

Tackling the salinity-pollution nexus in coastal aquifers from arid regions using nitrate and boron isotopes

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Abstract- Salinization and nitrate pollution are generally ascertained as the main issues affecting coastal aquifers worldwide. In arid zones, where agricultural activities also result in soil salinization, both phenomena tend to co-exist and synergically contribute to alter groundwater quality, with severe negative impacts on human populations and natural ecosystems wellbeing. It becomes therefore necessary to understand if and to what extent integrated hydrogeochemical tool can help distinguishing among possible different salinization and nitrate contamination origin, in order to provide adequate science-based support to local development and environmental protection.

The alluvial plain of Bou-Areg (North Morocco) extends over about 190 km² and is separated from the Mediterranean Sea by the coastal Lagoon of Nador. Its surface is covered for more than 60% by agricultural activities, although the region has been recently concerned by urban population increase and tourism expansion. All these activities mainly rely on groundwater exploitation and at the same time are the main cause of both aquifer and lagoon water quality degradation. For this reason, it was chosen as a case study representative of the typical situation of coastal aquifers in arid zones worldwide, where a clear identification of salinization and pollution sources is fundamental for the implementation of locally oriented remedies and long term management strategies. Results of an hydrogeochemical investigation performed between 2009 and 2011 show that the Bou-Areg aquifer present a high salinity (often exceeding 100 mg/L in TDS) due to both natural and anthropogenic processes. The area is also impacted by nitrate contamination, with concentrations generally exceeding the WHO statutory limits for drinking water (50 mg/L) and reaching up to about 300 mg/L, in both in the rural and urban/peri-urban areas. The isotopic composition of dissolved nitrates ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$) was used to constrain pollution drivers. Results indicates two main origins for human induced pollution: (i) manure and septic effluents, especially in urban areas and (ii) synthetic fertilizers in agricultural areas. In the latter, $\delta^{15}\text{N}$ enriched values highlight a mixture of those sources, possibly related to unbalanced fertilization and agricultural return flow. Boron isotopes ($\delta^{11}\text{B}$) were hence studied to further distinguish the nitrate origin in presence of multiple sources and mixing processes. Results indicate that in the study area the high geochemical background for B and Cl, coupled to the complex water-rock interaction processes, limit the application of the coupled $\delta^{11}\text{B}$ and $\delta^{15}\text{N}$ isotopic systematics to the detection of sources of groundwater pollution. In fact, despite the exceedingly high nitrate contents, the depleted $\delta^{11}\text{B}$ values that characterize synthetic fertilizers and sewage leakages could not be detected. Therefore, even if in saline groundwater the anthropogenic contribution has a negligible effect in terms of salinity input, being both sewage and irrigation water not very charged, the associated nitrate content fuels up water-rock interaction processes, eventually leading to a mineralization increase.

Keywords: Groundwater, contamination, salinization, Bou-Areg, Morocco, Mediterranean

Introduction

A clear understanding of salinization origin in groundwater is a fundamental prerequisite for the correct and long-term management of aquifer systems. In fact, aquifer and soil salinization represent a common issue worldwide and one of the main causes of water resources degradation (Foster and Chilton, 2003), often making it unsuitable for human consumption and contributing to biodiversity loss (Vengosh, 2003 and references and references therein). Groundwater salinity is generally defined by its chloride or Total Dissolved Solids (TDS) content, and groundwater use is often subject to its salinity level. For example, the World Health Organization (WHO) recommends that water for human consumption should not exceed 250 mg/L of chloride (WHO, 2011), while the suitability for agricultural practices mainly depends on the salt tolerance of the irrigated crops (Ayers and Westcot, 1985) and the knowledge of the long-term contribution of highly saline waters to reducing hydraulic conductivity and soil fertility (Vengosh, 2003).

All these issues can be even more crucial in areas where water resources are scarce, precipitation recharge is low, and groundwater represent the main freshwater supply local population rely on, like coastal zones in arid and semi-arid regions. The proximity to the sea generally drives the attribution of this phenomenon to seawater intrusion. However, an incorrect ascription of the salinity origin can have severe negative consequences such as ineffective mitigation measures, improperly abandoned wells and uncontrolled use of alternative water supplies. The unequivocal identification of its source is therefore a fundamental step for both the protection of natural ecosystems and human wellbeing. In fact, besides seawater encroachment, chloride concentration enrichment can be due to other phenomena associated to mobilisation and redistribution of salts changing the natural patterns of salt distribution and movement (Williams, 2001). Changes in the chemical composition of natural groundwater can be associated to both natural and human induced processes. The principal natural causes of groundwater salinity in aquifer bodies other than seawater intrusion are mixing with paleo-seawater and brines, water-rock interaction processes with direct dissolution of evaporites by fresh groundwater, infiltration of saline surface water (Kloppmann et al., 2014), and marine aerosols (either transported as liquid drops or evaporated materials) and airborne marine salts (Re and Zuppi, 2011).

On the other hand, anthropogenic sources of saline solutions can be associated to extensive groundwater extraction, potentially leading to seawater intrusion in coastal zones (Custodio, 2002), industrial activities, urban solid and liquid waste disposal, mining activities and agricultural activities related to both fertilizers inputs and agricultural return flow (Llamas and Custodio, 2003). Intensive irrigation can in fact enhance flushing and solutes migration from the surface to the underground system, contributing to the general salinity increase (Rosenthal et al., 1992) and consequent aquifer contamination.

In addition, in areas where agricultural activities are dominant and/or in areas interested by increasing population where households do not have access to adequate sanitation systems, dissolved nitrates can raise groundwater mineralization through either fertilizers re-mobilization with irrigation waters, or direct leaching from septic systems and domestic/industrial waste disposals (Kendall et al., 2007). The increase in groundwater nitrates hence represent a serious concern in regions of arable lands with sandy soils, with shallow groundwater table and high permeability aquifers (Vrba and Romijn, 1986), such as in the case of coastal aquifers in arid zones. The nitrate concentrations of groundwater in such cases frequently exceeds 50 mg/L (WHO statutory limit for drinking waters; WHO, 2011), with often negative impact on human population. The effects of high nitrate concentrations in water used for human consumption are widely

recognised and generally identified causing gastric cancer and methemoglobinemia in infants (Fan and Steinberg, 1996). Not only salinization and nitrate pollution can cause the deterioration of natural aquifers quality, but also, in coastal aquifers, submarine discharge of contaminated groundwater can lead to an alteration of marine life, caused by the presence of contaminants carried by groundwater, contributing eutrophication and eventually impairing the food security of the local populations (Saccon et al., 2013).

All these processes are expected to increase their impacts in the future, due to the combined effect of population growth and climate change, the latter associated to the frequency of extreme events, such as droughts and heat waves, exacerbating already existing water quality and quantity issues in coastal zones. Under these premises, the need emerges of reliable tools to tackle aquifer salinization processes.

As previously mentioned in coastal aquifers from arid zones the clear identification of salinity and pollution origin, besides being fundamental for ensuring the long-term protection of scarce water resources, is often challenging due to the co-existence of both natural and anthropogenic sources (e.g. Sanchez-Martos et al., 2002; Vengosh et al., 2005; Faye et al., 2005; Bouchaou et al., 2008). This is clearly due to the interaction of climate features enhancing evaporation processes, the proximity to the sea and the growing population in coastal zones with associated water-dependent economy (associated to an increase of the demand for groundwater to sustain food, energy and industrial processes). Environmental isotopes have proven to be crucial tools for the identification of the origin and fate of salinization and nitrates in groundwater (e.g. Aravena et al., 1993; Panno et al., 2001; Baily et al., 2011). The coupled use of the isotopic signature of O and N in the NO_3^- ion ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{N}_{\text{NO}_3}$) represent a fundamental instrument for assessing the occurrence of nitrification and denitrification processes in aquifers (e.g. Böttcher et al., 1990) and for discriminating among different anthropogenic nitrogen sources in ecosystems (Kendall, 1998). However they do not permit to distinguish manure from sewage-derived nitrates, since these sources have overlapping isotopic signatures ($\delta^{15}\text{N}_{\text{NO}_3} \sim 10\text{-}15\text{‰}$; Kendall et al., 2007).

For this reason, these isotopes are increasingly being used conjunction with other tracers, especially boron isotope ($\delta^{11}\text{B}$), based on the assumption that they co-migrate in many environmental settings (Seiler, 2005). The B isotopic composition in natural waters is mainly controlled by the aquifer matrix, and boron isotope analysis can also be used to effectively trace the different sources of salinity in groundwater: sea water intrusion, dissolution of soluble salts in the unsaturated zone, and/or flows of saline water from adjacent or underlying aquifers (Vengosh et al., 1998; Gonfiantini and Pennisi, 2006). On the other hand, anthropogenic sources can cause its variability and deviation from natural conditions (Xiao et al., 2013). In general, high boron concentrations can derive from the input of different compounds, characterized by different $\delta^{11}\text{B}$ imprints: (i) industrial and domestic effluents associated to the use of sodium perborate as an oxidation bleaching agent in domestic and industrial cleaning products ($\sim 1 \text{ mgL}^{-1}$; Vengosh et al., 1994; Vengosh, 2003); (ii) fly ash leachate ($\sim 14 \text{ mgL}^{-1}$; Davidson and Basset, 1993); (iii) landfill leachate ($\sim 7 \text{ mgL}^{-1}$; Eisenhut et al., 1996; Eisenhut and Heumann, 1997) or (iv) animal manure (e.g. liquid hog manure 0.4 to 8.2 mgL^{-1} ; Vincini et al., 1994; Komor, 1997). Moreover, while the nitrate isotopes evolution is controlled by redox conditions, oxidation and reduction reactions involving boron species can be neglected due to the large potential required to cause the reactions (Palmer and Swihart, 1996). However, B might not be conservative in sedimentary aquifers due to $\delta^{11}\text{B}$ fractionation, associated with the preferential removal of the light isotope by adsorption onto clay minerals (Vengosh et al., 1994).

The combined analysis of $\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{18}\text{N}_{\text{NO}_3}$ and $\delta^{11}\text{B}$ is therefore indicated to be the best approach for a complete identification of the origin of nitrate pollution and for evaluating the process associated with nitrogen transformation (Widory et al., 2005; Xue et al., 2009). Nevertheless, most of the case studies are developed in European countries (e.g. Widory et al., 2013; Sacchi et al., 2013) or in North America (e.g. Seiler, 2005; Badruzzaman, 2012), i.e. in low salinity environments and in temperate climates. The effectiveness of the use of the coupled $\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{18}\text{N}_{\text{NO}_3}$ and $\delta^{11}\text{B}$ systematics needs therefore to be assessed in other environments, like coastal aquifers in arid regions. The Bou-Areg aquifer (North Morocco) is an ideal situation to verify the applicability of this isotopic approach in such environments. Framed within the GEF/UNEP-Map MedPartnership project (UNEP, 2010) an investigation performed between November 2009 and June 2011 permitted to identify (i) groundwater recharge origin and aquifer-lagoon interactions (Re, 2011; Re et al., 2013a); (ii) the impact anthropic activities (i.e. agriculture and domestic pollution) on groundwater quality and nitrate pollution (Re et al., 2013b); and (iii) the high seasonal dependency that governs aquifer geochemistry, resulting in both a strong vulnerability to contamination, and a high resilience (Re et al., 2014). Based on these work outcomes, groundwater of the Bou-Areg aquifer shows an overall high salinity and nitrate pollution, with a hypothesized interconnection between the two contamination phenomena. Therefore, although the main processes occurring within the aquifer are relatively known, the nitrate-salinity nexus still remains an open question that needs to be solved in order to complete the hydrogeochemical assessment of groundwater salinization and pollution origin, and to support new management practices for groundwater protection at regional level. This paper presents new chemical and isotopic results together with a re-elaboration of already published data, with the main goal of testing the applicability of the coupled $\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{18}\text{N}_{\text{NO}_3}$ and $\delta^{11}\text{B}$ systematics to better discriminate salinity sources and nitrate origin in such an environment. Besides its relevance at regional level, the Bou Areg aquifer can be considered representative of the issues shared by different coastal aquifers in the Mediterranean Basin, and more in general, in arid and semi-arid regions.

Site description

The Bou-Areg coastal plain is located in the region of Nador, in the northern shore of Morocco, and covers a surface of about 190 km² (Fig. 1). The plain is limited by the Gourougou volcanic massif (NW), the Beni-Bou-Iffrou Massif and the Kebdana range (SE); its northern boundary coincides with the arched shape of the Lagoon of Nador (also known as Marchica or Sebkhia Bou-Areg), while to the south the plain is connected to the adjacent Gareb plain through the Selouane corridor (El Amrani et al., 2005).

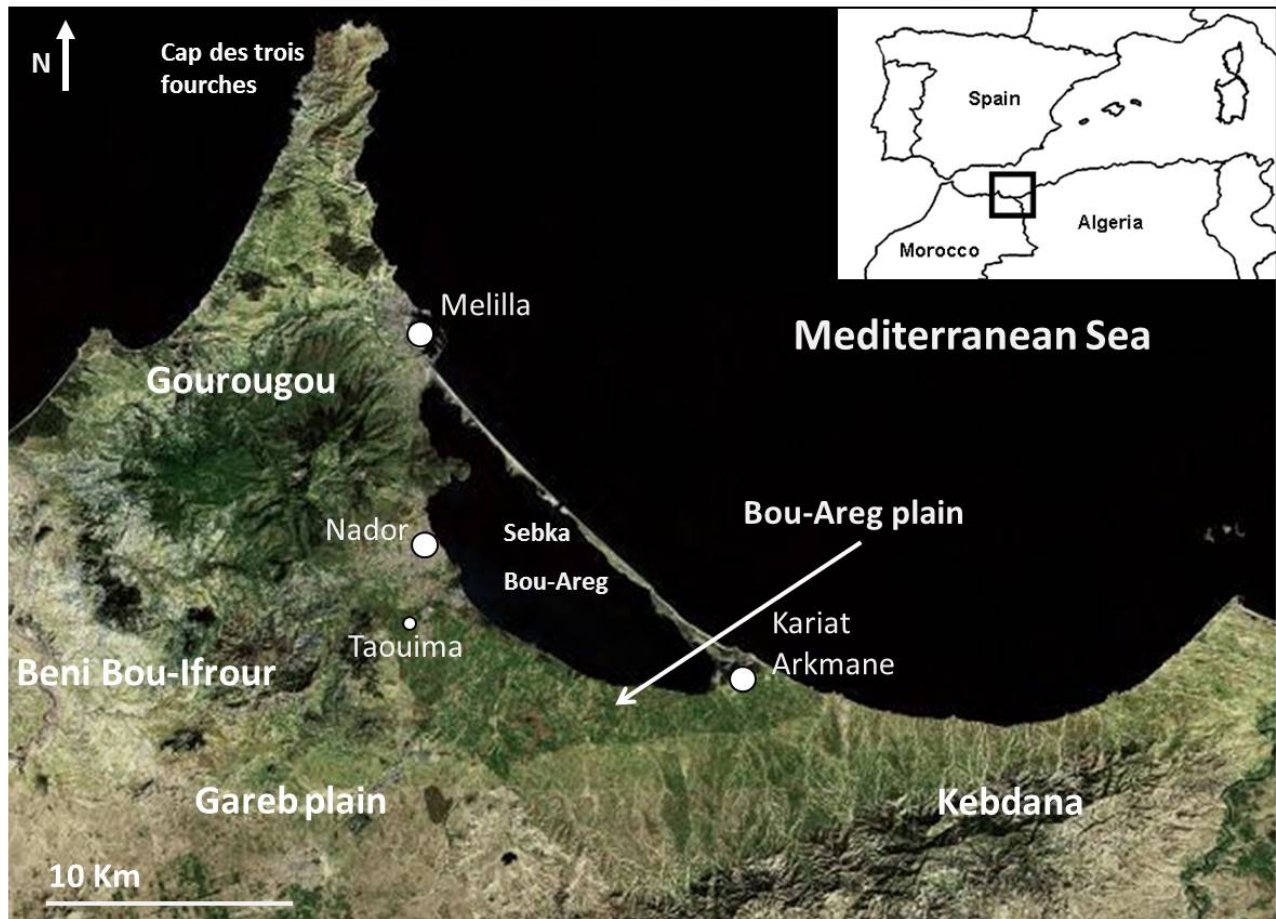
The climate of the region is semi-arid with two distinct seasons: the warm period, generally from May to October (average temperature of 23-24°C), and the cold season from November to April (average temperatures of 15°C) (data available from WeatherSpark, 2014). Seasonal climatic variations are usually moderate, with a general high level of humidity (50-80%) due to the proximity to the sea. Yearly average precipitations range from 300 to 400 mm/y, and these are generally more abundant in January-March and October-December.

The hydrologic network of the area is composed by numerous ephemeral rivers (*oueds*; often also recharged by sewage outflow from the urban areas upstream, Gonzalez et al., 2007), and few perennial streams, like the Selouane River located in the central part of the plain. The plain is also bordered by an artificial irrigation

channel, whose waters come from the Moulouya river (NE Morocco) and are diverted towards the cultivated areas through a network of minor superficial channels (Dakki, 2003). Therefore, the irrigation channel also represents the limit of the Bou-Areg irrigated area.

The Bou-Areg unconfined aquifer is constituted by late-Pliocene to early Quaternary continental sediments of variable thickness (up to about 100 m) and high permeability (up to $7 \times 10^{-4} \text{ m s}^{-1}$), limited to the bottom by a Pliocene substratum of gypsiferous marls (Chaouni Alia et al., 1997). Hydraulic head in the aquifer decreases from the bordering massifs towards the Lagoon of Nador (e.g. from 40 m a.s.l. close to the Kibdana range to sea level near the shore), which represents the natural outflow from the aquifer system (Dakki, 2003). The natural recharge to the aquifer is provided by groundwater from the adjacent Gareb aquifer, rainwater, stream water from the Selouane River and runoff coming from the massifs bordering the plain. An additional contribution to the natural recharge is also given by urban and industrial wastewaters (mainly from the cities of Nador, Selouane and Kariat Arkamane), together with irrigation waters and agricultural return flow (Re et al., 2013a). Indeed, the region of Nador, as many other coastal plains along the Mediterranean, is characterized by intense agricultural activities, covering more than 62% of the total surface area (El Yaouti et al., 2008; FAO, 2012), with more than 100 Km² of irrigated land (Agence Urbaine de Nador, 2013), exploited for both local consumption and for agro-industrial production (Khattabi and El Ghazi, 2008). The absence of large animal farms in the Bou-Areg region implies little production of manure, with the consequent dominant use of synthetic fertilizers (Re et al., 2013a). Considering the timing of recharge from precipitation and irrigation in the area it is possible to distinguish two distinct periods: (i) recharge from precipitation and low use of groundwater/irrigation channel water from October to April, and (ii) no recharge from precipitation and high water irrigation from wells and the irrigation network from May to October (El Yaouti et al., 2008).

In addition, the area is characterized by an increase in urban population (in the cities and suburbs of Nador, Beni Ensar and Kariat Arekmane) and by a development of tourism related activities (e.g. MarchicaMed), exerting additional pressures on local groundwater resources, that, besides being used for agricultural purposes together with the irrigation channel waters, also contribute sustaining domestic and industrial activities.



***Figure 1. Location of the Bou-Areg aquifer. Modif. after Microsoft® Bing™ Map, 2014.

Materials and Methods

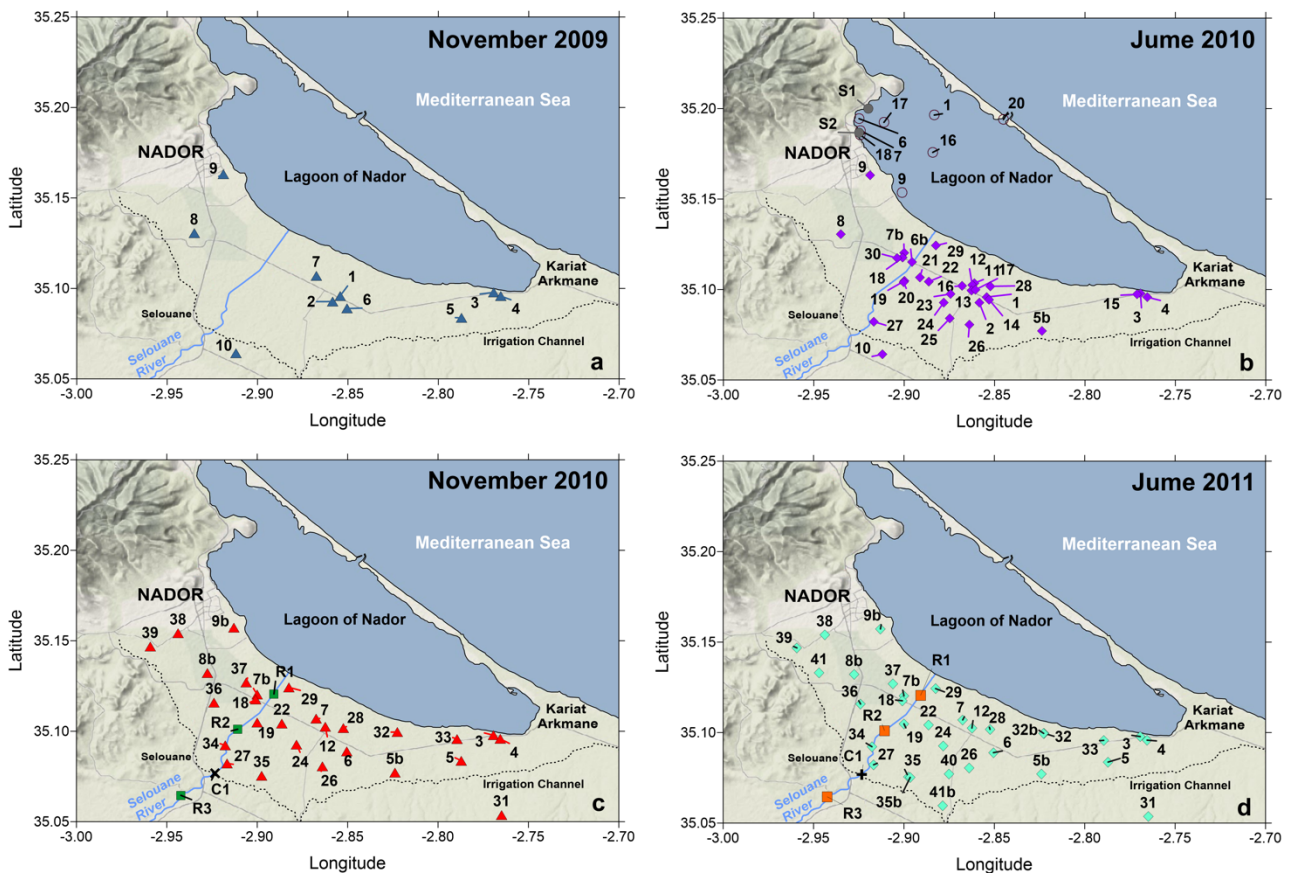
A total of 129 water samples were collected during four surveys carried out between November 2009 and June 2011 (Fig. 2), and more specifically:

- 94 groundwater samples from private hand-dug wells and boreholes (depth < 30 m) tapping the shallow Bou-Areg aquifer, and 2 in the adjacent Gareb Plain;
- 6 samples in the Selouane River and 2 from the irrigation channel;
- 21 samples in the Lagoon of Nador; and
- 4 springs

Samplings were performed over two years in November and June in order to provide evidences about the seasonal effect and possible local recharge in the area (Table 1). *In situ* measurements of Electrical Conductivity, pH, total alkalinity, Eh and water temperature were performed during all campaigns (Table 1, Table X1 and Table X2). Samples for major ion analysis were filtered through 0.45 µm cellulose membrane and stored in polyethylene bottles. Samples for cation analyses were preserved by addition of 5N HNO₃ soon after filtration. Samples for stable isotope analysis were collected and preserved according to the procedures indicated by Clark and Fritz (1997).

Chemical analyses of water samples were performed using ion chromatography at the hydrochemical laboratory of CNR-IGAG (Montelibretti, Italy; November 2009 campaign), at Department of Earth and Environmental Sciences of the University of Pavia (Italy; June 2010 and November 2010 campaigns), and at

Department of Earth Sciences of the University of Turin (Italy, June 2011 campaign). The error, based on the charge balance, was calculated to be <5%. Bromide analyses were performed at the CNR-IGG (Pisa, Italy) using ion chromatography. Boron analyses were performed at the Earth and Environmental Sciences Department at the University of Pavia (Italy), using ICP-AES (Jobyn Yvon 24). Hydrogen isotope composition was measured by water reduction over metallic zinc (Coleman et al., 1982), while $\delta^{18}\text{O}$ was analysed by water- CO_2 equilibration at 25 °C (Epstein and Mayeda, 1953). Both results are expressed in ‰ vs V-SMOW (Gonfiantini, 1978; Gonfiantini et al., 1995) and the analytical uncertainties (1σ) are $\pm 1\text{‰}$ and $\pm 0.1\text{‰}$ respectively. $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ of dissolved nitrate were analyzed following the procedures described by Silva et al. (2000) and refer to V-AIR and V-SMOW (Gonfiantini et al., 1995) with analytical uncertainties (1σ) of $\pm 0.5\text{‰}$ and $\pm 1\text{‰}$ respectively. All samples were prepared and analysed on a Finnigan™ MAT 250 Mass Spectrometer at ISO₄ private laboratory, Turin (Italy). Boron concentration was determined by ICP-AES. Boron isotopes (expressed as $\delta^{11}\text{B}\text{‰}$ vs NBS951) were determined by MC-ICP-MS at ALS Scandinavia AB, Sweden, with combined uncertainty (1σ) of ± 0.4 to $\pm 1\text{‰}$.



***Figure 2. Location of the sampling sites for the November 2009, June 2010, November 2010 and June 2011 campaigns in the Bou-Areg aquifer and Lagoon of Nador.

Results and discussion

Mineralization processes

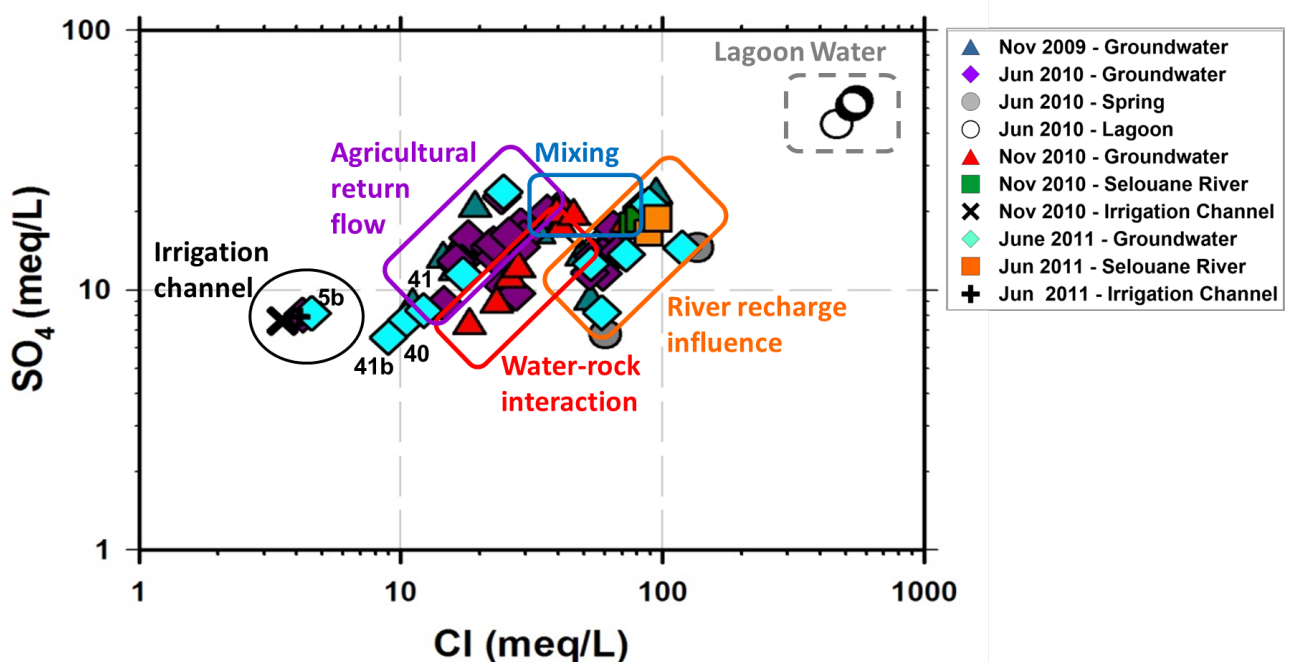
The comparison of the November 2009, June 2010 and November 2010 with previous studies performed in the Bou-Areg plain (Chaouni Alia et al., 1997; El Amrani et al., 2005; El Mandour et al., 2008; El Yaouti et al., 2008; El Yaouti et al., 2009) permitted to highlight some of the main features of the studied system:

- The aquifer is characterized by a generally high natural salinity, with most of the sampled groundwater with TDS values exceeding 100 mg/L. Salinity origin has been attributed to the combined action of water-rock interactions, dissolution processes of evaporative rocks and carbonates from Miocene substratum. Consequently, this groundwater is not adequate for irrigation purposes, although still being used by several farmers in the region (Re et al., 2011; Re et al., 2013a).
- The aquifer is highly vulnerable to irrigation practices (mainly performed from May to October), and agricultural return flow strongly contributes to increasing the natural groundwater salinization. However, when recharge from precipitations dominates (November to April) the system is less affected by human induced recharge and it shows a more natural composition, due to the dominant water-rock interaction processes. Therefore, the aquifer has a strong seasonal dependency but a good resilience (Re et al., 2014).
- External contribution to the background hydrochemical composition of the aquifer are also provided by: (i) Selouane River through natural lateral discharge and stream capture driven by groundwater abstraction in the irrigation season; and (b) groundwater flow from the Gareb Plain. Mixing processes also occur along the Selouane corridor, in absence of irrigation activities, and groundwater chemical composition is influenced by Selouane River, Gareb groundwater and water-rock interactions (Re et al., 2014).
- Saline water intrusion from the lagoon to the shallow aquifer is only limited to a few wells nearby the coastline, hence it is not a dominant process affecting aquifer geochemistry (Fig. 3). On the other hand, discharge of polluted groundwater has been found to partially alter the Lagoon of Nador quality (Re et al., 2011).

In order to support evidences from previous investigations, and to confirm both the high seasonal dependency and vulnerability to agricultural activities, June 2011 campaign aimed at identifying the samples more adequate to represent the end-members for the mixing processes and for recharge less affected by anthropogenic contamination. Results were compared to those from previous campaigns and particularly to the influence groups identified in Re et al. (2014). Fig. 3 shows the chloride and sulphate contents for all groundwater samples, and highlights that June 2011 groundwater samples mainly falls in the ranges characteristic of agricultural return flow ($\sim 10 \text{ meq/L} < \text{SO}_4^{2-} < \sim 30 \text{ meq/L}$ and $\sim 10 \text{ meq/L} < \text{Cl}^- < \sim 40 \text{ meq/L}$), and lateral river recharge ($\sim 10 \text{ meq/L} < \text{SO}_4^{2-} < \sim 21 \text{ meq/L}$ and $\sim 25 \text{ meq/L} < \text{Cl}^- < \sim 150 \text{ meq/L}$): For the first group high sulphates are associated to the salt remobilization due to irrigation practices, while lower chloride values (with respect to the other samples) are associated to the dilution effect provided by the irrigation channel water, as showed by the composition of well 5b, the closest to the irrigation channel (Fig. 3; Cl^- : 4.57 meq/L and SO_4^{2-} : 8.15 meq/L; irrigation channel Cl^- : 4.12 meq/L and SO_4^{2-} : 7.85 meq/L). Similarly, well 41b (Cl^- : 8.97 meq/L and SO_4^{2-} : 6.58 meq/L), located in the South-western part of the plain, close to the irrigation

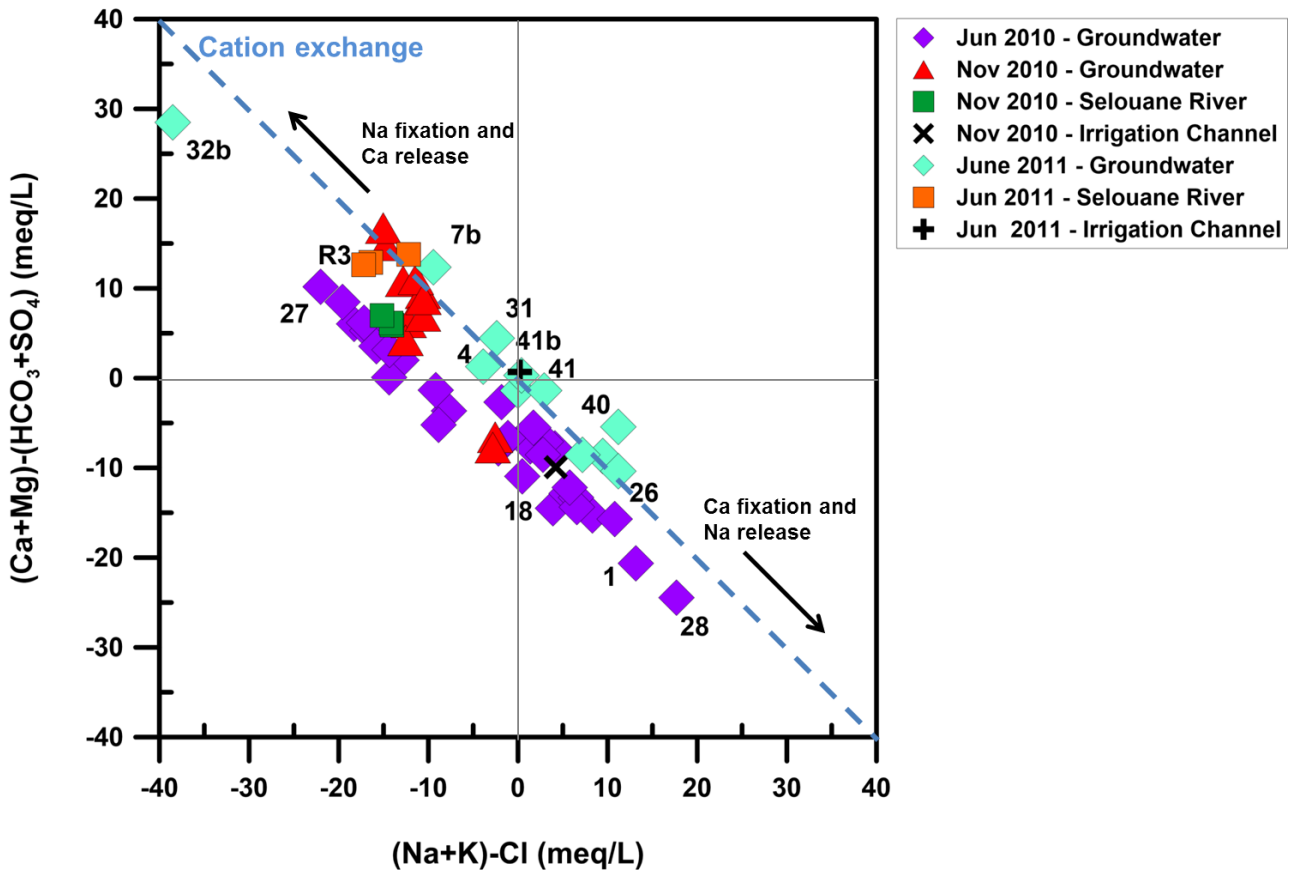
channel, shows a sulphate concentration similar to that of the irrigation channel, but higher chloride probably representative of a dominance of a more natural recharge, coherent with water-rock interaction processes. As a general rule, moving progressively away from the channel towards the centre of the plain, the dilution effect provided by irrigation water decreases resulting in both sulphates and chloride concentration increases.

On the other hand, the second group of wells show concentrations consistent with the composition of the Selouane River (average Cl^- : 92.53 meq/L and SO_4^{2-} : 18.04 meq/L), confirming the influence of local lateral recharge from the river and/or a higher contribution of groundwater from the Gareb Plain trough the Selouane corridor during the irrigation season.



***Figure 3. Plot of Cl^- vs. SO_4^{2-} for the samples collected November 2009, June 2010, November 2010 and June 2011 in the Bou-Areg (Modif. after Re et al., 2015).

A general Cl^- enrichment for all groundwater samples has been previously highlighted (Re et al, 2013) and attributed to pollution impact. Figure 4 shows that, in the correlation diagram between $[(\text{Na}+\text{K})-\text{Cl}]$ and $[(\text{Ca}+\text{Mg})-(\text{HCO}_3-\text{SO}_4)]$, all the samples from the June 2010 and November 2010 plot below the the -1:-1 line, highlighting this general enrichment in Cl^- due to anthropogenic origin. On the other hand, samples collected in June 2011 and generally located in the upstream part of the aquifer (recharge zone; e.g. 40, 41, 41b and 26) or in proximity to different salinity sources (e.g. Selouane River for well 7b, and Nador Lagoon for well 4) do not show this enrichment, highlighting the strong vulnerability of the aquifer to anthropogenic pollution and its high resilience when recharge from natural or less contaminated sources occurs. Concurrently, Fig. 4 highlights the occurrence of cation exchange processes modifying the relative abundance of Ca and Na, which are attributed to both salinization (Na fixation and Ca release) and “refreshening” (Na release and Ca fixation) processes.



***Figure 4. (Na+K)-Cl versus (HCO₃-SO₄)-Cl for the Bou Areg aquifer waters. Dashed line represents the cation exchange line (-1:-1).

Tracing Nitrate pollution origin

The isotopic compositions of dissolved nitrates in groundwater range between +4.13 and +27.23 ‰ vs AIR in $\delta^{15}\text{N}_{\text{NO}_3}$ and between +5.5 and +18.2‰ vs SMOW in $\delta^{18}\text{O}_{\text{NO}_3}$. In order to attribute each sample to a possible source of nitrates, the isotopic compositions were plotted in the classical $\delta^{18}\text{O}_{\text{NO}_3}$ vs $\delta^{15}\text{N}_{\text{NO}_3}$ diagram reporting the source compositional fields reported in the literature (Fig. 5a).

Some groundwater samples fall close to the compositional field of synthetic fertilizers, and follow the trend indicated for nitrification processes. Their nitrogen isotopic composition is rather enriched, since fertilizers generally range between -4‰ and +4‰, although some can reach up to +7‰ in $\delta^{15}\text{N}_{\text{NO}_3}$ (Kendall et al., 2007). Nevertheless, the original isotopic composition of fertilizers can be enriched by other processes occurring in the soil prior to be leached to groundwater, namely volatilization, which is enhanced in alkaline soils and arid climates (Kendall et al., 2007). Also, during nitrification, the $\delta^{18}\text{O}_{\text{NO}_3}$ ratio changes to lower values because of the incorporation or the exchange with $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of groundwater, with a normal range of $\delta^{18}\text{O}_{\text{NO}_3}$ for nitrified synthetic fertilizers usually of -5‰ to 15‰, depending on the isotopic composition of groundwater. Similar isotopic compositions for groundwater nitrates are reported by Shalev et al. (2015) in the arid region of the Arava Valley (Israel), and are attributed by the authors to synthetic fertilizers enriched by different degrees of ammonia volatilization.

Due to this $\delta^{15}\text{N}$ enrichment, none of the samples falls in the range indicated in the literature for mineralized synthetic fertilizers, but most are found in the compositional field of soil organic matter. Nevertheless, since

nitrate concentrations largely exceed the expected natural background level (16 mg/L, the lowest concentration displayed by sample 41 collected in the recharge area), samples falling in this field likely record a mixed contamination from both synthetic fertilizers and anthropogenic organic matter (animal or human waste). The latter source is characterized by $\delta^{15}\text{N}_{\text{NO}_3}$ in the range of +10‰ to +20‰; nevertheless, we considered this organic matter contribution dominant for samples showing a $\delta^{15}\text{N}_{\text{NO}_3}$ greater than +8.6‰. Finally, some samples are affected by a combined isotopic enrichment following the slope of 2:1 ratio indicative for denitrification phenomena.

Based on Fig. 5a, the main sources or processes controlling the nitrate concentration in each groundwater sample were inferred. Accordingly, in Fig. 5, yellow triangles identify synthetic sources; pink circles, mixtures of synthetic and organic sources; blue squares, anthropogenic organic matter (manure or sewage); and green diamonds denitrification.

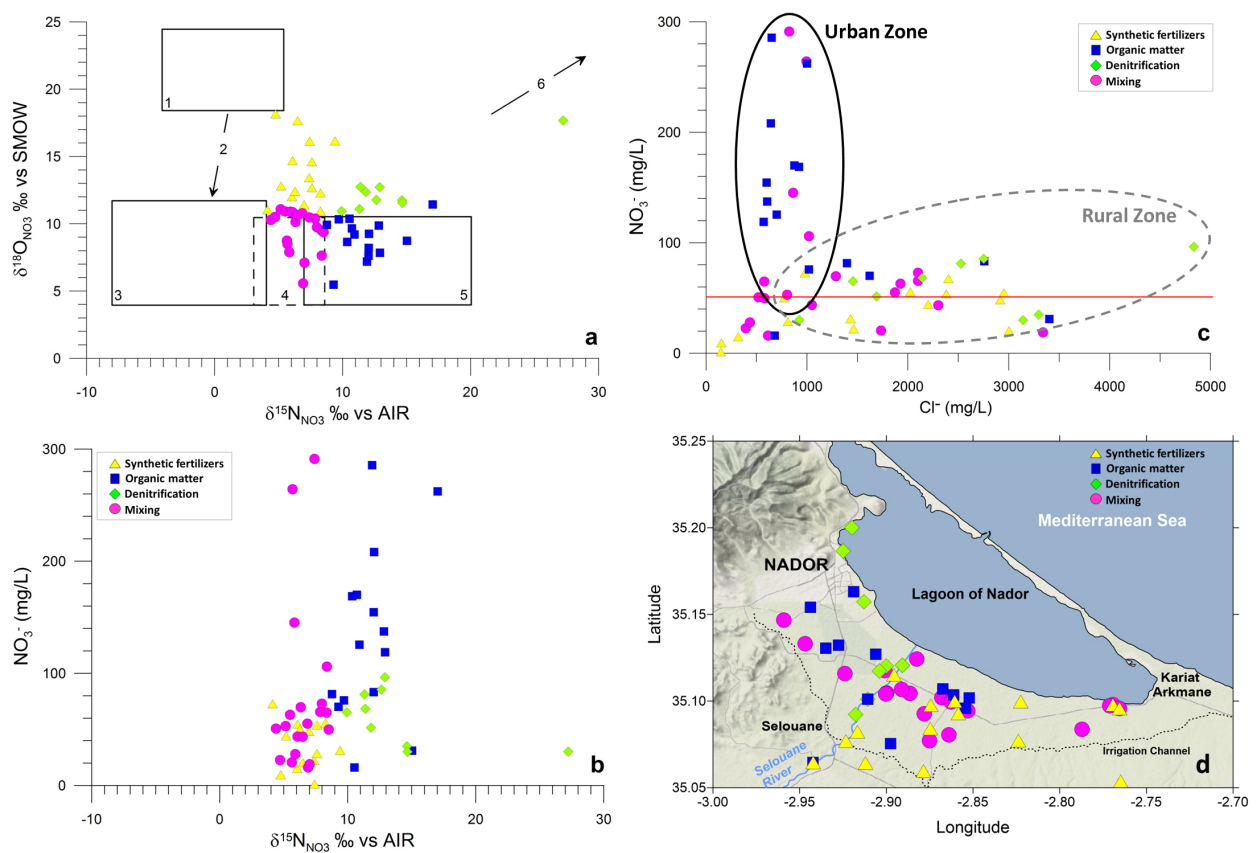
Fig. 5b reports the comparison between nitrate concentrations and $\delta^{15}\text{N}_{\text{NO}_3}$. Nitrates originated from synthetic sources are responsible for comparatively moderate nitrate contents (less than 80 mg/L). For nitrate contents greater than 100 mg/L (the double of the statutory limit for drinking waters; WHO, 2011), a range from +5.69‰ to +17.03‰ is observed, testifying for an increasing contribution of isotopically enriched sources like anthropogenic organic matter.

As far as denitrification is concerned, the identification of this process is mainly based on the position of the samples in Fig. 5a, where they show an enriched composition both in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, and in Fig. 5b where they show a limited nitrate content compared with samples from organic matter source. In addition, these samples are all located close to the Selouane river and to the coast (Fig. 5d) and could therefore be representative of longer and deeper groundwater circuits (Böhlke and Denver, 1995). Nevertheless, denitrification seems to have a limited influence, testified by a low isotopic enrichment (with the exception of sample 9b, with $\delta^{15}\text{N}_{\text{NO}_3} = 27.23$) and rather elevated residual concentrations (greater than 30 mg/L even at the highest isotopic enrichment). This suggests that, in the investigated area, denitrification is not an effective mechanism to limit nitrate contents in groundwater, in agreement with the high hydraulic conductivity of the aquifer (Chaouni Alia et al., 1997) and the oxic conditions measured in most wells (Table X1).

In Fig. 5c comparing the NO_3^- and the Cl^- contents, two trends are observed. One shows a progressive increase in chloride with nitrate contents not exceeding 100 mg/L. This trend is mostly displayed by samples containing nitrates originated from synthetic fertilizers and mixed sources, and can therefore be related to agricultural activities. In this interpretation, therefore, nitrates are associated to groundwater salinization, likely due to the use of mineralized irrigation water pumped from the aquifer performed in the past and discontinued after the construction of the irrigation channel (Dakki, 2003; El Amrani et al., 2005). A second trend, which is responsible for the highest nitrate concentrations recorded, is displayed by samples with relatively low chloride contents (up to about 1000 mg/L). This trend is followed by samples whose nitrate contents are mostly due to an anthropogenic organic matter source. Since cattle raising activities are not consistent in the area and manure spreading is limited (Boelee and Laamrani, 2003), a source from leaking septic tanks and wastewater is suspected, which would contribute nitrates contained in low-salinity water used from households.

The presence of an agricultural and an urban source of nitrates is further confirmed by the map showing the location of the analyzed wells, distinguished based on the nitrate sources indicated by their isotopic

signature (Fig. 5d). In the map, the Selouane river acts as a groundwater divide. Samples with nitrates originated by synthetic fertilizers are all located in the South-eastern plain, which is mostly dedicated to agriculture, whereas the North-western sector is more impacted by a contamination from anthropogenic organic matter and mixed sources. It is worth to note that samples in the agricultural area (e.g. 1, 7, 11, 28) showing an anthropogenic organic matter contribution are all collected from households and commercial activities along the main road leading to Kariat Arkmane. Also, samples with nitrates from mixed sources are mostly located close to the irrigation channel, in the proximity of the Selouane river or close to the lagoon shore, therefore in transitional areas where seasonal changes in nitrate input, water salinity and flow may reflect the impact of recharge from precipitation and irrigation.

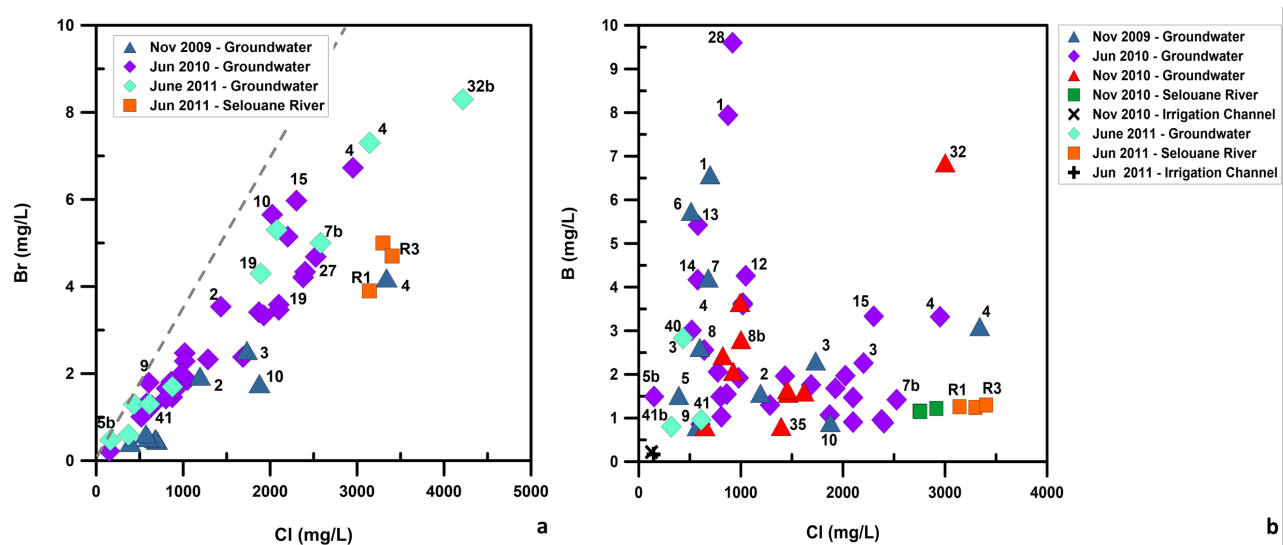


***Figure 5. (a) Stable isotope composition of dissolved nitrates in groundwater from the Bou-Areg aquifer, with Ranges for groundwater with $\delta^{18}\text{O}_{\text{H}_2\text{O}} \sim -4 \text{ VSMOW}$. 1) Synthetic fertilisers; 2) Evolution during nitrification; 3) Nitrified synthetic fertilisers; 4) (Soil organic matter and contamination from mixed sources; 5) Anthropogenic organic matter (sewage and manure); 6) Evolution during denitrification. Modified after Clark and Fritz (1997) and Kendall et al. (2007). (b) Concentrations vs isotopic composition of dissolved nitrates. (c). Dissolved nitrates vs chloride concentrations, highlighting the location of the groundwater samples in the urban and rural areas of the Bou-Areg aquifer. Red line: WHO statutory limit for drinking waters $[\text{NO}_3^-] = 50 \text{ mg/L}$; WHO, 2011). (d) Dissolved nitrates distributions in Bou-Areg groundwater with respect to potential N sources.

Insights provided by Br, B and $\delta^{11}\text{B}$ systematics

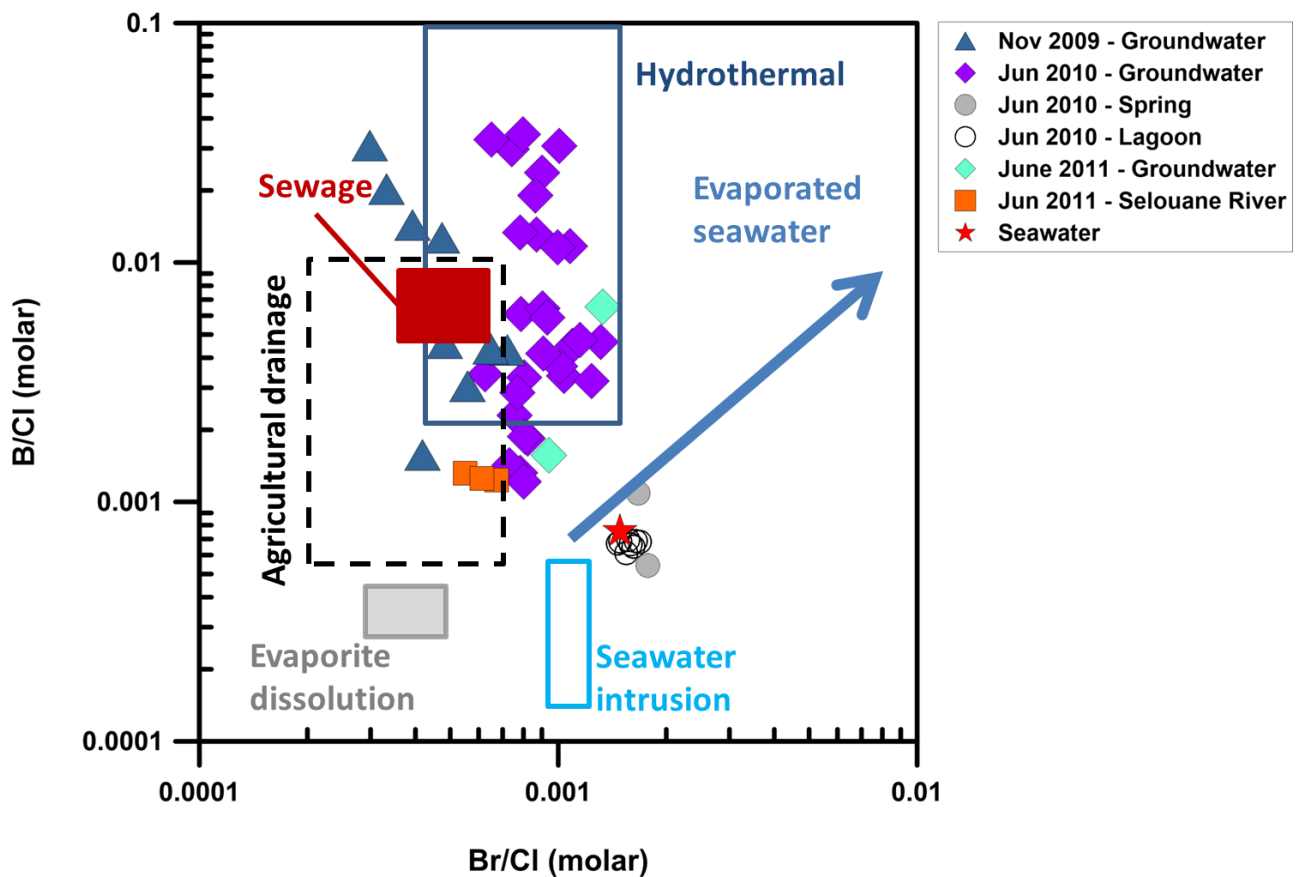
In order to further constrain the origin of nitrate contamination and groundwater salinization, the systematics of trace elements, such as Br and B, investigated together with Cl.

Groundwater from the Bou-Areg aquifer show Br concentrations ranging from 0.2 to 8.3 mg/L. Br, as expected, is well correlated with the Cl content (Fig. 6a), maintaining a Br/Cl ratio lower than sea water (dashed line). On the other hand, groundwater shows rather high B concentrations, reaching up to 9.6 mg/L, hence exceeding for most of the samples the WHO guidelines of 0.5 mg/L (WHO, 2011). At these concentrations not only can B directly harm human health, with its associated negative effects on fertility and pregnancy (Mastromatteo and Sullivan, 1994), but also indirectly undermine the food security of local population, being toxic for many plants (e.g. orange, lemon, apple) when >1 mg/L (Vengosh et al., 1998). On the B versus Cl plot (Fig. 6b), two main trends can be observed: one, with high Cl and low B contents, displayed by samples close to or from the Selouane river, and one, showing a B increase at Cl concentrations lower than 1000 mg/L. Samples belonging to this group are all located in the central part of the plain and in a rather small area, where no anthropogenic activities other than agriculture are present.



***Figure 6. (a) Chloride versus bromide, and (b) boron for the samples collected in the Bou-Areg aquifer.

The two systematics can be compared in the B/Cl vs Br/Cl plot (Fig. 7), evidencing the fields of the different sources and processes modifying their contents in groundwater (Vengosh, 2003). Here, none of the samples falls close to the marine end-member, permitting to confirm the exclusion of seawater intrusion as a major process affecting groundwater composition (Re et al., 2013a). Some of the samples might be affected by agricultural drainage or sewage leakage, but most of the samples fall in the field of hydrothermal waters, which are not known to be present in the area. Therefore, one or more different processes are likely affecting the concentrations of these three elements.



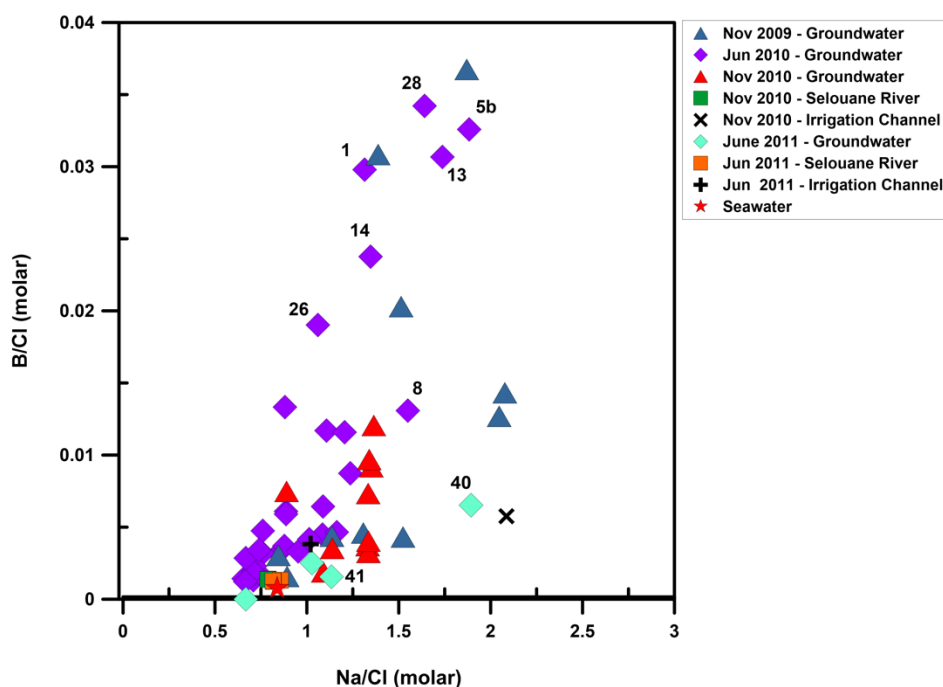
***Figure 7. Br/Cl versus B/Cl compared to different potential saline sources (e.g. seawater, evaporated seawater, brines, hydrothermal fluids, sewage effluents, agricultural drainage and evaporate dissolution). Modif. after Vengosh, 2003.

Chloride is considered the conservative ion by excellence and, although many sources can be identified adding chloride to groundwater, none are known to remove it, except NaCl precipitation which is very rare in freshwater environments (Stumm and Morgan, 1981). In the Bou-Areg study case, an input of chloride associated with increasing nitrate contents and a synthetic N source has been evidenced in the agricultural sector of the plain (Fig. 5c). To justify Br/Cl ratios lower than sea water, either a removal of Br or an input of Cl can be considered. Br removal is caused by an uptake from the organic matter (Edmunds 1996). In the studied area, the development of organic matter in a deep groundwater environment seems unlikely; rather, based on nitrate isotopes, we should expect an input of anthropogenic organic matter which, if degraded, would be a source of Br, as evidenced by $\delta^{13}\text{C}$ values (Re et al., 2013). Therefore, the low Br/Cl ratios are attributed to a Cl input provided by the dissolution of soluble salts in the unsaturated zone, as already evidenced by Re (2011). In order to elucidate the sources of B in groundwater, causing the high B/Cl ratios, $\delta^{11}\text{B}$ analyses were conducted on some samples selected based on the criteria reported in Table 2.

Notably, all samples show enriched $\delta^{11}\text{B}$, higher than 30‰. Sample 41, representative of the unpolluted groundwater far from the shoreline, has a $\delta^{11}\text{B}$ of +40‰, similar to that of seawater. Nevertheless, its Na/Cl ratio and B/Cl are higher than sea water. The same is observed for sample 7b, with a Na/Cl ratio close to that of sea water but enriched in B/Cl ratio. In both cases, ionic ratios are not compatible with sea water intrusion: rather, the isotopic composition could reflect the accumulation of B from marine aerosols in the

soils and its transfer to groundwater (Vengosh et al., 2005). The highly saline water of the Selouane river, drained from the Gareb plain (sample R3) shows an enriched $\delta^{11}\text{B}$, coupled to a slight decrease in the B/Cl ratio, which could be attributed to B adsorption on clays and/or a limited contribution from partially evaporated seawater. When looking at waters impacted by nitrate contamination, larger $\delta^{11}\text{B}$ differences, with respect to the less polluted samples, are observed. A relative isotopic depletion characterizes sample 8, showing high Na/Cl and B/Cl ratios. This could be due to Na release by cation exchange processes and B desorption from clays. Sample 9 and 28 instead show increasingly high B isotopic compositions but are also characterized by high B/Cl and Na/Cl ratios. Enriched B isotopic compositions are generally attributed either to the presence of evaporated seawater or to B adsorption on clays (Xiao et al., 2013 and references therein; Kloppmann et al., 2015). The first explanation is not applicable to these samples because of their relative low Cl content. B adsorption could be evoked for sample 9, and could be consistent with its relatively low total B content. Nevertheless, since this sample was collected in the Nador urban area, one would have expected a more depleted isotopic composition, since sewage is generally characterized by low $\delta^{11}\text{B}$. Even more difficult is the explanation for sample 28, where both high $\delta^{11}\text{B}$ and B contents are observed. Here, a single source or process cannot account for this composition.

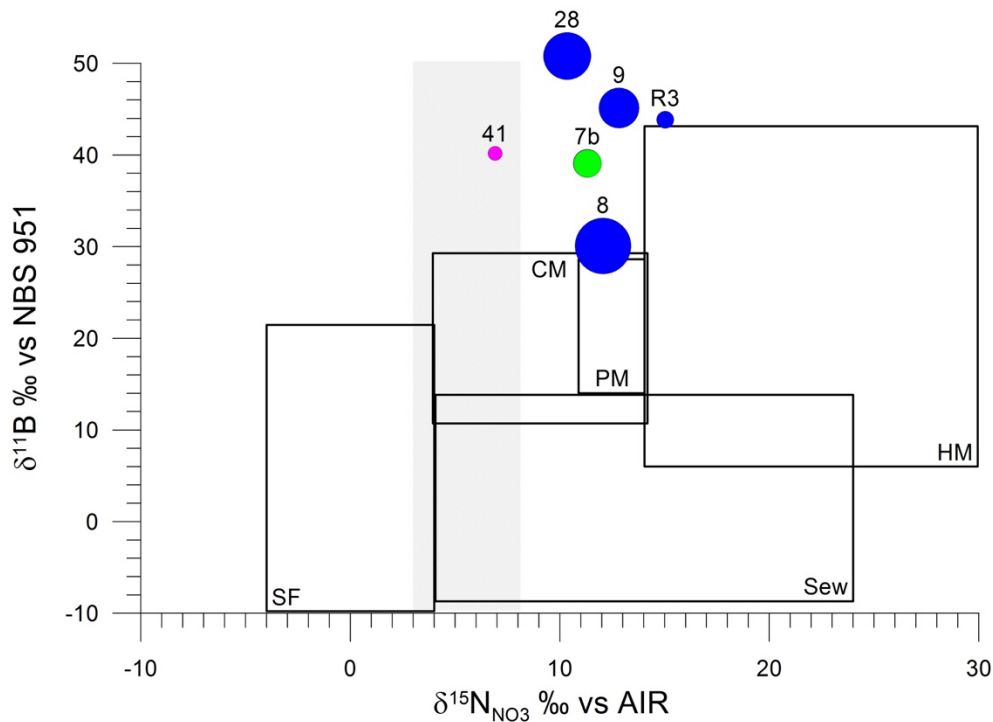
Similar high salinity groundwater with high Na/Cl, B/Cl and $\delta^{11}\text{B}$ is reported in the literature in the Gaza strip (Vengosh et al., 2005). In this case the high B content is provided by the leaching of loess deposits, while the dissolution of pedogenic calcium carbonates and gypsum would produce Ca-rich solutions that, exchanging with clay minerals saturated with Na^+ would cause the elution of Na^+ to the groundwater. This hypothesis is supported by the correlation of B/Cl ratios and Na/Cl ratios observed in both the saline groundwater and loess leachates, suggesting their common origin (Fig. 8). This correlation is also observed in Nador groundwater, especially in those samples showing the high B with moderate Cl contents found in the SE plain, and cation exchange reactions involving Ca-fixation and Na release as reported by Re et al., 2013 and shown in Fig. 4.



***Figure 8. B/Cl versus Na/Cl for water samples collected in the Bou-Areg coastal aquifer.

According to Vengosh et al. (2005), the progressive $\delta^{11}\text{B}$ enrichment in groundwater from the Gaza strip would be due to the long-term accumulation of marine aerosols in the loess deposits, resulting in an equilibrium between the dissolved ($>39\%$) and adsorbed ($<39\%$) boron phases. The boron-rich solution, percolating into the saturated zone, would establish a new equilibrium condition with the host clay minerals, in which the residual groundwater would become enriched in ^{11}B upon selective removal of ^{10}B to the adsorbed phase. This hypothesis could be valid also for Nador groundwater but due to the limited number of available isotopic data, this requires further investigation.

In Bou-Areg groundwater, the high geochemical background for B and Cl, coupled to the complex water-rock interaction processes, limit the application of this isotopic systematics to the detection of sources of groundwater pollution. Indeed, despite the exceedingly high nitrate contents of both agricultural and civil origin, the depleted $\delta^{11}\text{B}$ values that characterize synthetic fertilizers and sewage leakages could not be detected. This is well illustrated in Fig. 9, where $\delta^{11}\text{B}$ and $\delta^{15}\text{N}$ of groundwater samples are reported, together with the compositional fields of anthropogenic contamination sources. Nevertheless, the largest differences between a marine $\delta^{11}\text{B}$, characterizing the unpolluted end-member, and the depleted or enriched compositions, are observed in the most nitrate contaminated waters. It is generally acknowledged that during nitrification, microbial oxidation of ammonium generates acidity along with nitrate in soils, and that in many carbonate aquifers nitrate-rich waters are associated with high calcium derived from dissolution of the aquifer matrix (Vengosh et al., 2005; Menciò et al., 2016). Therefore, even if in saline groundwater the anthropogenic contribution has a negligible effect in terms of salinity input, being both sewage and irrigation water not very charged, the associated nitrate content fuels up water-rock interaction processes involving the carbonate dissolution and cation exchange reactions. In this context, the use of nitrate isotopes together with other geochemical tracers is crucial to understand the displacement from equilibrium conditions, and groundwater quality degradation, while boron isotopes can provide insights on the water-rock interactions processes triggered by the input of nitrates, and possibly on the reversibility of pollution effects.



***Figure 9. $\delta^{11}\text{B}$ vs $\delta^{15}\text{B}$ of groundwater. Bubble size is proportional to the dissolved nitrate content reported in Tab.2, and colours refer to the nitrate origin (purple = mixed sources; blue = anthropogenic organic matter; green = denitrification). Grey area = natural groundwater; SF = synthetic fertilisers; Sew = sewage and septic plumes; CM = cattle manure; PM = poultry manure; HM = hog manure (compositional fields after Widory et al., 2004; 2005; Tirez et al., 2010).

Conclusions

Salinity and nitrate contamination are widely recognised as the main issues associated to coastal aquifers degradation, especially in arid and semi-arid regions where shallow groundwater often represent the main freshwater source local populations rely on.

The proximity to the sea generally drives the attribution of aquifer salinization to seawater intrusion. However, all the possible natural and anthropogenic causes have to be adequately evaluated and controlled in order to avoid ineffective mitigation measures, and to ensure the reduction of its impacts also on soil and aquifer contamination. In addition, due to increasing water demand for sustaining human needs (associated both to population growth and a shift towards more water dependent economies), and the effect of climate change (with more frequent extreme events like droughts) these issues are likely to worsen in future years with severe negative consequences on both human wellbeing and natural ecosystems. It becomes therefore necessary to understand if and to what extent integrated hydrogeochemical tool can help distinguishing among possible different salinization and nitrate contamination origin, in order to provide adequate science-based support to local development and environmental protection.

The coupled systematic of $\delta^{11}\text{B}$ and $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ is generally indicated to be the best approach for a complete identification of the origin of nitrate pollution and for evaluating the process associated with nitrogen transformation. Within the framework a multi-tracer hydrogeochemical assessment, the Bou-Areg aquifer (Morocco) is presented as case study contributing to the identification of the most effective strategy

to assess the principal sources of groundwater salinization and pollution in arid zones, where high groundwater salinity can make the clear identification of nitrate pollution sources more complex.

Experimental findings on 129 samples collected over 2 years on a semi-annual basis confirmed that the high salinity of the aquifer is given by the both natural processes (i.e. evaporites dissolution and water-rock interactions) and anthropogenic impacts driven by irrigation activities and agricultural return flow. Bou-Areg aquifer salinization is strongly interconnected with nitrate pollution. The latter is mainly caused by manure and septic effluents, especially in urban areas and in the central part of the plain where houses are not adequately equipped with sanitation systems, and synthetic fertilizers in the agricultural zone. The analysis of the isotopic signal of dissolved nitrates ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$) permitted to highlight not only the presence the agricultural and urban source of nitrates, but also that the Selouane river, flowing in the central part of the plain, acts as a groundwater divide. In fact, samples with nitrates originated by synthetic fertilizers are all located in the South-eastern part of the plain, where agricultural activities are dominant, while the North-western sector, close to the city of Nador and its sub-urban neighbourhoods, is more impacted by a contamination from anthropogenic organic matter and mixed sources. In addition, in the agricultural area the lack of sanitation facilities in some households is highlighted by the isotopic signal corresponding to anthropogenic organic matter contribution. On the other hand, samples with nitrates from mixed sources are mostly located either close to the irrigation channel, to the Selouane river or the lagoon shore, hence in transitional areas where seasonal changes in nitrate input, water salinity and flow may reflect the impact of recharge from precipitation and irrigation, testifying the strong interactions between salinization and nitrate contamination.

Results also show that in the study area the high geochemical background for B and Cl, coupled to the complex water-rock interaction processes, limit the application of the coupled $\delta^{11}\text{B}$ and $\delta^{15}\text{N}$ isotopic systematics to the detection of sources of groundwater pollution. In fact, despite the exceedingly high nitrate contents of both agricultural and civil origin, the depleted $\delta^{11}\text{B}$ values that characterize synthetic fertilizers and sewage leakages could not be detected. Therefore, even if in saline groundwater the anthropogenic contribution has a negligible effect in terms of salinity input, being both sewage and irrigation water not very charged, the associated nitrate content fuels up water-rock interaction processes involving the carbonate dissolution and cation exchange reactions.

This study permitted a more complete identification of the impacted areas by both salinization and pollution, favouring the implementation of more appropriate science-based mitigation measures to achieve local sustainable development in the region. Ideally the process should be performed by taking into account the principles of socio-hydrogeology (Re, 2015), i.e. by acting in synergy with local authorities and farmers' associations to explain to groundwater end-users the potential harmful impact of high nitrate and boron concentration on their health, food security and wellbeing, and to promote the adoption of bottom-up strategies for pollution reduction, also in view of the rapid tourism expansion of the region.

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