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Integrated socio-hydrogeological approach to tackle nitrate contamination in groundwater resources. The case of Grombalia Basin (Tunisia)

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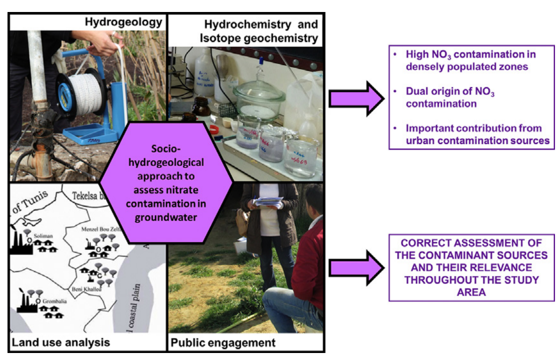
HIGHLIGHTS

- Effectiveness of socio-hydrogeology in groundwater quality assessment is proven.
- Dual origin of nitrate contamination: fertilizers and anthropogenic organic matter.
- High nitrates in the deep aquifer suggest hydraulic connections with the shallow.
- Dissolution of evaporites is triggered by nitrate contamination.
- Public participation provides essential information for correct data interpretation.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrate contamination still remains one of the main groundwater quality issues in several aquifers worldwide, despite the perduring efforts of the international scientific community to effectively tackle this problem. The classical hydrogeological and isotopic investigations are obviously of paramount importance for the characterization of contaminant sources, but are clearly not sufficient for the correct and long-term protection of groundwater resources. This paper aims at demonstrating the effectiveness of the socio-hydrogeological approach as the best tool to tackle groundwater quality issues, while contributing bridging the gap between science and society. An integrated survey, including land use, hydrochemical (physicochemical parameters and major ions) and isotopic ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) analyses, coupled to capacity building and participatory activities was carried out to correctly attribute the nitrate origin in groundwater from the Grombalia Basin (North Tunisia), a region where only synthetic fertilizers have been generally identified as the main source of such pollution. Results demonstrates that the basin is characterized by high nitrate concentrations, often exceeding the statutory limits for drinking water, in both the shallow and deep aquifers, whereas sources are associated to both agricultural and urban activities.

The public participation of local actors proved to be a fundamental element for the development of the hydrogeological investigation, as it permitted to obtain relevant information to support data interpretation, and eventually guaranteed the correct assessment of contaminant sources in the studied area. In addition, such activity, if adequately transferred to regulators, will ensure the effective adoption of management practices

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based on the research outcomes and tailored on the real needs of the local population, proving the added value to include it in any integrated investigation.

1. Introduction

A stronger integration between science and society could contribute solving nitrate contamination issues affecting rural regions worldwide. In these areas groundwater often represents the main freshwater source for both domestic and agricultural uses, providing farms and local households with -generally- free supplies in close proximity to the users and commonly without the need for complex treatment (Morris et al., 2003). Accordingly, worldwide 49% of the rural population depends on groundwater for domestic supply mostly extracted from private boreholes and/or hand dug wells (UNICEF and WHO, 2012). In addition, approximately 38% of global irrigated areas rely on groundwater resources (Siebert et al., 2013), which has contributed to a ten-fold increase of groundwater abstraction for agricultural irrigation over the last 50 years (WWAP, 2016).

Undoubtedly one of the main consequences of this high aquifer dependency is that any contamination of these waters can have serious repercussions on local population, either directly, when groundwater is used for drinking purposes or indirectly (e.g. affecting food security).

The intensification of agriculture to sustain human needs, occurred since the second half of the twentieth century, positively contributed to improve the wellbeing of many developing countries, where agriculture is a fundamental part of the economy (Hazell and Wood, 2008). On the other hand, however, the need to respond to rapid population growth and the shift towards more water-dependent economies resulted in severe aquifer exploitation and contamination, the latter mainly associated to high fertilizers' use rates (Foster and Chilton, 2003), contributing to increase the adverse impacts of agriculture on underlying groundwater resources. As a result, rural population is primarily affected by groundwater pollution, shown by an overall enhanced mineralization generally associated to nitrate contamination (FAO, 1996).

In fact, N-compounds are among the principal nutrients provided by synthetic fertilizers and manure spread on soils to improve crop growth and development, eventually increasing the grain/seed yield (Bose and Srivastava, 2001). However, mismanaged fertilizers use and irrigation practices can lead to an accumulation of nitrates in the subsoil that can leach into the aquifer, contribute to groundwater quality degradation, especially in shallow aquifers (Singh et al., 1995), and trigger complex water-rock interaction processes, ultimately enhancing salinization, particularly in coastal aquifers (Re and Sacchi, 2017, and references therein). In fact, when too large amounts of fertilizers are used (i.e. abundantly exceeding their use efficiency, as the percent recovery of fertilizer-N by a crop), a significant fraction of N can remain unutilized in the soil and create the potential for aquifer contamination. This is the case of many rural areas, especially in developing countries, where agricultural-led nitrate contamination is often associated to other anthropogenic sources (e.g. animal manure, sewage effluents, and untreated wastewaters) jointly increasing N concentration in groundwater bodies (Keeney, 1989). For example, in the sub-urban and rural areas of the Cap Vert Peninsula in the Dakar region, Senegal the interaction of agricultural activities, wastewater and septic effluent infiltration cause the occurrence of high nitrate concentrations in water for irrigation and human consumption, largely exceeding the statutory limits for drinking water (50 mg/L; WHO, 2011) and reaching concentrations up to 800 mg/L (Deme et al., 2006; Re et al., 2011; Diédhiou et al., 2012). High groundwater nitrate concentrations, both industrial and agricultural origin, have also been recorded in many rural areas in China, with concentrations up to 560 mg/L found in high-yielding areas of northern China (Liu et al., 2005; Yu et al., 2015, and references therein). In other regions the agricultural impact can be considered negligible, if compared with the on-site sanitation contribution. This is the case for example of different urban/peri-urban areas and high-density rural settlements in South Africa, Namibia and Botswana, where this anthropogenic source causes the occurrence of nitrate concentrations exceeding 800 mg/L (Tredoux et al., 2009).

In these situations, nitrate contamination of groundwater goes beyond the issue of water resources conservation per se, but also becomes a strong economic and social concern, given the severe impacts that excess of nitrates in groundwater can have on local populations, potentially arising food security and health (i.e. gastric cancer and methemoglobinemia in infants; Fan and Steinberg, 1996) issues. In addition, nitrate pollution, according to its origin, it is often associated with other contaminants, as pesticides or coliforms, therefore evidencing the aquifer vulnerability. This is why over the years the international scientific community widely analysed these effects and worked towards finding methods to identify the sources of contamination, such as the application of environmental isotopes (e.g. $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$; Aravena et al., 1993; Panno et al., 2001; Baily et al., 2011).

So why nitrate pollution continues being such a great issue worldwide? Why farmers continue over applying fertilizers and mismanage farm manure? Why local authorities underestimate the effects of the lack of proper sewage collection and treatment facilities on the subsoil and groundwater quality? This can be partially attributed to the "hidden nature" of both groundwater resources and nitrate contamination (i.e. odourless, absence of unpleasant taste, colour or turbidity), that makes more difficult its identification without specific analysis. But, leaving aside limitations in governance and central-local relations, which are out of the scope of this research, it is clear that a gap between the scientific community and the water end-users/managers/polluters still hampers adequate capacity building and knowledge transfer in this regard. The main effect of this fault is therefore the lack of awareness not only on the strong connections between human activities and the quality of the natural environment, but also on the fact that groundwater protection can lead to long-term benefits from the socio-economic point of view. This is why it is nowadays unrealistic to obtain effective solutions to water (and more generally environmental) issues keeping hydrogeology (and science) separate from the socio-economic and political domain. It is clearly important that the risks to groundwater quality (and consequently to human health) by the widespread use of fertilizers and unconstrained water use are assessed, so that the necessary control measures can be introduced. Nevertheless, effective durable solutions cannot be implemented without coupling sound scientific assessments with adequate public engagement and capacity building on the importance of water resources protection. In this regards it is crucial to strengthen the interactions between scientists and both farmers and water users, in order to make the most effective use of the outcomes of hydrogeological and environmental investigations tailored to water security. This implies bridging the gap between science policy and society, based on the assumption that a common understanding of the implication of scientific research would help solving the issues arising from opposing perceptions of environmental matters (Busche, 2015). Thus, improving information sharing and public engagement when different interests are at stake would be an asset in any research willing to lead to effective governance measures also in the groundwater sector. In this framework a new approach was proposed by Re (2015), named socio-hydrogeology, as a way of incorporating the social dimension into hydrogeological investigations and calling for a stronger engagement of hydrogeologists as advocates for public participation in water management and governance. In line with socio-hydrology (Sivapalan et al., 2012), aimed at studying the dynamic interactions and feedbacks between water and people, socio-hydrogeology focuses on the understanding of the mutual relations between people and groundwater (i.e., the impact of human activities on aquifer quality and the impact of groundwater on human wellbeing and life), by fostering the inclusion of the social dimension in hydrogeological investigations.

This paper aims at promoting the implementation of socio-hydrogeological approach as the best tool to tackle groundwater quality assessment, while contributing bridging the gap between science and society, by presenting the results of a research undertaken in the Grombalia Basin (North Tunisia). In particular, the effectiveness of performing specific groundwater quality assessments together with capacity building and participatory activities is tested. The public participation of local actors is a fundamental element for the development of the hydrogeological investigation, as it may ensure the effective adoption of management practices based on the research outcomes and tailored on the real needs of the local population. In this regard, direct engagement and confrontation with well owners and farmers allows hydrogeologists to tackle the investigation more productively, to retrieve reliable information on water and land use, and to create a relationship of mutual trust with local stakeholders. Hence the manuscript examines whether incorporating structured questionnaire administration to local farmers while performing hydrogeological samplings can value the effort, although it may seem time and money consuming. Indeed, these activities can provide precious information, useful for data interpretation, and at the same time favour dissemination and capacity building to support the implementation of new management practices based on the results of the scientific investigation.

2. Site description

The Grombalia region is located in south-western part of the Cap Bon Peninsula (Tunisia) and covers a surface of about 719 km^2. The basin is bordered by the Gulf of Tunis (N), the Takelsa Syncline (N-E), the anticlinal of the Abderrahmane Mountain and the oriental coastal plain (E), the plain of Hammamet (S) and the Bouchoucha and Halloufa reliefs (W; Fig. 1).

The climate of the region is semi-arid to Mediterranean sub-humid, with average precipitations of about 500 mm/y (1954–2006; DGRE, 2006), with maximum precipitations between October and January, and mean annual temperature of around 18 °C (max 28.9 °C in July, min 8.6 °C in January; 2003–2013, INM, 2014). The average monthly potential evapotranspiration is 76.8 mm, with lowest value in January (40.7 mm) and the maximum in July (134.5 mm) (2003–2012; INM, 2014). In the area several ephemeral rivers (*wadis*) are present, collecting surface runoff from the surrounding highlands towards the Gulf of Tunis.

The Grombalia Basin is situated astride the African–Eurasian plate boundary (Elmejdoub and Jedoui, 2009). Geologically, it is described as a graben delimited by two normal faults developed during the Middle Miocene (Hadj Sassi et al., 2006), namely the Borj Cedria NNW–SSE normal fault and the Hammamet NE–SW normal fault (Ben Ayed, 1993; Ben Salem, 1995; Chihi, 1995) and filled by 500 m of Quaternary sediments. These mainly consist of fine to coarse grained sands, clayey sands, sandstone, silt and abundant evaporate deposits (Schoeller, 1939; Colleuil, 1976; Ben Salem, 1995; Ben Moussa et al., 2010).

From a hydrogeologic point of view, the Grombalia aquifer is a multilayer system constituted by a shallow phreatic aquifer, with an average thickness of about 50 m, hosted in the Quaternary continental sand, clayey sand and sandstones deposits, and different confined aquifers with average thickness of about 100 m each separated by marl layers but communicating through discontinuities (Castany, 1948; Ennabli, 1980). The recharge in the shallow unconfined aquifer mainly occurs in the pediments of the surrounding mountains and converges to the central part of the basin. There, a general southeast–northwest flow carries groundwater to the Gulf of Tunis discharge areas (Ben Moussa, 2007; Gaaloul et al., 2014).

The Grombalia region is particularly devoted to arboriculture (mainly citrus -representing 82% of the national production-, grapes −80% of Tunisian vineyards- and olives) and horticulture (mainly tomatoes, strawberries and legumes). Most of the agricultural production, if not used for personal consumption, is sold on both the national and international markets (Gafsi and Ben Hadj, 2007), and the agro-industrial sector is also rapidly expanding with more than 1250 factories, including food processing plants located in surrounding areas of Nabeul, Grombalia and Soliman.

In the region, groundwater represents the main source of water supply for both agricultural and industrial use, and consequently, the aquifer is increasingly exposed to external pressure. More than 11,000 wells

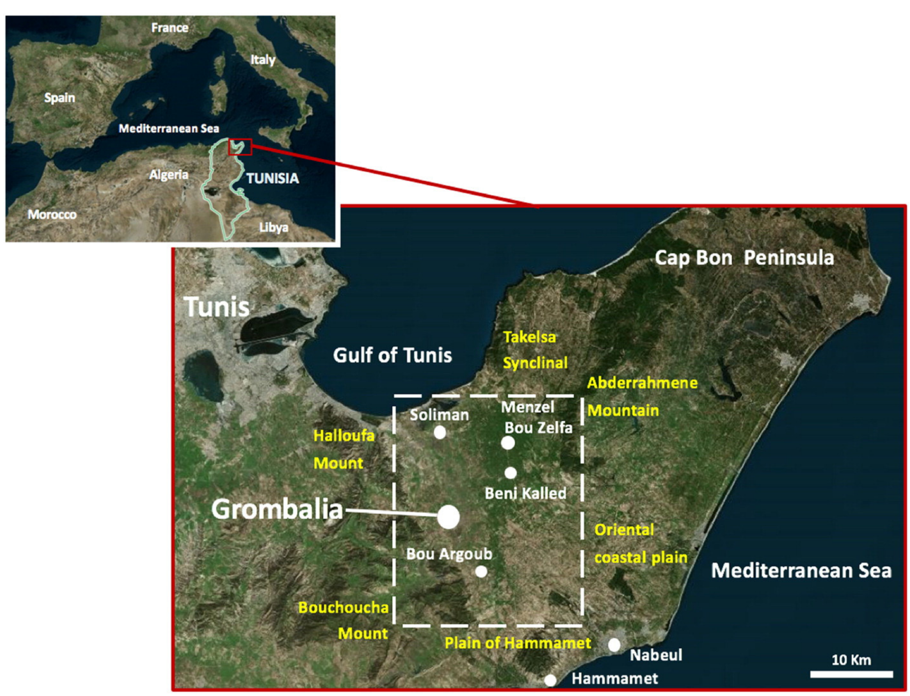

Fig. 1. Location of the Grombalia Basin. Background satellite image from Microsoft® Bing™ Maps. The white rectangle highlights the area represented in Fig. 2.

tap the shallow aquifer, with a current abstraction around 250 Mm^3/y, causing an estimated decrease of the water table depth of about 0.3 m/y (DGRE, 2010). Aquifer overexploitation had led to a severe piezometric level decrease over the years (about 10 m in the last 50 years; Charfi et al., 2013; Gaaloul et al., 2014), that is especially evident during the dry months, when abstraction rates exceed natural aquifer recharge from rainfall infiltration. In addition to scarcity, groundwater quality depletion is increasingly harming natural water resources. The latter is generally associated to aquifer salinization, salt water intrusion near to the sea shore and nitrate pollution due to anthropogenic activities (Ben Moussa et al., 2010; Ben Moussa and Zouari, 2011). As multiple contamination sources are present in the region of Grombalia, it is fundamental not only to clearly identify them, but also to effectively raise awareness among all the concerned stakeholders in order to promote shared strategies for contamination reduction and remediation, based both on sound scientific results and participative processes.

3. Methods

A socio-hydrogeological investigation, combining both classical hydrogeological analysis with socio-economic assessment (Re, 2015) was performed in the Grombalia plain (N-E Tunisia) targeted to a complete nitrate vulnerability assessment of the region. The sampling campaign combined the typical activities of a groundwater quality monitoring, together with a structured social analysis performed by the research team while conducting the field works.

3.1. Hydrogeochemical investigation

Between February and March 2014 (i.e. at the end of the rainy season/winter) a total of 51 groundwater samples were collected in both the shallow (depth generally <50 m b.g.l.) and deep Grombalia (depth generally >50 m b.g.l.) aquifers (26 and 25 respectively). Samples were collected from private hand-dug wells, mostly equipped with electrical pump, and from both private and public boreholes.

The sampling strategy took into account the historical sampling network and the previous studies in the region (Ben Moussa et al., 2010; Ben Moussa and Zouari, 2011; Ben Moussa et al., 2012; Charfi et al., 2013). This favored the design of the sampling network presented in Fig. 2, covering the whole Grombalia Basin and including the sites potentially more susceptible to nitrate contamination.

In situ measurements of electrical conductivity, pH and water temperature (Table X1 – Supplementary materials) were performed, using a WTW 340i multimeter. Samples for major ion analysis were filtered through 0.45 μm cellulose membrane and stored in high density polyethylene bottles. Chemical and isotopic analyses of the water samples were performed at the Laboratory of Radio-Analyses and Environment (LRAE) of the National School of Engineers of Sfax (Tunisia). Major elements were analysed using a Dionex DX 100 ion chromatograph equipped with a CS12 and an AS14A-SC Ion Pac columns and an AS-40 auto-sampler. The total alkalinity (as HCO_3^-) was determined by titration with standard hydrochloric acid (0.1 N) using methyl orange and phenolphthalein as indicators. The error, based on the charge balance, was calculated to be <5%. The isotopes of dissolved nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) were prepared and analysed at the ISO4 private laboratory (Turin, Italy) using a Finningan™ MAT 250 Mass Spectrometer, following the procedures described by Silva et al. (2000). Results are expressed in ‰ and refer to AIR and V-SMOW (Gonfiantini et al., 1995) with uncertainties (2σ) of ±0.5‰ and ±1‰ respectively.

3.2. Socio-hydrogeological approach

The socio-hydrogeological approach proposed by Re (2015) combines the groundwater quality assessment with capacity building and participatory activities, and it is cantered on the role of hydrogeologists as advocates for public engagement in water management and governance.

Therefore, during the previously described field work performed, all the farmers and well owners of the 51 sampled sites were asked to respond to structured interviews on water use and agricultural practices (Tringali et al., 2017). The main goal of this activity was to create a momentum for dialogue on local groundwater protection and capacity building, while also collecting relevant information on groundwater use and pollution issues. The interviews were administered directly by the research team and were focused on the collection of information related to sampled wells' features, groundwater uses and perceived anthropogenic impacts on water resources, crop production, irrigation and fertilizer use (Re, 2015; Table 1).

4. Results and discussion

4.1. Hydrogeochemical characteristics of the Grombalia aquifer

The high salinity recorded in the shallow aquifer has been pointed out by different authors, highlighting that mineralization processes in the region are relevant (Charfi et al., 2013) and concern areas where farming and agricultural activities are more intensive. The abundance of dissolved salts, especially of nitrates, chlorides and sulphates, indicates an alteration of physical-chemical properties due to anthropogenic activities (Ben Moussa and Zouari, 2011; Ben Moussa et al., 2012), thus constituting a serious threat for public health and crop production. Indeed, in their study on the unconfined aquifer, Tlili-Zrelli et al. (2013) indicate that all groundwater samples exceeded the drinking water limits for Na, Cl and SO_4, whereas 70% of the samples exceeded also that for Ca and Mg, imparting strong limitations on the use of groundwater for irrigation purposes.

Although numerous authors have investigated groundwater quality from the shallow aquifer, little is known about the composition of the deep groundwater and the factors regulating its chemistry. Our work therefore focused on the comparison between these two aquifer layers.

Samples collected in our study show electrical conductivity ranging from 1.04 to 9.18 mS/cm (mean 3.87 mS/cm) in the shallow aquifer and from 1.04 to 7.13 mS/cm (mean 2.37 mS/cm) in the deep one (Table X1 – Supplementary materials and Table 2). Chloride concentrations range from 112.4 mg/L (well 18), to 2932.4 mg/L (well 1), with average of 838.8 mg/L, in the phreatic aquifer, and from 107.3 mg/L (well 122) to 3436 mg/L (well 108), with average of 473.3 mg/L in the deep one. This confirms the high mineralization of the studied system for both the shallow and deep aquifer.

A Piper diagram, plotted in rectangular coordinates (Ray and Mukherjee, 2008) was used to highlight the different groundwater *facies* in the studied area. Nitrate concentrations were taken into account for the plot, due to its abundance in both the shallow and deep aquifers (Table X1 – Supplementary materials). Grombalia groundwater can be generally classified as Ca(Mg)-SO_4(Cl + NO_3) water type (Fig. 3). Only some samples from the deep aquifer (102, 103, 107, 112) display a Na-SO_4(Cl + NO_3) *facies*, while for others (110,113,119 and 122) bicarbonate is the dominant anion. From this diagram, no clear differences in water types between the shallow and the deep aquifer appear; only the composition of deep groundwater seems slightly more variable than that of the shallow.

Box plots comparing the major ion contents in groundwater from the two aquifers are reported in Fig. 4. Accordingly, the shallow aquifer displays higher contents in dissolved cations and anions, with the highest differences observed for nitrate, chloride, sulphate and calcium contents, while the distribution of the other ions is rather similar. This evidence is also supported by the Mann–Whitney *U* test (Table 2) highlighting that only for pH, HCO_3, K, $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ the two aquifers do not show statistically significant differences (p value > 0.05).

Previous studies (e.g. Ben Moussa et al., 2010), based on ion ratios and saturation indexes, indicated that the origin of mineralization is mostly from the dissolution of evaporites from the aquifer matrix,

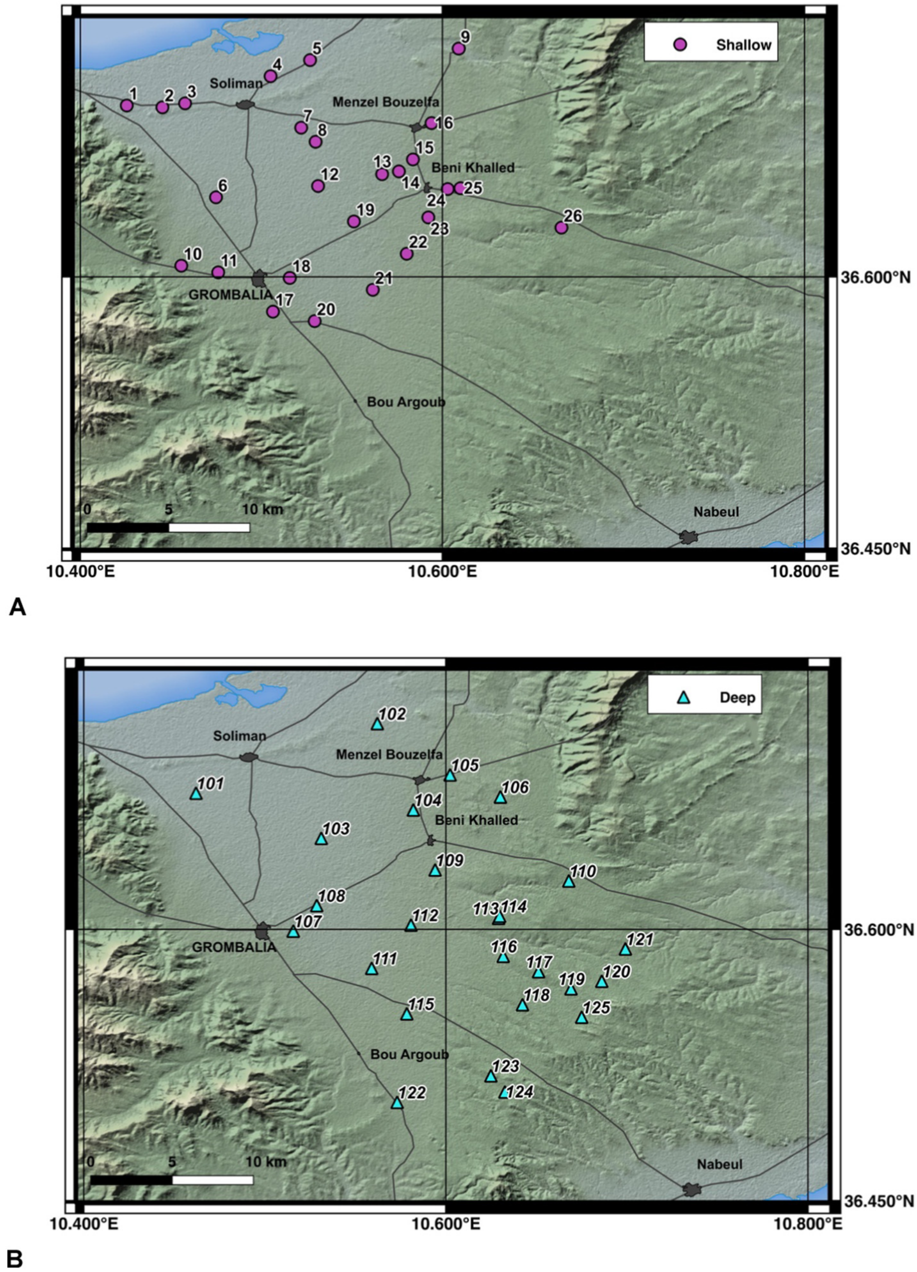

Fig. 2. Location of the sampling sites: (A) shallow aquifer; (B) deep aquifer.

namely halite and gypsum, whereas the high Ca excess, not balanced by sulphate ions, is due to cation exchange processes (aquifer salinization).

In the Na versus Cl plot (Fig. 5A), samples from the shallow aquifer align following the equation Na = 0.6036 ∗ Cl + 3.0061 ($R^2 = 0.903$) which does not correspond exactly to the 1:1 line expected for halite dissolution but shows an excess in Cl (or a deficiency in Na). Another source of Na and Cl could also be considered, i.e. sea water, but even in this case several samples (e.g. 7, 4, 10, 15, 17, 24, 25) plot below the seawater mixing line. Samples from the deep aquifer have a different behavior, and tend to align more clearly on both the halite dissolution and seawater mixing lines (Na = 0.8342 ∗ Cl + 0.8607; $R^2 = 0.962$), with the more saline sample (108) plotting directly on the latter, and two samples (109 and 119) with an excess in Na, plotting above the two previously mentioned lines. Also in the Ca vs SO_4 plot (Fig. 5B) samples do not align on the 1:1 line, indicative of gypsum dissolution, but show an excess in Ca for both the shallow and the deep aquifers. Two deep samples instead (108 and 109) plot close to the seawater composition. This excess in Ca, according to previous interpretations, is due to cation exchanges, which sequester Na and release Ca in solution. This process can be evidenced in the plot of (Na + K)-Cl versus (Ca + Mg)-(HCO_3 + SO_4) (Fig. 6) where samples should align on a −1 slope line (McLean et al., 2000). Indeed, for our case study, samples from the shallow aquifer are aligned and fall in the field of aquifer salinization (i.e. Na uptake and Ca release) but with a higher slope (−1.27), suggesting that other processes should be considered to account for mineralization. Samples from the deep aquifer are more in agreement with the aquifer salinization interpretation (i.e. fall on a −1 slope), although some samples (108, 109 and 119) deviate from this trend.

In conclusion, the processes regulating groundwater chemistry in the shallow and in the deep aquifers show similarities (salinity and hydrochemical facies) but also differences (some lower ionic content for the deep aquifer). A full understanding of water-rock interaction for these waters would require geochemical modelling and is out of the scope of this paper. Nevertheless, it should be noted that the most

Table 1
Summary of the structure and information retrieved with the structured questionnaires proposed by Re (2015).

Part	Goal	Information
Personal information	Obtain information (to be treated anonymously) on the rural population features	Gender, age, education, occupation, contacts
Water use	Retrieve information on regional and local characteristics to support data interpretation	Well features (age, depth, main characteristics), groundwater withdrawal rates, groundwater use trends, perceived or ascertained groundwater quality issues
Purposes of groundwater uses	Obtain information on local activities and priorities to support data interpretation	Groundwater use, kinds of crops cultivated, seasonal production, kinds and quantity of fertilizers used, irrigation type
Awareness of water issues	Know farmers and well holders perception about water issues	Perception of: water scarcity, climate change, integrated water resources management and groundwater pollution
Potential for participation	Evaluation of the potential for the implementation of participatory monitoring and management initiatives	Farmers' role in groundwater protection, perceived groundwater issues in the region, perception of scientists and policy makers regarding local groundwater management, willingness to be included in the groundwater monitoring network

mineralized waters from the shallow aquifer are located along the coast in the industrial area around Soliman: here groundwater overexploitation could have induced sea water intrusion and associated aquifer salinization processes, which modify the Ca/Na ratio. On the other hand, the highest mineralization in the deep aquifer is observed for wells 108 and 109, and is mostly due to the abundance of sulphate ions in solution. These samples are located at more than 15 km inland, between Beni Khalled and Grombalia, corresponding to an area where Tlili-Zrelli et al. (2013) already evidenced elevated sulphate contents not associated to Ca in groundwater. Hence, another source of salinity should be considered, of more continental origin and located at depth (e.g. evaporites containing $MgSO_4$).

4.2. Nitrate contamination

High nitrate concentrations in the shallow aquifer have been remarked over the years by different authors (e.g. Ben Moussa and Zouari, 2011; Charfi et al., 2013), and are confirmed by our survey. In the NO_3^- distribution map (Fig. 7), only few shallow wells (1, 7, 12, 18, 19, 20 and 21) show concentrations below the drinking water statutory limits of 50 mg/L (WHO, 2011), while most of the samples are not suitable for human consumption, with concentrations ranging from 67 mg/L (well 23) to 515 mg/L (well 15). Two pollution "hotspots" can be identified. The first is located in the central part of the plain (well 15 and surroundings), an area identified by Chenini et al. (2015) as high to very high groundwater contamination risk, due to the dominance of irrigated areas. This evidence would support the proposed strong contribution of agricultural activities to nitrate contamination, enhanced by long-term flood irrigation practices.

On the other hand, the second pollution hotspot is located along the coast (e.g. wells 4 and 5), where urban settlements and industrial activities dominate the land use (Chenini et al., 2015), testifying for the presence of multiple nitrate sources in the investigated area. Concerning the deep aquifers samples, 15 out of 25 can be considered suitable for drinking purposes, whereas in the others NO_3^- concentrations range from 55 mg/L (well 111) to 231 (well 118): these values, although significantly lower than those found in the phreatic aquifer, indicate that the deep aquifer may be severely impacted by nitrate pollution as well. Also in this case, the highest concentrations are recorded in the cultivated area (sample 104), but also closer to the recharge area to both aquifers (sample 118).

Another common feature to both aquifers is the presence of an area where nitrate contents are relatively low, located between the cities of Grombalia and Beni Kalled, the first identified pollution hotspot. In order to explain such low concentrations, Charfi et al. (2013) suggested the possible presence of denitrification processes.

The isotopic investigation was undertaken to identify the nitrate pollution sources and the processes affecting their concentration. The isotopic compositions of dissolved nitrates range between +4.65 and +25.38‰ vs AIR in $\delta^{15}N_{NO3}$ and between +7.8 and +19.4‰ vs SMOW in $\delta^{18}O_{NO3}$ in the shallow aquifer, and between +4.90 and +11.65‰ vs AIR in $\delta^{15}N_{NO3}$ and between +7.9 and +12.7‰ vs SMOW in $\delta^{18}O_{NO3}$ in the deep aquifer.

In order to identify the dominant sources, samples were plotted in a diagram displaying the NO_3^- concentration vs $\delta^{15}N_{NO3}$ (Fig. 8A) together with the normal ranges reported in the literature for each source. Even in this case, no significant differences can be observed for the shallow and the deep aquifer.

Some groundwater samples (22, 105) fall close to the compositional range of synthetic fertilizers, although their nitrogen isotopic composition is rather enriched, since fertilizers generally range between −4‰ and +4‰ in $\delta^{15}N_{NO3}$ (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). Similar isotopic compositions for groundwater nitrates are

Table 2
Descriptive statistics and Mann–Whitney *U* test results. Concentrations are expressed in mg/L, while isotopic values as permil. Underlined values correspond to not-statistically significant parameters. Values in bold indicate the group with the highest mean ranks relative to each statistically significant parameter.

		EC	pH	HCO_3^-	CO_3^{--}	SO_4^{--}	Cl^-	NO_3^-	Ca^{++}	Mg^{++}	Na^+	K^+	$\delta^{18}O$	δ^2H	$\delta^{15}N$	$\delta^{18}O_{NO3}$
Shallow	Min.	1.0	6.9	164.7	0.0	145.3	112.4	0.0	69.0	26.1	111.1	0.0	−5.4	−37.1	4.6	7.8
	Max.	9.2	7.8	481.9	0.0	723.1	1450.0	514.7	677.4	186.6	734.7	40.3	−3.5	−20.8	25.4	22.2
	Average	3.9	7.2	332.5	0.0	434.1	838.8	148.0	349.5	99.9	397.5	16.8	−4.6	−28.4	10.8	12.8
	Std. dev	1.5	0.2	75.8	0.0	165.0	534.1	140.9	156.8	54.2	220.0	10.7	0.5	3.2	5.3	4.4
	Mean M-W rank	**33.7**	23.5	27.8	23.5	**34.2**	**34.4**	**31.6**	**34.8**	**31.7**	**32.7**	**28.6**	**34.9**	**33.9**	11.6	10.6
Deep	Min.	1.0	7.0	128.1	0.0	23.8	107.3	2.0	31.6	12.7	72.8	4.2	−6.1	−34.8	4.9	7.9
	Max.	7.1	7.7	688.0	42.0	3105.0	3436.0	230.6	696.5	557.3	1888.4	63.6	−4.5	−28.7	11.6	12.7
	Average	2.4	7.3	321.3	4.8	383.0	473.3	55.7	181.8	89.7	275.9	16.1	−5.4	−31.8	8.1	10.7
	Std. dev	1.4	0.2	99.9	11.1	777.1	650.6	62.1	157.6	114.0	359.0	15.0	0.4	1.7	2.0	1.6
	Mean M-W rank	18.0	28.6	24.1	**28.6**	17.4	17.3	20.2	16.9	20.0	19.0	23.3	15.4	16.4	7.8	9.3
	Mann–Whitney *U*	125.0	260.5	277.5	260.0	111.0	108.0	179.0	97.0	176.0	150.0	258.0	69.0	93.0	26.0	38.0
	p value	0.0	0.2	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.1	0.6

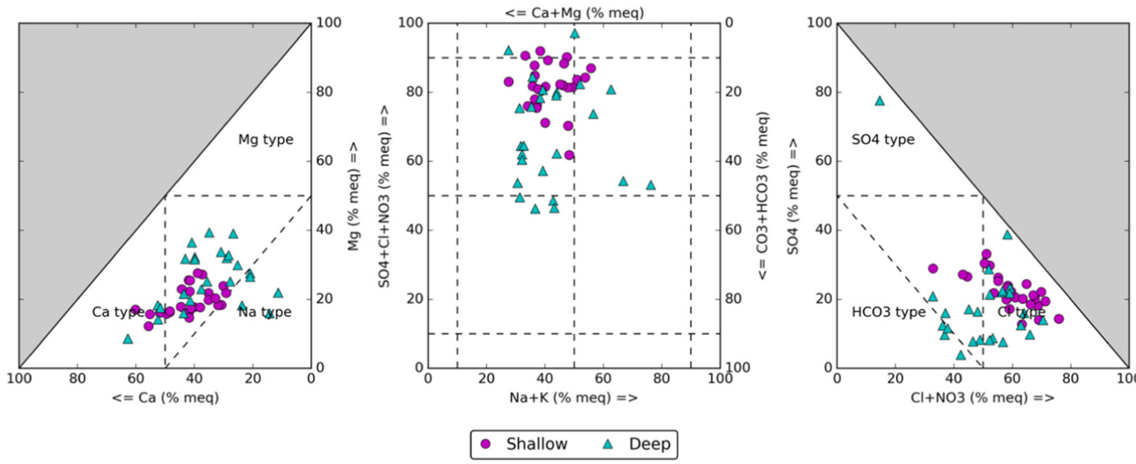

Fig. 3. Piper diagram in rectangular coordinates (Modif. After Ray and Mukherjee, 2008) for the samples collected between February and March 2014 in the shallow and deep Grombalia aquifers.

reported for the Bou Areg plain in Morocco by Re and Sacchi (2017, and references therein), and attributed by the authors to synthetic fertilizers enriched by different degrees of ammonia volatilization.

Most of the samples display an $\delta^{15}N_{NO3}$ in the compositional range of soil organic matter. Nevertheless, since nitrate concentrations largely exceed the expected natural background level (10–12 mg/L; Shand and Edmunds, 2008; Sacchi et al., 2013) these samples likely record a mixed contamination from both synthetic fertilizers and anthropogenic organic matter (animal or human waste). The latter source is characterized by enriched $\delta^{15}N_{NO3}$ values, exceeding +10‰; nevertheless, we considered this organic matter contribution dominant for samples showing a $\delta^{15}N_{NO3}$ greater than +8.6‰ (Re and Sacchi, 2017). It should be noted that the most enriched sample in $\delta^{15}N_{NO3}$ also displays a low nitrate concentration, which could be due to denitrification processes.

Indeed, when plotting $\delta^{15}N_{NO3}$ vs $\ln NO_3^-$ (Fig. 8B), samples affected by denitrification should plot on a straight line. Two of such trends can be identified in the plot: one, mostly displayed by samples from the shallow aquifer (15, 5, 6, 20), originates from rather enriched isotopic compositions and therefore would indicate the denitrification path followed by samples contaminated by organic matter sources. The second trend with the same slope, mostly displayed by samples from the deep aquifer (105, 125, 122, 111) originates from isotopic compositions in the range of synthetic fertilizers. Samples in between the two trends would represent a mixture of these two dominant sources with variable degrees of enrichment due to denitrification. The slope of the two identified trends corresponds to that indicated for a fractionation factor ε of about 10‰ (Kendall et al., 2007). In this case, the isotopic enrichment would be due to the denitrification of about 30–45% of the original nitrate content, reaching up to 80% in the case of sample 20. This sample is located in the previously mentioned area of low groundwater nitrate concentrations, despite the presence of a very shallow water table depth. Here, denitrification processes could be favored by the presence of clay rich vertisols (Chenini et al., 2015).

To verify the abovementioned hypothesis, the NO_3^- vs Cl^- diagram was plotted taking into account the localization of the samples in the Grombalia plain (Table X1 – Supplementary materials). In this graph (Fig. 9) it is possible to notice a remarkable enrichment trend of nitrate and chloride concentrations, especially characterizing the wells located in the peri-urban areas, confirming the relevance of anthropogenic pollution associated to domestic activities. Only two wells (e.g. 7, 1), with low or absent nitrate concentrations, show a significant enrichment in chloride concentration that can be associate to the occurrence of saline water intrusion in the coastal area near Soliman.

On the other hand, most of the wells located in the rural zones or in areas with no dominant land use (hence classified as intermediate) show relatively lower NO_3^- concentrations, corresponding to the

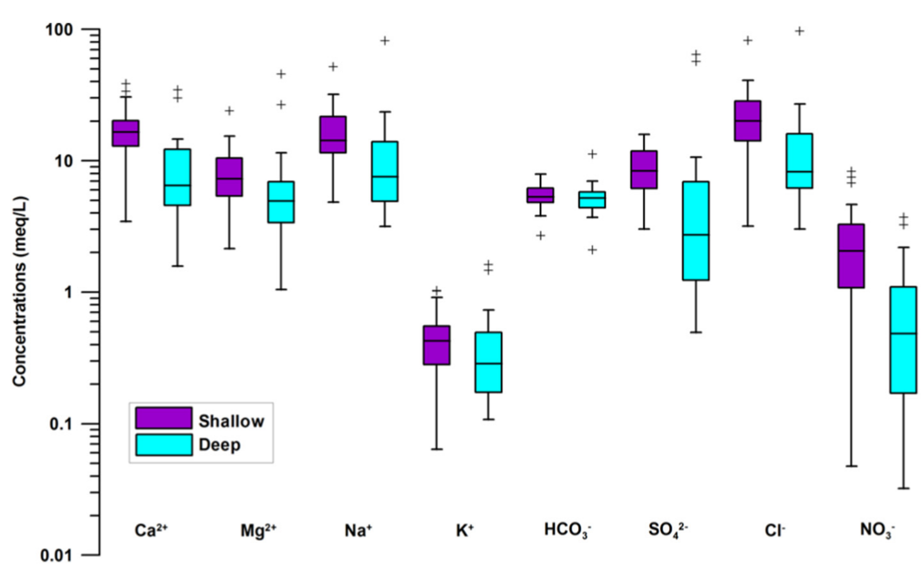

Fig. 4. Box plots of the major ion contents for the shallow and deep aquifers in the Grombalia basin.

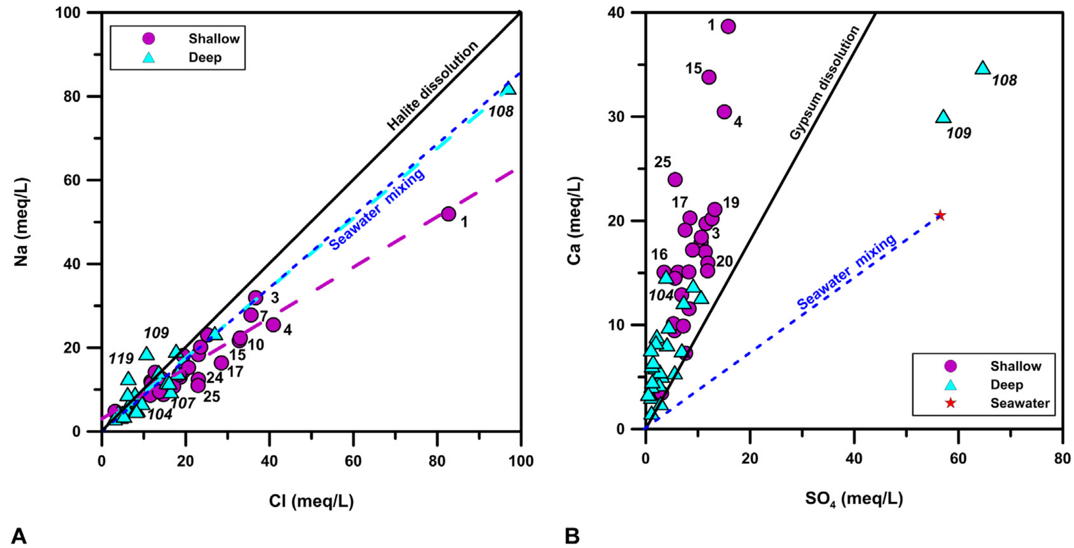

Fig. 5. (A) Plot of Na vs Cl and (B) Ca vs SO_4. Dashed blue line: seawater mixing trend; purple and cyan dashed lines correspond to the regressions for the shallow and deep aquifers respectively ($Na = 0.6036 * Cl + 3.0061$, $R^2 = 0.903$ and $Na = 0.8342 * Cl + 0.8607$, $R^2 = 0.962$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

previously identified trend of synthetic fertilizers pollution origin. Based on this observation, rural areas seem to be relatively less contaminated than peri-urban ones, although, the presence of most of the deep wells in these zones highlights the high vulnerability to agricultural pollution also in the deeper parts of the aquifer (Fig. 10).

To better understand the factors controlling nitrate contamination origin and evolution, the hydrogeochemical results have been analysed taking into account the territorial reality at regional level, based on the outcomes of the results of structured interviews performed during in situ measurements.

4.3. Socio-hydrogeological approach to identify nitrate pollution origin

Field surveys were completed for 85% of the sampled sites (78% of the shallow wells and 92% of the deep ones; Table 3).

Overall, well owners and farmers have shown high level of cooperation and interest in the outcomes of the hydrogeological assessment,

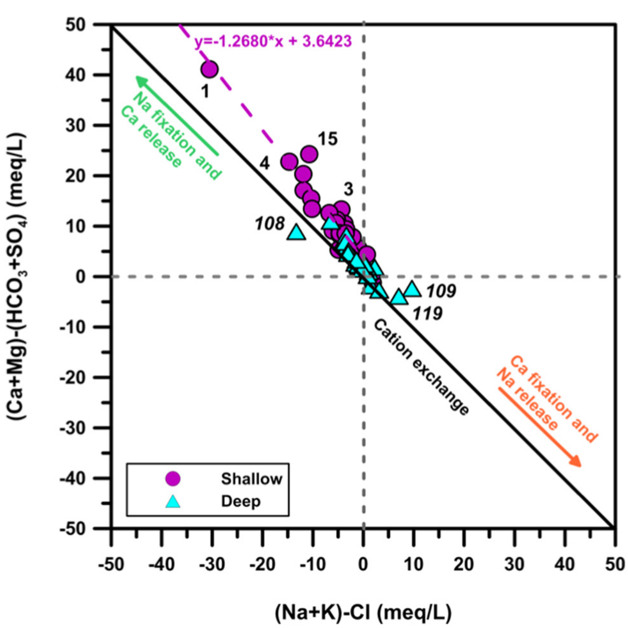

Fig. 6. (Na + K)-Cl versus (Ca + Mg)-(HCO_3 + SO_4). Black line: cation exchange (−1:1) line.

although few declined to respond to the interview but gave the permission to collect groundwater samples in their property. The interviews confirmed that local people are generally aware of the existence of groundwater issues in the region, and that they consider the most crucial problems to be: (i) the aquifer salinity increase, (ii) the decrease in the piezometric level due to groundwater overexploitation, and (iii) a clearly perceived degradation of water quality with respect to the previous years (Tringali et al., 2017). As a result of this high awareness, most of them expressed the willingness to be part of a collaborative water management process to improve groundwater quality in the region.

Considering all the sampled sites, deep wells are used to irrigate larger agricultural parcels (up to 75 ha; Table 3), probably due to the prevailing use of boreholes and resulting water availability. In fact, almost all the wells sampled in the deep aquifer are used for irrigation, often with a multiple utilization that includes drinking and domestic (i.e. household cleaning). The same groundwater use pattern can be observed for the shallow wells, mainly providing water for irrigation, but in some cases also used for household consumption, even though the high salinity makes people less inclined to its consumption for drinking water purposes except when other sources are not available. As it emerged during the interviews, local farmers are generally aware of groundwater salinity issues but have a scarce knowledge of the other potential contamination sources. As a result, besides the environmental and crops' productivity implications of using contaminated groundwater, many people are unaware of drinking water that is not so adequate for human consumption, with potential severe consequences on their health in the long run. This is why, as part of the proposed socio-hydrogeological approach, during interviews administration some time was also dedicated to knowledge transfer to farmers and wells' owners, and particularly targeted to information sharing on the general status of the studied aquifers and to raising awareness on the implication of groundwater misuse and pollution (Tringali et al., 2017).

As previously mentioned (Section 4.2), most of the authors have attributed the high NO_3^- concentration in the shallow aquifer to the impact agricultural return flow due to the fertilizers application rates and long-term flood irrigation. However, of all the interviewees only 33% of the shallow well's holders (i.e. 16% of the total) still uses flood irrigation in their fields, while the majority is opting for drip irrigation (78% of the total), generally considered the most effective irrigation practice in arid and semi-arid regions. Apparently, this shift towards more sustainable irrigation practices, occurred in late 90s, has had little influence on

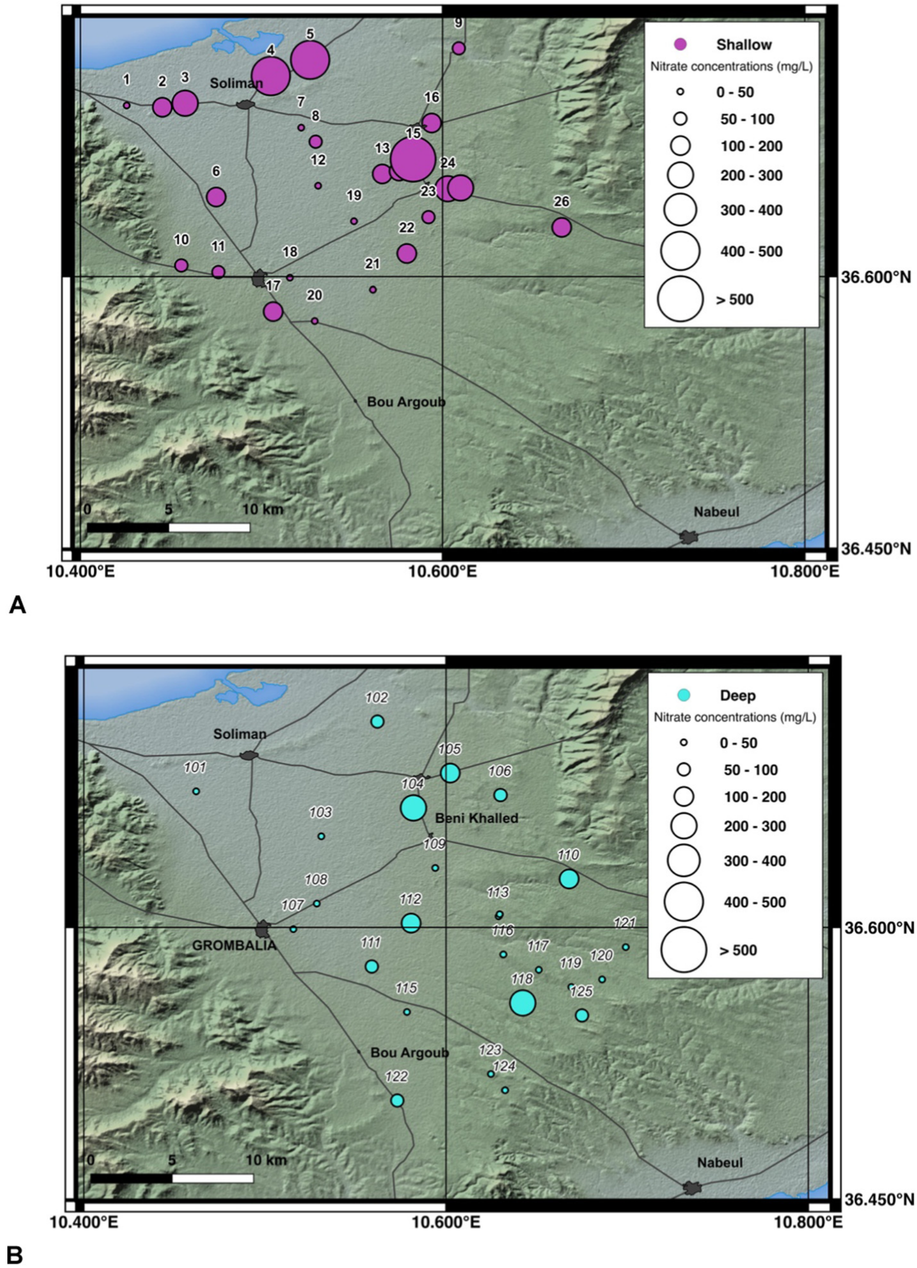

Fig. 7. Nitrate concentration distribution map in the Grombalia Basin: (A) shallow aquifer, (B) deep aquifer.

the nitrate contamination, which is still increasing (Henchiri, 2014), suggesting long recovery times for the aquifers.

Finally, it is interesting to note that the farmers' majority indicated the use of manure, alone or in combination with other types of synthetic fertilizers to increase crop production.

In order to identify the different sources of nitrate in the investigated area, the isotopic composition of nitrogen and oxygen ($\delta^{15}N_{NO3}$ versus $\delta^{18}O_{NO3}$) was compared to the information on fertilizer's use retrieved during semi-structured interviews. In Fig. 11 the isotopic compositions of the samples do not show a dominance of mineralized synthetic fertilizers as contaminants (as also evidenced in Fig. 8a), coherently with the information provided by interviewed wells owners. Denitrification processes are observed in both aquifers, following two trends: one originated from fertilizers (dashed brown oval in Fig. 11) and one (dashed blue oval in Fig. 11) from anthropogenic organic matter, confirming the previously described dual origin of nitrate contamination in the region. This supports the theory that agricultural activities are not the unique cause of aquifer pollution and that significant contribution also comes from domestic activities, and specifically from the lack of adequate sanitation facilities in the rural and peri-urban zones. For example sample number 6, which shows a composition fitting in the field of anthropogenic organic matter (i.e. manure or septic system effluents in Fig. 11), belongs to a site where the farmer declared to use only synthetic fertilizers, and consequently this contamination should have a civil origin.

5. Science-based management implications

Results of the socio-hydrogeological investigation performed in the Grombalia aquifer have important implication for the local water management.

The clear identification of pollution origin crucial for drawing new science-based reductions measures. To this end both the hydrogeochemical and social data have proved to be fundamental for the contamination source characterization, supporting the need for integrated investigations: socio-hydrogeology can hence be used to integrate vulnerability

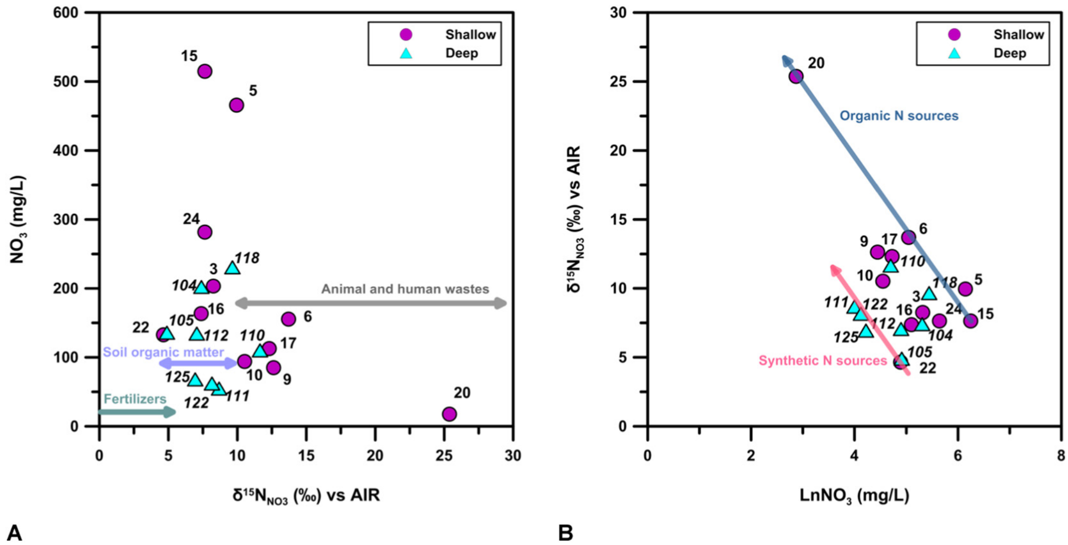

Fig. 8. (A) Nitrate concentration vs δ^{15}N. The reported ranges for nitrogen pollution sources are based on Clark and Fritz, 1997. (B) δ^{15}N vs lnNO_3, with the possible denitrification trends identified for synthetic (red arrow) and organic (blue arrow) nitrogen sources. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

assessment, especially in areas with intense anthropization, and might be considered as an asset in any hydrogeological investigation.

In particular, the study demonstrates the added value of socio-hydrogeology compared to classical hydrogeological assessment (Fig. 12). The integrated analysis permitted to better constraint the nitrate contamination sources in the studied region. Previous studies, where only hydrogeochemical analyses were performed, generally attributed nitrate contamination to agricultural activities, and particularly synthetic fertilizers, given the dominant land use in the region. However, the information retrieved with the interviews to local farmers and well owners revealed that farmers use manure in combination to synthetic fertilizers. The isotopic investigation also confirmed the presence of manure-induced contamination and highlighted the dual origin (urban/domestic and agricultural) of nitrate. In addition, a more detailed land-use analysis, also coupled with the interview administration, demonstrated that higher concentrations are found in more densely populated areas, evidencing the relevance of domestic pollution especially in the shallow aquifer. Indeed, only with the integrated approach the correct attribution of nitrate contamination would be possible, avoiding the implementation of improper management actions or penalizing farmers. The study also highlights the need to foster better sanitation and waste management at local and regional level. Therefore, results will be adequately shared with competent authorities to support new actions plans in the region.

As concerns the implementation of new management practices, it will be of paramount importance to take into account both the needs of the local stakeholders (including managers and water-end users) and the outcomes of the integrated socio-hydrogeological assessment. To this end, results will be shared with the key-stakeholders identified at the early stages of the project by means of a Social Network Analysis: the so called Groups of Agricultural Development (GDAs; composed by landowners, farmers and water users sharing water resources in each

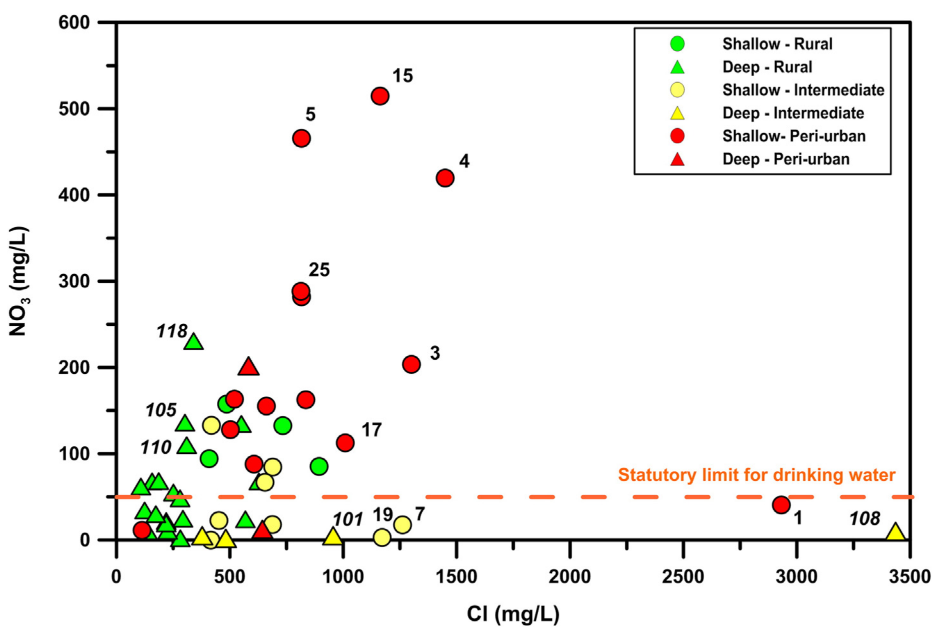

Fig. 9. Nitrate versus chloride concentrations for the samples collected in the Grombalia Basin in the February–March 2014 campaign. Orange dashed line: WHO (2011) statutory limit for drinking water (50 mg/L).

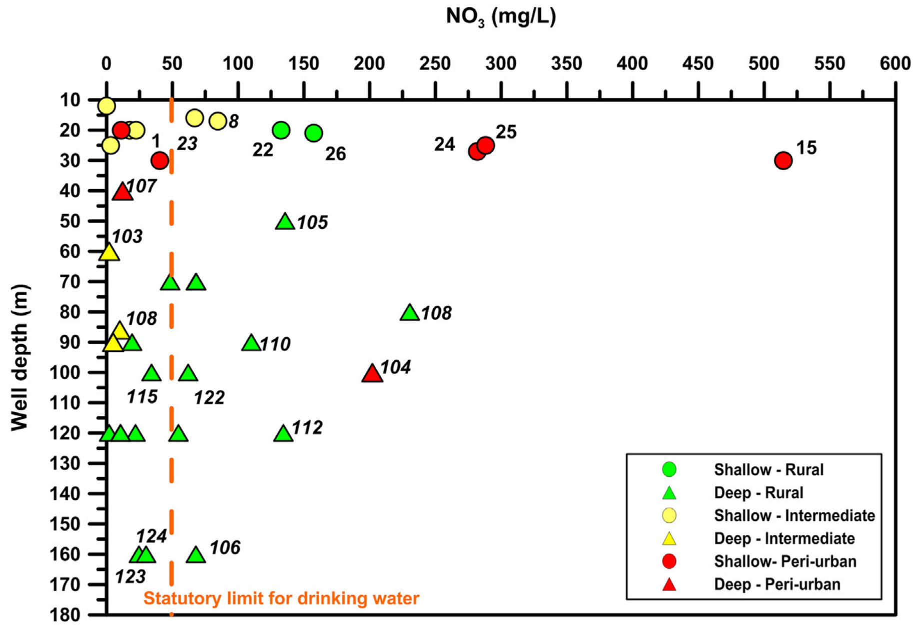

Fig. 10. Nitrate concentrations versus well depth.

irrigated area, and coordinated by a board of democratically elected local members), the Regional Commissariat for Agricultural Development (CRDA, i.e. the institution responsible for water resource management and control in the Grombalia region), and representatives of local farmers (Tringali et al., 2017). For the identification of a new and shared strategy for long-term groundwater protection priority will be given to the identification of new actions for groundwater protection that will not compromise the farmer's wellbeing and productivity and that will take into account the contribution of domestic and urban contamination sources. In this process the role of scientist and local mediators will also be fundamental to ensure adequate information sharing to the general public and civil society.

Table 3
Summary of the information retrieved with the structured interviews administered during the in situ measurements. Percentages indicated as "out of total" take into account that, for some categories responses are higher to the number of respondents (i.e. corresponding to possibility to have multiple groundwater use and crop production in the same site).

	Shallow	Deep
Administered interviews	21	23
Well owners	6	10
Tenants	15	13
Well type		
Hand dug well	23%	–
Pumped well	77%	32%
Borehole	–	68%
Irrigated area		
Average	2 ha	12 ha
Min.	1 ha	1 ha
Max.	4 ha	75 ha
Groundwater use (% out of total)		
Irrigation	63%	90%
Domestic	47%	81%
Drinking	32%	81%
Animal husbandry	5%	38%
Water type used for irrigation		
Groundwater	75%	86%
Groundwater and irrigation channel water	25%	14%
Irrigation type		
Flood	33%	–
Drip	54%	89%
Spray	–	–
Mix (flood-drip/spray-drip)	13%	11%
Crops (% out of total)		
Horticulture	28%	52%
Arboriculture	89%	90%
Fertilizers use		
Manure	16%	–
Binary synthetic fertilizers (DAP)	–	5%
Three-component synthetic fertilizers (NPK)	10%	43%
Manure and NPK	37%	19%
Manure, DAP and NPK	32%	28%
DAP and NPK	5%	5%

6. Conclusions

The Grombalia basin is characterized by a general high nitrate concentration, in both the shallow and deep aquifers. Results of an integrated investigation performed between February and March 2014 coupling hydrogeochemistry and isotope geochemistry highlighted the presence of a dual origin of such contamination, associated to both agricultural and urban activities, in a region where only synthetic fertilizers were generally identified as the main source of nitrate pollution. The presence of high nitrate contents also in the deep aquifer demonstrate its vulnerability to anthropogenic contamination and points to a hydraulic connection with the shallow aquifer for either natural (e.g. presence of discontinuities in the clay layer separating the two) or anthropogenic reasons (e.g. multilayer wells). This evidence would require further investigation as it is a crucial issue for the sound groundwater management in the area.

Interview administration provided useful information supporting the hydrogeochemical analysis, and, as in the case of fertilizers use, in agreement with the findings of the isotopic assessment. Indeed, when budget limitations do not permit a full isotopic assessment, public engagement activities could represent a useful tool to provide insight on possible contamination sources. Coherently, public engagement and capacity building are fundamental to inform farmers and households on the impact of agricultural practices and domestic activities (also with regard to the long-term health and food security implications) as well as to assess their needs and perceptions of environmental issues.

Overall, results of the investigation performed in the Grombalia basin supported the necessity to perform integrated investigations to correctly assess contaminant sources and their relevance throughout the study area. Multidisciplinary approaches, that also include socio-economic analysis can permit fostering connection between providers and users of water science, also including decision makers. In fact, for a correct long-term management of groundwater resources not only it is fundamental to know the hydrogeological characteristics of the

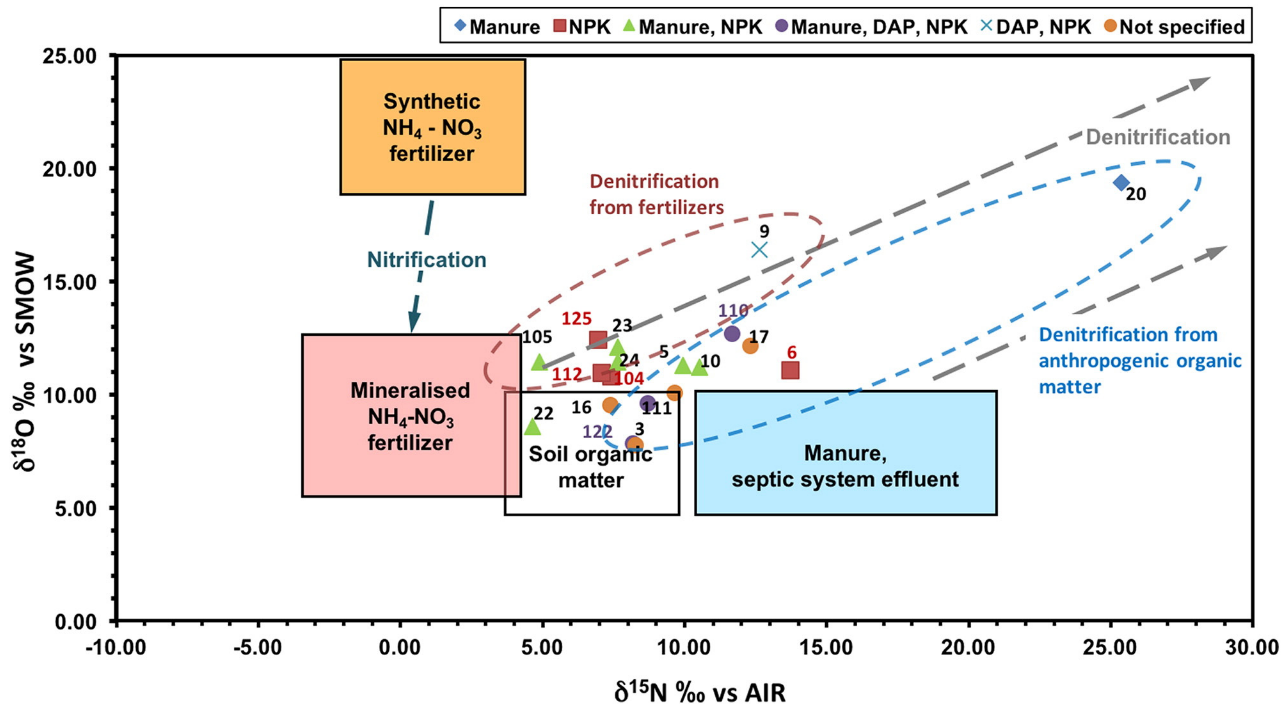

Fig. 11. Stable isotope composition of dissolved nitrates in groundwater from the Grombalia Basin, with ranges for groundwater with $\delta^{18}O_{H2O} \sim -4‰$ VSMOW. Modified after Clark and Fritz (1997) and Kendall et al. (2007). Dashed brown and blue oval corresponds to the denitrification trend originated from fertilizers and anthropogenic organic matter respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

studied region and the causes of aquifer contamination, but also to understand the socio-economic drivers that lead to such contamination. For example, only through public engagement it will be possible to understand if and why farmers over apply nutrients, or whether lacking sanitation facilities are still dominant. Additionally, this information could guide new policies prescriptions targeted to contamination reduction that also take into account the needs and issues of water end-users. Indeed, through socio-hydrogeology (ground)water scientists can act as advocates for good governance, and effectively contribute solving nitrate contamination issues.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.03.151.

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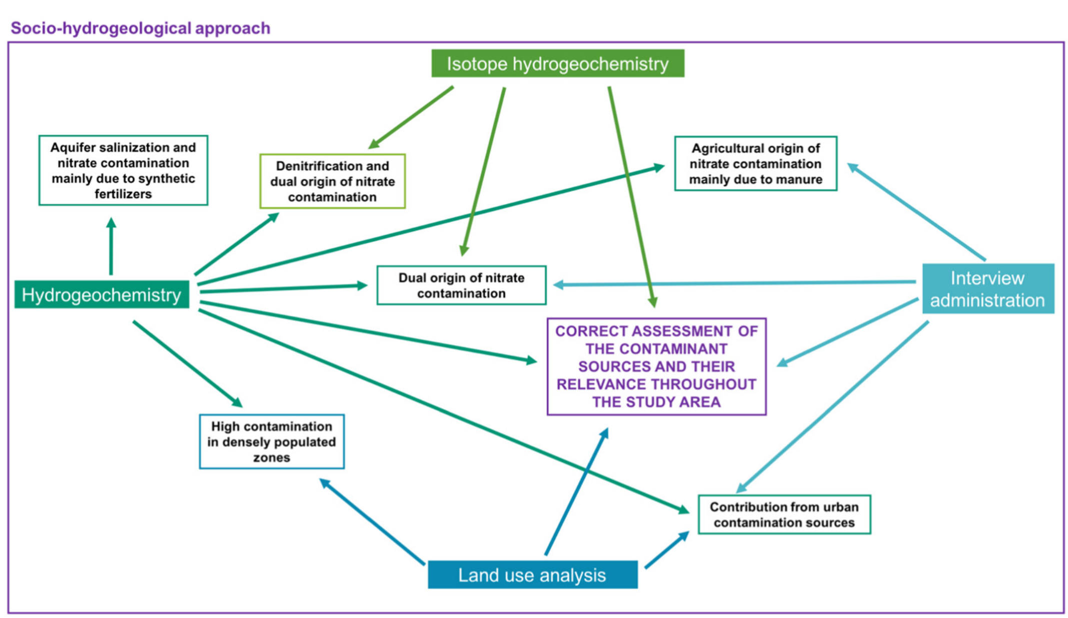

Fig. 12. Highlights of the information provided by integrating the different components of the socio-hydrogeological approach. The filled boxes indicate the activity, the empty boxes the conclusions that may be reached using the information provided by the activities. Partial or incorrect conclusions can be obtained if using only 2 or 3 information activities.

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