) range from approximately +4 to + 13‰, and are in the range of signatures for soil organic matter, manure and septic systems (Kendall, 1998). $\delta^{18}O_{-NO3}$ varies between +8 to +11‰, while the mean value for $\delta\ ^{13}C$ of DIC is -9.14‰. Mean $\delta^{18}O$ and $\delta^{2}H$ are -5.26 and -36.40 respectively.

Code	Nature	Latitude (degrees)	Longitude (degrees)	Altitude (m)	Air T (℃)	Depth (m)	Water T (℃)	pH	Conductivity (mSCm $^{-1}$)	Salinity (g)
P1	Well	35.0958	-2.8543	20	20.4	5.90	18.3	8.21	3.4	1.64
P2	Well	35.0928	-2.8585	20	21.5	7.18	21.3	7.61	5.23	2.61
P3	Well	35.0978	-2.7693	8	26.2	4.80	22.3	7.58	6.54	3.03
P4	Well	35.0958	-2.7655	40	29.8	5.00	20.6	7.74	8.12	4.04
P5	Well	35.0835	-2.7870	35	33.7	29.60	22.0	8.25	3.00	1.61
P6	Well	35.0889	-2.8506	30	32.1	12.93	20.6	7.83	3.80	1.90
P7	Well	35.1070	-2.8675	15	28	4.20	22.1	7.51	4.51	2.26
P8	Well	35.1305	-2.9350	4	29.7	3.30	21.3	7.76	3.78	1.88
P9	Well	35.1632	-2.9189	75	18	2.50	21.6	7.35	3.20	1.60
P10	Well	35.0642	-2.9120	15	19	8.03	15.4	7.63	6.22	3.10
T	Tap w.	35.0958	-2.8543	-	-	-	17.2	7.97	1.28	0.64

Table 4. 1. Results of the preliminary field investigation, November 2009.

Code	$\delta^{18}O$ (δ‰)	$\delta^{2}H$ (δ‰)	$\delta^{13}C$ (δ‰)	$\delta^{15}N_{\_NO3}$ (δ‰)	$\delta^{18}O_{\_NO3}$ (δ‰)
P1	-5.09	-36.71	-7.07	10.61	10.0
P2	-5.34	-37.82	-5.86	-	-
P3	-5.34	-35.23	-8.34	5.44	9.5
P4	-5.19	-35.65	-7.91	6.80	7.9
P5	-5.05	-35.78	-7.82	4.54	11.3
P6	-5.29	-38.18	-11.67	-	-
P7	-5.74	-39.89	-5.76	10.23	11.2
P8	-5.22	-34.33	-12.87	11.70	9.0
P9	-5.12	-34.05	-14.29	12.56	8.6
P10	-5.24	-35.54	-9.83	-	
T	-	-	-7.07	10.61	10.0

Table 4. 2. Isotopic composition (δ‰) of groundwater in the Bou-Areg plain (November 2009).

Code	Ca (mgL $^{-1}$)	Mg (mgL $^{-1}$)	Na (mgL $^{-1}$)	K (mgL $^{-1}$)	Cl (mgL $^{-1}$)	SO_4 (mgL $^{-1}$)	NO_3 (mgL $^{-1}$)	F (mgL $^{-1}$)	PO_4 (mgL $^{-1}$)	Br (mgL $^{-1}$)	B (mgL $^{-1}$)	Sr (mgL $^{-1}$)	Li (mgL $^{-1}$)	Si (mgL $^{-1}$)	Na/Cl (ratio)	Ca/Cl (ratio)	SO_4/Cl (ratio)
P1	134.5	30.2	629.9	4.3	699.5	-	125.6	2.16	8.49	0.47	6.58	0.82	0.07	6.9	1.39	0.170	-
P2	282.7	129.9	1178.3	-	1192.6	782.0	2.2	0.73	-	1.94	1.57	1.36	0.09	2.6	1.52	0.210	0.242
P3	366.1	110.0	1276.7	18.5	1732.4	645.4	20.5	1.21	-	2.53	2.31	1.68	0.08	7.6	1.13	0.187	0.137
P4	359.2	210.1	1831.8	23.5	3338.9	1118.04	19.0	1.14	-	4.2	3.1	2.91	0.13	10.79	0.84	0.095	0.124
P5	235.9	36.2	521.2	4.8	392.6	418.3	22.6	2.25	-	0.42	1.52	0.59	0.05	7.7	2.04	0.532	0.393
P6	214.2	87.7	621.5	41.0	512.3	633.2	2.0	1.6	-	-	5.74	0.88	0.2	1.1	1.867	0.370	0.456
P7	330.4	92.2	667.4	25.2	680.1	989.9	16.0	1.32	-	0.51	4.21	3.22	0.11	9.9	1.51	0.430	0.537
P8	187.3	112.6	808.4	22.5	599.7	714.4	154.5	3.19	-	0.53	2.62	0.88	0.09	16.7	2.07	0.278	0.440
P9	233.4	66.7	483.2	-	570.1	563.9	118.9	0.41	-	0.62	0.8	0.95	0.006	25.7	1.31	0.362	0.365
P10	449.1	177.8	1087.2	2.5	1876.5	435.8	-	0.46	9.09	1.77	0.9	2.84	0.097	12.1	0.89	0.212	0.086
T	298.0	38.1	74.5	-	101.6	310.1	1.4	0.03	-	0.12	-	-	-	-	1.13	2.60	1.126

Table 4. 3. Chemical data (in mgL $^{-1}$) in the Bou-Areg coastal plain (field investigation November 2009); ratios are expressed as molar ratio.

4.2. Spring campaign: June 2010

4.2.1 The Bou-Areg Aquifer

Water temperature varies between 19.7 ℃ and 38.2 ° C, with an average of 22.8 ℃, reflecting the seasonal temperature increase (Table 4.4).

Values of pH range from 7.2 (P30) and 7.9 (P28), with a mean value of 7.7, showing neutral or slightly basic nature. Electrical conductivity confirms high mineralization of the aquifer (average of 5,970 µScm^{-1}), with a maximum value in well 4 (10,52 µScm^{-1}) and a minimum in well 5b (1, 744 µScm^{-1}).

Redox potential values are positive for all the samples but well 5b (-8 mV) and if we exclude this Eh average for the Bou-Areg aquifer is about 178 mV.

Concentration data for groundwater (Table 4.5) indicate high cation contents, which are not balanced by the low alkalinity values (mean alkalinity value: 518 mgL^{-1}) but by elevated dissolved nitrates and chlorides. The abundance of major ions (especially of nitrates, chlorides and sulphates) suggests an elevated alteration of physical-chemical properties in fresh water resources and thus an increased risk. In particular such high values of nitrates, , with a maximum of 208 mgL^{-1} in P8, can pose serious risks for public health of local population withdrawing well waters for domestic uses.

As concerns trace elements, lithium is again the least abundant element, with values ranging from 0.01 to 0.23 mgL^{-1}. All the wells show values of B largely exceeding WHO drinkability limit (0.5 mgL^{-1}) and confirming the high salinization of the aquifer.

The $\delta^{15}N_{-NO3}$ values (Table 4.6) vary from approximately +4 to +13‰, and are in the range of signatures for soil organic matter, manure and septic systems (Kendall 1998). $\delta^{18}O_{-NO3}$ varies between +8 to +18‰, while the mean value for $\delta\ ^{13}C$ of DIC is -8.7‰. Mean $\delta^{18}O$ and $\delta^{2}H$ are -7.46 and -36.9 respectively.

4.2.2 The Lagoon of Nador

Lagoon water temperature mainly reflects air temperature, with an average value of 26.5 ℃, and this is mainly due to the fact that only surface water samples were collected. Values of pH are in the range of marine waters, ranging from 7.5 to 8.5 (average 8.2).

Most of the lagoon-sampled sites have conductivity values of about 55 mScm^{-1}, with a maximum of 55.70 mScm^{-1}in L5. However, the two sampled springs have conductivity values more coherent with the sampled groundwater: L2, with concentration of 7.84 mScm^{-1}, is the less saline site together with L19 (15.66 mScm^{-1}).

Dissolved Oxygen (D.O) values renge between a minimum value of 7.09 mgL^{-1} in L2 and a maximum of 8.6 mgL^{-1} in L15 (average value 8), while Eh ranges from 90 mV (L16) and 190 mV in L1.

Both major and trace elements do not present significant variations among all the sampling stations. Only L2 and L19, classified as springs, show inferior sodium and chloride concentrations (324- 696 mgL^{-1} and 2141-4834 mgL^{-1} respectively) but presence of dissolved nitrates (68-96 mgL^{-1}).

The same behaviour is shown for the isotopic signal of oxygen-18, whose mean value is 1.07‰.

Code	Nature	Latitude (degrees)	Longitude (degrees)	Altitude (m)	Air T (℃)	Depth (m)	Water T (℃)	pH	Conductivity ($mSCm^{-1}$)	Eh (mV)	CO_3^{2-} (mgL^{-1})	HCO_3^- (mgL^{-1})
P1	Well	35.0958	-2.8543	20	29.9	-5.90	19.7	7.83	4.80	150	27.0	720.0
P2	Well	35.0928	-2.8585	20	31.7	-6.46	21.5	7.60	6.54	122	27.0	552.0
P3	Well	35.0978	-2.7693	8	36.5	-3.90	22.5	7.41	7.94	146	24.0	396.0
P4	Well	35.0958	-2.7655	18	37.6	-4.30	21.6	7.43	10.52	153	<0.1	438.0
P5 b	Well	35.0772	-2.8239	25	34.9	-29.00	21.4	7.57	1.744	-8	9.0	327.0
P6 b	Well	35.1152	-2.8957	22	36.8	-3.50	21.5	7.32	8.25	190	6.0	366.0
P7 b	Well	35.1203	-2.9000	20	39.9	-3.30	27.2	7.50	9.06	222	15.0	405.0
P8	Well	35.1305	-2.9350	15	34.5	-2.90	20.1	7.36	4.64	217.	21.0	765.0
P9	Well	35.1632	-2.9189	4	18	-2.50	21.6	7.34	3.91	179.	0.0	543.0
P10	Well	35.0642	-2.9120	75	32.7	-9.00	22.5	7.28	7.28	180.	0.0	465.0
P11	Well	35.1035	-2.8612	22	30.7	-4.60	25.3	7.39	5.45	218	24.0	660.0
P12	Well	35.1024	-2.8624	22	33.5	-5.30	23.7	7.51	4.96	222	<0.1	462.0
P13	Well	35.0995	-2.8627	21	38	-6.00	21.9	7.84	4.01	166	18.0	738.0
P14	Well	35.0944	-2.8531	20	40	-5.60	22.4	7.40	3.81	182	<0.1	645.0
P15	Well	35.0974	-2.7713	10	36.9	-6.40	21.3	7.30	8.53	180	<0.1	483.0
P16	Well	35.1020	-2.8680	21	35.2	-5.60	21.5	7.60	5.01	170	<0.1	636.0
P17	Well	35.0999	-2.8606	20	35.8	-5.00	24.3	7.34	4.21	179	<0.1	642.0
P18	Well	35.1176	-2.9008	22	31	-3.50	20.1	7.73	5.92	205	<0.1	444.0
P19	Well	35.1047	-2.8999	22	34.1	-4.70	24.5	7.26	7.43	207	<0.1	462.0
P20	Well	35.1041	-2.9003	22	39.6	-4.60	22.2	7.21	7.21	186	<0.1	420.0
P21	Well	35.1067	-2.8913	22	38	-1.70	21.8	7.29	6.79	168	<0.1	492.0
P22	Well	35.1044	-2.8864	22	37.2	-3.00	21.8	7.24	6.97	208	<0.1	447.0
P23	Well	35.0976	-2.8743	31	35.2	-6.00	21.4	7.53	4.18	148	<0.1	561.0
P24	Well	35.0927	-2.8782	32	37.5	-7.50	38.2	7.53	4.25	157	21.0	546.0
P25	Well	35.0841	-2.8747	35	40.7	-10.00	21.7	7.70	4.48	156	15.0	420.0
P26	Well	35.0805	-2.8639	38	38	-17.00	22.6	7.59	3.00	204	12.0	447.0
P27	Well	35.0822	-2.9167	50	35.1	-7.00	23.4	7.16	8.17	165	0.0	441.0
P28	Well	35.1018	-2.8523	26	33.6	-3.40	20.6	7.85	5.59	160	30.0	840.0
P29	Well	35.1245	-2.8844	11	39.8	-4.00	22.6	7.38	7.78	167	<0.1	318.0
P30	Well	35.1174	-2.9039	21	40	-5.00	22.1	7.24	6.70	152	21.0	474.0

Table 4. 4. *In situ* measurements of the spring field investigation (June 2010).

Code	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO_4**	**NO_3**	**Br**	**B**	**Sr**	**Li**	**Saturation Index (SI)**				**Na/Cl**	**Ca/Cl**	**SO_4/Cl**
	(mgL^{-1})	**(mgL^{-1})**	**(mgL^{-1})**	**(mgL^{-1})**	**(mgL^{-1})**	**(mgL^{-1})**	**(mgL^{-1})**	**(mgL^{-1})**	**(mgL^{-1})**	**(mgL^{-1})**	**(mgL^{-1})**	**Calcite**	**Dolomite**	**Gypsum**	**Aragonite**	**(ratio)**	**(ratio)**	**(ratio)**
P1	46.2	62.2	745.1	21.3	874	500.2	170	1.46	7.94	1.68	0.09	0.75	1.09	-1.19	0.60	1.31	0.13	0.42
P2	110.2	120.5	1007.2	18.2	1431.6	985.8	31.3	3.54	1.96	1.9	0.09	0.66	1.03	-0.71	0.51	1.08	0.15	0.51
P3	129.8	138.5	1225.4	43.2	2201.2	708.2	44.2	5.14	2.26	2.38	0.09	0.38	0.51	-0.82	0.24	0.86	0.11	0.24
P4	149.2	206.5	1680.2	51.5	2951.2	990.4	54.8	6.73	3.32	3.26	0.15	0.56	0.74	-0.58	0.41	0.88	0.12	0.25
P5 b	41.2	43.1	183.2	15.5	149.9	385	9.50	<0.25	1.49	0.92	0.06	0.13	-0.02	-1.27	-0.02	1.88	0.51	1.90
P6 b	205.4	189.2	1095.4	47.5	2380.2	686.7	53.9	4.21	0.96	4.69	0.16	0.36	0.52	-0.72	0.22	0.71	0.14	0.21
P7 b	189.9	205.1	1205.9	75.9	2525.2	669.6	81.2	4.68	1.42	5.98	0.21	0.71	1.24	-0.68	0.57	0.74	0.14	0.20
P8	91.8	103.4	644.7	33	641.3	762.9	208.2	1.26	2.56	2.02	0.1	0.52	0.71	-0.81	0.37	1.55	0.29	0.88
P9	135.4	70.1	456.8	11.5	605.3	616.4	137.3	1.79	0.86	1.15	0.01	0.23	0.49	-1.03	0.08	1.16	0.20	0.75
P10	190.4	125.1	998.8	26.1	2024.7	590.2	55.6	5.65	1.97	2.45	0.1	0.29	0.53	-0.92	0.14	0.76	0.11	0.22
P11	120.2	115.2	731.8	90.4	1018.3	848.9	75.9	2.47	3.63	2.75	0.13	0.59	1.02	-0.74	0.45	1.11	0.20	0.62
P12	116.3	122	598.8	52.3	1048.6	765.3	43.7	1.85	4.26	2.92	0.16	0.57	0.91	-0.74	0.43	0.88	0.21	0.54
P13	22.6	41.9	653.2	42.1	579.4	599.1	49.8	1.31	5.42	0.78	0.08	0.66	0.80	-1.24	0.51	1.74	0.13	0.76
P14	76.5	78.2	503.2	32.3	575.7	620.1	64.9	1.17	4.17	2.06	0.1	0.43	0.62	-0.96	0.29	1.35	0.24	0.80
P15	193.4	187.2	1135.7	45.2	2301.1	829.2	43.5	5.97	3.33	2.26	0.12	0.45	0.67	-0.65	0.31	0.76	0.14	0.27
P16	79.6	83.2	797.3	25.3	1018.9	703.8	106	2.29	3.6	1.85	0.09	0.60	0.93	-0.94	0.45	1.21	0.14	0.51
P17	102.9	91.6	620.6	24.2	773.8	705.7	50.2	-	2.06	2.15	0.09	0.44	0.74	-0.87	0.30	1.24	0.21	0.67
P18	137.8	98.7	795.1	84.9	1285.8	958.2	69.7	2.33	1.3	6.34	0.15	0.59	1.06	-0.79	0.45	0.95	0.14	0.55
P19	190.7	183.1	976.5	36	2099	657.9	65.5	3.58	1.47	4.28	0.17	0.45	0.73	-0.72	0.31	0.72	0.15	0.23
P20	214.5	185.6	892.4	32.9	2099	555.2	72.9	3.46	0.91	4.39	0.15	0.33	0.50	-0.79	0.19	0.66	0.16	0.20
P21	184.3	154	861.8	38.8	1871.3	559.5	55.2	3.41	1.07	3.55	0.12	0.41	0.65	-0.85	0.26	0.71	0.15	0.22
P22	219.7	177.9	834.2	33.4	1925.9	646.7	63	3.34	1.68	3.88	0.13	0.37	0.59	-0.74	0.22	0.67	0.16	0.25
P23	125.4	92.5	531.9	41.2	809.7	640.4	28.6	1.66	1.03	2.35	0.08	0.54	0.95	-0.91	0.39	1.01	0.20	0.58
P24	129	134.5	461.4	55.8	801.6	723.8	53	1.42	1.49	3.36	0.09	0.95	1.85	-0.65	0.81	0.89	0.30	0.67
P25	61.2	60.7	690.4	13.6	978.6	466.6	72.8	1.99	1.92	1.1	0.07	0.42	0.59	-1.21	0.27	1.09	0.11	0.35
P26	78.7	83.9	356.6	33.8	518.7	425.9	50.7	1.01	3.01	1.54	0.11	0.52	0.79	-1.04	0.38	1.06	0.29	0.61
P27	281.9	166	1035.7	25.8	2401.5	675.9	67.6	4.33	0.89	3.88	0.14	0.25	0.53	-0.79	0.11	0.66	0.12	0.21
P28	33.8	55.8	979	40.8	919.9	782	168.8	1.65	9.6	0.86	0.1	0.78	1.07	-1.08	0.63	1.64	0.11	0.63
P29	189.4	196	496.1	35.7	861.8	1097.2	145.2	1.81	1.55	7.09	0.11	0.44	0.64	-0.42	0.30	0.89	0.40	0.94
P30	175.8	178.8	809.9	127.9	1689.1	814.3	51.5	2.38	1.76	4.58	-	0.40	0.57	-0.63	0.26	0.74	0.19	0.36

Table 4. 5. Chemical composition (mgL^{-1}) of the major and trace elements in Bou-Areg aquifer, and salinity indexes (SI) (Jun 2010). ratios are expressed as molar ratio .

Code	$\delta^{18}O$ (δ‰)	$\delta^{2}H$ (δ‰)	$\delta^{13}C$ (δ‰)	$\delta^{15}N_{\_NO3}$ (δ‰)	$\delta^{18}O_{\_NO3}$ (δ‰)
P1	-5.02	-37.54	-7.71	10.72	9.7
P2	-5.32	-38.23	-5.91	9.41	16.2
P3	-5.21	-36.58	-9.02	5.20	12.8
P4	-5.09	-37.51	-7.83	6.09	14.7
P5 b	-5.49	-41.46	-12.56	4.77	18.2
P6 b	-5.10	-37.64	-6.36	7.61	14.6
P7 b	-4.90	-36.80	-8.00	11.31	11.1
P8	-4.92	-36.96	-14.20	12.06	9.3
P9	-4.74	-33.86	-13.97	12.82	9.9
P10	-5.08	-37.20	-8.78	8.27	10.9
P11	-5.10	-38.48	-8.08	9.71	10.3
P12	-4.90	-38.70	-9.91	6.08	10.9
P13	-5.30	-38.77	-5.79	8.51	9.4
P14	-5.01	-35.89	-10.52	8.35	9.5
P15	-5.12	-36.52	-9.61	6.49	10.6
P16	-5.25	-37.50	-6.49	8.37	7.6
P17	-5.25	-37.97	-6.85	6.28	12.4
P18	-4.57	-32.82	-10.88	6.33	10.1
P19	-5.20	-37.32	-6.67	7.85	10.4
P20	-5.19	-37.39	-5.46	7.99	9.7
P21	-5.11	-35.49	-5.31	6.84	10.8
P22	-5.13	-36.42	-6.27	5.49	10.9
P23	-5.47	-39.13	-8.63	7.60	12.7
P24	-5.03	-36.62	-11.22	5.16	11.1
P25	-5.26	-38.25	-7.67	4.13	11.0
P26	-5.11	-36.52	-9.24	4.39	10.3
P27	-5.15	-33.96	-5.21	8.27	12.3
P28	-5.07	-36.10	-9.64	10.35	8.7
P29	-4.77	-34.01	-12.38	5.83	7.9
P30	-4.98	-35.48	-10.74	11.81	9.7

Table 4. 6. Isotopic composition (δ‰) of groundwater in the Bou-Areg plain (June 2010).

Code	Station name	Nature	Latitude (degrees)	Longitude (degrees)	Air T (℃)	Water T (℃)	pH	Conductivity (mSCm-1)	D.O. (mgL-1)	Eh (mV)	CO_3^{2-} (mgL^{-1})	HCO_3 (mgL^{-1})
L1		Lagoon	35.1964	-2.8834	34.7	27.6	8.25	55.00	7.54	190	<0.1	176.9
L2		Spring	35.2000	-2.9198	-	24.7	7.84	7.94	7.09	182	<0.1	387.4
L3		Lagoon	35.2057	-2.9072	33.3	27.1	8.35	55.30	7.95	178	<0.1	204.4
L4		Lagoon	35.2195	-2.9086	33.0	26.7	8.39	55.50	7.97	163	<0.1	186.1
L5		Lagoon	35.2477	-2.9276	32.4	27.0	8.40	55.70	7.80	163	<0.1	180.0
L6	*Oued* Tirakaa	Lagoon	35.1944	-2.9250	32.1	27.6	8.47	55.10	8.15	165	<0.1	176.9
L7	Sidi Ali	Lagoon	35.1879	-2.9242	31.9	27.1	8.50	55.10	8.20	158	<0.1	180.0
L8	*Oued* Bousardun	Lagoon	35.1664	-2.9048	31.0	26.1	8.41	55.50	8.00	174	<0.1	176.9
L9	STEP	Lagoon	35.1536	-2.9011	31.7	26.0	8.30	55.00	7.59	149	<0.1	186.1
L10	Oued Selouane	Lagoon	35.1360	-2.8817	31.7	25.6	8.26	54.90	8.24	138	<0.1	186.1
L11	Canal d'irrigation	Lagoon	35.1289	-2.8683	30.9	25.4	8.25	54.90	8.46	125	<0.1	183.0
L12	Delta BouAreg	Lagoon	35.1272	-2.8586	30.6	25.3	8.31	55.10	8.50	138	<0.1	180.0
L13		Lagoon	35.1194	-2.8461	29.7	25.1	8.25	55.10	8.50	134	<0.1	173.9
L14		Lagoon	35.1286	-2.8412	29.2	25.3	8.18	55.20	8.60	153	<0.1	176.9
L15		Lagoon	35.1540	-2.8631	28.6	25.2	8.20	55.20	8.59	120	<0.1	176.9
L16		Lagoon	35.1758	-2.8842	28.2	25.9	8.16	55.30	8.28	90	<0.1	173.9
L17		Lagoon	35.1924	-2.9112	29.2	27.3	8.18	55.30	7.70	96	<0.1	176.9
L18	Port Sidi Ali	Lagoon	35.1855	-2.9244	30.1	30.4	8.11	49.70	7.71	123	<0.1	216.6
L19		Spring	35.1866	-2.9249	32.6	25.0	7.50	15.66	7.90	150	<0.1	372.1
L20	Bokana	Inlet	35.1940	-2.8451	30.5	30.5	8.17	55.10	7.80	131	<0.1	173.9
Mean			-	-	31.0	26.7	8.30	54.90	8.08	143.8	-	182.49
Standard deviation			-	-	1.7	1.6	0.10	1.31	0.35	27.0	-	11.13

Table 4. 7. Physicochemical parameters for the Lagoon of Nador (field investigation June 2010). Mean and standard deviations are calculated for all the sampling sites without considering the two springs (L2 and L19).

Code	Ca	Mg	Na	K	Cl	SO_4	NO_3	Br	B	Sr	Li	Saturation Index				Na/Cl	Ca/Cl	SO_4/Cl
	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	Calcite	Dolomite	Gypsum	Aragonite	(ratio)	(ratio)	(ratio)
L1	1100.1	265.7	11002.8	304.8	19196.1	2476.0	0.0	73.10	3.99	7.09	0.14	1.60	2.49	0.16	1.46	0.88	0.10	0.095
L2	191.5	75.8	1185.9	52.7	2141.4	324.2	68.4	8.05	0.71	1.09	0.02	1.00	1.41	-0.97	0.86	0.85	0.16	0.112
L3	1135.2	334.0	10745.7	388.5	19173.4	2468.3	0.0	64.61	-	-	-	1.77	2.90	0.17	1.63	0.86	0.10	0.095
L4	1149.9	365.3	10733.4	427.3	19126.8	2466.0	0.0	67.23	-	-	-	1.77	2.92	0.17	1.63	0.87	0.11	0.095
L5	1199.9	375.2	10664.2	461.8	19246.1	2486.6	0.0	67.92	-	-	-	1.79	2.96	0.19	1.64	0.85	0.11	0.095
L6	1260.4	404.3	10962.3	504.4	19193.9	2489.0	0.0	64.36	4.00	7.02	0.13	1.88	3.17	0.21	1.74	0.88	0.12	0.096
L7	1198.1	401.8	10879.0	477.8	19566.0	2552.1	0.0	64.66	4.00	6.99	0.13	1.89	3.19	0.20	1.74	0.86	0.11	0.096
L8	1332.7	428.8	10803.0	529.1	19221.5	2494.8	0.0	63.28	-	-	-	1.82	3.02	0.23	1.67	0.87	0.12	0.096
L9	1311.1	422.8	10923.5	525.4	18746.9	2439.7	0.0	66.23	3.96	6.92	0.14	1.72	2.83	0.21	1.58	0.90	0.12	0.096
L10	1342.8	435.1	10933.2	533.1	18620.0	2398.0	0.0	63.61	-	-	-	1.68	2.75	0.21	1.54	0.91	0.13	0.095
L11	1397.9	516.1	11019.2	553.4	19092.1	2475.9	0.0	71.686	-	-	-	1.68	2.79	0.24	1.54	0.89	0.13	0.096
L12	1398.5	470.2	11057.2	554.2	19125.0	2493.0	0.0	65.39	-	-	-	1.73	2.85	0.24	1.59	0.89	0.13	0.096
L13	1371.7	455.1	10508.7	543.1	19378.8	2451.7	0.0	66.01	-	-	-	1.64	2.67	0.23	1.50	0.84	0.13	0.093
L14	1460.0	493.0	11358.4	581.3	19209.6	2481.0	0.0	61.29	-	-	-	1.61	2.62	0.25	1.47	0.91	0.13	0.095
L15	1477.6	501.1	11448.3	585.0	19253.7	2512.1	0.0	68.777	-	-	-	1.63	2.66	0.26	1.49	0.92	0.14	0.096
L16	1520.0	568.1	11532.5	594.1	19269.0	2498.0	0.0	71.518	4.03	7.00	0.13	1.61	2.67	0.27	1.47	0.92	0.14	0.096
L17	1510.2	506.7	11649.2	598.1	19343.7	2520.3	0.0	69.395	3.93	6.85	0.13	1.66	2.74	0.28	1.52	0.93	0.14	0.096
L18	1369.0	550.0	9728.0	485.7	16461.0	2082.5	0.0	57.376	3.07	5.79	0.07	1.70	2.94	0.21	1.56	0.91	0.15	0.093
L19	486.7	318.1	2760.9	104.5	4834.4	696.5	96.5	19.378	0.8	2.32	0.05	0.92	1.48	-0.47	0.78	0.88	0.18	0.106
L20	1567.2	578.2	11880.9	607.5	19593.9	2569.2	0.0	71.473	3.89	6.92	0.12	1.71	2.94	0.32	1.57	0.93	0.14	0.097
M	1339.03	448.41	10990.5	514.14	19045.4	2464.12	-	73.10	3.86	6.82	0.12	-	-	-	-	-	-	-
STD	140.91	83.61	484.20	79.88	685.53	102.79	-	8.05	0.32	0.42	0.02	-	-	-	-	-	-	-

Table 4. 8. Chemical composition (mgL^{-1}) of the major and trace elements in Bou-Areg aquifer, and salinity indexes (SI) (Jun 2010). ratios are expressed as Molar ratio. M=mean; STD= Standard Deviation. Mean and standard deviations are calculated for all the sampling sites without considering the two springs (L2 and L19).

Code	**$\delta^{18}O$** **(δ‰)**	**$\delta^{2}H$** **(δ‰)**	**$\delta^{13}C$** **(δ‰)**	**$\delta^{15}N_{\_NO3}$** **(δ‰)**	**$\delta^{18}O_{\_NO3}$** **(δ‰)**
L1	1.14	7.58	-0.88	-	-
L2	-4.59	-27.76	-13.35	11.38	12.7
L3	1.13	7.62	-	-	-
L4	1.18	7.93	-	-	-
L5	1.29	6.65	-	-	-
L6	1.19	6.68	-1.27	-	-
L7	1.16	6.01	-1.47	-	-
L8	1.13	6.94	-	-	-
L9	1.16	7.21	-1.84	-	-
L10	1.15	6.01	-	-	-
L11	1.16	7.20	-	-	-
L12	1.13	6.43	-	-	-
L13	1.12	7.04	-	-	-
L14	1.14	7.10	-	-	-
L15	1.12	7.27	-	-	-
L16	1.20	6.55	-0.48	-	-
L17	1.16	7.91	-0.36	-	-
L18	-0.31	-3.29	-6.84	-	-
L19	-4.79	-31.50	-13.85	12.90	12.7
L20	1.08	6.61	0.11	-	-
Mean	1.07	6.41	-	-	-
STD	0.35	2.49	-	-	-

Table 4. 9. Isotopic composition (δ‰) of groundwater in the Nador Lagoon (June 2010). Mean and standard deviations are calculated for all the sampling sites without considering the two springs (L2 and L19).

4.3. Fall campaign: November 2010

4.3.1 The Bou-Areg Aquifer and *oued* Selouane

Water temperature varies between 18 ℃ and 27 ℃, w ith values relatively higher with respect to the prevoous fall campaign (November 2009), but with the same average of 20.5 ℃ (Table 4.10).
Values for pH are confirming the neutral or slight alkaline nature of Bou-Areg groundwater with values ranging from 7.1 to 8 and a mean of 7.5 (if we exclude the value of 3. 01 for well 26, thet hase to be verified as a possible bias).
Electrical conductivity suggests the presence of exceedingly mineralized waters, with an average of 6,081 μS/cm, and a maximum of 10,066 μS/cm in well 32 (well 5b is always the least mineralized).
Redox potential values are positive for all the samples but well 5b (-176 mV) and if we exclude this Eh average for the Bou-Areg aquifer is about 1163 mV.
As concerns the physico chemical parametersfor the *oued* Selouane (Table 4.11), the mean temperature is 18.6 ℃, again reflecting air temperature and sl ichtly changing according to the different altitude, as only surface samples have been collected. o*ued* water have a alkaline pH, with mean value of 8.2, while the conductivity is again quite high (mean of 10,080 μS/cm), especially if compared to the sample collected in the irrigation channel (1,342 μS/cm).

Hydrochemical data for this campaign are not yet available; therefore, only physicochemical parameters are shown. Nevertheless, as this work is part of an ongoing project, all the data for this campaign will be used (together with the one that will be obtained in Spring 2011) to support the proposed interpretation on processes occurring in the Bou-Areg plain and in the lagoon of Nador.

Code	Nature	Latitude (degrees)	Longitude (degrees)	Altitude (m)	Depth (m)	Water T (°C)	pH	Conductivity (mSCm^{-1})	Eh (mV)
P3	Well	35.09783	-2.76933	8	-3.90	20.7	7.53	6.56	166.0
P4	Well	35.09577	-2.76550	18	-4.78	19.8	7.16	10.50	153.0
P5	Well	35.08370	-2.78712	40	-30.43	21.0	7.95	3.81	178.0
P6	Well	35.08890	-2.85054	35	-12.63	20.1	7.70	5.35	171.0
P7	Well	35.10700	-2.86745	30	-4.02	20.3	7.29	4.25	205.0
P5 b	Well	35.07713	-2.82385	25	-28.30	20.5	7.71	1.78	-176.0
P7 b	Well	35.12025	-2.90003	20	-3.07	18.0	7.60	9.09	260.0
P8 b	Well	35.13220	-2.92755	13	-3.30	20.8	7.56	5.58	188.0
P9 b	Well	35.15725	-2.91297	4	-1.00	20.0	7.51	4.96	161.0
P12	Well	35.10247	-2.86238	22	-4.42	20.4	7.45	4.96	182.0
P18	Well	35.11760	-2.90086	22	-3.84	19.8	7.61	6.72	172.0
P19	Well	35.10484	-2.89997	22	-5.17	20.6	7.76	6.73	182.0
P22	Well	35.10424	-2.88635	22	-3.46	20.0	7.24	7.26	193.0
P24	Well	35.09267	-2.87826	32	-8.11	20.8	7.74	4.35	180.0
P26	Well	35.08053	-2.86392	38	-16.28	21.3	3.01	3.09	182.0
P27	Well	35.08223	-2.91675	50	-7.67	20.7	7.12	7.99	200.0
P28	Well	35.10177	-2.85235	26	-4.00	20.4	7.92	5.39	185.0
P29	Well	35.12428	-2.88252	11	-2.37	18.8	7.36	6.64	220.0
P31	Well	35.05371	-2.76484	70	-175.00	27.6	7.18	6.67	83.0
P32	Well	35.09961	-2.82249	13	-6.00	19.7	7.40	10.66	51.0
P33	Well	35.09566	-2.78947	20	-13.16	18.1	8.04	5.82	115.0
P34	Well	35.09221	-2.91765	30	-3.80	19.8	7.49	7.80	180.0
P35	Well	35.07545	-2.89752	50	-7.28	20.5	7.38	6.32	186.0
P36	Well	35.11578	-2.92398	40	-8.05	20.5	7.68	5.28	197.0
P37	Well	35.12702	-2.90614	16	-2.15	19.2	7.49	8.70	192.0
P38	Well	35.15414	-2.94380	16	-2.00	22.4	7.26	3.49	199.0
P39	Well	35.14675	-2.95921	36	-8.40	21.1	7.45	4.43	196.0

Table 4. 10. *In situ* measurements of the November 2010 field investigation for the Bou-Areg groundwater.

Code	Nature	Latitude (degrees)	Longitude (degrees)	Altitude (m)	Water T (℃)	pH	Conductivity (mSCm^{-1})	Eh (mV)
S1	River	35.12062	-2.89076	12.00	21.30	8.46	9.91	128
S2	River	35.10112	-2.9108	26.00	20.60	8.36	9.94	112
S3	River	35.06458	-2.94224	101.00	18.10	7.78	10.39	166
C1	Irrigation channel	35.07685	-2.9233	53.00	18.60	8.11	1.34	111

Table 4. 11. *In situ* measurements of the November 2010 field investigation for the *oued* Selouane (S-) and Irrigation channel (C1).

Code	Nature	Latitude (degrees)	Longitude (degrees)	Altitude (m)	Water T (℃)	pH	Conductivity (mSCm^{-1})	Eh (mV)
L19	Lagoon-Spring	35.18664	-2.92497	5.00	17.9	7.90	55.1	136
L21	Lagoon	35.16463	-2.9109	5.00	17.7	7.87	41.5	113
L22	Lagoon	35.17918	-2.92133	5.00	17.8	7.87	58.1	117

Table 4. 12. *In situ* measurements of the November 2010 field investigation for three lagoon sites.

5. Discussion: the Bou-Areg Aquifer

5.1. Groundwater classification

Piper trilinear diagram (Figure 5.1) show that Bou-Areg aquifer waters are mostly classified as

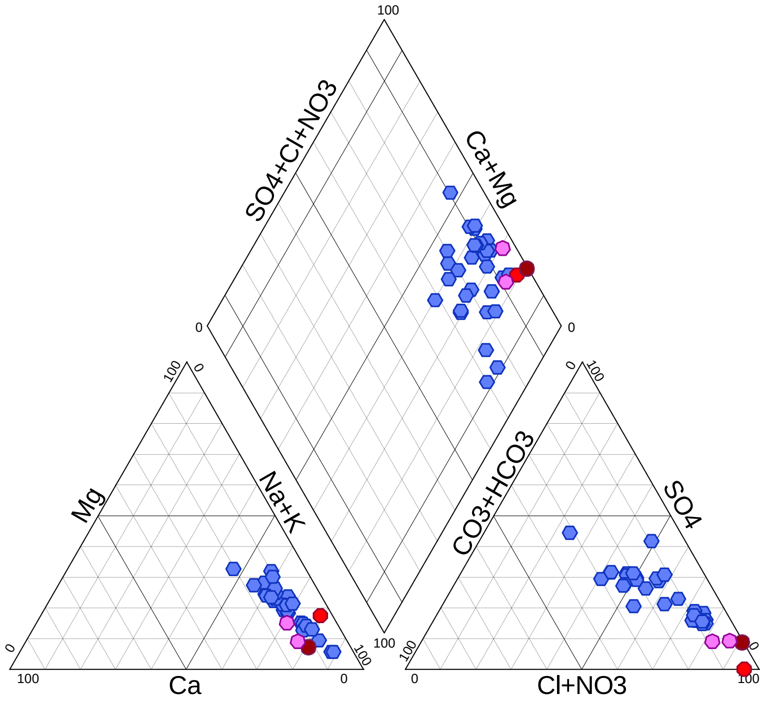


Figure 5. 1. Piper tirilinear diagram. Blue dots represent June 2010 data for the Bou-Areg plain. Red dots represent Sea Water, dark red dot represents L20 (Bokana), pink dots represent L2 and L19 (springs).

Stability diagram of dissolved species (N-O-H) show that the samples lie in the range of aqueous N (Figure 5.2 A). Few samples are in the metastable NO_3, while most of them appear to be in denitrification phase. Isotope analysis of dissolved nitrates presented in the last paragraph will be applied to support the possible occurrence of denitrification processes in the aquifer;

Considering the diagram S-O-H, (Figure 5.3 B), all the samples appear to be in the SO_4.phase.

It must be noticed that well 5b shows a different behaviour if compared to the other wells, suggesting a possible different recharge origin.

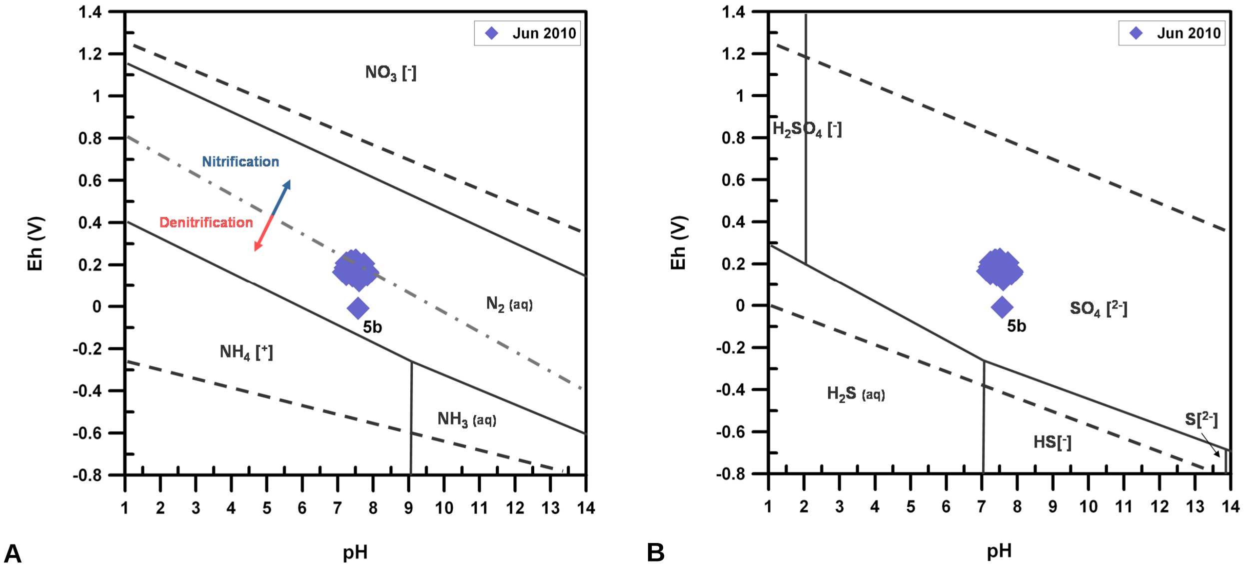


Figure 5. 2. Stability diagrams of dissolved species: (A) N-O-H and (B) S-O-H, for the data of the spring campaign. Modif. from atlas Eh-ph.

Given this preliminary classification, data of the two sampling campaigns, described in the previous chapter were used to:

i. Trace groundwater recharge;
ii. Define the origin of water salinity, either natural or human induced;
iii. Define and quantify human induced pollution.

5.2. Tracing groundwater recharge

In order to define the main sources of recharge, $\delta^{18}O$ and $\delta^{2}H$ values for groundwater sampled in the Bou-Areg plain, were plotted and compared with the Global Meteoric Water Line (Figure 5. 4 A; GMWL: $\delta^{2}H= 8.17\ \delta^{18}O+10.35$; Rozanski *et al*., 1993;). In addition, data were also compared with the composition of local precipitation, to better identify the isotopic signal of water entering into the underground system. Due to the absence of information on isotopic fingerprint of local precipitation, data were compared with the dataset of the nearest meteoric station. As the main rain sources in the sampling area are Atlantic driven precipitations, the chosen Local Meteoric Water Line (LMWL) was the one provided by Ouda *et al*. (2005; $\delta^{2}H= 8\ \delta^{18}O+13.7$).

Figure 5.3 shows that for both the surveys groundwater in the Bou-Areg aquifer plot below the GMWL, suggesting the occurrence of evaporation prior to recharge

Deviations from the GMWL, with an average slope of 6.72 in June 2010, also supports the occurrence of evaporative processes with high relative humidity (Gonfiantini, 1986) and mixing with external saline sources. Higher oxygen-18 values, compared with the reference ones for precipitation, corresponds to isotopic enrichment in $H_2{}^{18}O$ in the liquid phase, therefore evaporation of the lighter isotope (^{16}O).

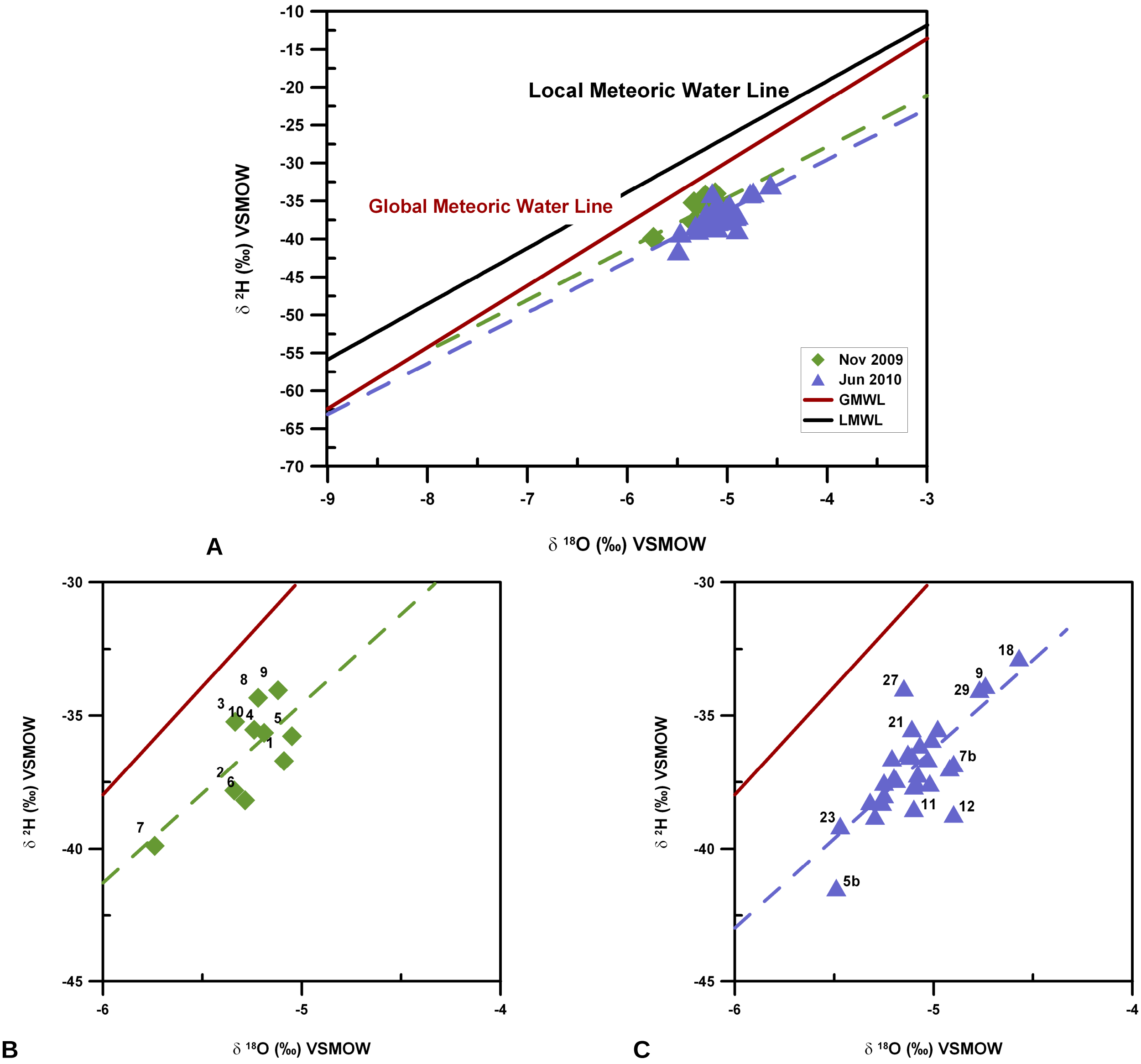


Figure 5. 3. Delta Deuterium and oxygen-18 variations in groundwater from the Bou-Areg coastal plain.

Dashed green line = Fit linear data NOV 2009, equation: $\delta^2H = 6.72\ \delta^{18}O - 0.95$;

Dashed blue line = Fit linear data JUN 2010, equation: $\delta^2H = 6.71\ \delta^{18}O - 2.7$;

Ruby red line = Global Meteoric Water (GMWL), $\delta^2H = 8.17\ \delta^{18}O + 10.35$ ‰ VSMOW (Rozanski *et al.*, 1993);

Black line = Local Meteoric Water Line (LMWL), $\delta^2H = 7.34\ \delta^{18}O + 10.19$ ‰ VSMOW (Ouda *et al.*, 2005).

The deviation even from the LMWL (Ouda *et al.*, 2005) therefore support the evaporative loss of the aquifer (Clark and Fritz, 1997) and possible continental contribution.

To sustain the latter assumption, the isotopic signal of groundwater samples (June 2010 Bou-Areg: $\delta^2H = 6.71\ \delta^{18}O - 2.7$) was compared with the one of the closest freshwater body with available data: Tafna river basin in central Algeria (from the underground source to the sea estuary; $\delta^2H = 6.18\ \delta^{18}O - 2.36$; Lambs and Labiod, 2009). As one can see, the two lines have quite close slope, confirming that runoff flowing from the Atlas chain to the North West and the runoff from the mountains, flowing toward S-E direction, are possible sources of natural recharge for the Bou-Areg aquifer (Chaouni *et al*., 1999).

In addition to local recharge water, mixing with external saline sources as well as surface evaporation may potentially modify the stable isotope composition of the investigated water (Bouchaou *et al*., 2008). In those cases $\delta^{18}O$ and $\delta^{2}H$ values would deviate from GMWL and LMWL slopes, towards elevated $\delta^{18}O$ and $\delta^{2}H$ values (and lower $\delta^{18}O/\delta^{2}H$ slope), as in Bou-Areg aquifer (Figure 5.3).

By comparing $\delta^{18}O$ values with chloride and nitrate concentrations in groundwater samples one can see that some waters having high chloride (>1000 mgL^{-1}) and nitrate (>50 mgL^{-1}) concentrations are associated with relatively high $\delta^{18}O$ values (Figure 5.4). This association might suggest that agricultural return flow can be another important recharge source in the aquifer (Ahkouk *et al*., 2003; Bouchaou *et al*., 2008). On the other hand, wells with relatively high oxygen-18 values and low chloride concentrations might be associated to a mixing with an already evaporated solution (e.g. the irrigation channel water).

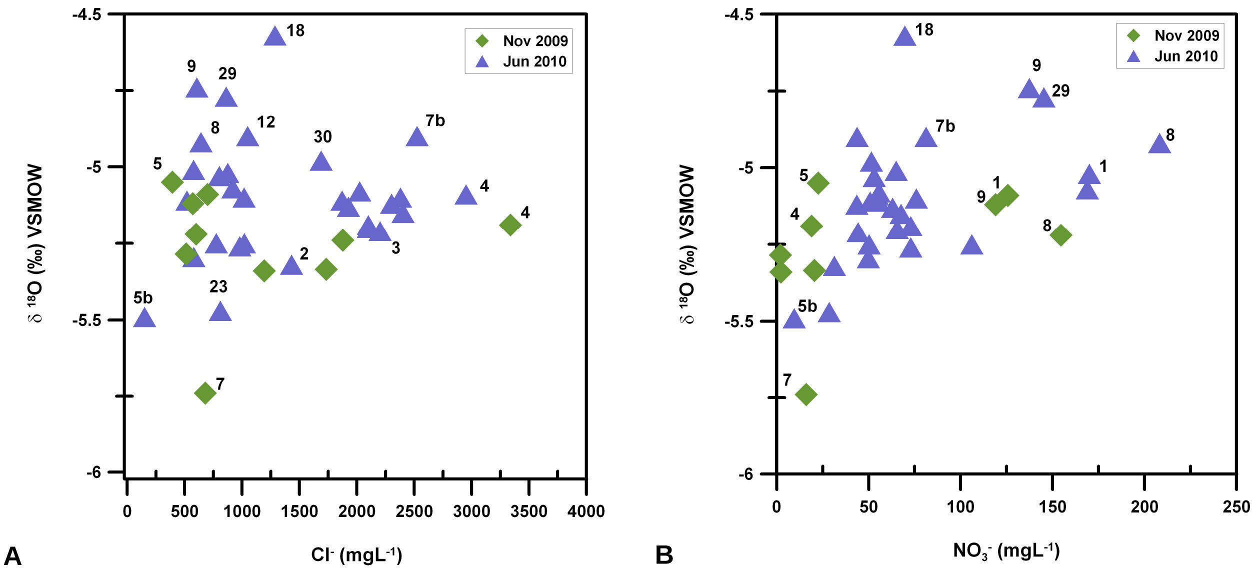


Figure 5. 4. Variations of $\delta^{18}O$ values (‰) versus chloride (A) and nitrate (B) concentrations.

Wells 5 and 5b, although showing a different chemical composition are considered the isotopic signal of deep recharge, given the depth of the wells and the location at the limit of the irrigated area. Those two wells are also the most reductant (with well 5b also having the most negative values of oxygen-18), representative of the deep recharge coming from the peripheral areas of the system, and not affected by human pollution or water-rock interaction with the carbonate system. In addition, the wells are separated to the whole system by a flexure, parallel to the lagoon (Figure 1.6), acting as hydraulic barrier, thus limiting the exchanges with the whole system. Hence, those wells can be assumed to belong to a confined system, close to the atmosphere. Well 26 (Figure 5.5) can represent a possible mixing point between deep freshwater and more saline shallow waters.

As previously explained the aquifer is assumed to be mainly recharged by mountain runoff, therefore its composition is possibly influenced by water rock interaction and other sources of salinization.

Plots of dissolved species versus wells' depth (Figure 5.5) allowed to point out the occurrence of other phenomena in the downstream zone.

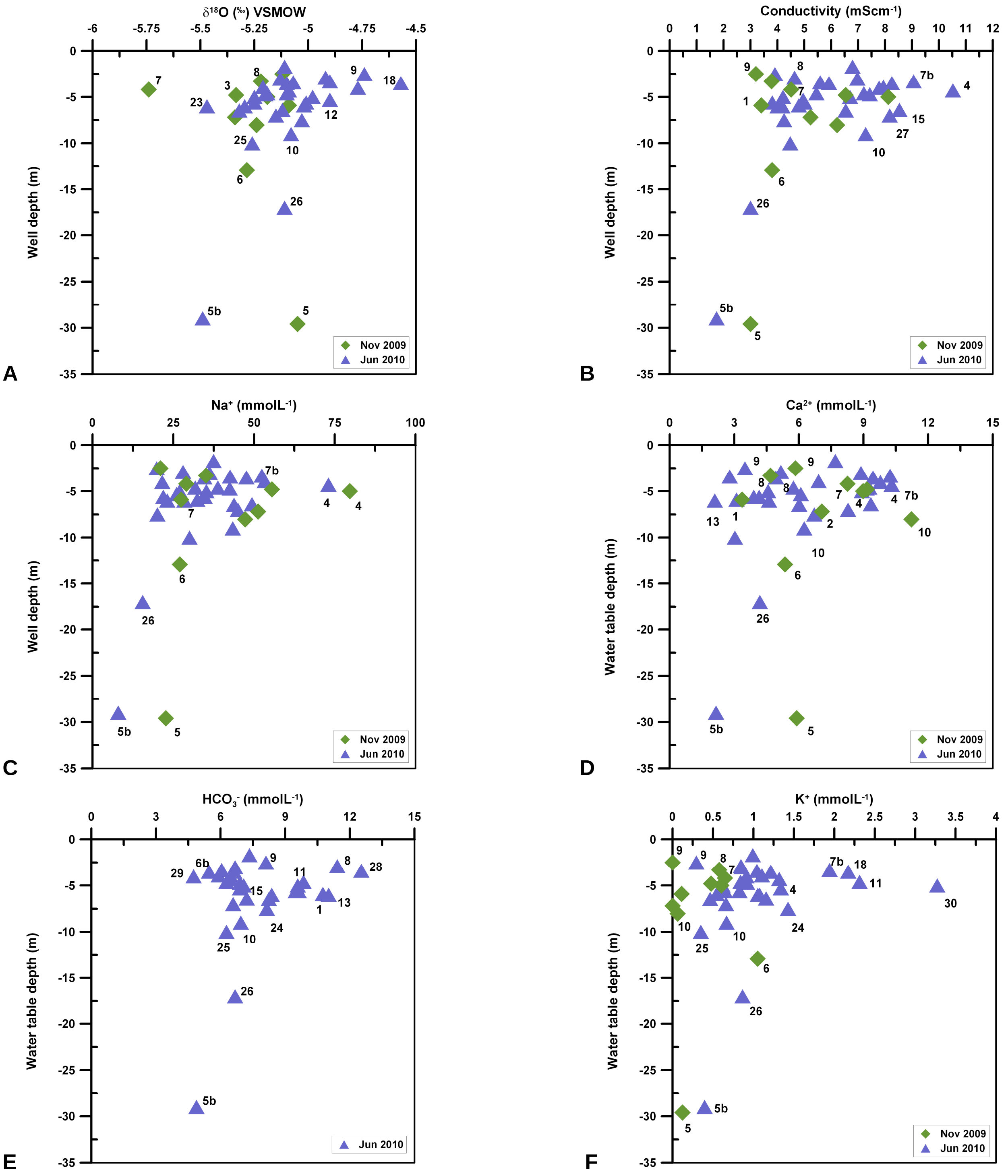


Figure 5. 5. Well depth variation in the Bou-Areg aquifer versus (A) δ^{18}O; (B) Conductivity; (C) sodium; (D) calcium; (E) magnesium and (F) potassium.

Well 7b, 18 and 30 are all located in the left bank of the *oued* Selouane and quite close to each other. Welll 30 is the deepest among the three, showing a more negative oxygen-18 signal (-4.98‰). On the other hand well 7b has high EC (9.1 mScm^{-1}), chloride concentration (2,525.2 mgL^{-1}) and oxygen-18 signal of -4.94‰ (Figure 5.5 A and B), while well 18 has the most enriched signal for both deuterium and oxygen-18. These discrepancies can be associated to different local recharge processes possibly interacting with the common effect of agricultural inputs, explaining their high potassium concentrations (Figure 5.5 F). For example, due to its isotopic composition, well 7b might be a sub-alveo, laterally recharged by the *oued* which is interacting with the inputs of agricultural return flows. For the November 2010 campaign the high Electrical Conductivity of this well (9.1 mScm^{-1}) is confirmed, and reflects the one of the closest sampled station in the *oued* Selouane (S1 9.9 mScm^{-1}). Geochemical results for this campaign will be used to support this theory.

High alkalinity values for most of the wells (Figure 5.5 E) might reflect elevated concentrations of Dissolved Inorganic Carbon in the aquifer, typical of open system conditions.

Therefore, based on the preliminary chemical and isotopic investigation, we can assume that in the plain there are two kind of waters: deep freshwater separated from the whole system and water recharged by mountain runoff that are interacting with different saline sources of local recharge, creating complex interactions between diluted waters mainly, under open system conditions (Figure. 5.6).

Results on the chemical composition of the irrigation channel (November 2010) will allow to identify end-members for mixing processes and to possibly discriminate among the different sources of recharge within the aquifer.

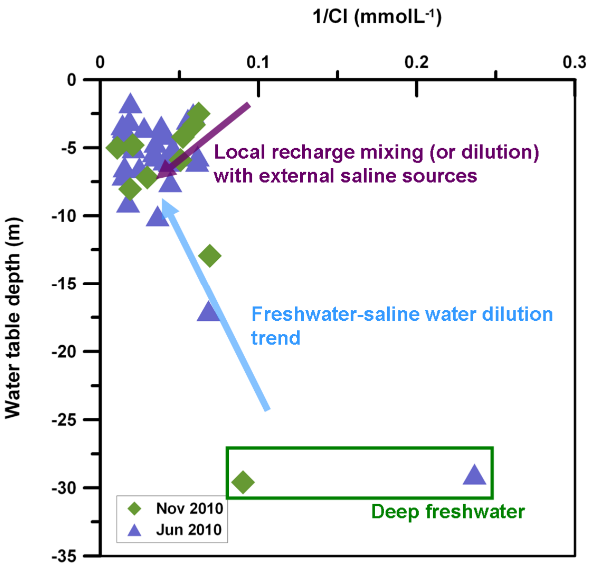


Figure 5. 6. Schema of processes occurring in the Bou-Areg aquifer. Arrows are indicating general trends and their slope does not any mathematical meaning.

5.3. The origin of groundwater salinity

Salinization of underground resources and soils is e a problem of particular relevance in coastal areas, especially in arid and semi-arid regions (Rosenthal *et al*., 1992; Mas-Pla *et al*., 1999; Sanchez-Martos *et al*., 2002; Faye *et al*., 2005; Di Sipio *et al*., 2006; Panno *et al*., 2006; Bouchaou *et al*., 2008; Lenahan *et al*., 2010; Re *et al*., 2011). Groundwater salinity is determined by the Total Dissolved Solids (TDS; Bouchaou *et al*., 2008); however water mineralization can be also pointed out considering its Electrical Conductivity (EC), that, when correlated with TDS measurements, provides an approximate value for TDS concentrations usually within 10% accuracy. Therefore, for the purpose of this study, EC was used as a proxy for mineralization processes.

Based on Handa (1969) waters have been first classified according to their Electrical Conductivity (Table 5.1) to obtain the Salinity Index (Ravikumar *et al*., 2010), that gives preliminary characterization on the suitability of water samples for agricultural proposes. This Salinity Index can also define the salinity hazard or total concentration of soluble/dissolved salts computed by measured EC values that could give a first proxy of groundwater salinization in the aquifer.

None of the samples collected in the November field investigation can be classified as freshwater (<1000 µScm^{-1}), therefore all the groundwater are considered as mineral waters (Civita, 2005).

Electrical Conductivity (µScm^{-1})	Water Salinity	November 2009	June 2010
0-250	Low	-	
251-750	Mediium	-	
751-2,250	**High**	**Tap**	
2,251-6,000	**Very high**	**1**, **2**, 5, 6, 7, **8**, **9**	**1**, **8**, **9**, 11, 12, 13 14 , 16, 17, 23, 24, 25, 26, 28
6,001-10,000	**Extensively high**	**3**, **4**, **10**	**2**, **3**, 6b, 7b, **10**, 15, 18,19, 20, 21, 22, 27, 29, 30
10,001-20,000	Brines weak concentration	-	**4**
20,001-50,000	Brines moderate concentration	-	
50,001-100,000	Brines high concentration	-	
> 100,001	Brines extremely high concentration	-	

Table 5. 1. Classification of groundwater based on their Electrical conductivity and ranges proposed by Handa (1969).

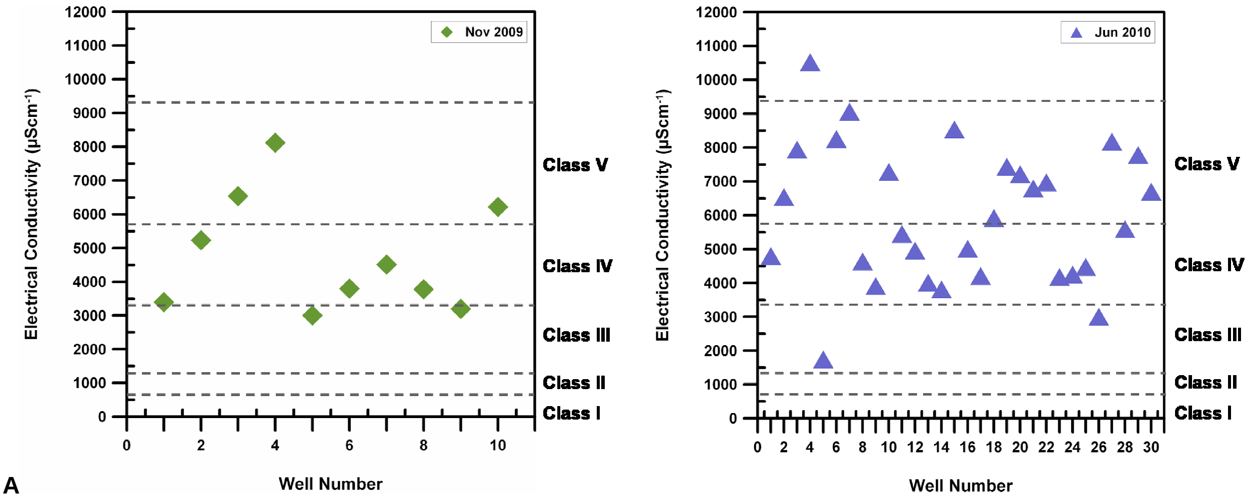


Figure 5. 7. Salinity Index (based on Ravikumar *et al*., 2010) for groundwater samples in the Bou-Areg Aquifer: (A) November 2009 and (B) June 2010).

In particular, no sample shows a Salinity Index compatible with water suitable for agriculture and irrigation purposes (class I and II). Well number 5 (November 2009; EC= 3,000 μScm-1) as well as P5b and P26 can be considered to belong to class III, which refers to waters usually suitable for irrigating the medium and high salt-tolerant crops. Highly saline waters (class IV: 1, 6, 7, 8, 9 for the November campaign; 1, 8, 9, 11, 12, 13 14, 16, 17, 23, 24, 25, 26, 28) are suitable for irrigating high salt-tolerant crops, while waters in salinity class V (i.e. 2, 3, 10 for the November campaign and 2, 3, 10, 15, 18, 19, 20, 21, 22, 27, 29, 30), or above (well 4), are generally unsuitable for irrigation. Therefore, if we consider this classification, only few of the sampled wells can provide waters suitable for irrigation.

Moreover, it is important to stress the increase of salinity for all the wells from June to November (Figure 5.7), that could be associated to an increase in leaching in the unsaturated zone, thus recharging the underground system with more dissolved salts (Allison *et al*., 1994). In fact the remobilization of salts from the unsaturated zone is a phenomenon of particular relevance in arid zones after heavy rains episodes, allowing for a more rapid and strong infiltration.

Once stated that the aquifer is characterized by high salinization levels, it is important to establish if these conditions are related to natural characteristics of the system, or these are resulting from human activities, such as excessive exploitation thus inducing, in coastal zones, to saline water intrusion (Custodio, 2002; Edmunds, 2003; Faye *et al*., 2005; Vengosh, 2003).

Natural salinization can be related either from the influence of marly gypsum-bearing terrains or it can be associated to marine aerosols. In particular marine sprays (either transported as liquid drops or evaporated materials) and airborne marine salts can contribute to the base cation content in coastal soils (Art *et al*., 1974; Whipkey *et al*., 2001). Water evaporation surfaces, as a ponds, lakes or, as in the case of the Bou Areg plain irrigation channel, could also yield saline waters that might enter the ground, possibly favoured by the increased water density (Custodio, 2004). Besides, irrigation return flows can alter natural groundwater salinity (Llamas and Custodio, 2003).

In the plot of Na^+ concentration versus Cl^- concentration (Figure 5.8 A) one can observe that almost all the samples have quite high values for both the ions, confirming the salinization processes affecting the aquifer. The chemical composition of the salts in groundwater is slightly different from seawater's one, due to differences in the hydrochemical processes occurring in those systems. This explains why most of the samples plot above the freshwater-seawater dilution line (while 5b, 7b, 9, 10, 20, 21, 22, 27, 30 plot below it). Only few samples (3, 4, 12, 24 and 29) have a composition coherent with the progressive dilution with seawater, thus suggesting the possible existence of old seawater intrusion or presence of connate water (Chaouni *et al*., 1997; El Yaouti *et al*., 2009) interacting with the recent recharge in this sector of the aquifer.

In the plot of Na/Cl molar ratio versus chlorine (Figure 5.8 B), the same enrichment in Na^+ relative to Cl^- is observed. This enrichment could indicate water-aquifer interaction, and cation exchange reactions between the silicates fractions of the aquifer and groundwater rich in dissolved calcium; therefore in first approximation we could assume that the circulation is slow, facilitating the exchange with silicates, with liberation of Na^+ (El Yaouti *et al*., 2009) and a possible associated decrease in Ca^{2+}.

By plotting calcium versus chlorine, (Figure 5.8 C) an excess in Ca^{2+}, with respect to the seawater dilution trend, is observed, suggesting the occurrence of carbonates or gypsum dissolution. Moreover, lithium and strontium (Figure 5.11 C and D) have a good correlation with calcium thus confirming the probable occurrence of carbonates minerals dissolution.

This can occur when rainwater or irrigation water entering into the aquifer dissolve carbonates rocks, and explain the high HCO$_3^-$ concentrations throughout the aquifer (ranging from 318 to 840 mgL^{-1}).

The highest value of Ca/Cl molar ratio for well 10 (Figure 5.8 D) might be representative of its origin, therefore associated to its baseline conditions, as this well is located in the confining Gareb Plain.

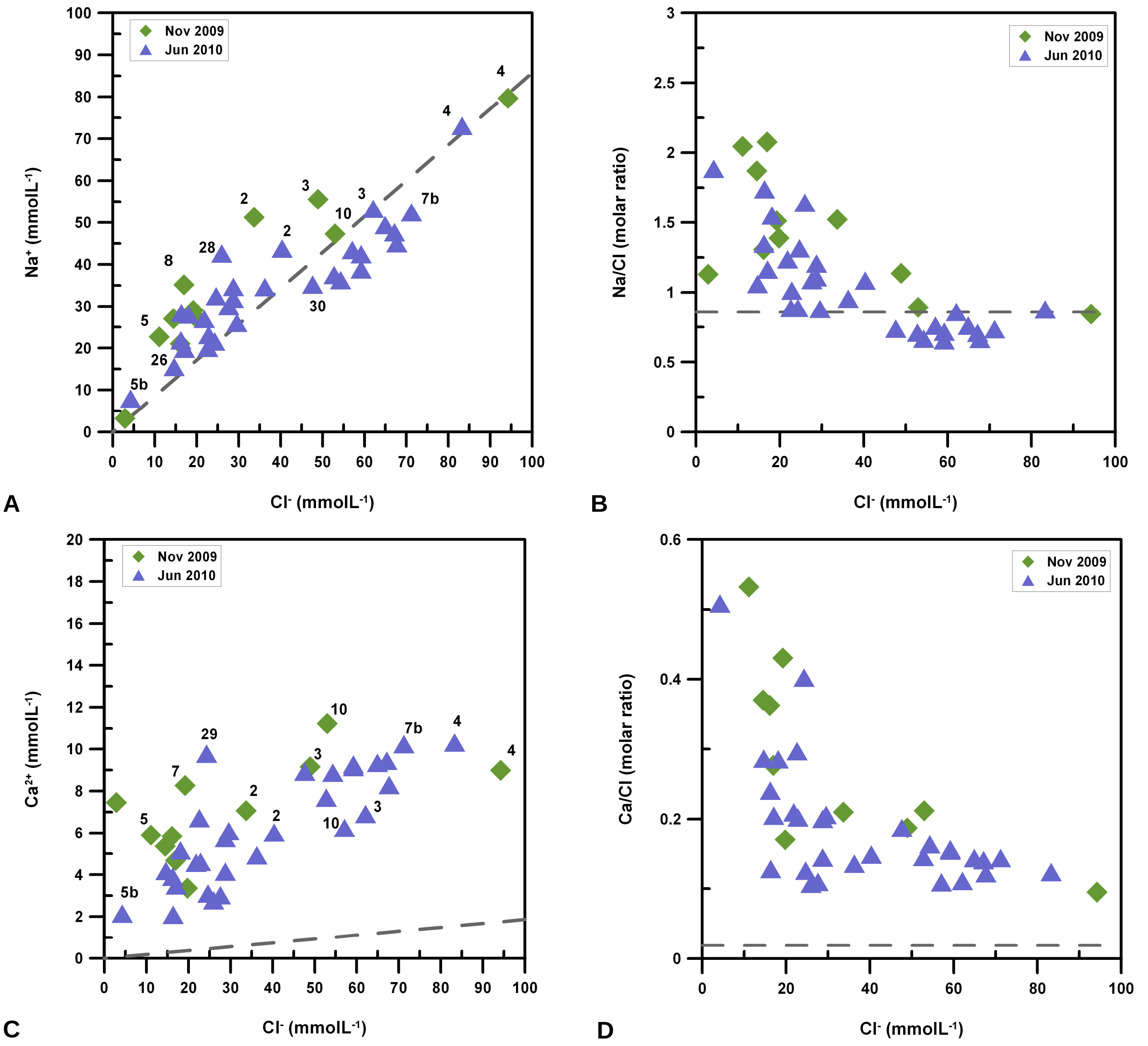


Figure 5. 8. Plots of dissolved species versus chloride concentration (in mmolL^{-1}): (A) Na vs. Cl; (B) Na/Cl (molar ratio) vs. Cl; Ca vs. Cl; (D) Ca/Cl (molar ration) vs. Cl; dashed lines represent Seawater Dilution Line (SWDL).

The correlation diagram between [(Na+K)-Cl] and [(Ca+Mg)-(HCO3-SO4)] supports the possible occurrence of cation-exchanges processes, in addition to carbonates dissolution, as the samples plots coherently with the -1:-1 line (Figure 5.9). Consistently with what previously assumed, the more mineralized wells (i.e. the ones showing enrichment in sodium with respect to chloride in Figure 5.8 A) are plotting in the fourth quadrant, pointing out Ca^{2+} fixation and release of Na^{+}. On the other hand well plotting below the seawater-freshwater dilution line are falling in the second quadrand indicating possible Na^{+} fixation and release of Ca^{2+} or Mg^{2+}.

As one can see, all the samples plot slightly below the -1:-1 line, highlighting a general enrichment in Cl^{-}, possibly due to pollution sources.

This is once again suggesting that human activities are alterating the natural chemical composition of the aquifer.

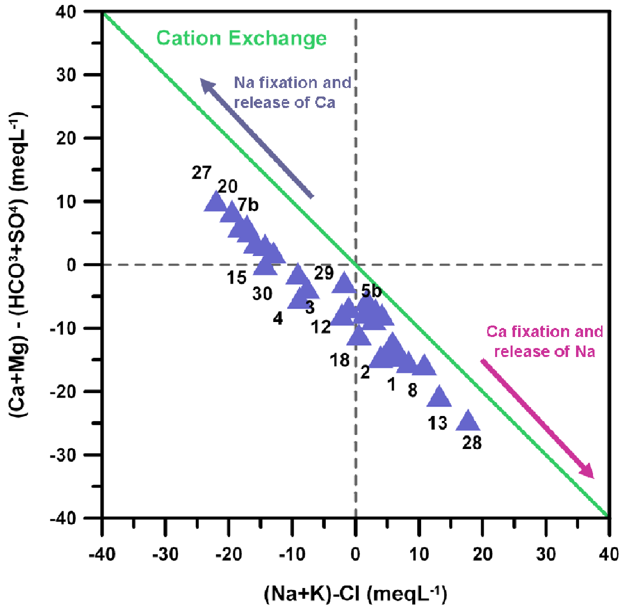


Figure 5. 9. Plot of (Na+K)-Cl versus [(Ca+Mg)–(HCO$_3$-SO$_4$)] for the Bou-Areg Aquifer groundwater. Light green line represents the cation exchange line (-1:-1). Modif. after Trabelsi, 2009.

As mentioned in Chapter 1, the area surrounding the lagoon of Nador is mainly dominated by the Gourougou volcanic massif, the Beni-Bou Ifrour Mountain and the Kebedana massif. Therefore, sediments coming from those three units influence the minealogic composition of both the lagoon and the Bou-Areg plain. In particular the northern part (i.e. where wells 8 and 9 are located) is dominated by the presence of minerals such as calcium plagioclase, silica, olivine and pyroxene coming from the Gourougou mountain, while the soils of southern part (where all the other wells are located) are rich in quartz, calcite and clays. In particular, the clay fraction is dominated by illite and chlorite by (Bloundi, 2005) which generally characterize areas at weak pedologic evolution, as young soils or, as in this case, arid and semi-arid regions.

In addition to carbonates dissolution, another source of salinization is represented by marine aerosols, whose composition is mainly dominated by Na and Cl, associated with high Mg/Ca ratio values (Edmunds and Shand, 2008).

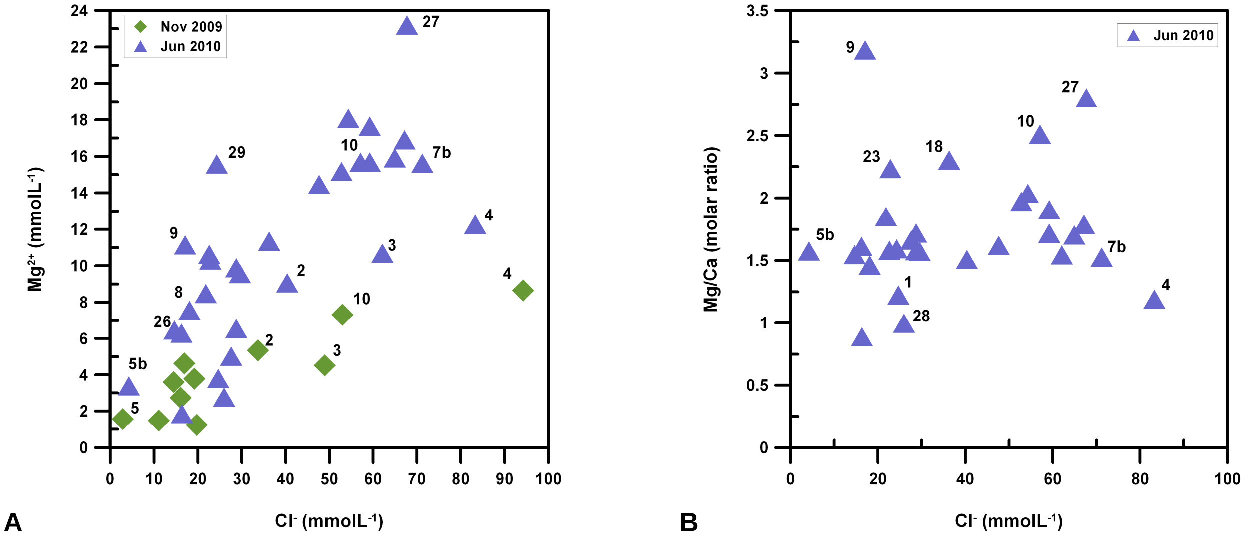


Figure 5. 10. (A) Magnesium variations versus chloride and (B) magnesium (calcium molar ratio versus chloride (Mg-Ca ratio for sea water = 5.2).

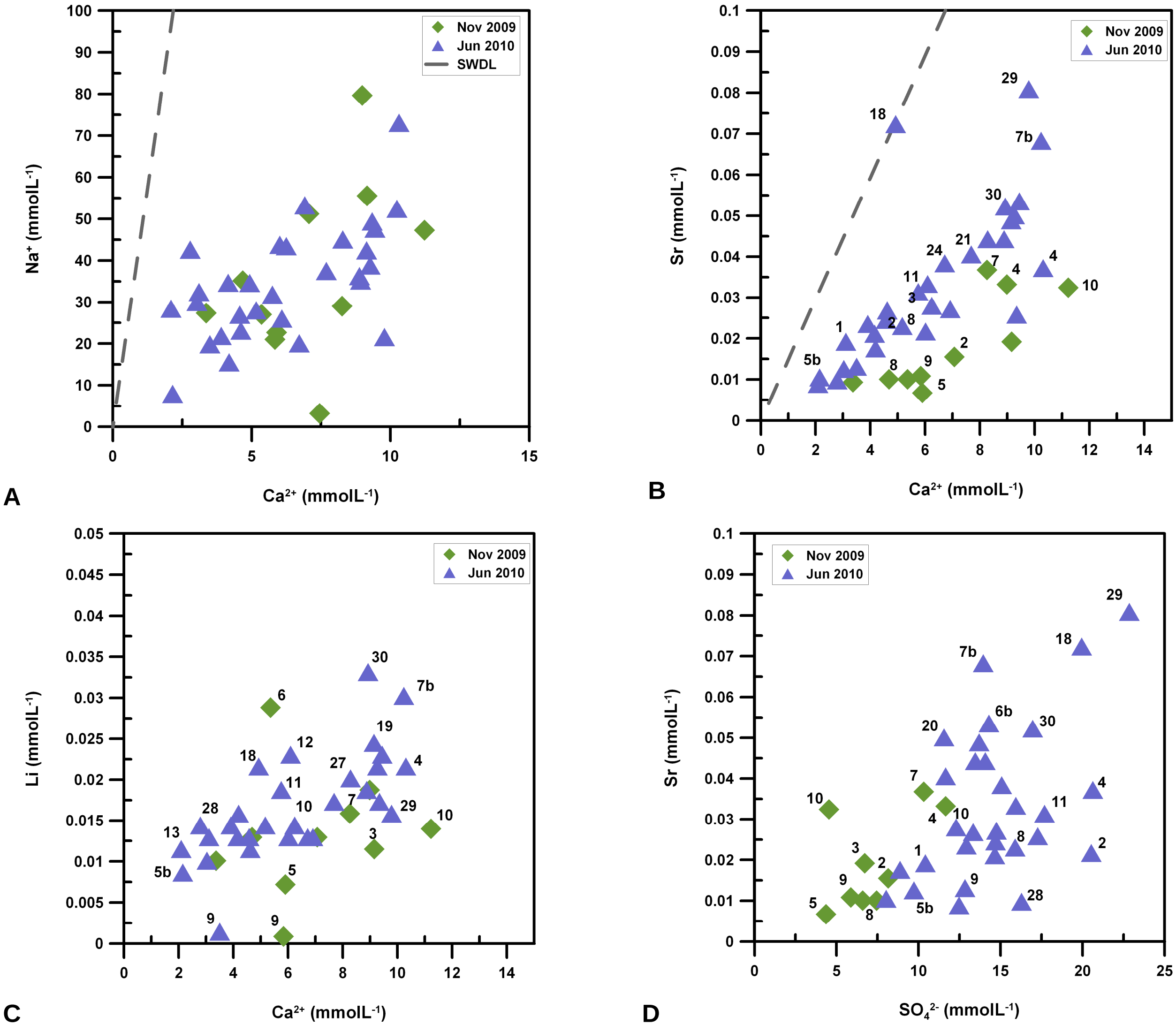


Figure 5. 11. Plots of sodium (A), (B) strontium and (C) Lithium versus calcium; (D) plot of sulphates versus strontium.

Figure 5.10 B shows that wells 10 and 27 meets those characteristic suggesting a possible origin of salinization mainly influenced by marine sprays, or a stronger mixing with Gareb plain waters, due to the proximity of well 27 to the border of the Bou-Areg and the Gareb plains.

As concerns the other wells, relatively high Mg concentrations could be associated to water-rock interaction with volcanic sediments, silicates dissolution or cation exchanges processes (Figure 5.9).

To confirm the proposed trends for salinization origin, Saturation Indices for calcite, dolomite, gypsum and aragonite have been calculated and plotted versus Total Dissolved Solids (Figure 5.12).

Almost all the groundwater samples appear to be supersatuatated with respect to calcite, dolomite and aragonite, suggesting that those minerals are present in the hosting rocks. The presence of limestone in the aquifer deposits and the existence of calcite and dolomite detected by X-ray diffraction analysis (Mahjoubi *et al*., 2003; Bloundi, 2005) can lead, as also proposed by El Yaouti *et al*. (2009), to an increase in Ca^{2+}, Mg^{2+} and HCO_3^- concentrations in the aquifer, when calcite is dissolved.

On the other hand, all the samples appears to be undersaturated with respect to gypsum, suggesting that evaporative mineral phases are minor or absent in the host rock (Bloundi *et al*., 2005), and that water will dissolved gypsum (if present in the aquifer).

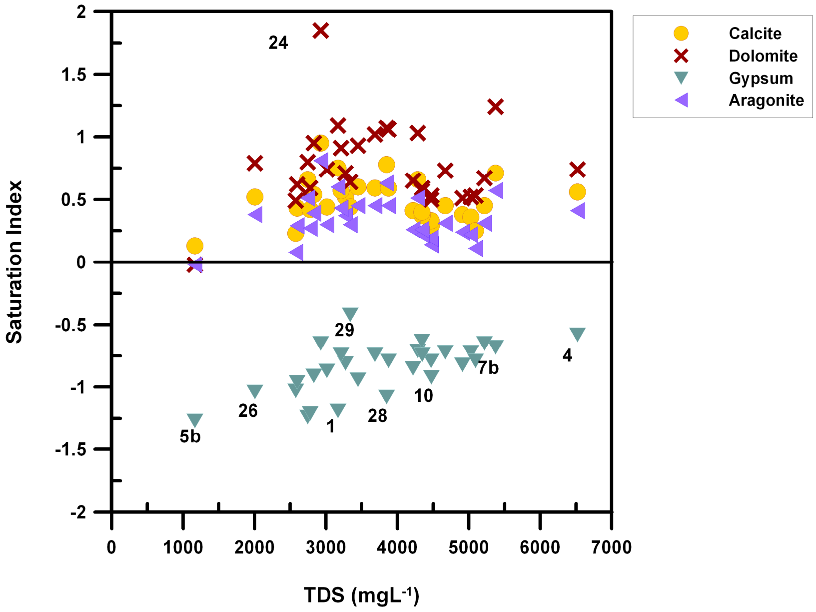


Figure 5. 12. Plot of saturation Index (SI) with respect to carbonate and evaporative minerals.

When dealing with groundwater salinization in coastal areas it is also important to consider bromide and boron concentrations, which allow for a better understanding of possible anthropogenic contributions.

As previously mentioned, taking into account the hydrogeological and climatical context of the region, several potential sources of groundwater salinity can be invoked: marine intrusion, dissolution of marine aerosols, sedimentary marine salinity that impregnates Quaternary layers, evaporitic deposits of the geological formations, or anthropic activities (Edmunds, 1996b; Hsissou *et al*., 1999).

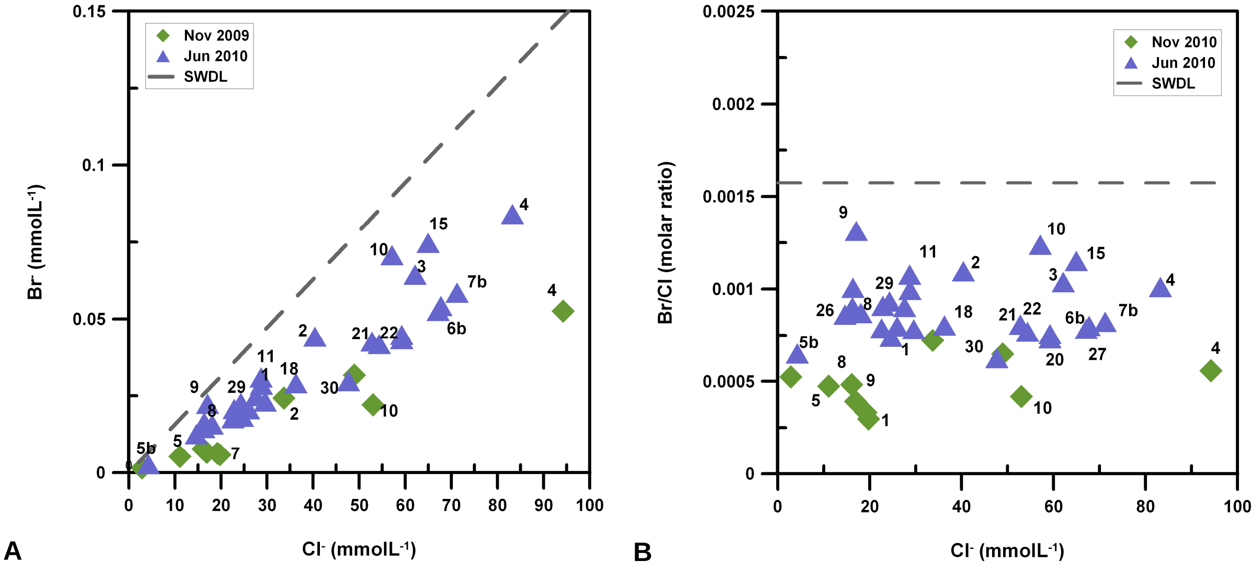


Figure 5. 13. (A) Bromide variations versus chloride. (B) Br/Cl (in molar units) Cl

The enrichment in Cl over Br, with respect to the fresh water-seawater dilution trend characterizing all the samples for both the campaigns (Figure 5.13) can be indicative of human induced pollution, or presence of marine aerosols, and absence of seawater contribution.

Increasing of Br/Cl versus seawater would confirm the marine aerosol input or percolation of seepage water through the bromide-rich organic horizons of soils (Hsissou *et al*., 1999). However, Figure 5.13 B shows that actually none of the wells of the Bou-Areg aquifer can be due to marine aerosol contribution.

This, together with the increase in Cl, can be associated to natural salinity, halite precipitation or mixing with other saline sources. In particular irrigation water or sewadges percolating in the soli can redissolve the halite, thus raise chloride concentration.

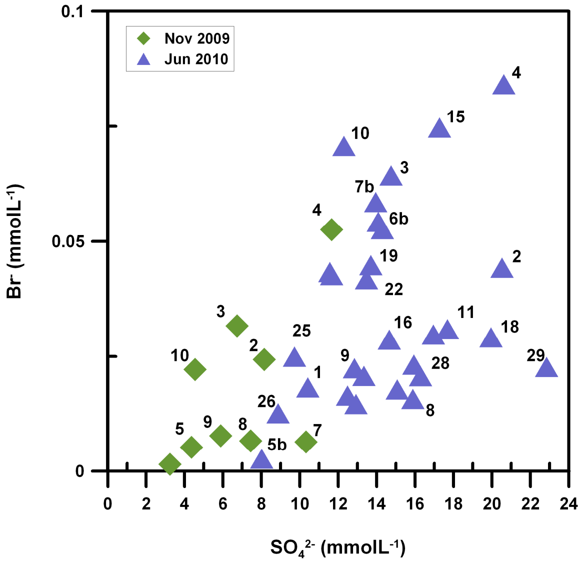


Figure 5. 14. Bromide variations versus sulphates.

High salinity and low Br/Cl (Figure 5.13 B) also confirms the presence of a different source from seawater/lagoon waters, i.e. wastewaters discharged directly in to the system.

Wells 3, 4, 7b and 15 shows the highest walues for both in SO_4 and Br supporting the possible occurrence of for gypsum dissolution and remobilization due to agricultural return flow. In the same way, the high values of SO_4 for wells 2, 11, 18 and 29(showing relatively low Br), might be associated to the presence of sulphate-based fertilizers inputs.

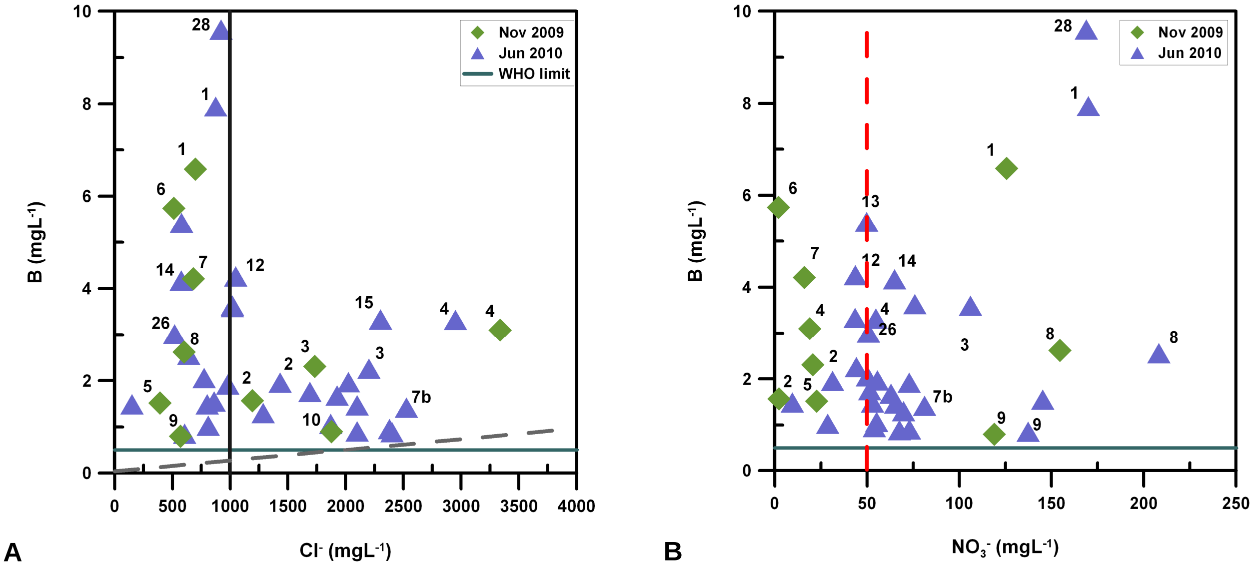


Figure 5. 15.Variations of boron versus (A) chloride and (b) nitrates. WHO limit for drinking water (B= 0.5 mgL^{-1}); Black line: limit for water to be considered as freshwaters; dashed red line: WHO limit for nitrates in drinking waters (NO_3=50 mgL^{-1}). Dashed grey line: fresh water-sea water dilution line.

The relationship between boron and chloride (Figure 5.15 A) provide evidence of the relative enrichment of B in the aquifer. In general B is used, together with Cl to constrain salinity sources and mixing processes between freshwater and seawater (dashed grey line in Figure 5.15 A; $[B]_{sw}$= 4.45 mgL^{-1}).

All groundwater samples of the Bou Areg plain plot above the SWDL, and show values exceeding the WHO limit for drinking water (Figure 5.15 B) also testifying the high salinity of the aquifer. Moreover, boron concentrations exceeding 0.75 mgL^{-1} are considered toxic for crops growth (Vengosh, 2003), thus making waters from wells 1 and 28 unsuitable for agricultural practices. In general, as groundwater in the plain are mainly used as irrigation waters the relatively high values for all the samples might pose serious problems in agricultural production.

As concerns the general high boron concentrations (Figure 5.16), they can derive from (i) industrial and domestic effluents associated to the use of sodium perborate as an oxidation bleaching agent in domestic and industrial cleaning products (~1 mgL^{-1}; Vengosh *et al*., 1994; Vengosh, 2003); (ii) fly ash leachate (~14 mgL^{-1}; Davidson and Basset, 1993); (ii) landfill leachate (~7 mgL^{-1}; Eisenhut *et al*., 1996; Eisenhut and Heumann, 1997) or animal manure (i.e., liquid hog manure 0.4 to 8.2 mgL^{-1}; Vincini *et al*., 1994; Komor, 1997).

In particular, the high values of both B and NO_3 for wells 1 and 28 (Figure 5.15 B) can be associated to domestic or animal pollution. On the other hand, the presence of wells showing a progressive increase in boron and chloride (e.g. 2, 3, 4, 7b and 15) can confirm the proposed remobilization of dissolved salts in the agricultural sector.

As a general feature, by comparing boron and dissolved nitrates one can notice that many samples exceed the regulatory drinking water limits for both the elements, thus suggesting the possible occurrence of severe human induced pollution in the aquifer. In the last paragraph the origin of nitrates in groundwater will be investigates.

Source apart, B concentration in some waters is related to leaching of rock, boric minerals and clay minerals. Other possible origins of boron in the aquifer system are associated to the wide range of applications of boric acid and borate minerals (glass and porcelain manufacture, production of leather, carpets, cosmetics, and photographic chemicals, fertilizers, wire drawing, and welding and brazing of metals). To better determine the origin of B in the natural system, especially in cases where no clear distinction can be done (Figure 5.16), isotopic signal of ^{11}B needs to be analyzed.

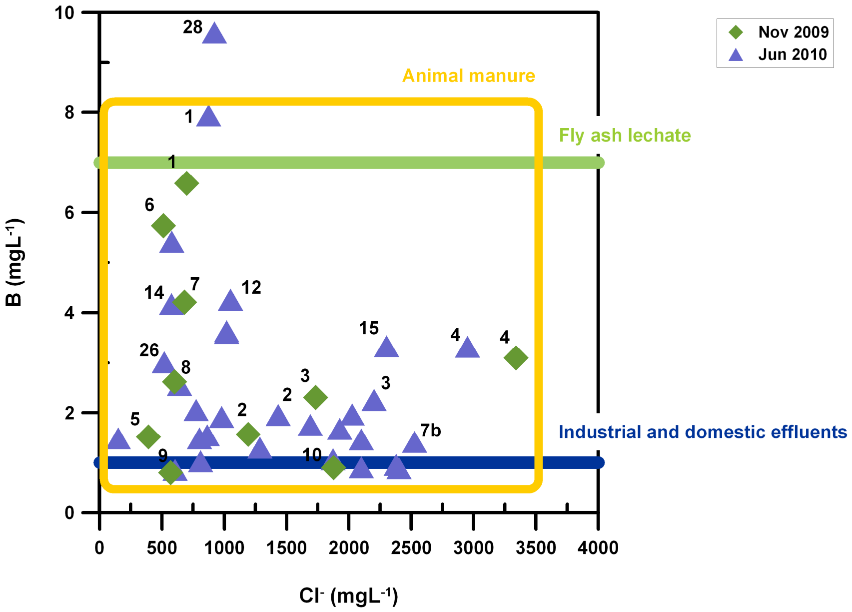


Figure 5. 16. Plot of boron versus chloride associated to the chemical composition of the possible pollution sources in the aquifer. Values for each group and their references are reported in the text in the previous page.

To conclude the investigation on salinization origin, results were compared with literature ones (Figure 5.17), for the periods April 2004 (El Mandour *et al*., 2008) and December 2006 (El Yaouti *et al*., 2009).

By comparing the obtained results with the ones of other surveys over the last six years, the same high salinity of the aquifer is remarkable (Figure 5.17 A). For both the surveys in April 2004 and December 2006 higher levels of chloride (> 4000 mgL^{-1}) and calcium (> 500 mgL^{-1}) concentrations are shown for some wells located in the downstream area, closer to the lagoon. Other water types in the eastern and western zones of the plain contain a net enrichment in calcium and magnesium. This high salinization has been explained by both El Mandour *et al*. (2008) and El Yaouti *et al*. (2009) as linked to sea water intrusion in the coastal zone and evaporative processes in the upstream zone. Cation exchanges with clay fractions were also seen to occur, explaining for some wells the decrease of calcium in favour of sodium.

The present study confirms the high saline characteristics of the chatchment, although any evidence of seawater intrusion can be derived from the chemical and isotopic data.

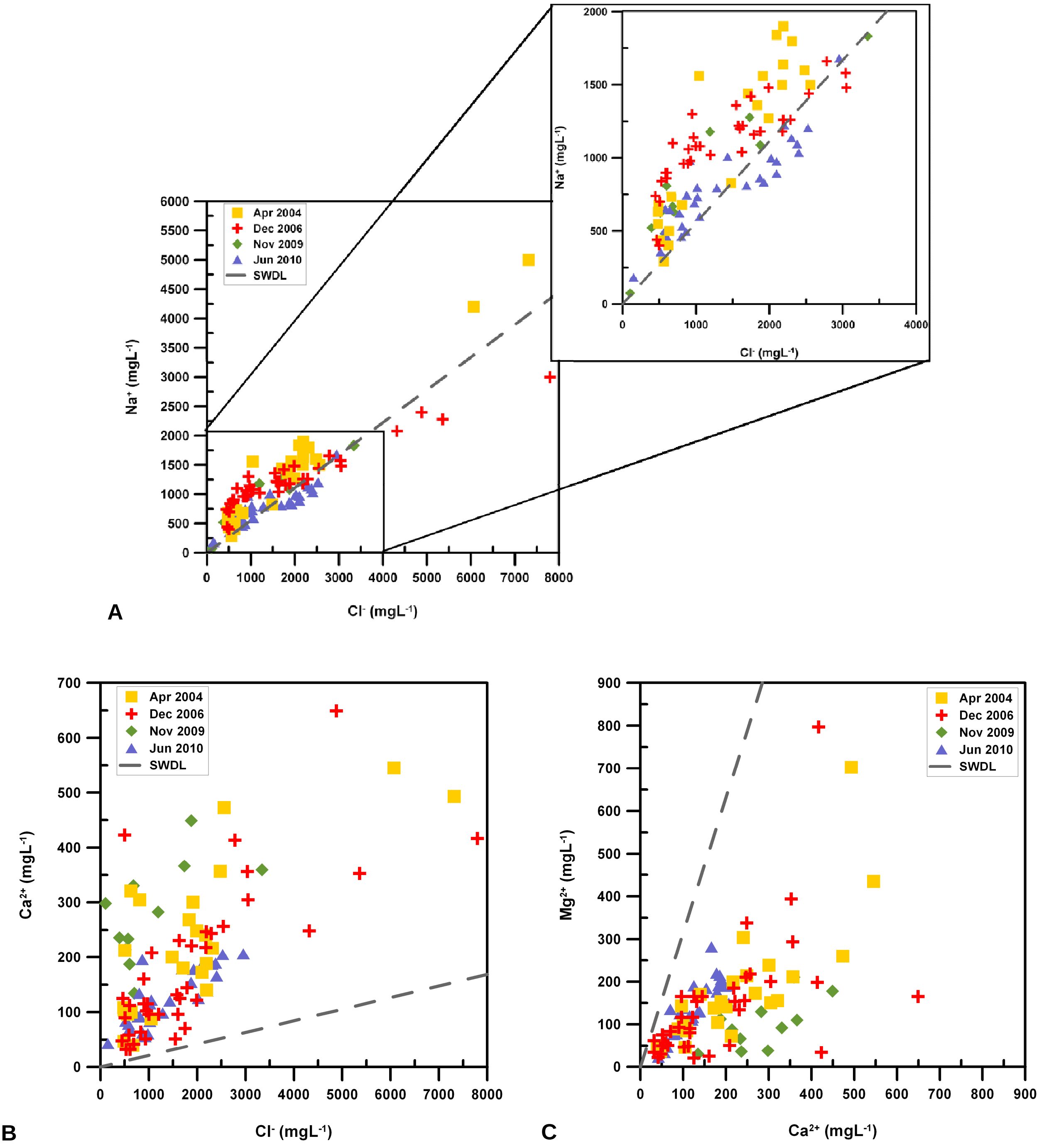


Figure 5. 17. Plots of (A) sodium and (B) calcium versus chloride concentrations. (C) Plot of magnesium versus calcium for the Bou-Areg coastal plain. Data of the surveys of November 2009 and June 2010 are compared with published data for the same area: April 2004 (El Mandour *et al*., 2008) and December 2006 (El Yaouti *et al*., 2009).

5.4. Evaluation of human induced pollution: Nitrates in Groundwater

As emerged in the previous section the salinization of the aquifer is also caused by the increase of human induced pollution.

The main anthropic activities in the investigated area are associated to agricultural practices and urban (or rural) development, sometimes derived from inadequate sanitation systems. For this reason, the analysis in this section focuses on dissolved nitrates, as data of the investigated area often exceed the Moroccan drinking water standard (40 mgL-1, El Yaouti *et al*., 2009).

In the case of the June 2010 survey only 3 wells (2, 5b and 23; Figure 5.19) respect the drinking standard limits, though even wells 3, 12, 13 and 15 are below the WHO limit of 50 mgL-1 (WHO, 2006).

The distribution map of dissolved nitrates for the June 2009 campaign (Figure 5.18) shows that the highest concentrations occur in the centre of the plain (agricultural zone) and in the urban area (P8 in Taouima and P9 in Nador).

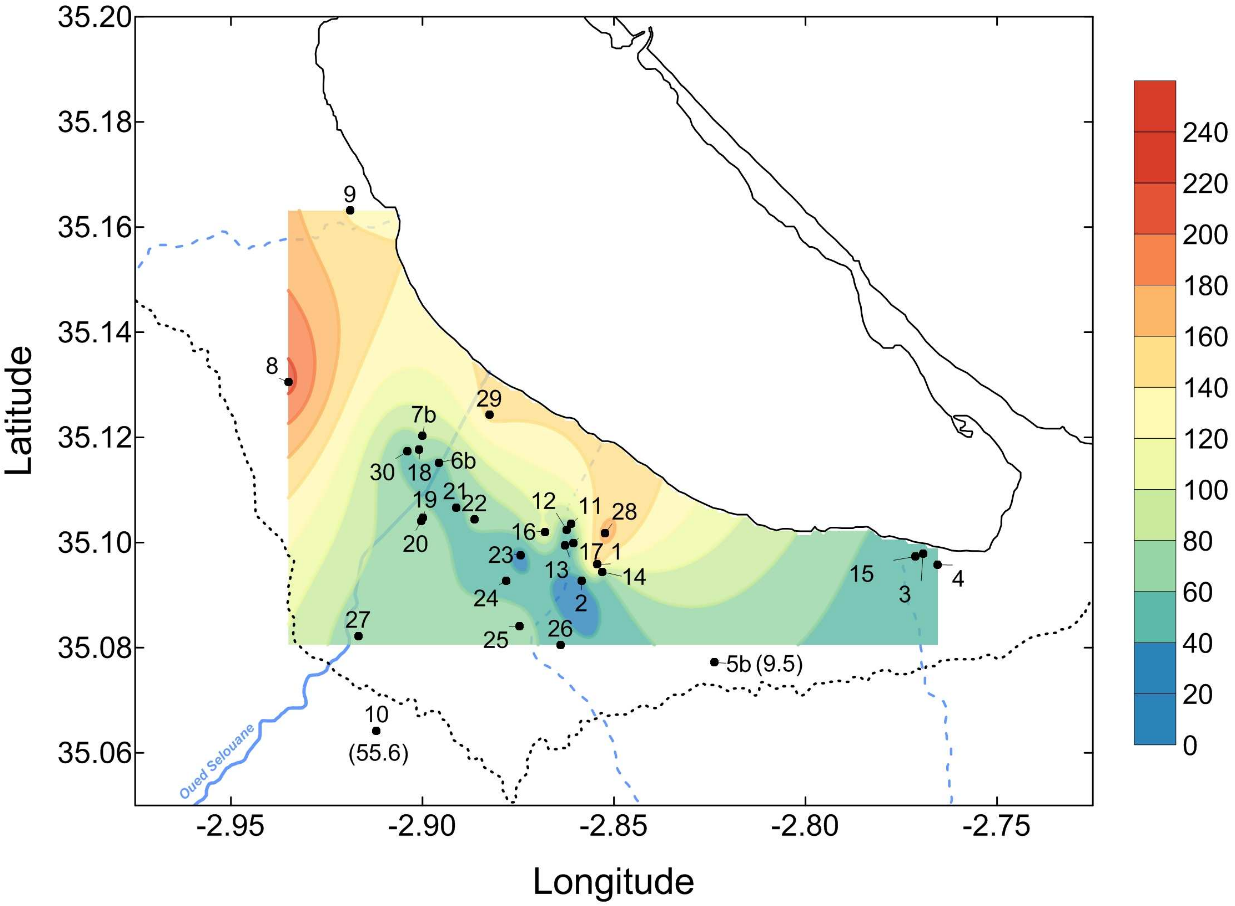


Figure 5. 18. Distribution map of dissolved nitrates (mgL^{-1}) in the Bou-Areg Aquifer (June 2010). The interpolation was done without considering P10 (belonging to the Gareb Plain) and P5b (as previously assumed to be separated from the system).

Although most of the households declared they normally do not directly drink waters from their wells, the fact that the majority of them use those waters for domestic purposes (cooking, washing and cleaning) urge to focus the attention also to the related sanitation issues. Indeed it is necessary to take into account the side effects of irrigational practices and the associated recirculation of contaminated waters.
For this reason, it is fundamental to determine the origin of pollutants in the catchment.

Figure 5.9 A shows that some wells present an increase in chloride concentration, that can be indicative of pollution loads. The same enrichment in Cl is evident in Figure 5.19, associated to a progressive increase in dissolved nitrates (Group B, e.g. wells 4, 7b, 27 and 30). This can be due to agricultural pollution. On the other hand, a second trend (group A) can be highlighted, associated to relatively low Cl concentrations (~1000 mgL^{-1}, e.g wells 1, 9 and 8) but strongly enriched in NO$_3$ that could be related to manure or septic effluents. The same trends appear to be present also in literature data (Figure 5.9 B) and are confirmed by an associated increase in sulphate (Figure 5.20 A). Low potassium values (Figure 5.21 A) can confirm absence (or very low) agricultural inputs for those wells.
Higher values for the June 2010 survey can be indicative of the aforementioned local recharge due to leaching trough the unsaturated zone after the rainy season, allowing for the remobilization of pollutants.
Figure 5.21 A also shows that wells of Group B, are affected by a progressive enrichment in potassium. This increase is expected in groundwater interested by infiltration from agricultural land use, as a consequence of nutrient leaching (Griffioen, 2001).

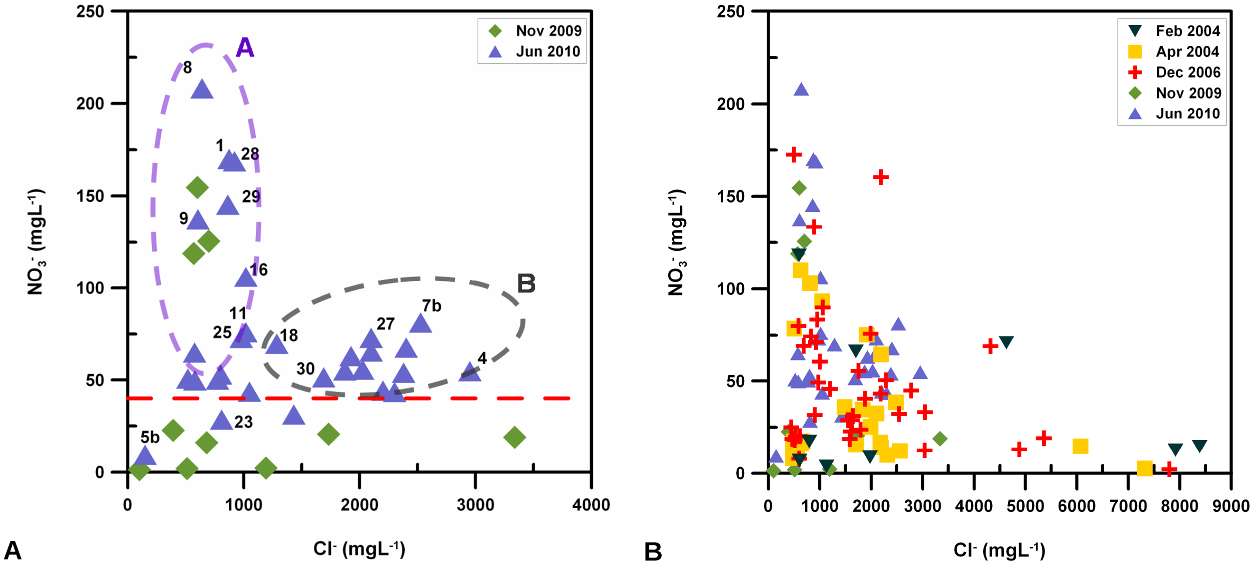


Figure 5. 19. Plots of dissolved nitrates vs. chloride. (A) Data for the November 2009 and June 2010 campaigns. Dashed red line: Moroccan drinking water standard (El Yaouti *et al*., 2009). (B) Comparison with the available data on Bou-Areg Aquifer geochemistry: February 2004 (El Amrani *et al*., 2005), April 2004 (El Mandour *et al*.,2008) and December 2006 (El Yaouti *et al*., 2009).

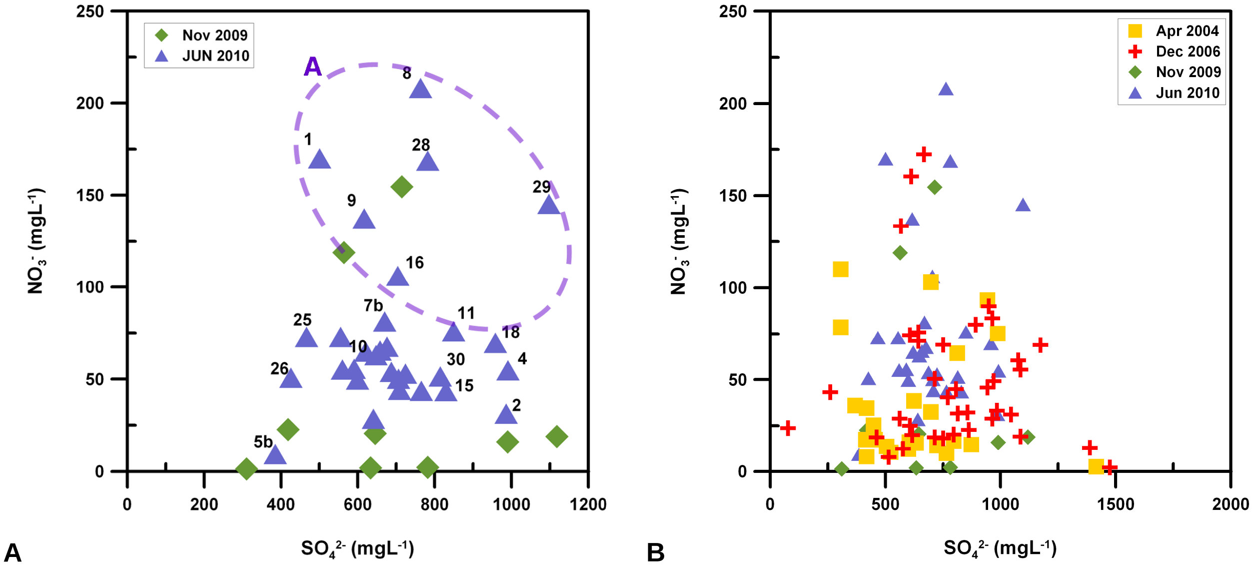


Figure 5. 20. Plots of dissolved nitrates vs. sulphates. (A) Data for the November 2009 and June 2010 campaigns. (B) Comparison with the available data on Bou-Areg Aquifer geochemistry: April 2004 (El Mandour *et al.*,2008) and December 2006 (El Yaouti *et al.*, 2009).

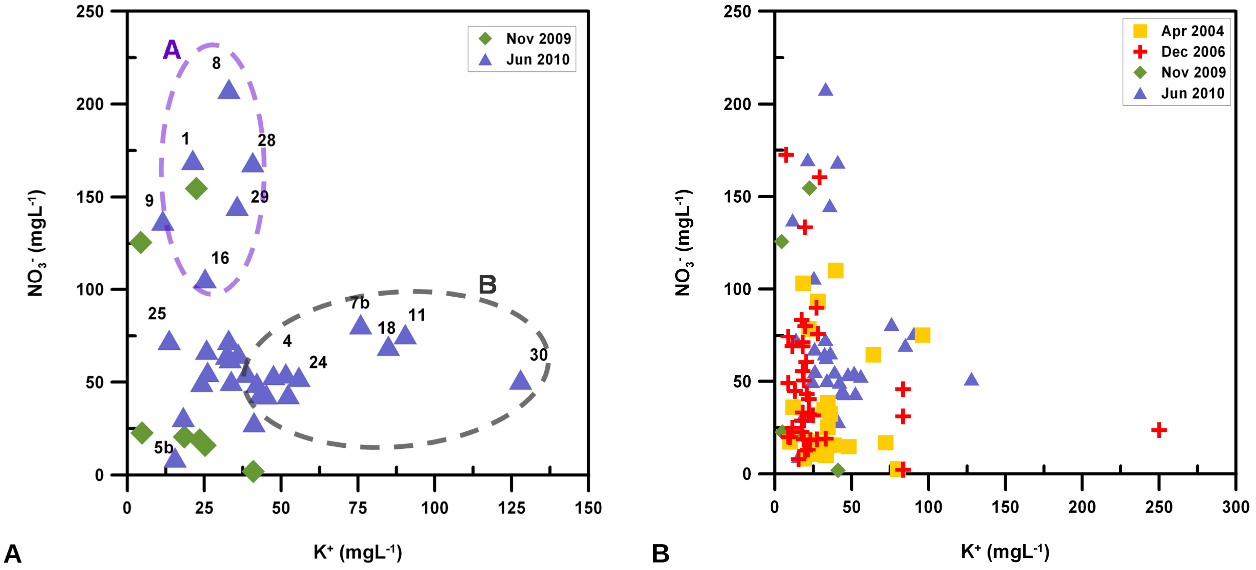


Figure 5. 21. .Plots of dissolved nitrates vs. potassium. (A) Data for the November 2009 and June 2010 campaigns. (B) Comparison with the available data on Bou-Areg Aquifer geochemistry: April 2004 (El Mandour *et al.*,2008) and December 2006 (El Yaouti *et al.*, 2009).

Bromine variations support the proposed trends (Figure 5.22 A). All the samples (apart from P5b) show concentration higher than 1 mgL^{-1} in the aquifer thus confirming the presence of two different groups of water (A: high Br and relatively low nitrates -P4, P10, P21- and B: with progressive increase of both the elements). A general increase in Br from November to June is also evident, suggesting the occurrence of remobilization processese during the winter season.

Figure 5.22 B, compares the Br/Cl ratio and the Cl concentrations with NO_3 abundance (bubbles areas) in the groundwater samples. The more polluted wells (relatively higher NO_3^-) are coherent with the proposed trend of anthropogenic source based on the study by Andreasen and Fleck (1997; green arrow in Figure 5.22 B).

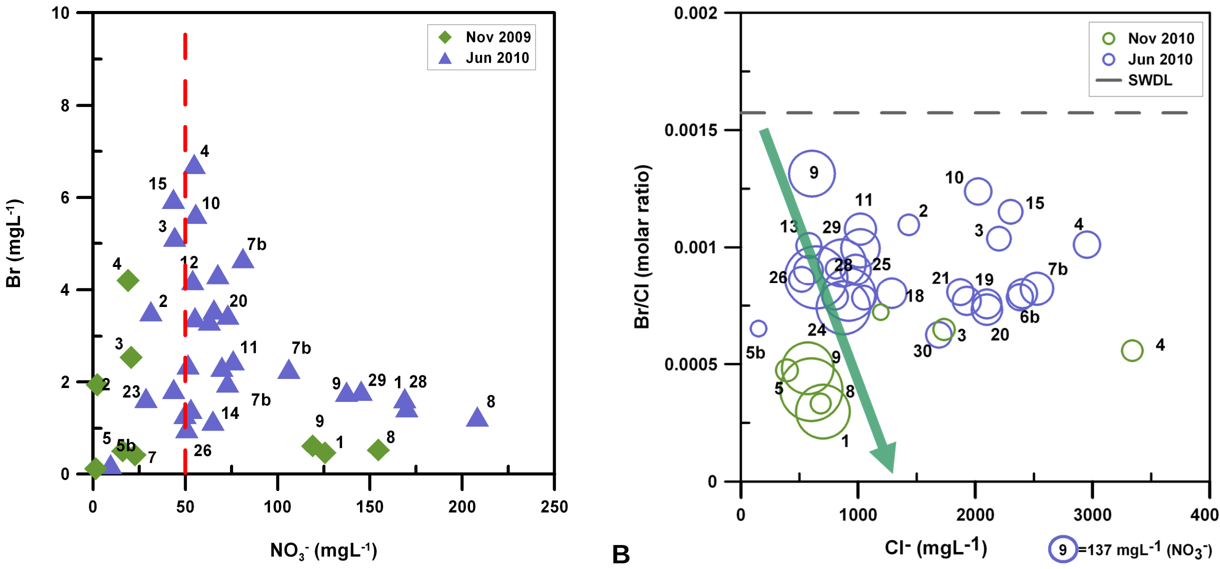


Figure 5. 22. (A) Plots of dissolved nitrates vs. bromine for the Bou-Areg coastal plain. Dashed red line: Moroccan drinking water standard (El Yaouti *et al.*, 2009); (B) Bubble plot of Br/Cl (molar ratio) versus Cl concentration. Modif. after Kagabu *et al.*, 2011). The green arrow represents the proposed trend for anthropogenic contribution.

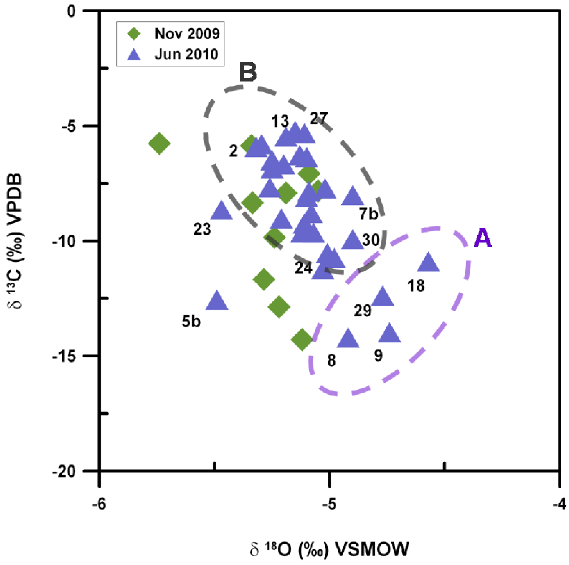


Figure 5. 23. Plot of carbon-13 (‰) versus oxygen-18 (‰) for samples of Bou-Areg aquifer.

To better understand the sources of pollution of the aquifer and the associated recharge process, $\delta^{13}C$ was studied. By comparing carbon-13 and oxygen-18 (Figure 5.23) one can notice that the isotopic signal of the oxygen is more uniform, meaning that the waters are affected by the same fractioning processes (evaporation in the aquifer, evaporation during the irrigation processes and water recycling), whereas carbon's signal is more variable due to water interaction with the carbonates system, soil organic matter or pollutants.

Wells of Group A have a more negative isotopic signal, typical of local recharge remobilizing pollutants in the unsaturated zone. This interaction causes changes in the isotopic composition of carbon-13. On the other hand, well 5b has a signal of deep recharge, hence water circulating in a system without interactions with the parent rock, supporting the interpretation proposed in the previous section.

In group B, a tendence towads more positive carbon-13 valuse is observable. This can be coherent with pocesses of carbonates dissolution ($\delta^{13}C$ of marine carbonate ~ 0‰) in intensively irrigated areas; in fact as carbonate is dissolved, $\delta^{13}C_{DIC}$ will evolve to more enriched values. Of course, how far it evolves and the rate of carbonates dissolution depends on the “openness” of the system, therefore by the soil CO_2, and possible interaction of photosynthetic uptake (fixation of CO_2 by C_3 or C_4 plants (Clark and Friz, 1997). For example, C_4 plants (e.g. common agricultural plants likesugar cane, corn and sorghum) have $\delta^{13}C$ ranging from -10 to -16‰, thus coherent with the signal of the Bou Areg water samples. A survey on the speciation of agricultural and natural species might be useful to support this theory.

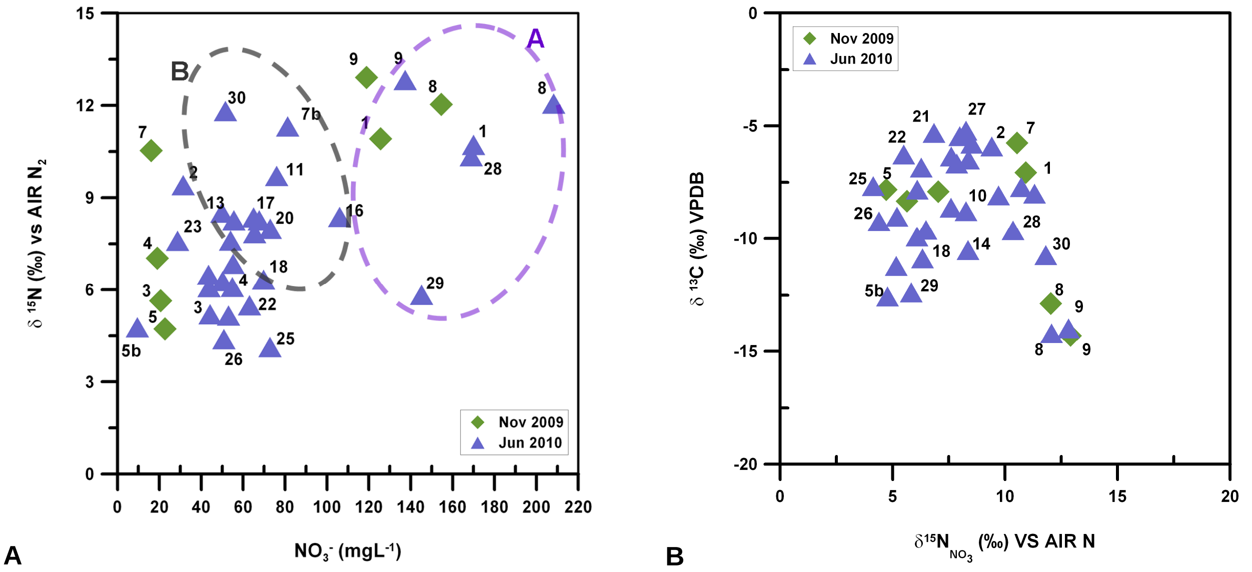


Figure 5. 24. Isotopic signal of the groundwater in the Bou-Areg aquifer. (A) Delta nitrogen 15 (‰) versus Nitrates and (B) verus carbon-13 (‰).

Isotopic signal of $^{15}N_{\_NO3}$ was finally investigated to clarify nitrate origin in the system. By comparing it with NO_3 concentrations (Figure 5.24 A) the same groups (and behaviour) can be highlighted.

Discrimination among different nitrate origin was also supported by comparing $\delta^{15}N_{\_NO3}$ with $\delta^{13}C$ (Figure 5.24 B). Wells 8 and 9 seems to be affected by the same processes as they have quite close signal for both the isotopes. However, the proposed grouping is not evident, suggesting complex interaction with the carbonate system and pollution loads/recharge processes.

To shed some light on those processes, the isotopes of dissolved nitrates were studied. In fact the use of natural abundance of $\delta^{15}N$ allows to multiple nitrate origin, namely fertilizers, organic matter and manure inputs, as well as pointing out the occurrence of nitrification and denitrification processes (Clark and Fritz 1997). By comparing the obtained isotopic data for groundwater of the Bou-Areg aquifer, with the isotopic composition of $\delta\ ^{15}N_{\_NO3}$ in manure, septic system effluents (10-15‰) in soil organic matter (~ 5‰) and fertilizers (~ 0‰; Clark and Fritz, 1997), two main sources of nitrogen input to groundwater distinguished (Figure 5.25).

Wells 8 and 9 are clearly affected by pollution from manure and septic effluents systems while 25 and 30 have signals coherent with mineral fertilizers, thus explaining the high K concentration for well 30.

On the other hand, wells 1, 16, 28 and 29 are more likely to be a mixing with two sources: manure systems and syntetic fertilizers. Despite their isotopic signal is coherent with the one of soil organic matter ($\delta^{15}N$ ~ +4 to +10 ‰), the natural origin can be exluded, as their concentrations are quite above 15 mgL^{-1} (Clark and Fritz, 1997).

The other wells showing $\delta^{15}N$ values around 10 ‰ can be interested by mixing processes, rather than a complete contribution from soil organic matter.

Well 5b emerged in the previous sections to be the less polluted well as located at the limit of the irrigated zone. Its isotopic composition (+18.2 ‰; +4.77 ‰) therefore, can be peculiar of long-term accumulation of NO_3^- by photochemical reactions in atmosphere (Michalski *et al*., 2004), rather than being due to synthetic fertilizers.

For the other wells mixing processes seems to occur thus affecting the isotopic signal of dissolved nitrate, the same process appears evident for L2 and L19, classified as springs, hence groundwater emerging at the surface at the lagoon's border.

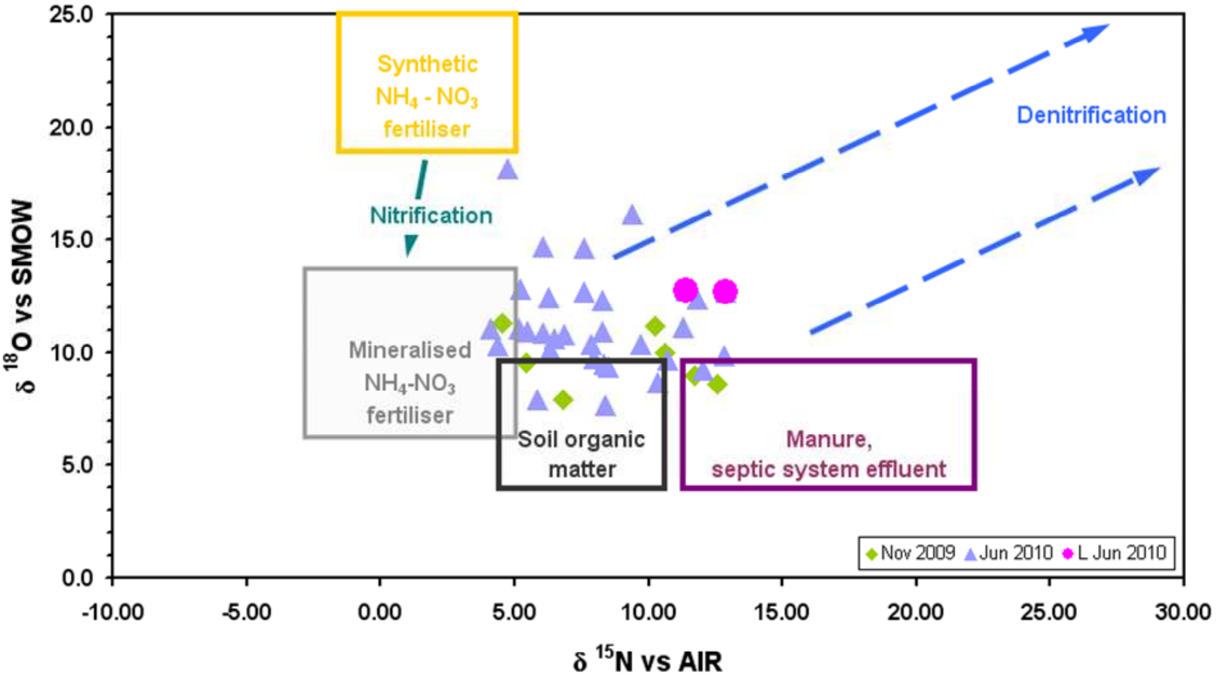


Figure 5. 25. $\delta^{18}O$ (‰) versus $\delta^{15}N$ (‰) of dissolved nitrates in groundwater from the Bou-Areg plain (modified after Kendall, 1998). Neon red dots correspond to L2 and L19, classified as springs.

6. Discussion: the Lagoon of Nador

6.1. Water classification

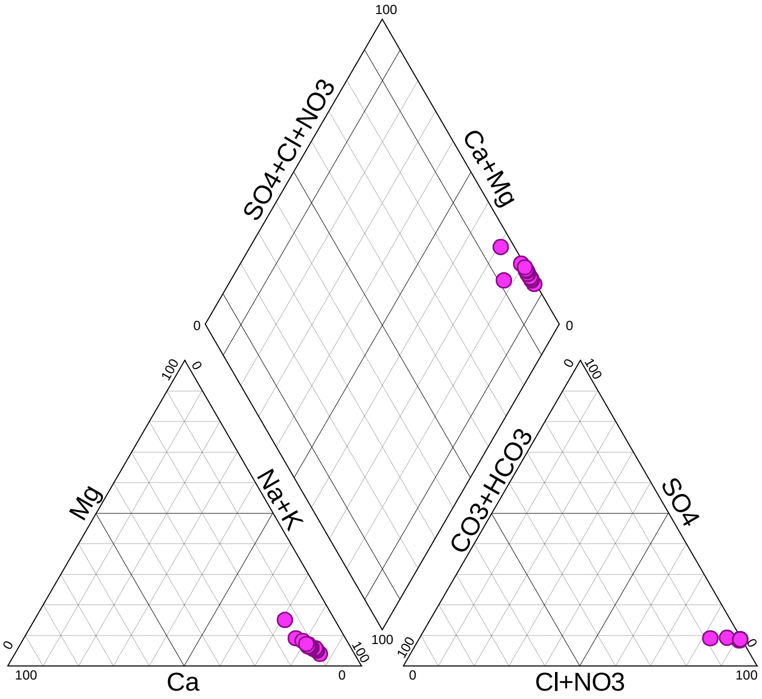


Figure 6. 1. Piper Diagram for the waters of the Lagoon of Nador (Jun2010).

Lagoon waters are all classified as sodium chloride type (Figure 6.1). Almost all the samples have behaviour coherent with the dilution with sea water (Figure 6.2), although in most of the cases exceeding sea water concentration and showing a slight enrichment in sodium. This confirms the hypersaline nature of the lagoon. The same dominant composition is shown in Figure 6.3 with the Langelier Ludwig square diagram (LL; Langelier and Ludwig, 1944). In the diagram, with %HCO_3 as x-axis (LL-HCO3), lagoon water samples can be chemically classified as Na, K-Cl waters, as well as most of the groundwater samples. Only well 5b, whose chemical composition has been discussed in the previous section, can be classified as bicarbonate water, while in well 29 Ca and Mg dominates.

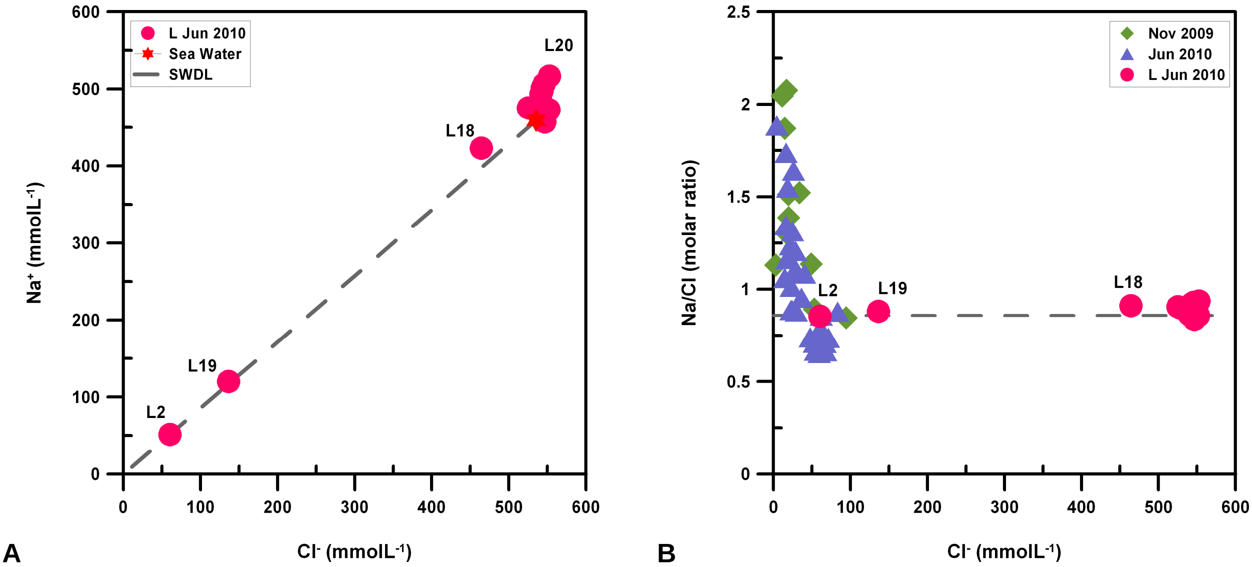


Figure 6. 2. Chloride variations versus (A) sodium and (B) Na/Cl molar ratio for the lagoon of Nador. Dashed lines represent the seawater dilution trend. Samples are also compared with groundwater data for both November 2009 and June 2010.

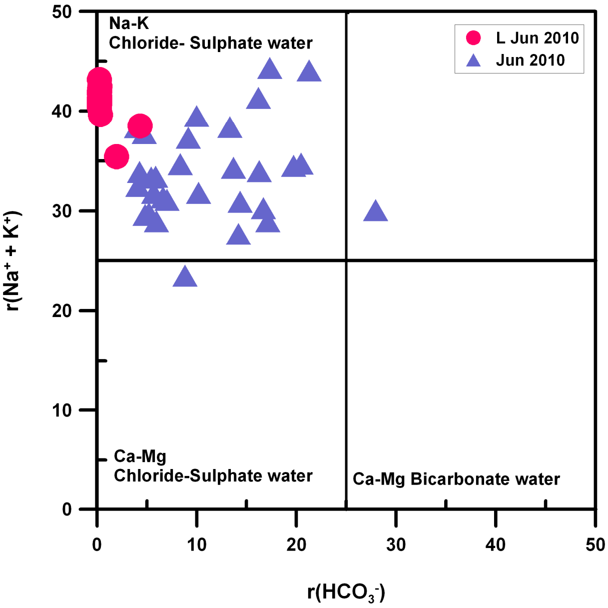


Figure 6. 3. LL-HCO3 diagram for lagoon water and groundwater samples (Jun 2010).

The dominance of chloride is also evident in Figure 6.4 A, while the plot of LL-SO_4 (Figure 6.4 B) shows that all the samples are situated in the second quadrant, with a relatively smaller percentage of sulphates. The triangular diagram HCO_3^--SO_4^{2-}-Cl^- (Figure 6.5) underlines the aforementioned dominance of chloride ions for the surface water samples collected in the lagoon of Nador, and the associated depletion in sulphate.

By plotting Na versus K it is evident the lagoon water samples, previously classified as Chloride-Alcaline, belong to the Na-Cl type, as Na prevails on K (Figure 6.6), and it is the dominant cation for all the samples. As already mentioned in the previous chapter, two points L2 and L19, are not really lagoon waters, but are classified as springs discharging groundwater in the lagoon. This could be seen also considering the chemical composition of that water, having a nature more coherent with freshwaters passing trough polluted systems than salt water (Figure 6.2. B). The different behaviour of sample L18, collected in the Sidi Ali port, could be associated to lagoon waters with very circulation and poor mixing.

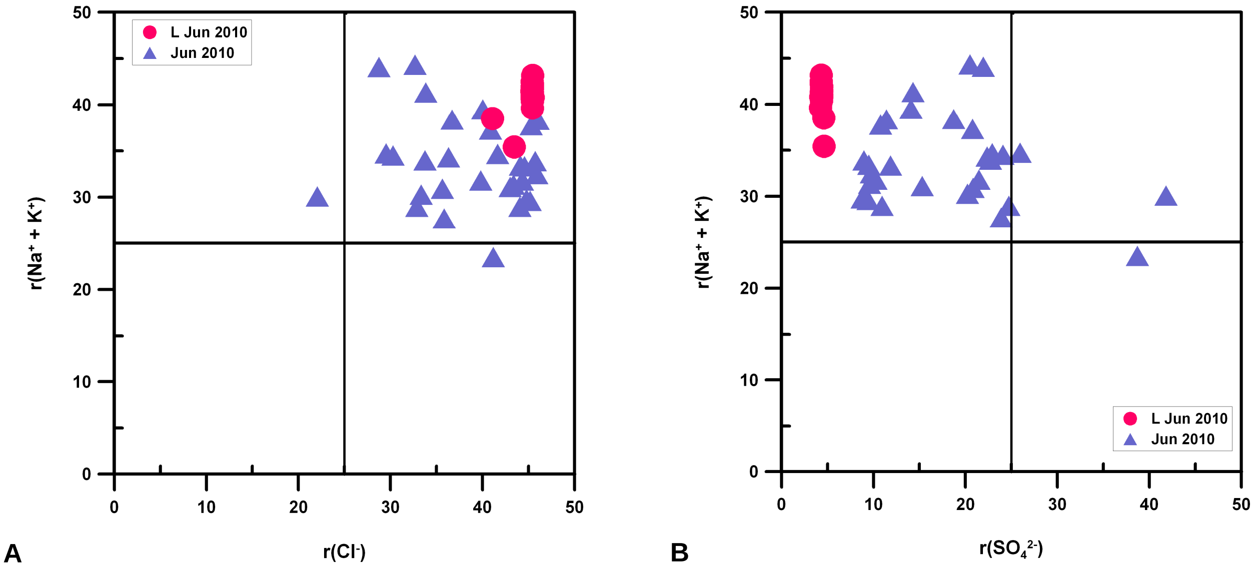


Figure 6. 4.(A) LL-Cl diagram and (B) LL-SO_4 diagram for lagoon water and groundwater samples (Jun 2010).

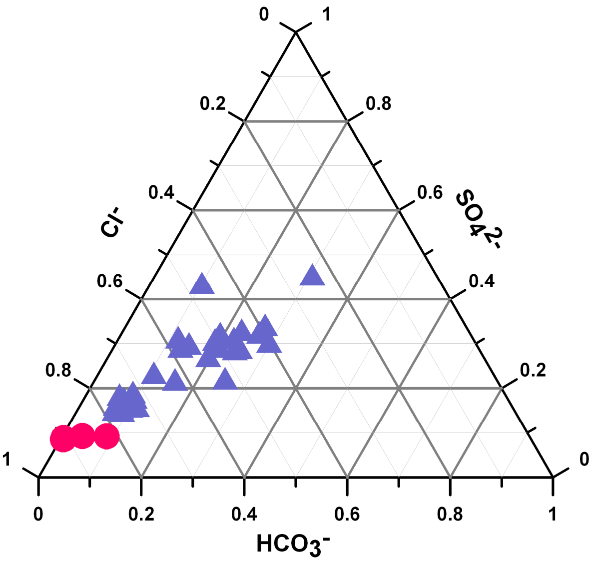


Figure 6. 5. Triangular diagram HCO_3^--SO_4^{2-}-Cl^- for the lagoon and ground water samples (June 2010).

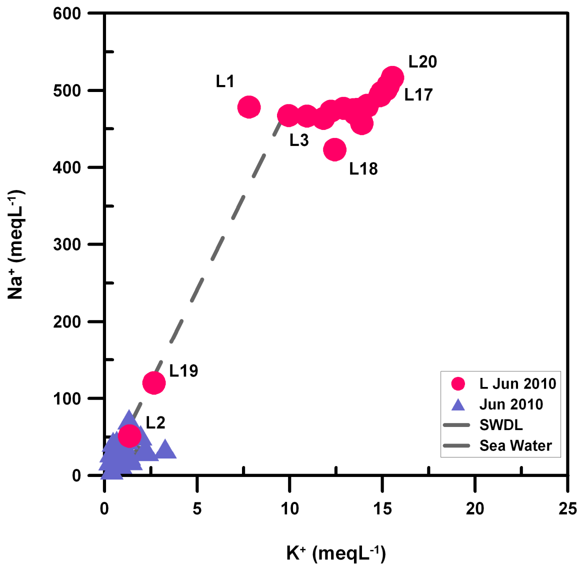


Figure 6. 6. Plot of sodium versus potassium for the lagoon and ground water samples (Jun 2010).

6.2. Geochemical processes

As in the previous chapter, the geochemistry of both major and trace elements was investigated to better understand the geochemical processes occurring in the Lagoon of Nador, as a basis for further assessments on its interactions with the Bou-Areg aquifer.

Due to the hypersaline nature of the lagoon, one can assume that there are three main processes controlling its chemical composition: (i) evaporation, (ii) inflow from agricultural sources and (iii) groundwater flow, discharging directly in the lagoon (Baneschi, 2007), associated to the influence of seawater entering from the inlet.

Figure 6.7 and Figure 6.8 allow one to observe enrichment in calcium with respect to the other ions but sodium (Figure 6.7 A) that has been highlighted as the dominant cation. Moreover, Ca^{2+} concentrations variations are not associated to significant changes in SO_4^{2-}, HCO_3^- or Sr (Figure 6.7 and 6.8) content. This can reflect the chemical composition of the lagoon sediments in the sampling stations of the survey, whose mineralogical composition is dominated by feldspar ($KAlSi_3O_8$ - $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$) and clays coming from Gourougou rocks alteration (Bloundi, 2005). Samples L1, L13, L14 L15, L16 and L20 are more likely to belong to a zone, characterized by a dominance of quartz (SiO_2) and calcite ($CaCO_3$). These minerals derive from hydrolysis of calcareous or sandy-limestone terrains of the Kebedana and Beni-Bou Ifrour mountains. Moreover, a part of calcite also comes from intra-lagoon calcareous organisms (e.g. ostracods and foraminifera).

Calcium versus magnesium diagram (Figure 6.7 B) shows an increase in Ca associated to Mg, as well as the presence of two trends on the lagoon water samples: on the one hand samples L2 and L19 (i.e. the two springs) with a Ca/Mg ratio close to 1, on the other all the samples with a Ca/Mg ratio higher than 1. The excess of calcium can be attributed to the dissolution of Ca-minerals (e.g., calcite, anhydrite or gypsum). However, for the system of the lagoon of Nador, high values of calcium are associated to no significant increase in SO_4 concentrations, thus suggesting that gypsum leaching is unlikely to occur.

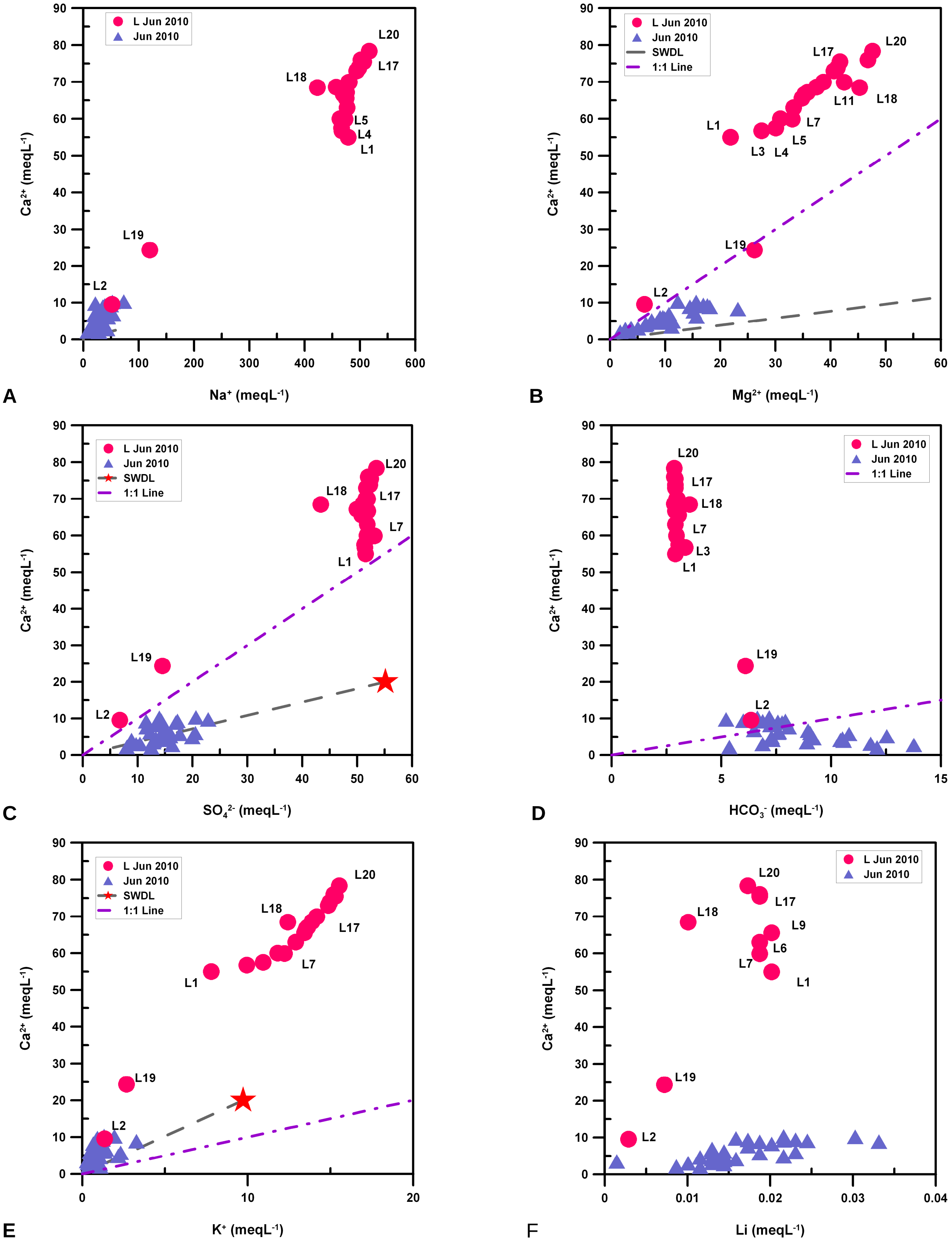


Figure 6. 7. Calcium variations versus (A) sodium, (B) magnesium, (C) sulphates, (D) bicarbonates, (E) potassium and (F) lithium for the lagoon of Nador. Dashed grey lines represent the seawater dilution trend (SWDL); purple lines correspond to the 1:1 Ca: element ratio.

In fact in Figure 6.9 an excess in [Ca+Mg] is observed, once again, associated with no variations in [SO_4+HCO_3]. This allows one to exclude the occurrence of dissolution of calcite, gypsum and dolomite as those processes releases Ca, Mg, SO_4 and HCO_3 according to a [(Ca + Mg)/(SO_4 + HCO_3)] ratio equal to 1 (Purple line in Figure 6.9). On the other hand, calcite precipitation can be present, highlighted by the high calcium values, associated to relatively low HCO_3^- concentrations (Figure 5.7 D).

If one considers the studied elements it is possible to summarize that only Mg, Li and K varies together with Ca.

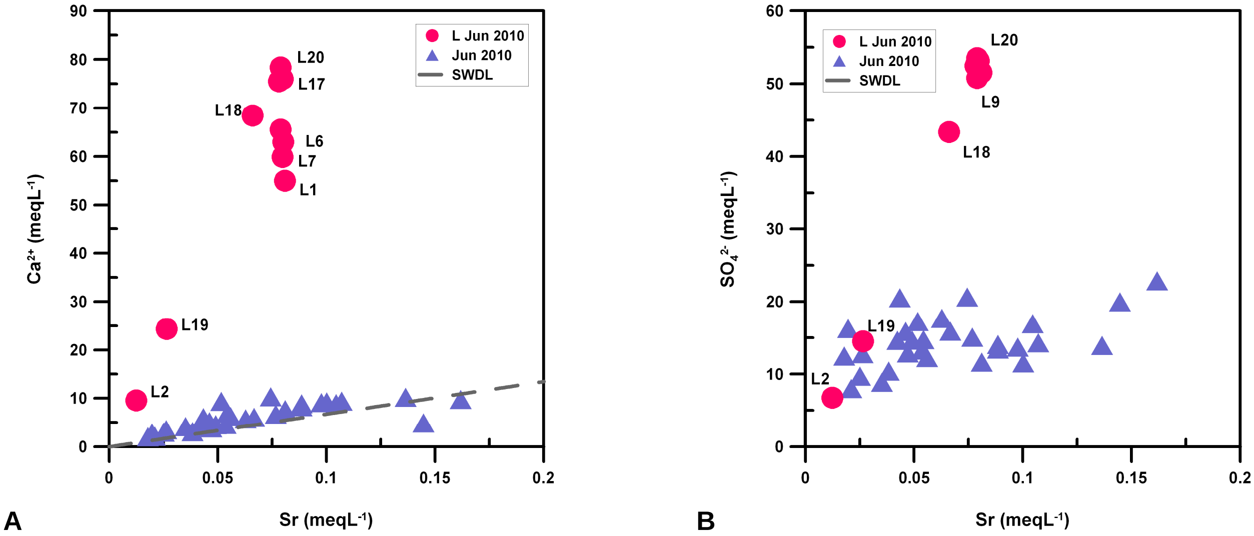


Figure 6. 8. Plot of calcium versus strontium (A), where grey dashed linerepresents Sea Water Dilution Line, and (B) sulphate versus strontium.

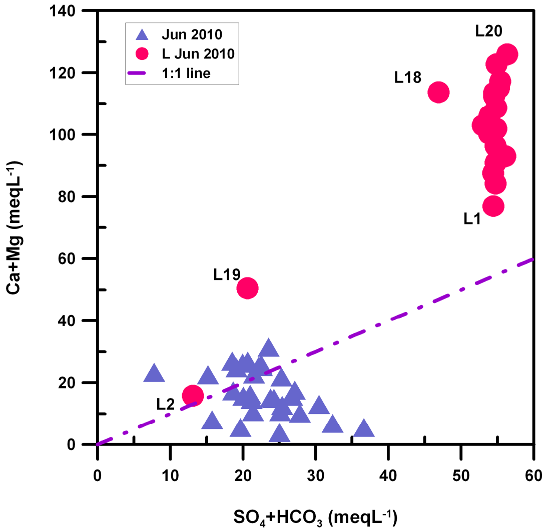


Figure 6. 9. Bivariate diagram of (Ca+Mg) vs. (SO_4+HCO_3). Purple line corresponds to the 1:1 (Ca+Mg)/(SO_4+HCO_3) ratio.

By considering the different Saturation Indices (Figure 6.10) it is possible to highlight the occurrence of evaporation of Aragonite, while, the supersaturation with respect to calcite, gypsum and dolomite, confirms their precipitation within the lagoon system.

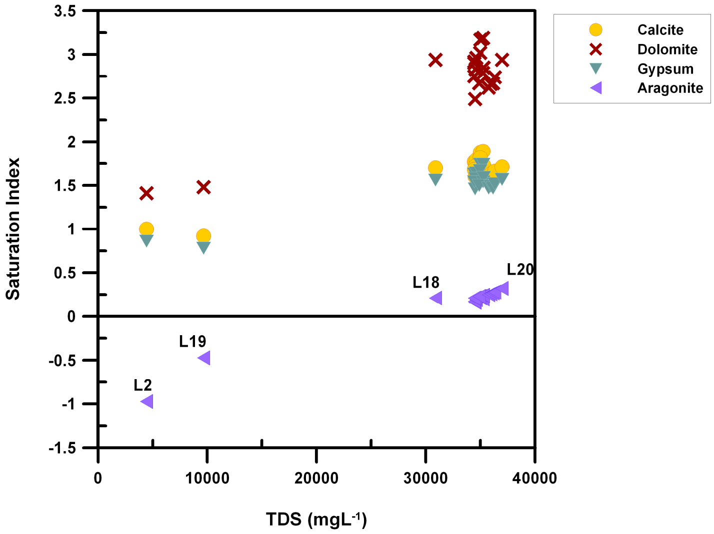


Figure 6. 10. Plot of saturation Index (SI) with respect to carbonate and evaporative minerals.

To confirm and define the occurrence of evaporative processes, chemical data were compared with the geochemical characteristics of marine water (Fontes and Matray, 1993; Conti *et al*., 2000) and major ions were plotted against chloride (Figures 6.11 and 6.12).

As it was already pointed out in the previous section, all the samples falls along the fresh water-sea water dilution trend, showing a Na/Cl ratio coherent with the sea water one (Figure 6.11 A). The excesses in calcium for all the samples is also evident (Figure 6.11 B), with a shift towards the calcite precipitation (apart from L2 and L19). The same behaviour is shown for SO_4 (Figure 6.11 C). L2 and L19 appears to be slightly below the mixing line, with values coherent with more concentrated waters (Conti *et al*., 2000), due to the presence of oxidation-reduction reactions. In fact, groundwater rising at the surface, as in the case of these two springs, sulphide minerals are readily oxidised giving rise to sulphates. Alternatively, this could be related to human activities or leaching from the bed-rock.

Potassium variations for almost constant values of chloride (values coherent with the seawater one) might suggest continental water contribution associated to agricultural runoff. In fact all the irrigational channel (and groundwater recharge) flows directly into the lagoon; the fact that L2 and L19 present an increase in Cl with respect to K can confirm this assumption. Indeed, those two springs are located in the urban part of the aquifer, therefore affected by possible human pollution loads, but with no direct agricultural input. The associated increase in Ca (Figure 6.8 A) needs a more detailed investigation. The high Ca values can be associated to a possible microbiological contribution that increased its content in the solution. As all the sampled have been collected as surface water a biological investigation of the processes occurring in the photic zone, and hence possibly alterating the chemical composition, should be further performed.

Bromine variations compared to chloride, show a geochemical composition coherent with the one of marine water (Fontes and Matray, 1993; Conti *et al*., 2000), with some sites slightly exceeding sea wateer value. This supports the absence of carbonates precipitation in the lagoon, and possible occurrence of mineralization of organic matter. Points L2 and L19 once have a concentrations characteristic of groundwater mixing with more saline (lagoon) water.

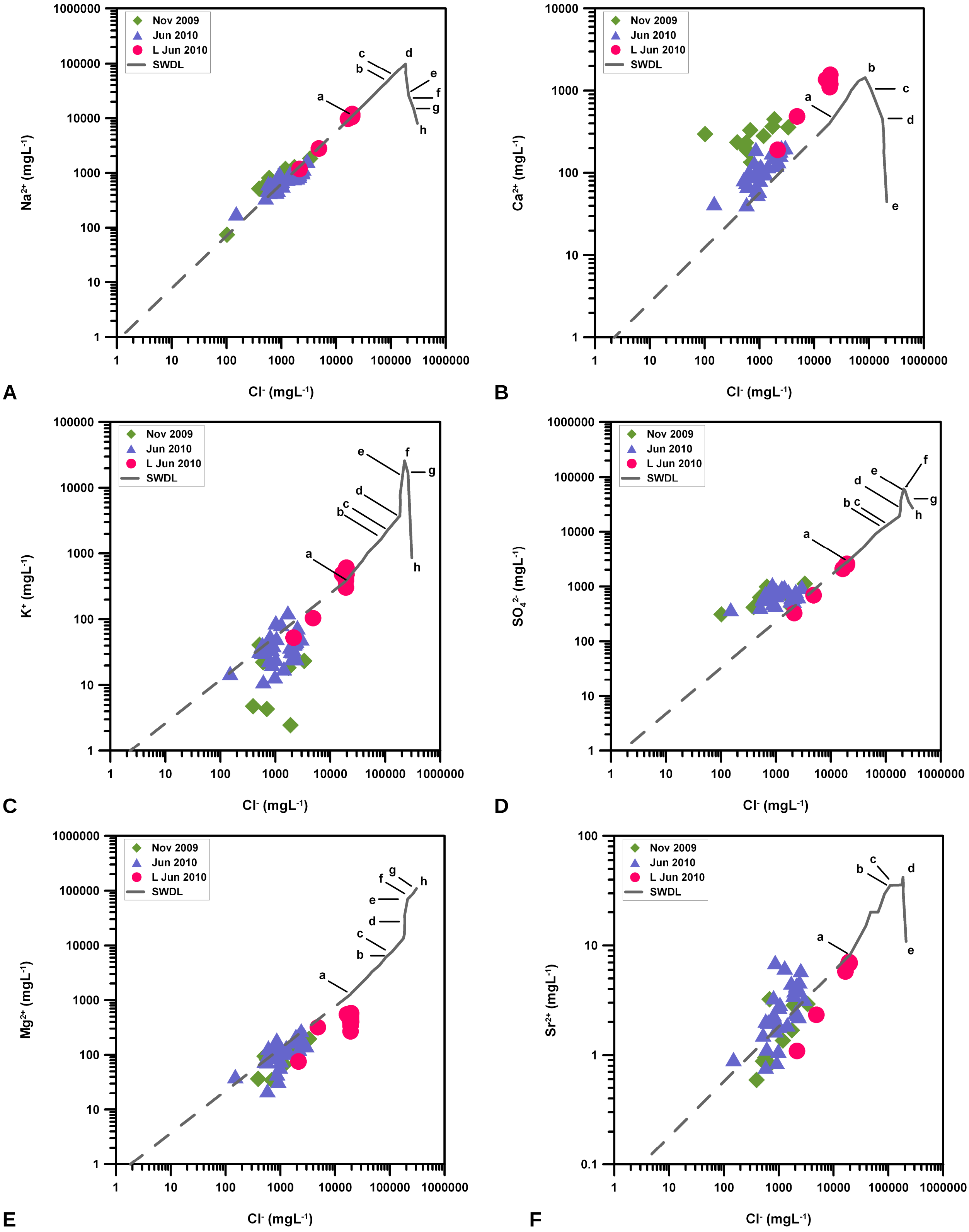


Figure 6. 11. Chemical composition of Bou-Areg groundwater and Lagoon of Nador water. Major elements vs. chloride concentration, Logartitmic Scale. (A) Sodium; (B) calcium; (C) potassium; (D) sulphates; (E) magnesium; (F) Strontium; a=seawater; b=beginning of calcite precipitation; c=beginning of gypsum precipitation; d=beginning of halite precipitation; e=beginning of epsomite precipitation; f=beginning of sylvite precipitation; g=beginning of carnallite precipitation; h=beginning of bischofite precipitation;dashed line=Sea Water Dilution Line (Fontes and Matray, 1993).

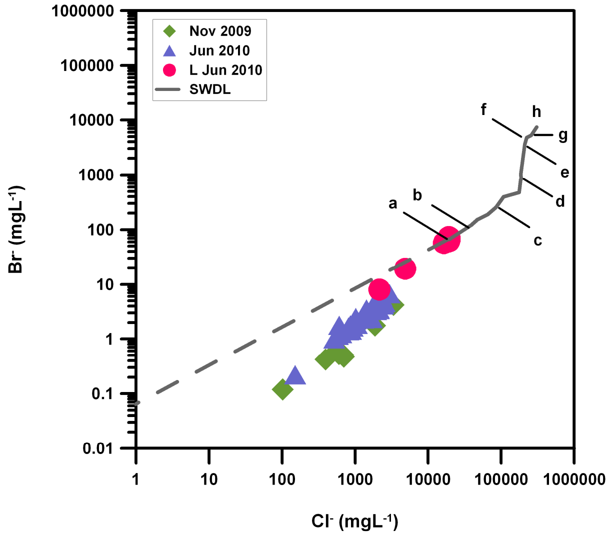


Figure 6. 12. Chemical composition of Bou-Areg groundwater and Lagoon of Nador: bromine versus chloride. water. a=seawater; b=beginning of calcite precipitation; c=beginning of gypsum precipitation; d=beginning of halite precipitation; e=beginning of epsomite precipitation; f=beginning of sylvite precipitation; g=beginning of carnallite precipitation; h=beginning of bischofite precipitation;dashed line=Sea Water Dilution Line (Fontes and Matray, 1993).

In chapter 5 sources of Boron causing excessive concentrations with respect to sea water have been discussed. Lagoon water samples all plot below the fresh water seawater dilution trend, highlighting that sea water mixing is not the dominant process affecting lagoon geochemistry.

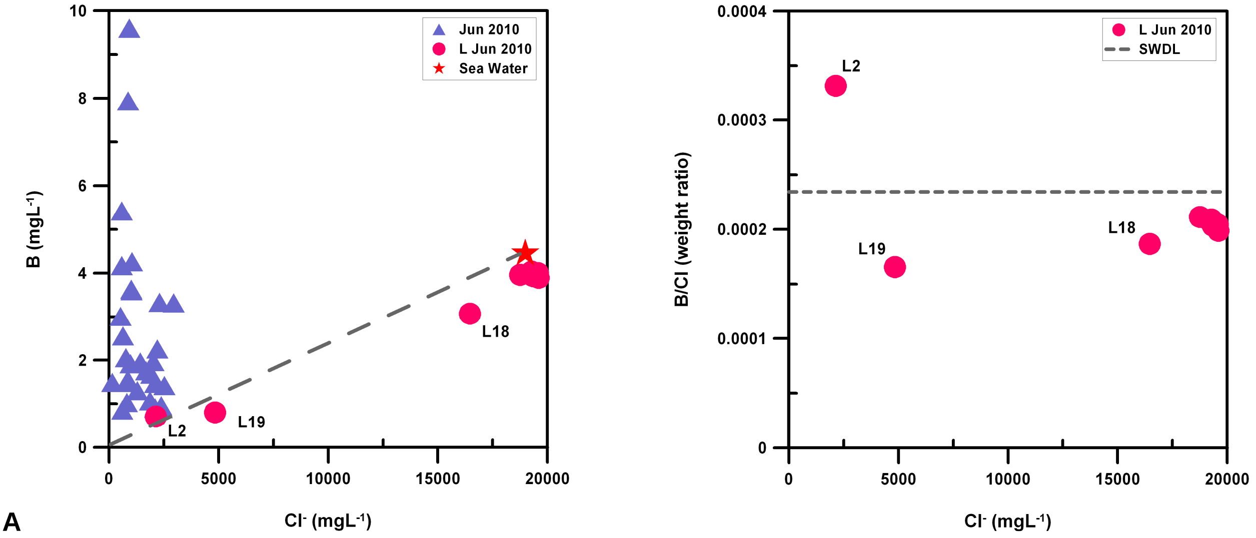


Figure 6. 13. (A) Plot of B versus Cl for both the lagoon and groundwater samples (Jun 2010); (B) Br/Cl weight ratio versus Cl. Dashed grey line: fresh water-seawater dilution line.

As emerged in this paragraph, the geochemical composition of the lagoon of Nador derives from both seawater mixing and other intermixed processes such as evaporation and groundwater inflows.

However, investigation on the absolute and relative concentrations of specific solutes, e.g. Cl, Na, Br and B, did not allow for a clear distinction of the effect of seawater mixing from evaporative processes.

In order to characterize the influence of the evaporation on the chemical composition of the lagoon and to understand its hydrogeochemical variations, stable isotopes of water molecule were investigated.

As in Chapter 5, data were plotted and compared to the Global Meteoric Water Line (Rozanski *et al*., 1993).

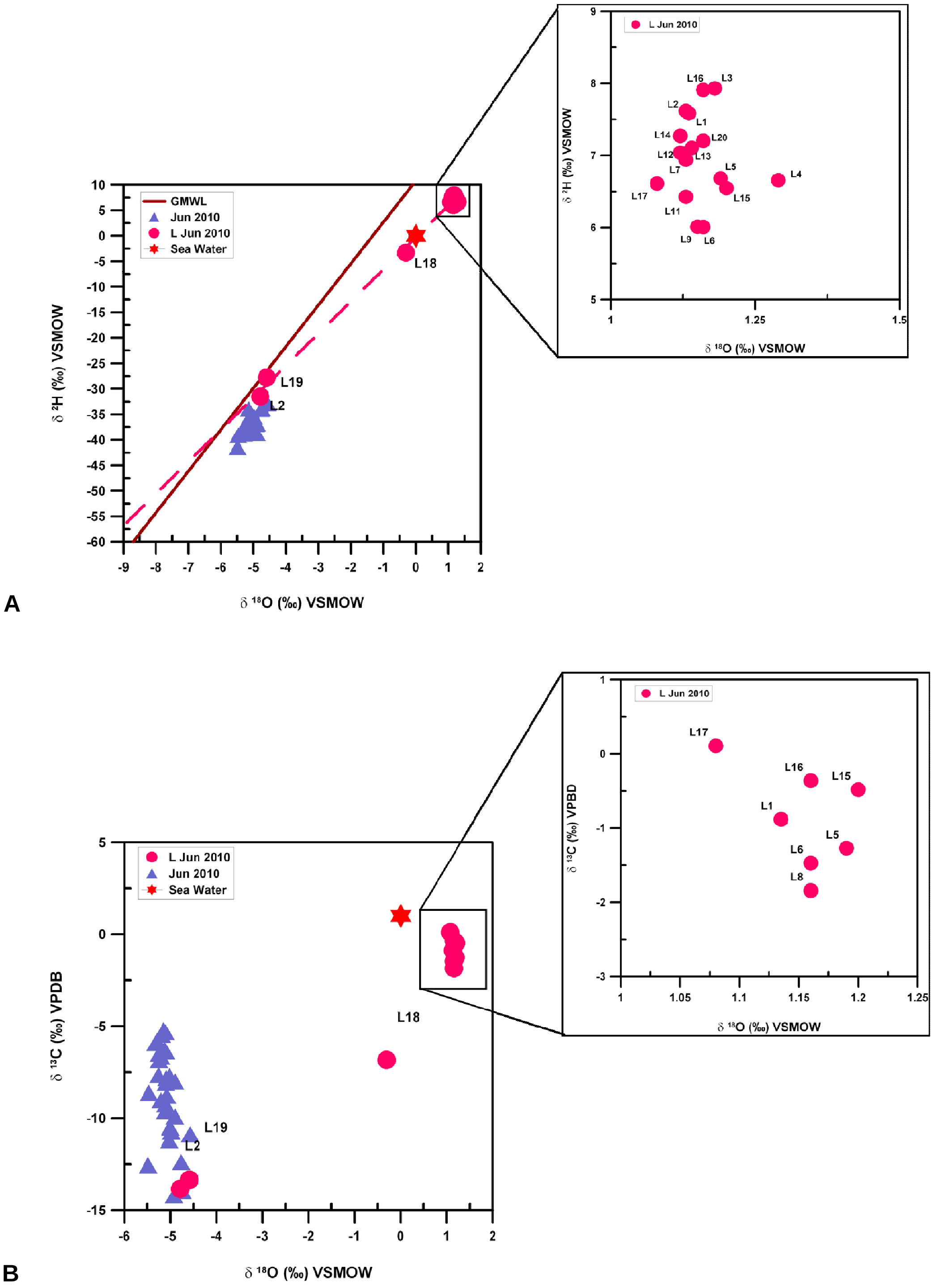


Figure 6. 14. (A) Delta Deuterium and oxygen-18 variations in the Lagoon of Nador waters (June 2010). Red star represents the Sea Water Value. Dashed pink line = fit linear equation.: $\delta^{2}H = 6.28\ \delta^{18}O - 0.31$; (B) Delta carbon-13 (‰) variations vs. oxygen-18 (‰) for the Lagoon of Nador (June 2010). Samples are also compared with the groundwater data obtained for June 2010.

When considering the isotopic signature of water molecule (Figure 6.14) one can notice that lagoon waters are quite homogeneous, all enriched in both oxygen-18 and deuterium if compared to the sea water composition. This enrichment, associated to the deviation from the GMWL suggests the occurrence of evaporative phenomena, as emerged in the previous sections.

The isotopic signal of carbon-13 show the tendency toward the sea water composition (+ 1‰), while L2 and L19 clearly show a signal that is not influenced by sea water mixing, thus confirming the continental origin of the waters (as the signal is more coherent with groundwater DIC of freshwater carbonates (~ +13‰). L18 (+7‰) has a tendency towards seawater values as well, thus confirming the lower mixing of the area.

In the same way by comparing chloride content and oxygen-18 (Figure 6.5) these tendencies can be pointed out. In fact, the isotopic enrichment in oxygen-18 is not associated with a change in chloride concentration, suggesting once again that the main active process involves an exchange of water molecules between the atmosphere and the lake, whereas the net change in the mass of water can be less important (Baneschi, 2007).

Figure 6.15 also show that most of the samples have a oxygen-18 signal towards the beginning of calcite evaporation. Quantification of evaporation or isotopic mass balance might be important to be determined.

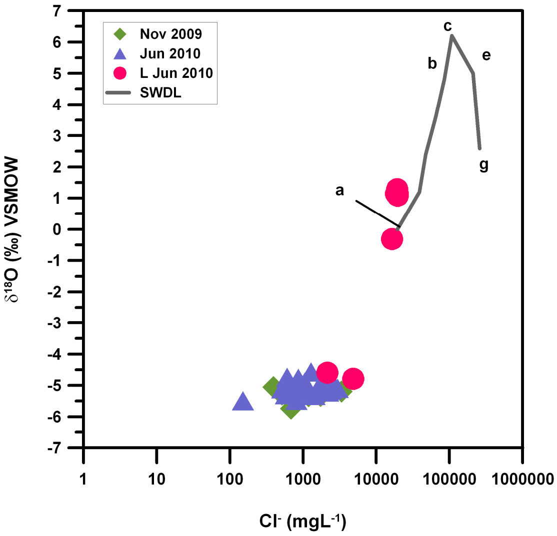


Figure 6. 15. Oxygen-18 versus chloride concentrations for both the Bou-Areg plain and lagoon of Nador. a=seawater; b=beginning of calcite precipitation; c=beginning of gypsum precipitation; d=beginning of halite precipitation; e=beginning of epsomite precipitation; f=beginning of sylvite precipitation; g=beginning of carnallite precipitation; h=beginning of bischofite precipitation;dashed line=Sea Water Dilution Line (Fontes and Matray, 1993).

7. Preliminary results of the November 2010 campaign

Distribution maps of physicochemical parameters have been used to show evidences of the aforementioned processes. The interpolation was done excluding well 31, as belonging to the Gareb Plain, as welll as wells 5 and 5b, as previously described to by separated from the others by a hydrochemical barrier. However if we exclude electrical conductivity and Eh interpolation values for P5b and P5 are coherent with the measeured ones.

Piezometric level (Figure 7.1 A) is decreasing towards the lagoon, thus confirming that the aquifer is recharging, and contributing as its freshwater input, the lagoon of Nador.

The lowest piezometric levels are found in the urban areas of Nador and Kariat Arekmane, hence making groundwater more sensitive and vulnerable to human induced pollutions (e.g. lecheate, septic effluents…)

Groundwater in the Bou-Areg Plain has pH values ranging from 7.1 and 8, with highest values in the upstream (exluding well 38) and downstream regions (Figure 7.1 B). On the other hand, lowest values are found in correspondence to the upper part and the mouth of the *oued* Selouane, and close to Kariat Arekmane.

The opposite trend seems to characterize groundwater temperature (Figure 5.2 B), with warmer waters in the central area.

The spatial distribution of conductivity shows that highest conductivity values (>7 Scm-1) characterize the wells closest to the lagoon border (3, 4 and 32 in the downstream area) and the zone stretching down *oued* Selouane towars the lagoon (Figure 7.2 A). This trend confirms the results obtained by Chaouni Alia *et al*. (1999).

Eh distribution appears to be quite homogeneous apart form the two extremes of the highest values in P7b and P29 (highest values), and P32 (lowest one).

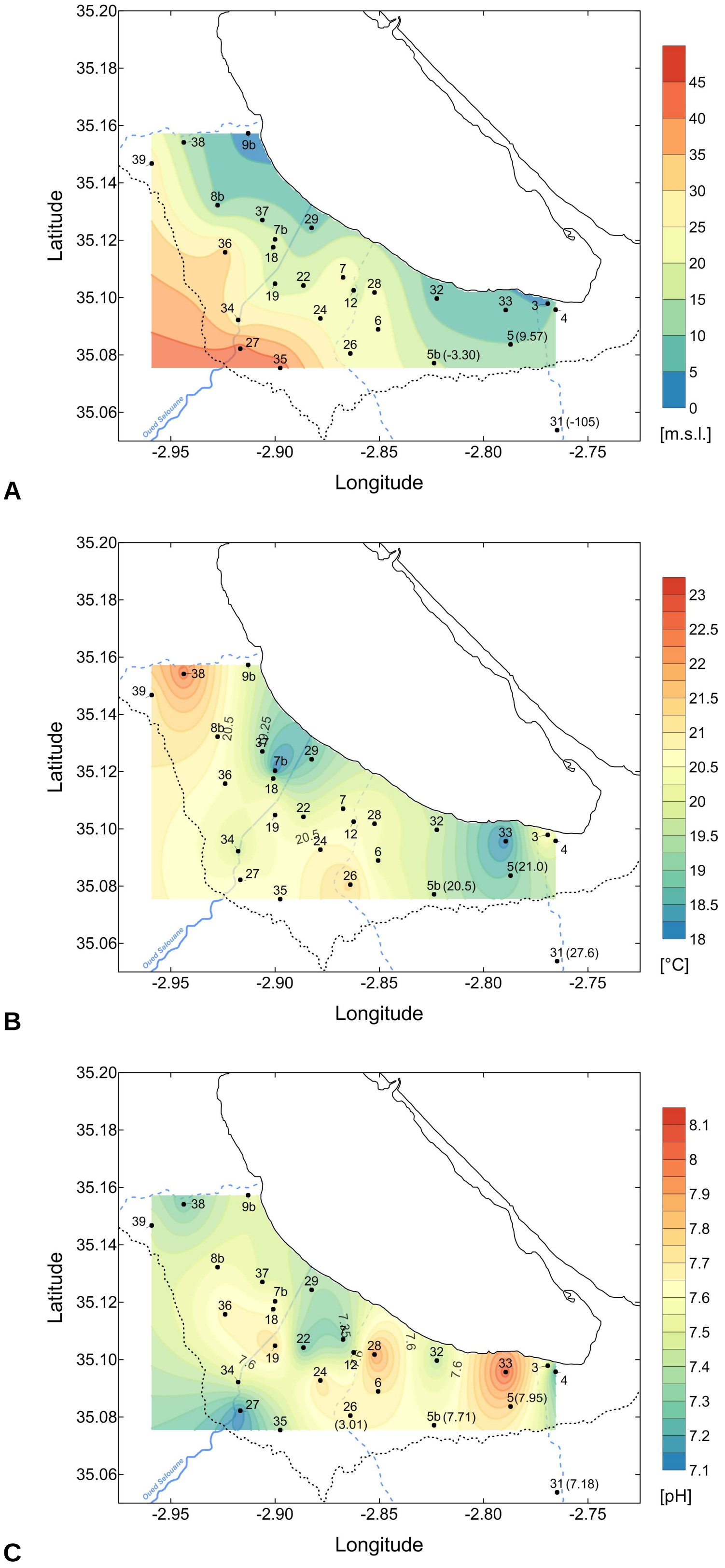


Figure 7. 1. Spatial distribution of physic-chemical parameters in the Bou-Areg Plain for the November 2010 survey, obtained with Kriging method. (A) Aquifer Level (m.s.l.); (B) groundwater temperature (°C); (C) pH. The distribution have been calculated excluding P5, P5b, and P31 and separated from the Bou-Areg plian system. Values for those wells are reported in the map.

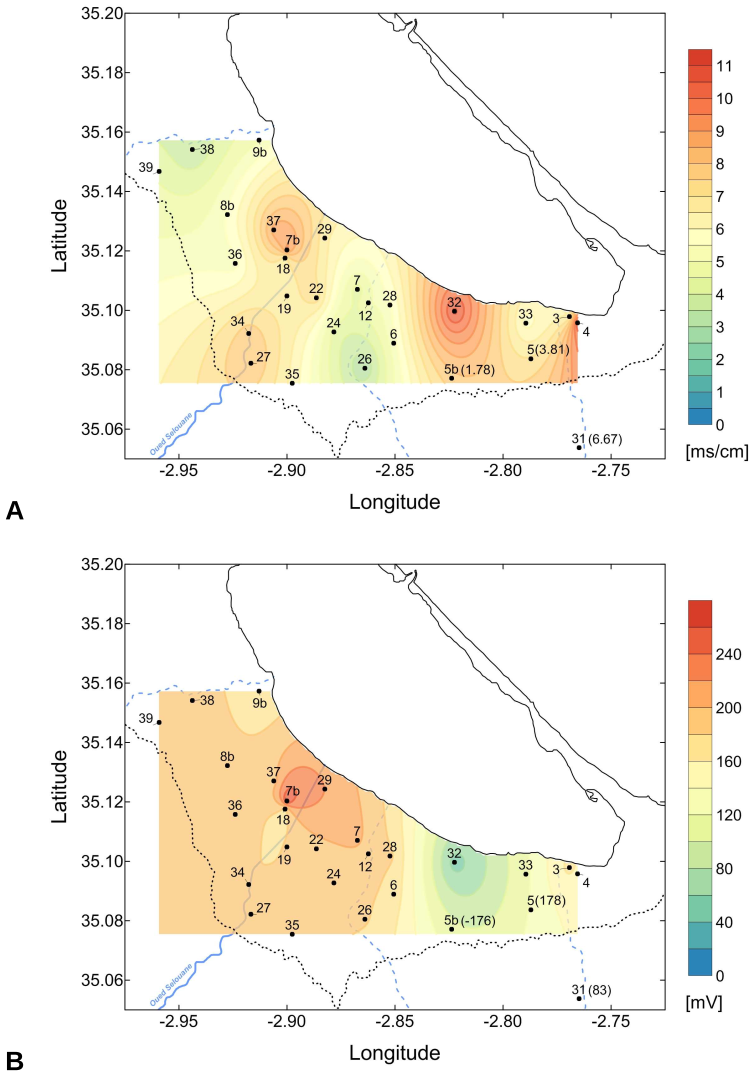


Figure 7. 2. Spatial distribution of physic-chemical parameters in the Bou-Areg Plain for the November 2010 survey, obtained with Kriging method. (A) Electrical Conductivity (mScm^{-1}) (B) Eh (mV).

Salnity index was again used to check groundwater suitability for agricultural practices (Figure 7.3) and verify seasonal variations of electrical conductivity.

Results confirm the non suitability for crop irrigation of most of the Bou-Areg aquifer waters. Some wells (P3, P19, P29) show a slight decrease conductivity values with respect to June 2010, while the others remained constant.

It is important to underline the high conductivity values of the *oued* Selouane, which salinity can be possibly associated to human contribution. On the other hand, the irrigation channel water (C) appears to be more siuitable for agricultural activities. The relatively low salinization of those waters coming from the Moulounya river are less saline, more suitable for agricultural purposes and more adequate to replace be groundwater from the Bou-Areg aquifer for those activities.

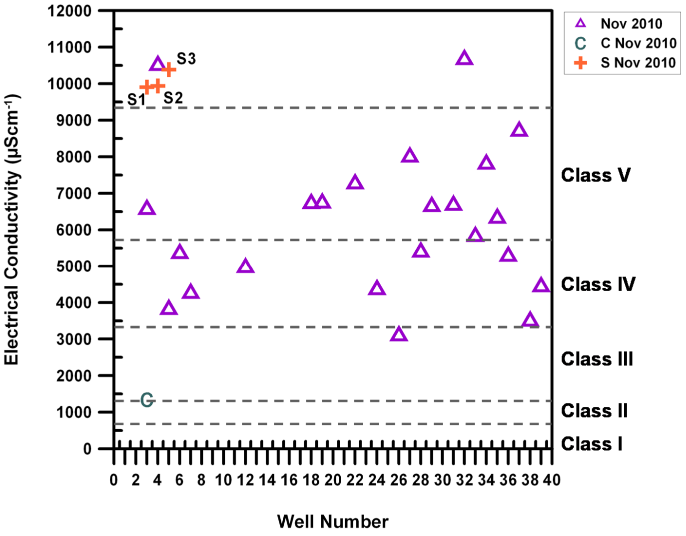


Figure 7. 3. Salinity Index (based on Ravikumar *et al*., 2010) for groundwater samples in the Bou-Areg aquifer,Irrigation channel (C) and o*ued* Selouane (S1, S2 and S3) sampled in November 2010.

8. Statistical analysis

8.1. Principal Component Analysis (PCA)

Statistical analysis on geochemical data for the Bou-Areg aquifer and the lagoon of Nador was applied, with the attempt to confirm the occurrence of processes described in the two previous chapters and to identify the main parameters controlling them.

In the first analysis, seventeen hydrochemical and isotopic variables (pH, EC, HCO_3, Na, K, Ca, Mg, Cl, NO_3, SO_4, Br, B, Sr, Li, $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$) and forty samples (30 groundwater and 10 lagoon water) Were investigated using multivariate statistical technique, to evaluate the occurrence of mixing processes between the lagoon and the aquifer.

This analysis was held considering only the parameters common to all the samples collected during the June 2010 campaign. As concerns lagoon water samples, only the ten with the complete results were included into the analysis.

The correlation matrix of the analyzed variables (Table 8.1) allowed for the distinction of the most relevant hydrochemical relationships. For example, high correlations of oxygen-18 and deuterium with EC, Cl, SO_4, K, Ca, Mg and Br, reflect the occurrence of mixing processes combined to the evaporative ones, as previously demonstrated by the deviations from the GMWL (Figure 5.3). Cl correlations with SO_4, Na, K, Ca and Br are representative of salinization processes in the aquifer.

The low determinant of the correlation matrix (6.46E-025) means that the variables have a high correlation and confirms that the data are adequate for the PCA to be performed (López Roldán and Lozares Colina, 2000). In the same way Barlett chi-square statistic test gave a value of 1,810.2 (with 136 degrees of freedom and a minimum significance level of 0.000) confirms the existence of a good intercorrelation within the variables. Moreover, the Kayser Meyer Olkin method (KMO) gives a quite high value (0.848), which allows one to consider valid the PCA application.

To reduce the overlap of original variables over each principal component, a varimax rotation was performed (Kaiser, 1958).

Table 8.2, shows the results after the rotation: the loadings of each obtained factor (F1, F2, and F3), the eigenvalues, the amount of variance explained by each factor and the cumulative variance.

	pH	EC	HCO_3	Cl	NO_3	SO_4	Na	K	Ca	Mg	Br	B	Sr	Li	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C$
pH	1																
EC	0.845	1															
HCO_3	-0.439	-0.655	1														
Cl	0.842	0.999	-0.659	1													
NO_3	-0.460	-0.601	0.637	-.614	1												
SO_4	0.826	0.977	-0.573	0.973	-0.568	1											
Na	0.853	0.998	-0.637	0.998	-0.602	0.975	1										
K	0.825	0.970	-0.614	0.969	-0.598	0.955	0.975	1									
Ca	0.808	0.987	-0.670	0.986	-0.599	0.960	0.989	0.986	1								
Mg	0.575	0.887	-0.708	0.886	-0.563	0.854	0.881	0.906	0.929	1							
Br	0.848	0.997	-0.656	0.997	-0.605	0.969	0.998	0.966	0.986	0.877	1						
B	0.491	0.258	0.359	0.251	0.136	0.298	0.278	0.266	0.222	0.011	0.258	1					
Sr	0.504	0.764	-0.651	0.759	-0.460	0.797	0.742	0.747	0.757	0.789	0.738	-0.042	1				
Li	-0.073	0.150	-0.107	0.155	-0.200	0.211	0.132	0.167	0.132	0.215	0.117	0.023	0.560	1			
$\delta^{18}O$	0.867	0.992	-0.622	0.991	-0.576	0.977	0.992	0.969	0.976	0.852	0.991	0.284	0.757	0.137	1		
$\delta^{2}H$	0.862	0.991	-0.644	0.990	-0.573	0.968	0.991	0.964	0.976	0.858	0.991	0.257	0.751	0.110	0.996	1	
$\delta^{13}C$	0.609	0.756	-.0366	0.767	-0.625	0.751	0.762	0.723	0.729	0.663	0.748	0.292	0.623	0.367	0.739	0.729	1

Table 8. 1. Correlation matrix of the physicochemical parameters for the Bou-Areg plain and lagoon of Nador (data: June 2010). Underlined values represent relevant correlations.

	F1	F2	F3
Na	0.989	-0.050	0.119
Br	0.987	-0.073	0.102
$\delta^{18}O$	0.985	-0.032	0.121
EC	0.984	-0.072	0.137
$\delta^{2}H$	0.984	-0.060	0.094
Cl	0.983	-0.079	0.142
Ca	0.976	-0.116	0.121
K	0.965	-0.059	0.150
SO_4	0.958	-0.006	0.209
pH	0.901	0.214	-0.114
Mg	0.843	-0.307	0.228
$\delta^{13}C$	0.725	0.081	0.436
Sr	0.673	-0.281	0.575
NO_3	-0.579	0.435	-0.191
B	0.332	0.901	0.013
HCO_3	-0.608	0.702	-0.056
Li	0.013	-0.013	0.978
Eigenvalue	11.954	1.759	1.751
% of variance explained	70.266	10.349	10.297
% of cumulative variance	70.266	80.615	90.912

Table 8. 2. Matrix of rotated component. Rotation method: Varimax (Kaiser, 1958). Underlined values represent relevant loadings.

Factor 1 resulting from this analysis explains the 70.3% of the total variance and it is mainly participated by Na, Br, $\delta^{18}O$, Electrical Conductivity, $\delta^{2}H$, Cl, Ca, K, SO_4, pH, Mg, $\delta^{13}C$ and Sr.

This factor can represent the Salinization Component, partially due to agricultural contribution (as the high loads of K, Br and carbon-13), salts remobilization in the non-saturated zone, or influence of evaporative rocks dissolution.

It must be noticed that NO_3 has a relatively high negative score in Factor 1, suggesting that it is antithesis with the total mineralization.

Factor 2, explaining 10.35% of the variance, includes NO_3, B and HCO_3, and is likely to be the pollution component. Those high scores can be attributed to water infiltration from irrigation recharge and leaching of domestic wastewaters and manure into the aquifer, passing through a carbonate system.

Factor 3, includes only Li, thus suggesting that this element has a very low correlation with all the others, also supported by the low scores with all the other variables in the correlation matrix (Table 8.1). This can be related to the chemical behaviour of lithium, a conservative element, as once brought into solution it tends to remain in the dissolved state (Hem, 1985).

Variables’ distribution with respect to the three principal components (Figure 8.1) supports the definition of the main characteristics of the components, which coincide with the main phenomena assumed to be affecting water composition in the region in chapters 5 and 6.

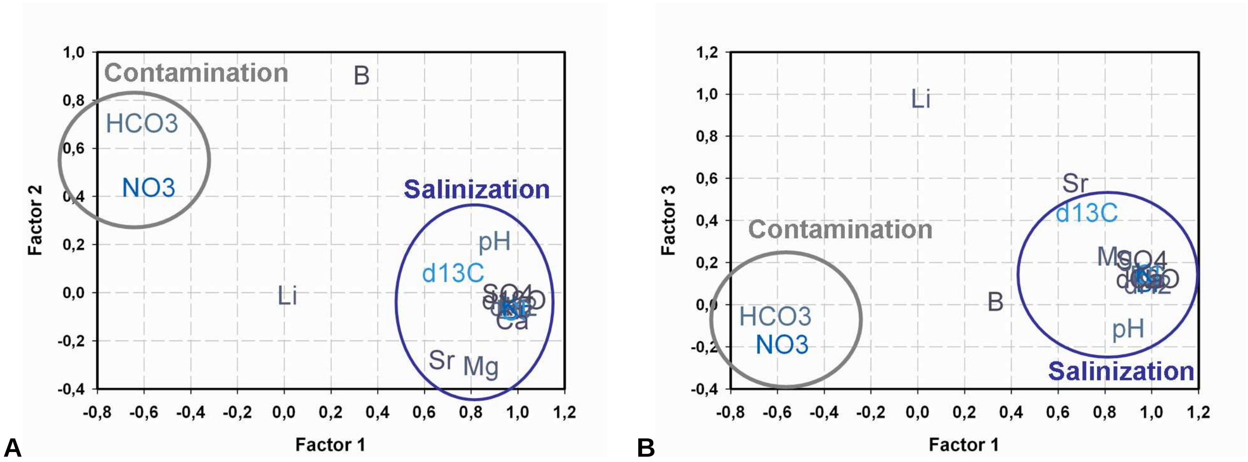


Figure 8. 1. Distribution of the studied hydrochemical parameters with respect to the factors resulting from the PCA (June 2010 data): (A) Factor 1 vs. Factor 2, and (B) Facto1 vs. Factor 3.

The separation between continental waters (Bou-Areg aquifer) and lagoon water appears evident, highlighting the different origin of those systems. Once again, springs behaviour is not completely coherent with groundwater’s one, nor with lagoon water.

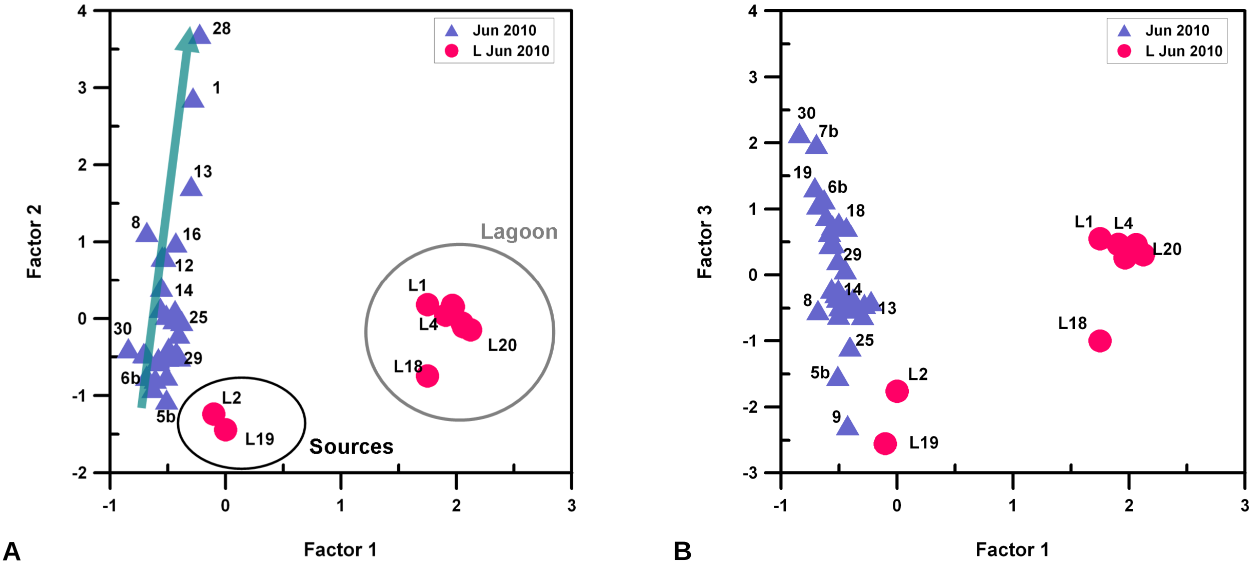


Figure 8. 2. (A) Plot of Factor 1 vs. Factor 2 and (B) Factor 1 vs. Factor 3.

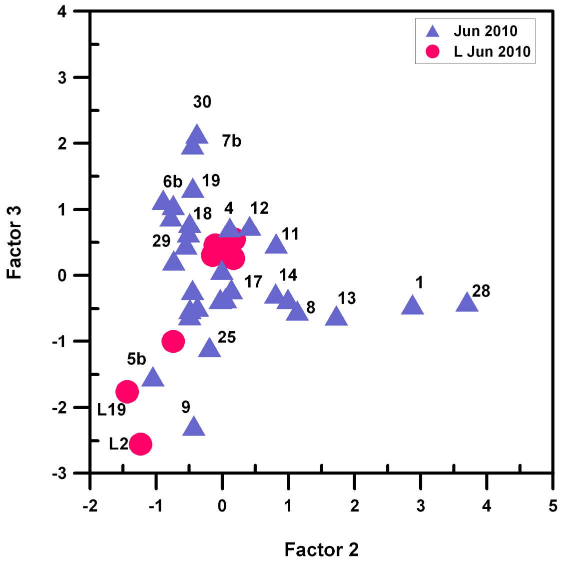


Figure 8. 3. Plot of Factor 1 vs. Factor 3.

To verify the relevance of Factor 3 for the explaining the processes occurring within the aquifer/lagoon system, lithium was excluded by the factorial analysis. As a result, only two factors were obtained, explaining the 75.22% and 13.03% of the variance.

Also in this case the analysis can be considered good, given the low determinant of the correlation matrix (5.17E-024), and the good intercorrelation within the variables (Barlett chi-square statistic test gave a value of 1,760.5, with 126 degrees of freedom and a minimum significance level of 0.000). Again, the Kayser Meyer Olkin method (KMO) gives a quite high value (0.877), allowing for considering the PCA application acceptable

As in the previous case, Factor 1 can be assumed to be the salinization factor, thus including the same variables and being characterized by the high negative correlation between nitrates.

Those results support the separation between aquifer and lagoon water, thus not allowing for a clear identification of salinization end-members.

	F1	F2
Cl	0.995	0.035
EC	0.995	0.043
Na	0.994	0.067
Br	0.991	0.047
Ca	0.988	0.000
$\delta^{18}O$	0.988	0.085
$\delta^{2}H$	0.986	0.060
K	0.977	0.051
SO_4	0.975	0.094
Mg	0.899	-0.222
pH	0.836	0.348
Sr	0.792	-0.263
$\delta^{13}C$	0.780	0.111
HCO_3	-0.680	0.612
NO_3	-0.647	0.375
B	0.229	0.929
Eigenvalue	12.035	2.084
% of variance explained	75.221	13.028
% of cumulative variance	75.221	88.249

Table 8. 3. Matrix of rotated component of the PCA analysis (June 2010 data for both the aquifer and the lagoon of Nador) performed without Li. Rotation method: Varimax (Kaiser, 1958). Underlined values represent relevant loadings.

This first result of the PCA allow one to exclude the lagoon water as a possible end-member of mixing processes within the aquifer.

Moreover, due to the high number of variables (and their good correlation) in Factor 1, from this analysis it is not possible to clearly discriminate between natural salinization and human induced one.

Once stated that, the adequateness of the dataset for an integrated water resource assessment of the aquifer was checked performing a PCA only on groundwater data, based on the possible identification of the needed end-members.

This analysis was performed considering 30 groundwater samples (June 2010 survey) and all the available physicochemical and isotopic parameters (19 variables).

In the obtained correlation matrix (Figure 8.3; determinant 9.03E-014) the most relevant hydrochemical relationships are again displayed (underlined values).

The Barlett chi-square statistic test gave a value of 655,78 (with 171 degrees of freedom and a minimum significance level of 0.000) and confirms the existence of a good intercorrelation within the variables (López Roldán and Lozares Colina, 2000). Kayser Meyer Olkin method (KMO) gives a relatively high value (0.632), thus allowing for considering the PCA application acceptable.

	pH	EC	HCO_3	Cl	NO_3-	SO_4	Na	K	Ca	Mg	Br	Sr	Li	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C$	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$	CO_3
pH	1	1																	
EC	-0.451	1																	
HCO_3	0.425	-0.392	1																
Cl	-0.512	$\underline{0.935}$	-0.449	1															
NO_3-	0.186	-0.047	0.507	-0.243	1														
SO_4	-0.082	0.505	0.001	0.249	0.139	1													
Na	-0.213	$\underline{0.889}$	-0.136	$\underline{0.895}$	-0.065	0.385	1												
K	-0.090	0.278	-0.063	0.242	-0.147	0.415	0.205	1											
Ca	$\underline{-0.683}$	$\underline{0.864}$	$\underline{-0.559}$	$\underline{0.824}$	-0.168	0.431	$\underline{0.609}$	0.369	1										
Mg	$\underline{-0.811}$	$\underline{0.729}$	$\underline{-0.576}$	$\underline{0.755}$	-0.191	0.243	0.445	0.208	$\underline{0.859}$	1									
Br	-0.417	$\underline{0.889}$	-0.406	0.925	-0.229	0.287	$\underline{0.883}$	0.142	$\underline{0.704}$	$\underline{0.637}$	1								
Sr	-0.396	0.601	$\underline{-0.544}$	0.490	-0.024	0.480	0.267	0.505	$\underline{0.755}$	$\underline{0.700}$	0.315	1							
Li	-0.339	0.600	-0.310	0.616	-0.172	0.298	0.474	$\underline{0.724}$	$\underline{0.708}$	0.536	0.402	$\underline{0.695}$	1						
$\delta^{18}O$	-0.051	0.199	-0.040	0.038	0.487	0.425	0.017	0.370	0.208	0.214	0.028	0.516	0.258	1					
$\delta^{2}H$	-0.244	0.325	-0.093	0.205	0.360	0.367	0.132	0.207	0.289	0.446	0.163	0.497	0.166	$\underline{0.753}$	1				
$\delta^{13}C$	-0.071	0.360	-0.024	0.488	-0.361	-0.150	0.465	-0.109	0.237	0.264	0.354	0.046	0.258	-0.484	-0.202	1			
$\delta^{15}N_{NO3}$	-0.035	0.047	0.521	-0.016	$\underline{0.553}$	0.116	0.106	0.210	-0.052	-0.012	-0.025	-0.047	0.110	0.293	0.193	-0.157	1		
$\delta^{18}O_{NO3}$	-0.113	0.072	-0.423	0.212	$\underline{-0.619}$	-0.049	0.162	-0.036	0.103	0.065	0.196	-0.094	0.029	-0.476	-0.463	0.098	-0.244	1	
CO_3	0.500	-0.177	0.442	-0.229	0.273	0.020	0.006	0.212	-0.303	-0.491	-0.190	-0.318	-0.064	-0.092	-0.209	-0.100	0.319	0.065	1

Table 8. 4. Correlation matrix of the physicochemical parameters for the Bou-Areg plain (data: June 2010). Underlined values represent relevant correlations.

Again, to reduce the overlap of original variables over each principal component, a varimax rotation was performed, giving the five factors presented in Table 8.4.

	F1	F2	F3	F4	F5
Na	0.971	-0.051	0.025	0.108	-0.032
Br	0.915	0.203	-0.136	0.031	0.010
EC	.0.915	0.261	-0.013	0.224	0.164
Cl	.0.892	0.330	-0.097	0.226	-0.080
Ca	0.648	0.515	-0.124	0.420	0.145
CO_3	-0.010	-0.797	0.185	0.207	-0.058
pH	-0.262	-0.769	0.013	-0.169	0.074
Mg	0.512	0.759	-0.041	0.264	0.080
NO3	-0.049	-0.153	0.778	-0.195	0.384
$\delta^{15}N_{NO3}$	0.077	-0.183	0.756	0.235	-0.008
$\delta^{18}O_{NO3}$	0.173	-0.165	-0.737	0.064	-0.255
HCO_3	-0.188	-0.540	0.683	-0.121	-0.171
K	0.085	-0.106	0.010	0.908	0.218
Li	0.378	0.234	0.005	0.832	-0.005
Sr	0.272	0.502	-0.074	0.559	0.438
$\delta^{18}O$	-0.011	0.180	0.365	0.229	0.803
$\delta^{13}C$	0.466	0.126	-0.008	0.029	-0.659
$\delta^{2}H$	0.149	0.394	0.379	0.049	0.651
SO_4	0.420	-0.154	-0.013	0.263	0.637
Eigenvalue	4.877	3.209	2.550	2.499	2.462
% of variance explained	25.666	16.891	13.423	13.153	12.956
% of cumulative variance	25.666	42.557	55.980	69.134	82.090

Table 8. 5. Matrix of rotated component of the PCA analysis (June 2010 data for the Bou-Areg aquifer). Rotation method: Varimax (Kaiser, 1958). Underlined values represent relevant loadings.

As a result of this analysis, Factor 1 has high loading of Na, Br, EC, Cl (with lower but significant scores for Ca, Mg and ^{13}C) and accounts to the 25.7% of the total variability. The highest scores for this factor are given by wells 2, 3, 4, 10, 15 and 27. It must be noticed that wells 3, 4 and 15 are located in the eastern zone, close to each other, thus suggesting a possible common origin of those waters, that might be related to evaporites dissolution. As Chaouni *et al*. (1997) pointed out the occurrence of saline water intrusion in this sector of the plain, the high salinity of those samples might also be associated to existence of old seawater intrusion or presence of connate water (El Yaouti *et al*., 2009). On the other hand wells 10 and 27 were described in Chapter 5 as possibly showing a composition being affected by marine aerosol, although bromine values did not supported this theory, and the need for further investigation have been highlighted.

Hence, this factor can represent, as in the previous case, the salinization factor, somehow related to seawater.

Factor 2 is characterized by a high negative correlation between CO_3 and pH and HCO_3 with Mg. The good positive correlations also between Mg, Ca and Sr might suggest this can be assumed as the carbonated pole. In addition, the negative correlation between HCO_3 and Mg (and Ca) may reflect also the occurrence of cation exchange within the system. The samples with the highest scores for this factor are in fact wells 20, 22 and 27 (Figure 8.4 A), as the ones more enriched in Mg. However, by plotting samples' scores for Factor 1 and Factor 2 a clear separation between the two proposed processes is not possible, thus confirming that the salinization in the aquifer results from the complex interaction of both the components.

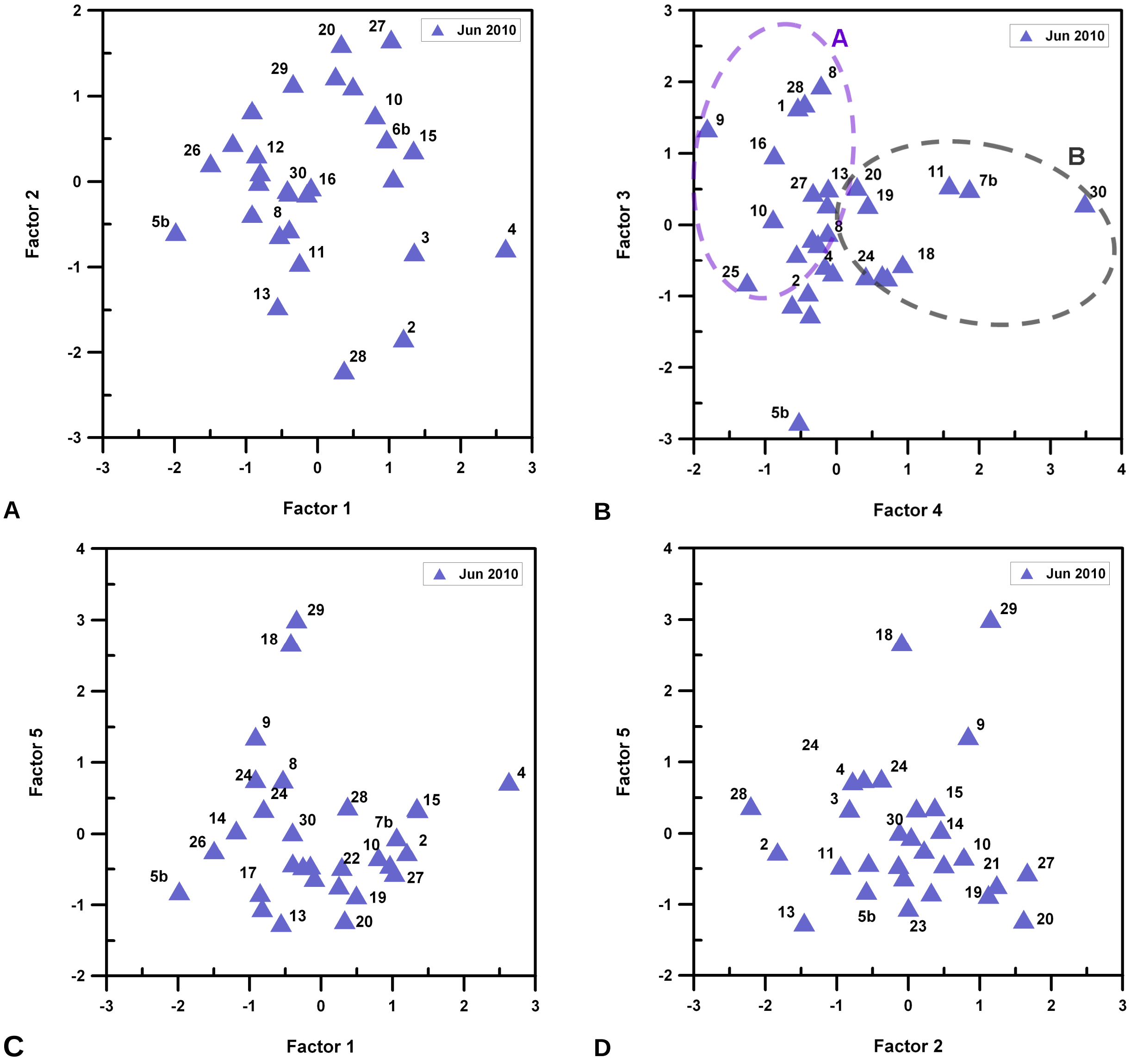


Figure 8. 4. Plots of factors' scores for samples collected in June 2010 for the Bou-Areg Aquifer: (A) Factor 1 vs. Factor 2; (B) Factor 3 vs. Factor 4. The groups A and B correspond to the ones proposed in chapter 5 (cfr. Figure 5.19 A9; (C) Factor 1 vs. Factor 5 and (D) Factor 2 vs. Factor 5.

Factor 3, can be assumed to be the factor of human induced (organic) pollution, mainly associated to dissolved nitrates in groundwater. The samples that are mostly represented by this factor are 1, 8, 9 and 28, as the wells described in Chapter 5 to be affected by manure and septic effluents contamination.

The high negative correlation between the two isotopes of dissolved nitrates can in this case suggest a mixing with synthetic fertilizers and manures (higher ^{15}N and lower ^{18}O), hence confirming the occurrence of mixing processes as proposed in chapter 5 (Figure 5.25). On the other hand, the correlation between HCO_3 and NO_3 can be associated to nitrification processes, producing an increase of H^+ in the system. This increase can favour $CaCO_3$ dissolution thus leading to an increase in HCO_3 (Stumm and Morgan, 1981).

Factor 4 (highest correlation with K and Li) can represent the pole of agricultural (and synthetic) pollution. In this case, the most represented well is well 30, previously assumed to be strongly affected by agricultural pollution.

By plotting Factor 4 versus Factor 3 (Figure 8.4 B) the samples present a clearer distinction between the two components reinforcing the grouping proposed in Chapter 5 for nitrate pollution.

To conclude, Factor 5 present a good correlation among oxygen-18, deuterium and sulphates, associated with a negative correlation with carbon-13. This negative correlation can be due to the progressive enrichment in δ^{13}C associated to carbonates dissolution or, on the other hand, influence of evapotranspirative processes related to the presence of cultivated plants (decrease in δ^{13}C and increase in δ^{18}O signal).

The highest factor scores are found for well 18 and 29, previously assumed to be the most evaporated ones, and hence supporting the idea that this factor can be representative of evaporative processes.

By plotting Facto5 1 versus Factor 5 (Figure 8. 4 C) the separated influence of the two components can be seen, especially for wells 4 and 15 with respect to 18 and 29. This distinction might support the proposed presence of old salt water (or connate water) in the western part of the aquifer, affecting groundwater quality with a higher extent than salinization. In the same way Factor 2 plotted against Factor 5 (Figure 8.4 D) allow to better separate the wells mostly characterized by salinization due to carbonates dissolution/cation exchange, from the ones for which the evaporative processes are dominant.

However, despite those general distinctions, what emerges from the PCA is that some wells are highly represented by the factors, but at the same time most of the samples are homogeneously plotting. Meaning that the data are probably not so adequate for describing the problem at regional level (the majority of the samples is fact located in the central/agricultural part of the plain), also due to the interaction of many different processes affecting the quality of the aquifer.

Those findings support the decision of changing the sampling net occurred for the November 2010 campaign.

8.2. Clustering

To conclude, cluster analysis was used to reinforce the results obtained so far, with both the hydrochemical and statistical approaches, and to group groundwater samples (June 2010 survey) according to their common characteristics, based on the 5 components obtained from the second PCA (Table 8.5).

The clustering mainly reflects the distinctions among the wells described in chapter 5 and in the previous section. In particular can be seen that wells 1, 8, 9 and 28 are grouped together with 18 and 19, consequently being associated to the agricultural/organic pollution. On the other hand wells 11, 17 and 30 are related to agricultural/synthetic pollution.

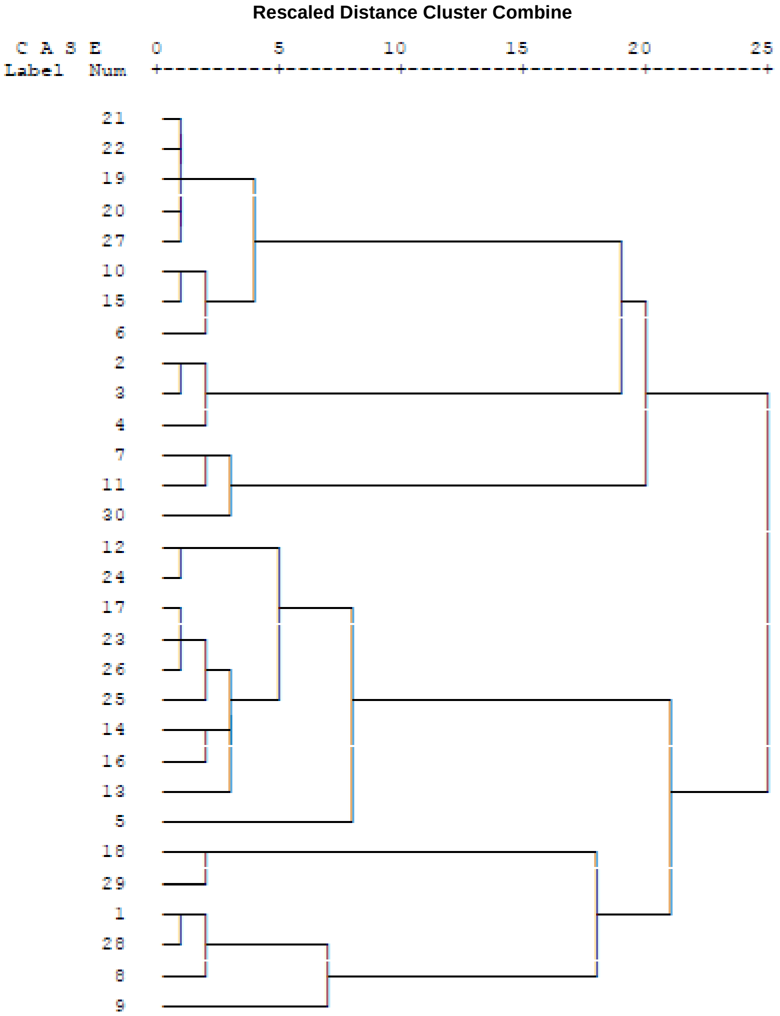


Figure 8. 5. Dendrogram based on agglomerative hierarchical clustering, Ward's method, for the samples collected in the Bou-Areg aquifer (Jun 2010).

However, due to the complexity of the system and the combined action of several processes affecting water quality in the system, the subgroups obtained from the clustering do not give any information about the zonation of the sites associated to the main hydrochemical processes. Therefore the PCA and the clustering can not be considered as fully describing the main characteristics of the sampling sites.

Indeed, although the multifactor analysis allowed for a preliminary distinction among the main factors affecting groundwater composition, and a grouping of wells according to those common factors, it appears clear that, for an integrated management to be performed the dataset is not completely adequate.

As already mentioned, this work is part of an ongoing project, therefore, once obtained the results for the November 2010 campaign a new PCA will be performed and the possible end-members will be identified, allowing for the mixing analysis to be performed.

9. Conclusions and future perspectives

Urban and coastal aquifers in arid and semi-arid climates mainly depend on groundwater resources. Their continuous withdraw to respond to human needs, often leads to a deterioration of the natural quality of the aquifers, with severe effects on natural ecosystems and human health.

These issues were addressed in the research project, by applying hydrogeochemical tools to support groundwater management practices. Stress was put on the role of groundwater in sustaining coastal lagoons and wetlands, including their habitats and ecosystems, in both the general case of the Mediterranean shores, and the specific case study of the Grand Nador area (Morocco). The understanding of the hydrogeochemical characteristics of the Bou-Areg coastal aquifer and its interactions with the lagoon will serve as a basis for future local management practices. In fact, mitigation and remediation policies addressed to the reduction of salt concentrations in the aquifers have to be based on a robust knowledge on the mineralization causes. Therefore, it is of primary importance to clearly identify salinity origin, as well as to characterize its sources and quantify their specific contributions.

The present study also highlighted the importance of including aquifer systems in coastal zones management plans, due to their fundamental role in controlling environmental processes. On the other hand, due to their high vulnerability, special attention should be paid in preserving them from human impacts or in improving their characteristic if the natural quality has been already altered.

In the framework of the UNESCO-IHP SAP/MED component, this research aimed to translate scientific findings into objective criteria for developing sustainable coastal zone management policies in coastal district of Nador and, on a broader perspective, to serve as example along the Southern Mediterranean shore.

Geochemical analysis was applied to describe the main processes occurring in the Bou-Areg coastal plain and its interactions with the lagoon of Nador.

Two kinds of waters are assumed to characterize the aquifer, deeper freshwater, separated from the whole system, with relatively high quality, and water mainly recharged by mountain runoff, interacting with different saline sources of local recharge, thus creating a complex system of diluted waters. The presence of a flexure in the southern part of the aquifer creates a hydraulic barrier, which further contributes to the differentiation in the geochemical compositions of the studied groundwater.

Experimental findings confirm that the high salinity of the aquifer is given by the coexistence of dissolution processes of evaporative rooks and carbonates from Miocene substratum, water-rock interactions, and human impacts due to agricultural return flows. The latter represent the main contribution to groundwater salinization, especially in the central part of the aquifer, as well as one of the main causes of the general increase in nitrate concentrations. A possible influence of marine aerosols is partially supported by the general chemistry, yet it should be verified studying the isotopic signal of strontium. In addition, the high salinization observed in the southern part of the aquifer, close to the city of Kariate Arekmane, might be attributed to the presence of connate water.

Estimates of the Salinity Index (SI) confirmed a high degree of salinization for this system, thus suggesting that the waters of the Bou-Areg aquifer are inappropriate for irrigation purposes. Moreover, the SI might represent a powerful and straightforward indicator not only to support the findings of the study, but also for dissemination purposes.

Given the hydrochemical results, isotopic investigation of dissolved nitrates, allowed for the identification of two main drivers for human induced pollution: (i) manure and septic effluents, especially in the urban areas and in the central part of the plain where houses are not adequately equipped with sanitation systems, and (ii) synthetic fertilizers in the agricultural zone.

One must also note that, the sum of the abovementioned pressures and the effects of agricultural return flows are acting in a synergic way and contemporaneously affecting the aquifer quality. Adequate policies should indeed focus on both urban and agricultural pollution in the region, in order to prevent the natural system from further contamination and protect human wellbeing in the Nador district. Consequently, the non-drinkability and non-adequateness of groundwater for irrigational practices should be better highlighted at local level also to reduce the potential risks for human health.

As a major threat of the system, the agricultural return flow has significantly modified the chemistry of the system and it is a prime example of the human induced changes over coastal environments. Management plans for the preservation of the aquifer and the reduction of anthropogenic impacts on the lagoon should promote the reduction of groundwater use for agricultural practices and the consequent increase in the use of the waters distributed by the irrigation channel.

The hydrogeochemical investigation allowed to consider the saline water intrusion from the lagoon in the shallow aquifer to be negligible, while discharge of polluted groundwater into the lagoon has been found to partially alter its quality. As many springs are present in the lagoon shore, further studies should be extended also to the evaluation and quantification of Submarine Groundwater Discharge (SGD) in order to better assess the impact of the aquifer to the lagoon. In fact, the decline of direct pollution loads into aquifer will produce an improvement in the quality of the general environment, which is a relevant prerequisite considering the future development planned for the area, foreseeing the construction of tourism facilities and recreational sites

The statistical data treatment was used to support the hydrogeochemical findings and to verify the adequateness of the dataset to explain processes occurring at a regional level. As the multivariate analysis supported absence of saline water intrusion from the lagoon, the latter can not be assumed to be an end-member for mixing processes. Therefore, as already highlighted by the hydrogeochemical results, other sources are influencing the properties of the Bou-Areg system.

The sampling data appear to be representative to the main pollution processes, although not allowing for a clear spatial distinction or quantification of the different mixing processes. Those results support the decision to partly redesign the spatial structure of the November 2010 field campaign, which was carried out over a broad investigation area and included both the permanent river and the irrigation channel. The geochemical and statistical analysis on those samples will allow for obtaining a clearer vision on the general processes occurring in the area, and to retrieve adequate criteria for supporting integrated water management at catchment level. Furthermore, those results could strengthen the possibility of promoting different alternatives for water supply, which the current data set cannot confirm.

All the scientific findings of this work enclose important **management implications** for the future development of groundwater resources in the Bou-Areg plain. A management priority should be represented by the reduction of groundwater extraction and synthetic fertilizers employment for farming practices, since the agricultural return flow was shown to have severe impacts on the general quality of the system. A strategic alternative is instead represented by the alternate exploitation of the water distributed through the artificial channel with the treated (and purified from bacteria) one coming from the STEP (wastewater treatment plant). The latter solution would allow to employ an irrigation water characterized by a controlled nutrients concentration and composition, with the consequent decrease of synthetic components discharge into the system. Obviously, this option will involve the periodic control of the water quality across the plain to avoid the possible drawbacks (,e.g. the increase of dissolved nitrates concentration). Besides the remediation actions at the regional level (catchment), the complex pressures exerted by different pollution sources (punctual and diffused) highlight the need to enforce an adequate groundwater protection trough specific, local actions at the single well level. To this regard communication plans should promote the awareness of households and farmers, as well as, the public participation within the management process.

Future investigations should engage a direct confrontation with wells holders and local farmers associations to better address the study (ensure possibility of seasonality studies given the permission to include the selected wells in the sampling network), and to retrieve reliable information about the amount and nature of fertilizers and other substances spread on the soil or poured into the wells.

To conclude, the present work highlighted that the low water quality of the aquifer is mainly related to anthropogenic pressures, namely (i) high fertilizers inputs, (ii) inadequate irrigation practices, and (iii) lack of sufficient sanitation facilities. The improvement of groundwater exploitation, together with the enhancement of sanitation structures and the use of non polluted and wastewater disposal, will allow to considerably ameliorate the quality of the subsurface waters and, consequently, to reduce their impacts on the lagoon. Alternative water sources for irrigation practices have necessarily to be considered, also including non polluted waters coming from the peripheral parts of the aquifer, as long as an efficiency enhancement of the irrigation channel. Finally, public participation of local farmers and landowners represent an essential step to enforce the adoption of effective and sustainable management practices.

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ANNEXES

Annex 1: Geological map of the Bou-Areg coastal plain

Annex 2: Environmental isotope in hydrogeology

Isotopes are atoms of the same element having different numbers of neutrons.

The nuclear structure of a nuclide is classically defined by its number of protons (**Z**) which defines the element, and the number of neutrons (**N**) defining the isotope of that element. For a given nuclide, the sum of neutrons and protons gives the atomic weight (**A**), expressed by the notation $^{A}_{Z}\mathbf{Nu}_{N}$. In reality, the mass of a nuclide is slightly less than the combined mass of its neutrons and protons. The “missing” mass is expressed as the nuclear binding energy (according to Einstein’s mass-energy relationship), which represents the amount of energy required to break the nucleus into its constituent nucleons. Conventional notation for a nuclide uses only the elemental symbol and the atomic weight (e.g. ^{18}O or ^{34}S) (Clark and Fritz, 1999).

Naturally occurring nuclides define a path in the chart of nuclides, corresponding to the greatest stability of the neutron/proton (**N/Z**) ratio.

For nuclides with low atomic mass, the greatest stability is achieved when the number of neutrons and protons are approximately equal (N = Z); these are the so-called stable isotopes (denoted as yellow nuclides in Figure 1). However, as the atomic mass increases, the stable neutron/proton ratio increases until N/Z = 1.5.

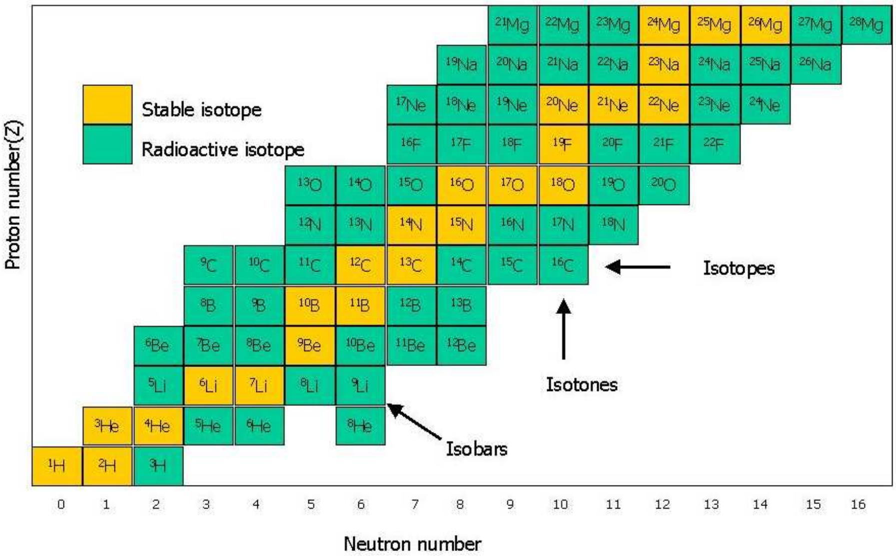

Figure 1. Detail of the chart of nuclides. The isotopes of an element (equal Z) are in the horizontal rows,while isobars (equal A) along diagonal lines,and isotones (equal N) in vertical columns. The natural radioactive isotopes are marked green.

Radioactive decay occurs when changes in N and Z of an unstable nuclide cause the trans-formation of an atom of one nuclide into that of another, more stable, nuclide; these radioactive nuclides are called unstable nuclides (denoted as the green nuclides in Figure 1).

Environmental isotopes are natural occurring isotopes of elements found in abundance in our environment, e.g. H, C, N, O and S. These are also the principal elements of hydrogeological, geological and biological systems.

Environmental isotopes have become an integral part of geochemical studies in groundwater projects. New analytical technologies now allow rapid, routine measurement of a growing number of isotopes in a wide variety of sample types.

Isotopes provide information that complements geochemical data, giving insights to geochemical pathways and processes in ground water resource and ground water quality studies (Clark and Fritz, 1997).
Table 1 shows the mayor stable environmental isotopes used in hydrogeology.

Isotope	**Ratio**	**% natural abundance**	**Reference Standard**
^{2}H	$^{2}H/^{1}H$	0.015	VSMOW
^{3}He	$^{3}He/^{4}He$	0.000138	Atmospheric He
^{6}Li	$^{6}Li/^{7}Li$	7.5	L-SVEC
^{11}B	$^{11}B/^{10}B$	80.1	NBS 951
^{13}C	$^{13}C/^{12}C$	1.11	VPDB
^{15}N	$^{15}N/^{14}N$	0.366	AIR N_2
^{18}O	$^{18}O/^{16}O$	0.204	VSOMW VPDB
^{34}S	$^{34}S/^{32}S$	4.21	CDT
^{37}Cl	$^{37}Cl/^{35}Cl$	24.23	SMOC
^{81}Br	$^{81}Br/^{79}Br$	49.31	SMOB
^{87}Sr	$^{87}Sr/^{86}Sr$	$^{87}Sr = 7.0$; $^{86}Sr = 9.86$	Absolute ratio measured

Table 1. The stable environmental isotopes and the specific references (Clark and Fritz, 1997).

Stable environmental isotopes are measured as a ratio (**R**) of the two most abundant isotopes of a given element.

$$R = \frac{Abundance\ of\ rare\ (or\ heavier)\ isotope}{Abundance\ of\ lighter\ isotope}$$

In practice, rather than the effective ratio, isotopic concentrations are expressed referring to specific international standard, using the delta (**δ**) notation:

$$\delta^{18}O = \left[\frac{R_{sample} - R_{reference}}{R_{reference}}\right] \qquad \text{e.g.: } \left[\frac{{}^{18}O/{}^{16}O_{sample} - {}^{18}O/{}^{16}O_{reference}}{{}^{18}O/{}^{16}O_{reference}}\right]$$

These values are usually expressed as part per thousand or permil difference from the reference.
For example $\delta\ ^{18}O$ and $\delta^{2}H$ are reported referred to SMOW (Standard Marine Ocean Water) or the equivalent VSMOW (Vienna Standard Marine Ocean Water).
"δ" values can be negative or positive; negative values indicate lower abundances pf the rare isotope in the sample than in the standard, while positive values mean higher abundance (Mook, 2001)
The various isotopes of an element have slightly different chemical and physical properties because of their mass differences. These variations are an expression of the socalled isotopic fractionation: Mook (2001) has expresses its consequences as:
i) Heavier isotopic molecules have a lower mobility.
The kinetic energy of a molecule is solely determined by temperature: $kT = ½mv^2$ (k = Boltzmann constant, T = absolute temperature, m= molecular mass, v = average molecular velocity). Therefore, molecules have the same $½mv^2$, regardless of their isotope content. This means that the molecules with larger molecular mass necessarily have a smaller molecular velocity.

Some practical consequences are that heavier molecules have a lower diffusion velocity, and the collision frequency with other molecules (i.e. the primary condition for chemical reaction) is smaller for heavier molecules; this is one of the reasons for the rule: lighter molecules react faster.

ii) The heavier molecules generally have higher binding energies, explaining why the energy required for breaking the chemical bond between ^{2}H-^{2}H is about 2Kcal/mole less than between H-H.

Isotopic fractionation occurs in any thermodynamic process, due to differences in the rates of reaction for different molecular species (Clark and Fritz, 1997). This is expressed by the fractionation factor (**α**), indicating a different concentration of one isotope over the other on one side of the reaction.

$$\alpha = \frac{R_{reagent}}{R_{product}} \qquad \text{e.g: } \alpha^{18}O_{water-vapour} = \frac{\left({}^{18}O/{}^{16}O\right)_{water}}{\left({}^{18}O/{}^{16}O\right)_{vapour}}$$

In general, isotope effects are small (α~1) hence the fractionation factor is expressed as a deviation from 1, or ε, named fractionation (Mook, 2001) and defined as follow:

$\varepsilon = \alpha - 1 \quad \left(x\ 10^3\ ‰\right)$ and ε represents the enrichment factor (ε>0) or the depletion factor (ε<0) of the rare isotope (reagent).

In one-way processes (A → B) ε is the change in isotopic composition, or, in other words the new isotopic composition compared to the old one (Mook, 2001).

There are two types of isotope fractionation, defined in function of the process causing them:

i) kinetic fractionation, resulting from an irreversible physical or chemical process,

ii) thermodynamic fractionation, as a consequence of a thermodynamic (equilibrium) reaction.(Kendall and McDonnell, 1998)

Based on these premises, the following section present a brief description of the environmental isotopes and the relative processes, that have been applied in the present work to investigate water quality and quantity in the Bou-Areg aquifer and in the lagoon of Nador.

1. $\delta^{15}N_{-NO3}$ and $\delta^{18}O_{-NO3}$

Recent concern about the potential danger to water supplies, mainly posed by the use of agricultural, chemicals has raised attention on the mobility of various solutes, especially nitrate and pesticides, in shallow hydrologic systems.

Nitrate concentrations in public water supplies have risen above acceptable levels in many areas of the world, largely resulting by overuse of fertilizers and contamination by human and animal waste (Kendall and McDonnell, 1998).

Several studies have shown that a nitrate concentration of 10 mg NO_3–N/L (USA federal maximum level for drinking water) can adversely affect, at least during long-term exposures, sensitive aquatic animals (Camargo *et al.*, 2006).

An excess of nitrate in drinking water can also cause several health problems, especially for children, who can contract methemoglobinemia (Fan and Steinberg, 1996) and gastric cancer (Feast *et al.*, 1998). Methemoglobinemia is the most significant health problem associated with nitrate in drinking water. This syndrome is caused by the reduction of nitrate in nitrite, under anaerobic conditions in the digestive tract. When nitrite is present in blood, hemoglobin (an iron-based compound) can be converted to methemoglobin, which cannot carry oxygen (Camargo *et al.*, 2006). This blood condition, resulting in cyanosis, is also known as blue-baby disease.

Other consequence of the presence of high nitrate concentration in the environment, are all the eutrophication phenomena of in lakes and rivers (Kendall and McDonnell, 1998).

In order to decrease nitrate levels in groundwater and soils it is fundamental to identify the different nitrate sources and to understand the processes affecting its concentration.

Since different sources of nitrate often have isotopically distinct nitrogen and oxygen isotopic composition (Kendall and McDonnell, 1998; Figure 2), they can be used to achieve these goals.

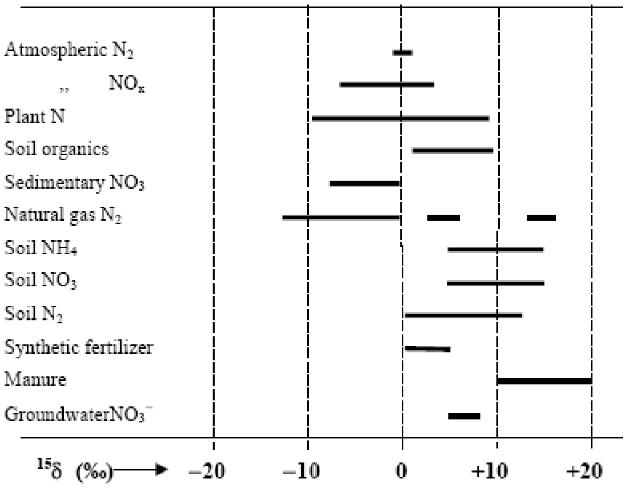

Figure 2. Figure 2 Survey of δ15N values of nitrogen containing compounds in nature. The values are referred to the isotopic composition of air-N_2. (Mook, 2001).

Nitrogen has two stable isotopes: ^{14}N (99.63% of abundance) and ^{15}N (0.37%) (Clark and Fritz, 1997).

The average abundance of ^{15}N in air is constant (Junk and Svec, 1958) and the isotopic signature of nitrogen is expressed as $\delta^{15}N$, generally reported in permil (‰), referred to N_2 in atmospheric air (Kendall and McDonnell, 1998. Kellman and Hillaire-Marcel, 2002):

$$\delta^{15}N = \left[\frac{{}^{15}N/{}^{14}N_{sample}}{{}^{15}N/{}^{14}N_{atmospheric\, N\, 2}} - 1 \right] 1000$$

Nitrogen cycling through environmental reservoirs is subject to different physical, chemical, and biological controls converting nitrogen, in its inert atmospheric molecular form,into forms more useful to biogeochemical processes.

Biologically-mediated reactions (e.g., assimilation, nitrification and denitrification) strongly control nitrogen and nitrogen isotopic compositions in both soil and water (Figure 3).

Since ^{14}N is readily assimilated, these reactions frequently result in increases in the $\delta^{15}N$ of the substrate and a decrease in the $\delta^{15}N$ of the product (Kendall and McDonnell, 1998).

Nitrification is a chemical process that produces nitrate (NO_3^-) through the oxidation of ammonium (NH_4^+). After gaseous N_2, nitrate is the most stable form of nitrogen and is present in most groundwater. The nitrification reaction occurs under aerobic conditions, whereas denitrification occurs under anaerobic conditions.

Nitrification: $NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$

Denitrification: NO_3- + $5/_{4CH2O}$ = $1/2N_2$ +$5/4HCO_3^-$ +$1/4H^+$ +$1/2H_2O$

A bacterium known as Thiobacillus denitrificans is responsible for most of the denitrification in groundwater although other bacteria can denitrify, in the absence of carbon, using electron sources such as Mn_2^+, Fe_2^+, sulphide and methane (Clark and Fritz, 1998).

The use of $\delta^{15}N$ analyses, combined with $\delta^{18}O$ analysis, allow for identifying the diverse effects of denitrification and assimilation.

If plant uptake alone is responsible for NO_3^- remediation, the isotopic composition of the remaining NO_3^- remains unchanged. If both denitrification and assimilation are occurring, the isotopic composition of the residual nitrate is enriched and the overlying plants reflect the isotopic composition of the NO_3^- source. Therefore isotopic composition of the plants will remain the same and the water will become more enriched, if denitrification is the only process occurring.

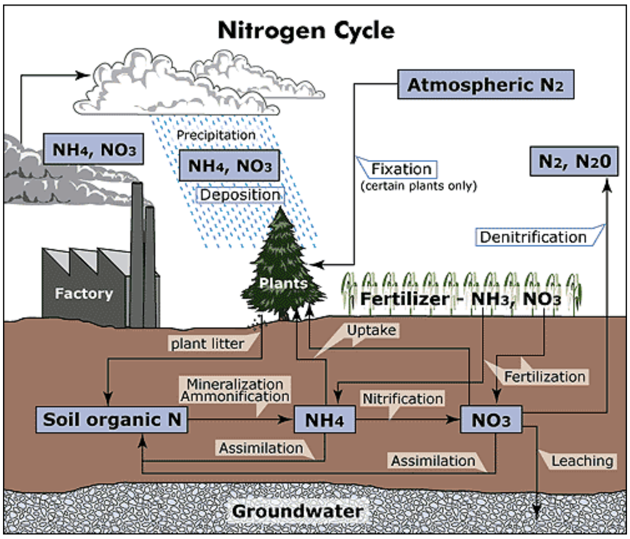

Figure 3. Nitrogen cycle and process affecting $\delta^{15}N$ values (SAHRA.edu)

The $\delta^{18}O$ composition of nitrate adds some more information on the origin of NO_3^-, because, for example, it allows distinguishing between synthetic and natural fertilizers (Clark and Fritz, 1998). In biologically formed nitrate, one oxygen atom comes from atmospheric O_2 and the other two comes from water. On the contrary, in synthetic fertilizers nitrate receive its oxygen primarily from atmospheric O_2. Since the two oxygen sources are different, nitrate form natural and synthetic fertilizers should show different isotopic composition.

2. $\delta^{18}O_{-H2O}$ and $\delta^{2}H_{-H2O}$

Because of their close relationship, linked to the abundance and importance of water on the planet, oxygen, hydrogen and their isotopes are usually studied together (Kendall and McDonnel, 1998).

Oxygen has three stable isotopes, ^{16}O (99.76% of abundance), ^{17}O (0.04%), and ^{18}O (0.20%); hydrogen has two stable isotopes, ^{1}H (protium, 99.985%) and 2H (deuterium, 0.015%), and one radioactive isotope, 3H (tritium, $t_{1/2}$= 12.32 yrs).

Most importantly, oxygen and hydrogen combine to form water, thus making their isotopic composition a powerful tracer of the hydrosphere and an important tool to determine the origin and the history of waters.

There are nine isotopic configurations for water molecule, distinguishable by their differenmass numbers as well as their characteristics. However, due to the low abundance of the heavier isotopes, almost all water molecules have one of these isotopic combinations: $^{1}H_2{}^{16}O$ (the most common), $^{2}H_2{}^{16}O$, $^{1}H_2{}^{18}O$.

As a result of fractionation, waters develop unique isotopic compositions that can be indicative of the source or the processes that formed them.

Oxygen and hydrogen isotopic compositions are reported as “delta” (δ) values, and expressed as the parts per thousand or permil (‰) difference from reference (Clark and Fritz, 1997):

$$\text{e.g.: } \delta^{18}O = \left[\frac{^{18}O/^{16}O_{sample}}{^{18}O/^{16}O_{reference}} - 1\right]1000 \text{ VSMOW,}$$

where VSMOW (Vienna Standard Marine Ocean Water) is the name of the used reference.

In the same way deuterium isotope is expresses as “delta” (δ^2H), corresponding to the ratio of ($^2H/^1H$).

Meteorological processes affect water molecule, providing a characteristic signature, fundamental to investigate the provenance of groundwater (Clark and Fritz, 1997).

On global scale and annual basis, the flux of moisture can be considered close to equilibrium (Clark and Fritz, 1997), although each step of the water cycle is strictly dependant on climatic regimes and it is characterized by different partitions of ^2H and ^{18}O amongst the different freshwater reservoirs (Figure 4).

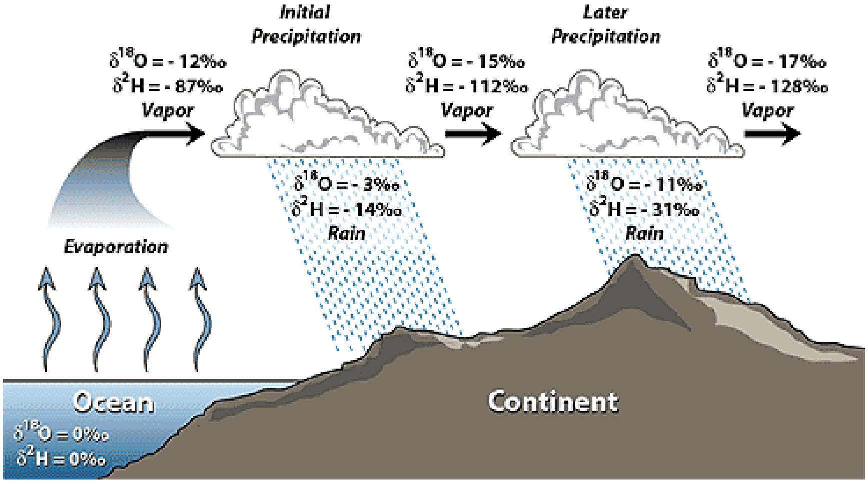

Figure 4.Rainout effect on δ^2H and $\delta^{18}O$ values (SAHRA.edu).

These differences in partition of isotopic composition are due to global and local effects.

The evolution of the $\delta^{18}O$ and δ^2H composition of meteoric waters begins with evaporation form the oceans.

When water evaporates, the water vapour becomes enriched in the molecules carrying the lighter isotope as compared to the water it leaves behind. On the contrary when water vapour condenses into water, it becomes enriched in molecules carrying the heavier isotope as compared to the vapour it leaves behind. Such a process, similar to a multiple stage distillation is the Rayleigh fractionation and it is responsible for the partitioning of oxygen and deuterium isotopes between warm and cold regions, since during all the steps of evaporation and condensation isotope fractionation occurs.

Precipitation composition is very important in hydrogeological studies because allows to reconstruct their origin and history.

Despite the complexity of hydrological water cycle, the δ^2H and δ^{18}O values for precipitation worldwide behave predictably, falling along a line described by Craig (1961a) as the Global Meteoric Water Line (GMWL, Figure 5).

The relationship between ^{2}H and δ^{18}O in meteoric water is approximately:

$$\delta^2 H = 8.13\delta^{18}O + 10.8$$

This relationship for ^{18}O and ^{2}H isotopes is primarily a reflection of differences in their equilibrium fractionation factors. The slope of the GMWL expresses this ratio, which is eight times greater for oxygen than hydrogen (Craig, 1961b).

Craig's line shows also that isotopically depleted waters (δ^2H and δ^{18}O lighter than -160 and -22 ‰ respectively) are associated with cold regions and enriched waters are found in warm regions. This distribution derives from Rayleigh distillation and temperature effect on precipitation (Clark and Fritz, 1997).

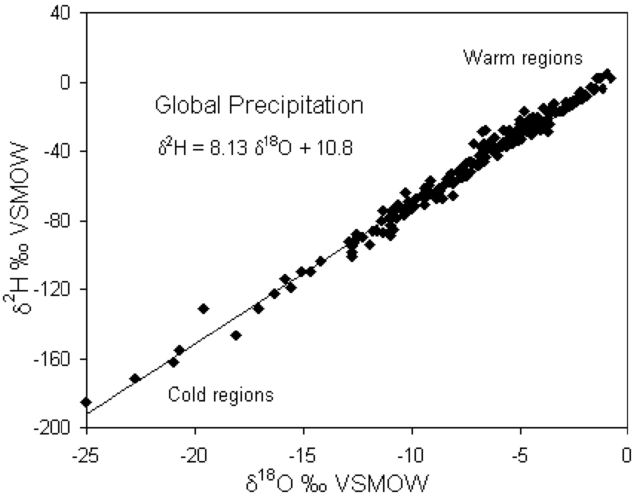

Figure 5. Meteoric relationship for 18O and 2H in precipitation (Clark and Fritz, 1997).

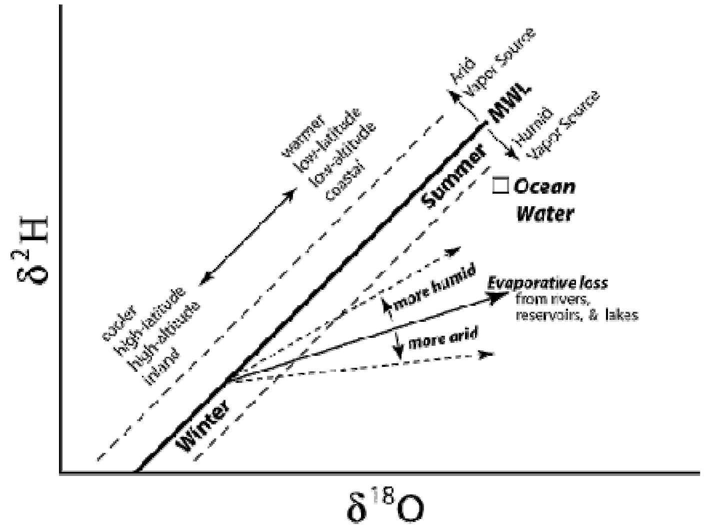

Figure 6. Summary diagram of how hydrologic processes affect oxygen and hydrogen isotopic composition of water (SAHRA.edu).

The Global Meteoric Water Line, obtained from many samples of water from rivers, lakes and precipitation (Craig, 1961b), corresponds to an average of local meteoric water lines (Clark and Fritz, 1997).

Local lines differ from GMWL in both slope and intercept because of the variation of climatic and geographic parameters (Figure 6).

For a clear and complete analysis of groundwater origin, using δ^2H and $\delta^{18}O$, both GMWL and LMWL must be considered.

3. $\delta^{13}C$

Carbon in natural waters is present both in the aqueous and in the solid phase. The C-bearing species in the aqueous phase are: DIC (Dissolved Inorganic Carbon) ad DOC (Dissolved Organic Carbon) defined as C in dissolved organic matter (DOM). In the solid phase C species is the particulate organic carbon (POC) defined as the carbon in particulate organic matter (POM).

The study of carbon chemistry in waters is of primary importance as it gives details of the kinetics of transport and of the exchange processes of CO_2 between atmosphere and water masses.

When CO_2 diffuses into water, it forms four main species of DIC: $CO_2(aq)$, H_2CO_3 (hydrated carbon), HCO_3^- (Dissociated carbon acid) and CO_3^{2-} (Clark and Fritz, 1997). Their distribution or relative concentration is function of pH (Figure 7).

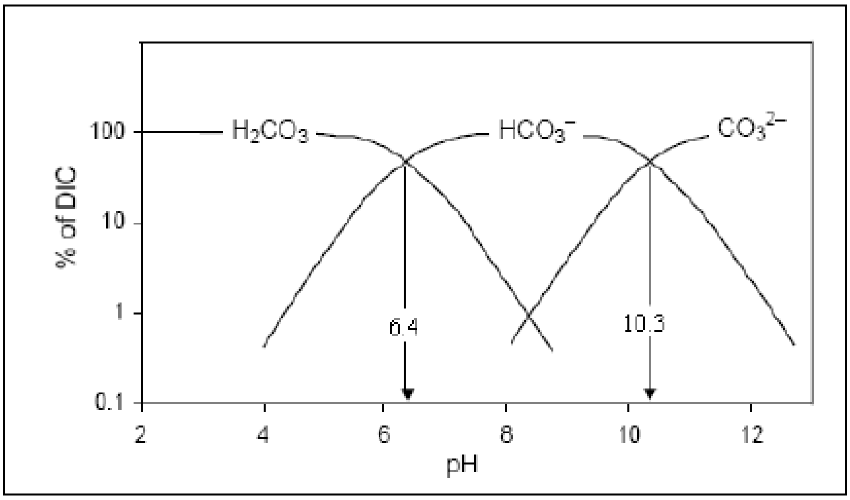

Figure 7. Distribution of carbonate species in pure water as a function of pH at 25 °C(Clark and Fritz , 1997).

Dissolution of $CO_2(g)$ in water takes place according to the reactions:

CO_2 dissolution in waters	$CO_2(g) \leftrightarrow CO2(aq)$
CO_2 hydration	$CO_2(aq) + H_2O \leftrightarrow H2CO3$
1st dissociation of carbonic acid	$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$
2nd dissociation of carbonic acid	$HCO_3- \leftrightarrow H^+ + CO_3^{2-}$

As one can be observe, HCO_3^- is the dominant species at pH between 6.4 and 10.3 (Figure 8), therefore in seawater ($pH \cong 8.2$) this will be the major ion. However, CO_3^{2-} is also present. The co-existence of these species in seawater creates a chemical buffer system, regulating the pH and the pCO_2 of seawaters.

DIC can derive from CO_2 (from soil, atmosphere, or organic) and carbonate mineral dissolution.

$CaCO_3 + CO_2 + H2O \leftrightarrow Ca_2^+ + 2HCO_3^-$

In seawater calcite dissolution is the most common and effective buffering reaction, and is sensitive to the partial pressure of CO_2.

In addition, silicate weathering by carbonic acid, such as albite hydrolysis, increases DIC according to the reaction:

$2NaAlSi_3O_8 + 2CO_2 + 3H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 2Na_+ + 2HCO_3^- + 4SiO_2$

Carbon has two stable isotopes ^{12}C (98.89%) and ^{13}C (1.11%) and one radioactive ^{14}C ($t_{1/2}$=5715 yrs). Natural variation of the two stable isotopes of carbon (Figure 9) can be useful for understanding food webs and carbon cycling in ecosystems.

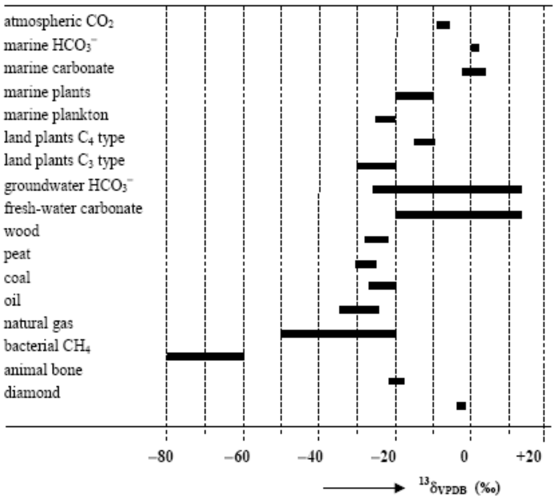

Figure 8. General view of $\delta^{13}C$ variations in natural compounds, referred to VPDB (Vienna Pee Dee Belemnite). The ranges are indicative for the materials shown (Mook, 2001).

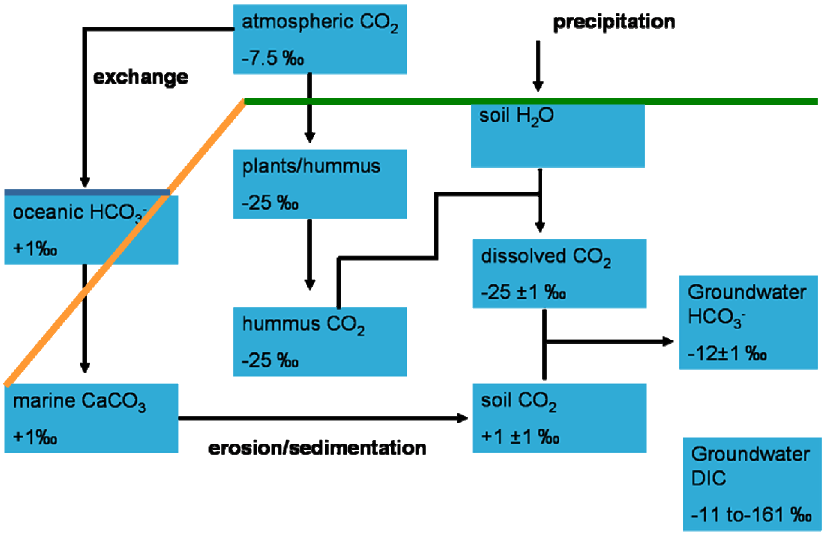

Figure 9. Schematic representation of the formation of dissolved inorganic carbon in groundwater from soil carbonate and soil CO2 (adapted from Mook, 2001).

Figure 9 presents a general survey of natural abundances of various compounds. The lowest ^{13}C value range (-80/-60 ‰) is represented by bacterial methane (marsh-gas) while at the high end is found the bicarbonate fraction of groundwater under special conditions. In the carbonic acid, system variations up to 30‰ are normally observed. Wider variations occur in systems in which carbon oxidation or reduction reactions take place, such as the CO_2 (carbonate) - CH_4 (methane) or the CO_2 -$(CH_2O)_x$ (carbohydrate) systems.

Values of δ13C are used to in this work to establish the origin of dissolved organic carbon content of groundwater (Figure 10), and, as well as DIC species, the distribution of δ13C is determined by pH (Figure 11).

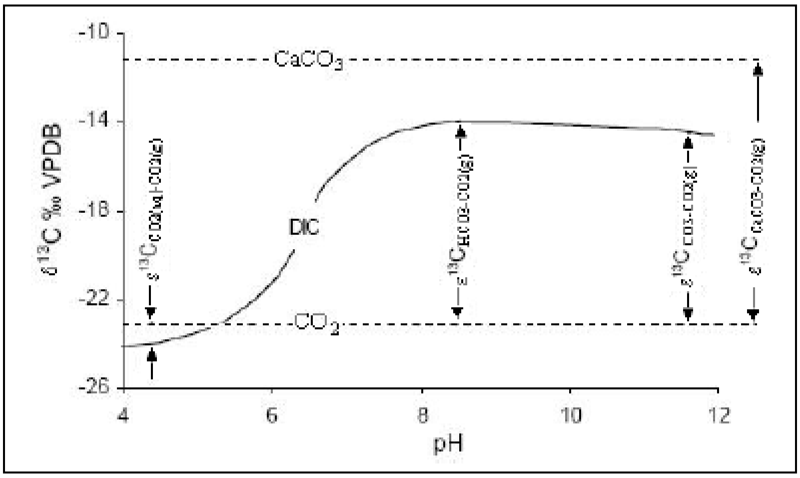

Figure 7. δ ^{13}C of DIC in equilibrium whit soil CO_2 at 25℃ (Clark and Fritz, 1997).

Since ^{13}C is promptly fractionated during biogeochemical reactions, the range of $\delta^{13}C$ in waters is significant and different compounds of carbon will have characteristic values. Thus, some processes, such as CO_2 exchange between atmosphere and open water bodies, photosynthesis and bacterial respiration will modify the $\delta^{13}C$ of DIC in aqueous media and consequently will give information about the evolution of DIC.

During DIC reactions isotope fractionations occur, the largest pertaining to CO_2 hydration. Table 2 shows the enrichment factor and reactions involving DIC species.

CO_2 dissolution in waters	$CO_{2(g)} \leftrightarrow CO_{2(aq)}$	$\varepsilon^{13}C_{CO2(aq)-CO2(g)} = -1.1‰$
CO_2 hydration	$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3$	$\varepsilon^{13}C_{HCO3-CO2(aq)} = 9‰$
Dissociation bicarbonate	$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$\varepsilon^{13}C_{CO32-HCO3} = -0.4‰$

Table 2. Fractionation factors associated with the sequence of reactions that occur when CO2 dissolves in water to generate DIC species (Clark and Fritz, 1997).

DIC and δ13C in groundwater evolve to higher values during weathering reactions in the soil and in the aquifer. Control on this evolution includes the degree to which it takes place under open or closed system conditions, and whether the parent material is carbonate or silicate. In carbonate terrains, dissolution of calcite or dolomite provides an additional source of carbon to the DIC pool. As these carbonates are generally enriched in 13C, this contribution has a large effect on the δ13C.

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Università
Ca'Foscari
Venezia

DEPOSITO ELETTRONICO DELLA TESI DI DOTTORATO
DICHIARAZIONE SOSTITUTIVA DELL'ATTO DI NOTORIETA'
(Art. 47 D.P.R. 445 del 28/12/2000 e relative modifiche)

Io sottoscritto **Viviana Re**
Nata a **Torino** (prov. TO) il **18 Aprile 1981**
residente a **Novi Ligure (AL)** in **Via Venezia** n. **5**
Matricola **955409** Autore della tesi di dottorato dal titolo:
Groundwater in urban coastal areas: hydrogeochemical based approach for managing the transition areas. The example of the lagoon of Nador (Morocco)
Dottorato di ricerca in Analisi e Governance dello Sviluppo Sostenibile
(in cotutela con _)
Ciclo 23
Anno di conseguimento del titolo **2011**

DICHIARO

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Estratto per riassunto della tesi di dottorato

Studente: **Viviana Re** matricola: **955409**

Dottorato: **Analisi e Governance dello Sviluppo Sostenibile**

Ciclo: **23**

Titolo della tesi: **GROUNDWATER IN URBAN COASTAL AREAS: HYDROGEOCHEMICAL BASED APPROACH FOR MANAGING THE TRANSITION AREAS. The example of the lagoon of Nador (Morocco)**

Riassiunto

Nell'ambito del progetto SAP MED, la laguna di Nador rappresenta il caso di studio Marocchino per la sottocomponente gestita da UNESCO-IHP. Lo studio dell'acquifero di Bou-Areg e della laguna di Nador ha due obiettivi principali: (i) dimostrare l'importanza degli studi idrogeochimici a supporto della gestione degli acquiferi costieri e (ii) definire la qualità delle acque sotterranee ed le loro interazioni con la laguna.
Questo lavoro ha permesso di identificare le acque di ruscellamento e flussi di ritorno agricoli come le due principali fonti di ricarica dell'acquifero. In base all'analisi idrochimica e statistica, è possibile escludere la presenza di processi di intrusione salina, mentre, le attività agricole e domestiche sono considerate le principali cause dell'alterazione della normale salinità dell'acquifero. L'analisi isotopica ha infine permesso di individuare due principali fonti di azoto nelle acque sotterranee: (i) fertilizzanti sintetici e (ii) effluenti di fosse settiche.

Abstract

The hydrogeochemical investigation on the Bou-Areg Plain and Lagoon of Nador (Morocco) is, framed within the UNESCO-IHP sub component of the MED MAP project, as the Moroccan pilot case study.
Its main research goals were (i) to demonstrate the effectiveness of hydrogeochemical tools for coastal aquifers management, with focus on urban coastal areas in semi-arid climates and (ii) to unravel the role of groundwater in sustaining transition areas.
The study allowed for the identification of surface runoff and agricultural return flows as the main sources of aquifer recharge. Moreover, the effects of agricultural practices are increasing the natural high salinization of the aquifer. The isotopic signal of dissolved nitrates allowed for the identification of two main nitrogen sources in the system: (i) fertilizers and (ii) manure and septic effluent. The PCA analysis supported the absence of saline water intrusion in the aquifer.

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