11

Hydrochemical Investigation of Groundwater Contamination in the Grombalia Shallow Aquifer, Cap Bon Peninsula, Tunisia: Impact of Irrigation with Industrial Waste Water

Amor Ben Moussa and Kamel Zouari
Ecole Nationale d'Ingénieurs de Sfax,
Tunisia

1. Introduction

During the last two decades, demands for groundwater from urban, industrial development and extensive agricultural activities in the Grombalia basin, Cap Bon peninsula, north-eastern Tunisia, particularly in the Beni Khalled, Menzel Bou Zelfa and Soliman regions have resulted in increased withdrawals from the Quaternary shallow aquifer. As an example of water supply related problem generalised water level decline and the deterioration of groundwater quality. In deed, in recent times, soils have become increasingly polluted by waste water and agricultural chemicals (fertilisers, pesticides, herbicides). In shallow groundwaters this pollution can easily be transported.
The major economic role of the shallow aquifer has raised concerns relating to the effects on groundwater resource as (i) the recharge rate of the shallow aquifer is not known with precision and (ii) the detrimental effect on the environment in relation with the groundwater contamination and salinization, which put a strain on the existing fresh water that supports the regional development. Subsequently there is a requirement for agreed and consistent examination and assessment activities to recognize the source of the pollution and evaluate its current amount and future expansion. It's within this framework that is undertaken the present study, which aims to provide reliable information about the hydrochemical characteristics of groundwater and the main groundwater mineralization processes. It also investigates the impact of regional agricultural and industrial activities on groundwater quality.

2. Study area

The study area belongs to the NW–SE troughs domain of the Cap Bon Peninsula, north-eastern Tunisia and cover an area extent of about 720 km² (Elmejdoub and Jedoui 2009). It is boarded to the north by the Gulf of Tunis and the Tekelsa Hills, to the east by the Abderrahman Mountain and the oriental coastal highlands, to the south by the Hammamet Hills and to the west by the Bou Choucha and the Halloufa mountains (Fig. 1). The climate of the study area is classified as Mediterranean, semi-arid; with mild, wet winters and warm, dry summers. The average annual rainfall ranges between 500 and 600 mm (Ben

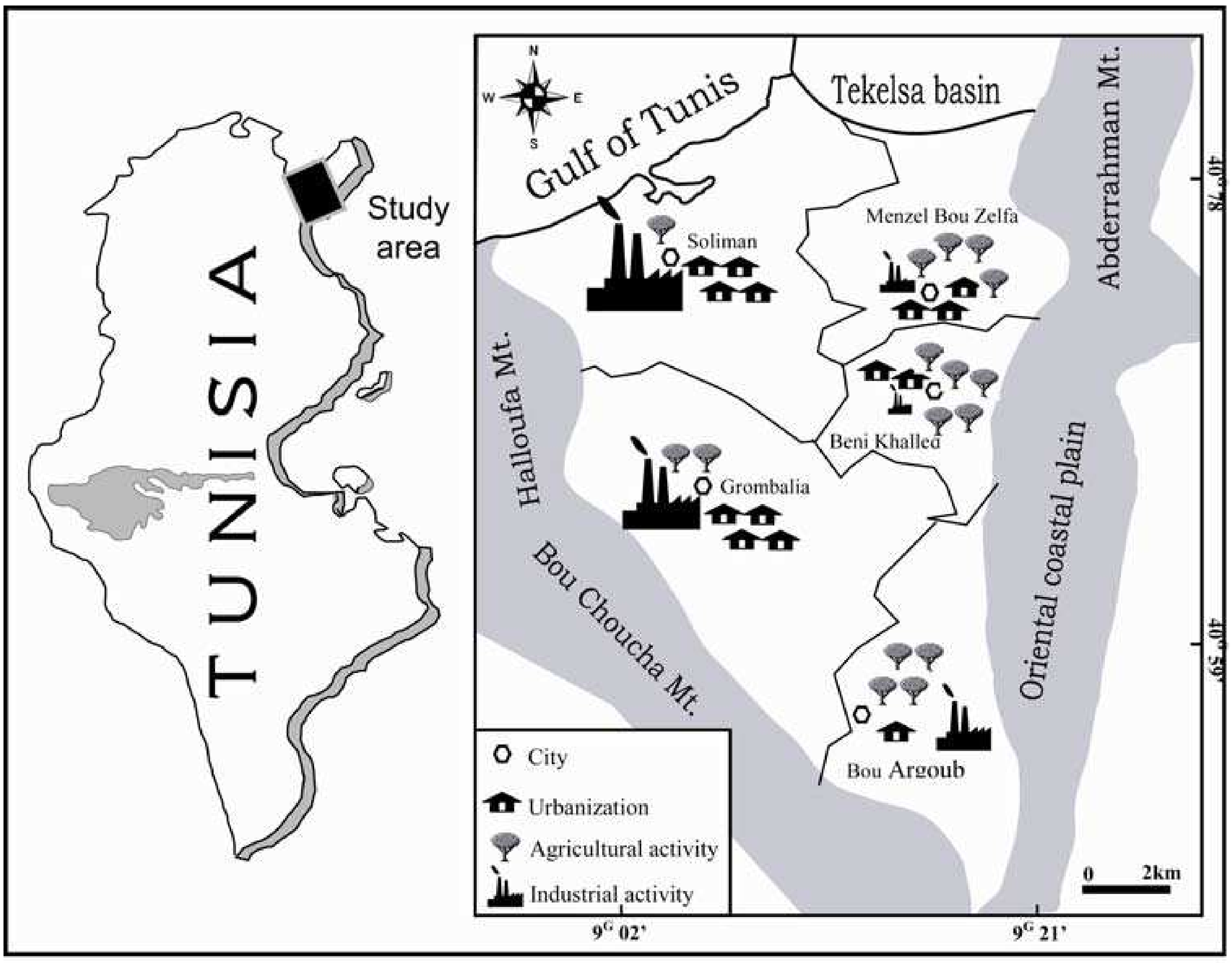


Fig. 1. Location map of the study area

Moussa 2007). About 80% of this precipitation occurs between September and March. The potential evapotranspiration is about 1,200 mm year-1. The average annual temperature is about 18°C with maximum temperatures up to 30°C in summer. Regionally, the surface drainage is toward the north reflecting regional topographic gradients. It is constituted by several ephemeral Wadis, which collect surface runoff from the surrounding highlands toward the Gulf of Tunis.

3. Geology and hydrology

The Grombalia Basin is located in the south-western part of the Cap Bon Peninsula, which is situated astride the African–Eurasian plate boundary (Elmejdoub and Jedoui 2009). Geologically, it is described as a graben oriented NW–SE and filled by Quaternary sediments. The edges of this graben were related to two normal faults that appeared during the Middle Miocene (Hadj Sassi et al. 2006). These are the Borj Cedria NNW–SSE normal fault and the Hammamet NE–SW normal fault (Ben Ayed 1993; Ben Salem 1995; Chihi 1995). The sedimentary units outcropping in the basin are represented by recent Quaternary soil and terraces that partially cover the Eocene, Oligocene and Miocene Formations. The Eocene deposits are mainly constituted of Glauconeous sands of the Souar Formation, which locally outcrops in the north of the Halloufa Mountain. The Oligocene unit is principally made up of coarse to medium-grained sandstone belonging to the Fortuna Formation

(Burollet 1956; Blondel 1991). It largely outcrops along the Halloufa and Bou Choucha mountains in the western part of the basin. The Miocene sandstone and clay series are found essentially in the Oriental costal hills and in some restricted areas along the foot of the Halloufa and Bouchouch mountains. The Quaternary detrital sedimentations of the Rejich Formation mainly consist of fine to coarse-grained sands, clayey sands, sandstone, silt and abundant evaporate deposits (Schoeller 1939; Colleuil 1976; Ben Salem 1995).

From a hydrogeologic point of view, the Grombalia alluvial aquifer that is characterized by an average thickness of about 50 m is hosted in the Quaternary continental sand, clayey sand and sandstones deposits, which repose on a 15 m-thick clayey bed-rock (Fig. 2). The potentiometric map, realized on the basis of water level measurements of 41 wells, displays the main groundwater flow patterns in the Grombalia unconfined aquifer. It shows that the recharge occurs in the pediments of the surrounding mountains and converges to the central part of the basin. There, a general southeast–northwest flow carries groundwaters to the Gulf of Tunis discharge areas (Ben Moussa 2007). The exploitation of groundwater from the Grombalia shallow aquifer started in the 1950s; the number of shallow wells increased through time. At present, this number exceeds 11,000, with a total extraction of 249 Mm3 (DGRE 2005). Consequently, the water level has dropped between 1 and 10 m, with an annual rate of about 0.3 m.

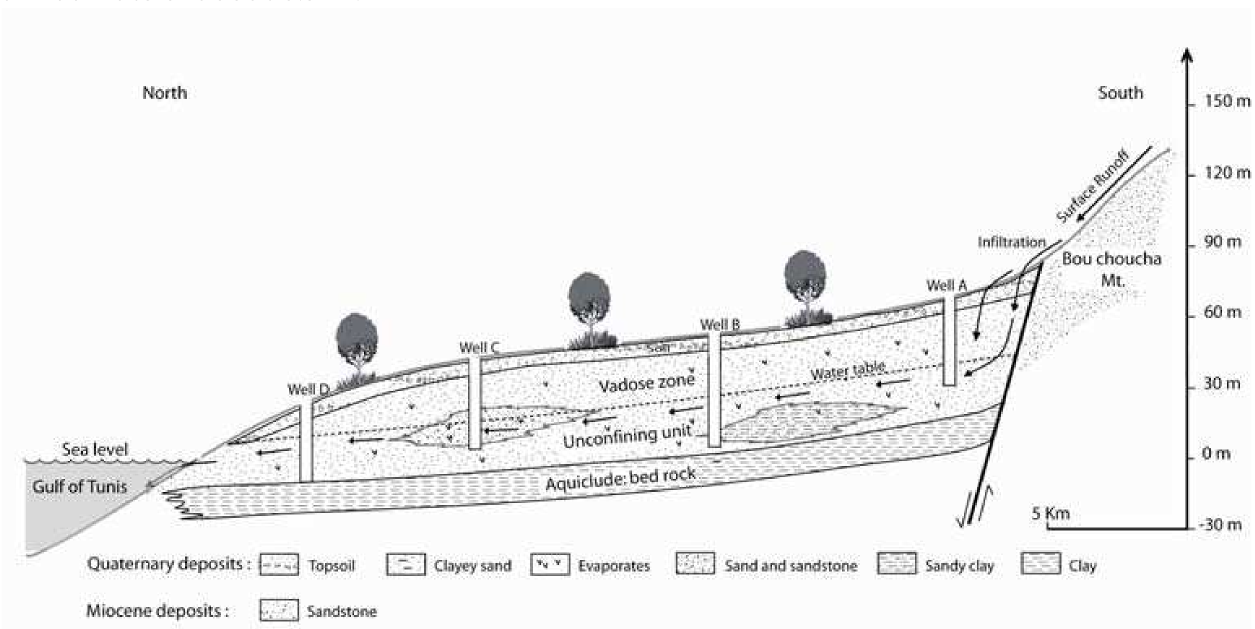


Fig. 2. Hydrogeological cross section of the Grombalia unconfined aquifer

4. Sampling and analytical procedure

A field sampling campaign was carried out during September 2005. A total of 38 groundwater samples was collected from dug wells tapping the shallow aquifer at depths ranging between 6 and 35 m. In situ measurements of pH, Temperature, electric conductivity (EC) and the total dissolved solids (TDS) were performed in the field. Water samples were filtered and collected in 100 ml polyethylene bottles with poly-seal caps for major and minor elements analysis which have been done at the ''Laboratoire de Radio-Analyses et Environment'' of the ''Ecole Nationale d'Ingenieurs de Sfax'' (Tunisia), using titration method (for HCO_3) and standard ion chromatographytechniques.

5. Results and discussion

5.1 Partial pressure of carbon dioxide (pCO_2) and in situ measurement

The pCO2 values, calculated with WATEQ4F program (Ball & Nordstrom, 1991), in situ parameters, total dissolved solids (TDS) and analytical data of the major and minor ions in groundwater samples are measured. The pCO_2 values range from 0.29 10^{-2} and 4.63 10^{-2} atm. The highest contents of pCO2 characterize wells located downstream suggesting an increasing along flow path. The lowest values are registered in the recharge area, which signify that fresh groundwater displays lower pCO_2 levels upstream the basin close to the recharge area and in the vicinity of the Wady courses. However, groundwaters with higher pCO_2 levels provide insight into the more extensive water rock interaction and the microbial mediated reactions that produce CO_2 (Rightmire, 1978; Adams et al., 2001). Groundwater samples show relatively heterogeneous values of temperature, varying between 13.9 and 21.2°C. Relatively high temperatures, close to that of the atmosphere, characterize Soliman and Menzel Bou Zelfa regions. These high temperatures are probably related to the shallow depth of the groundwater table. However, deeper wells of Grombalia, Beni Khaled and Bou Argoub regions are distinguished by relatively low temperatures, indicating that they are not or slightly influenced by the atmosphere. Groundwater samples, which are almost neutral, show very homogeneous pH values ranging between 6.9 and 7.8. The EC values vary in a wide range from 1.1 to 7.8 mS/cm that lend support to the interference of numerous natural and anthropogenic processes.

5.2 Origin of groundwater mineralization

5.2.1 Water type

The Piper diagram (Piper 1944) has been established in order to precisely specify the water types in the Grombalia shallow aquifer. Nitrate concentration was taking into account when plotting this diagram because of its relative abundance in the groundwater (Fig. 3). The data plotted in Piper classification diagram display show the same Na–Cl–NO_3 water type.

5.2.2 Nitrate

The nitrate contents in the studied aquifer show a large range of variation, from 0 to 384 mg/l. Ninety percent of the groundwater samples taken during this study, show nitrate concentrations exceeding the maximum European admissible nitrate concentration limit in drinking water (50 mg/l). The examination of the nitrate distribution map (Fig. 4) reveals that high nitrate concentrations appear to be related to agricultural land-use patterns and suggests that the application of nitrogen fertilisers and the irrigation with treated waste water lead to increased nitrate leaching. The areas with nitrate concentrations, exceeding 50 mg/l, are located in the Soliman and Beni Khaled region where agricultural activities are more developed (Fig. 5). This may reflect the influences of agricultural practices that introduce a long-term risk of groundwater pollution by over-fertilization and pesticides leached downward in conjunction with the excess use of treated waste water, particularly in the Soliman region. In fact, the nitrification is likely related to the return flow phenomenon as the most enriched samples were collected from the agricultural areas. In this region, where flood irrigation is applied at a large-scale, the excess of irrigation water undergo excessive nitrate enrichment at the ground surface; after that it eventually returns to the unconfined aquifer. Indeed, the positive relationship between NO_3 and SO_4 (Fig. 6) suggests that both N and S are used in the study area in the form of $(NH_4)2SO_4$-fertilisers (Bohike et

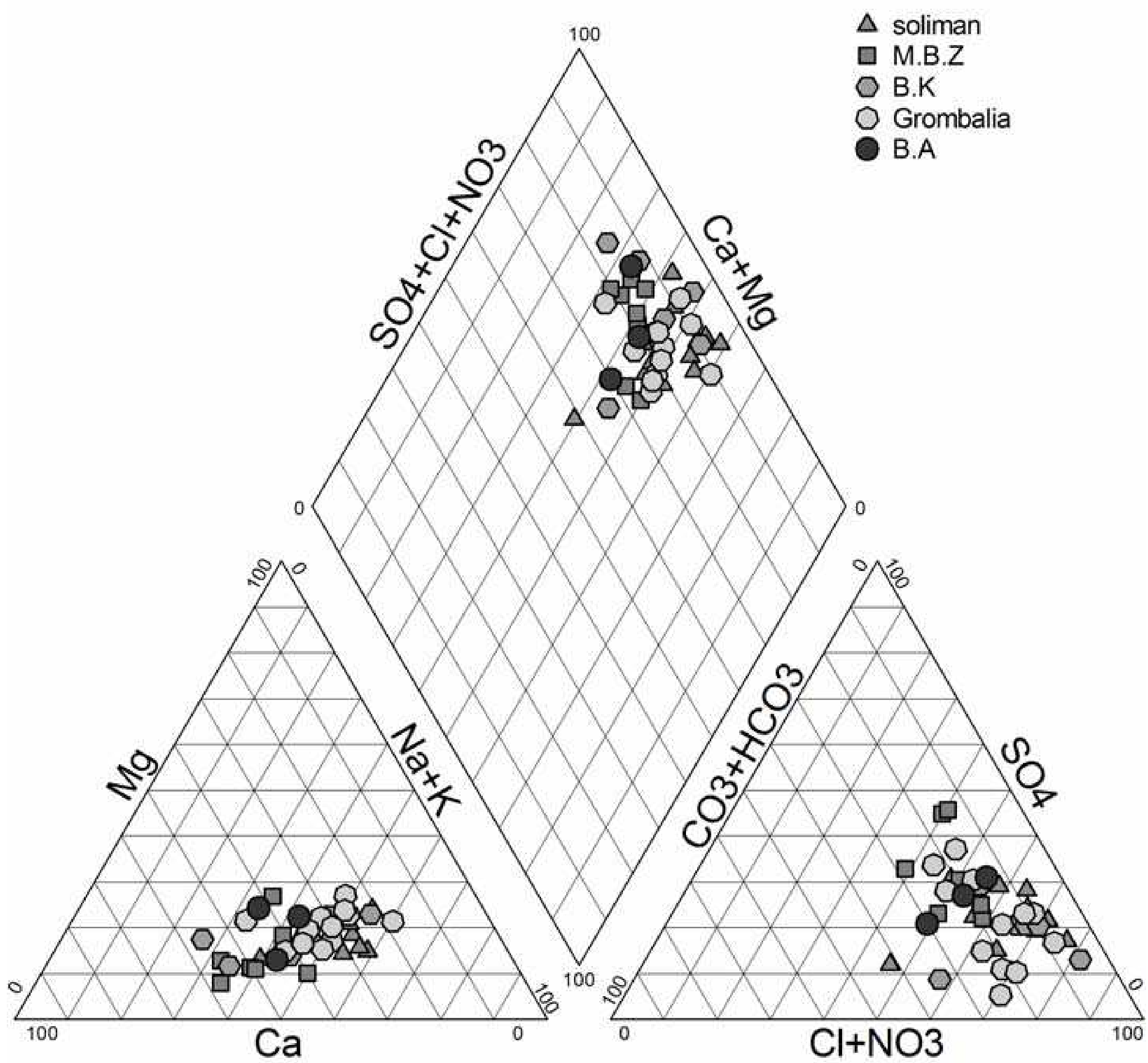


Fig. 3. Piper diagram of the Grombalia unconfined aquifer

al., 2007). Moreover, some groundwater samples show a well-defined relationship between NO_3 and Ca (Fig. 7), highlighting that both elements are mostly originated from the excessive use of $Ca(NO_3)_2$-fertilizers (Stigter et al., 2006). Therefore, the nitrate contamination is a result of the local hydrogeological setup coupled with the traditionally applied flood irrigation and the complete lack of environmental awareness regarding the over-fertilisation and the utilisation of recycled waste water.

5.2.3 Strontium and bromide

Strontium and bromide are generally used as tracer due to their geochemical characteristics, in particular when they are used in conjunction with other conservative elements such as chloride. These elements are relatively abundant in the Grombalia shallow groundwater and they are used to identify sources of groundwater contamination as well as hydrogeochemical reactions accompanying salinization processes.

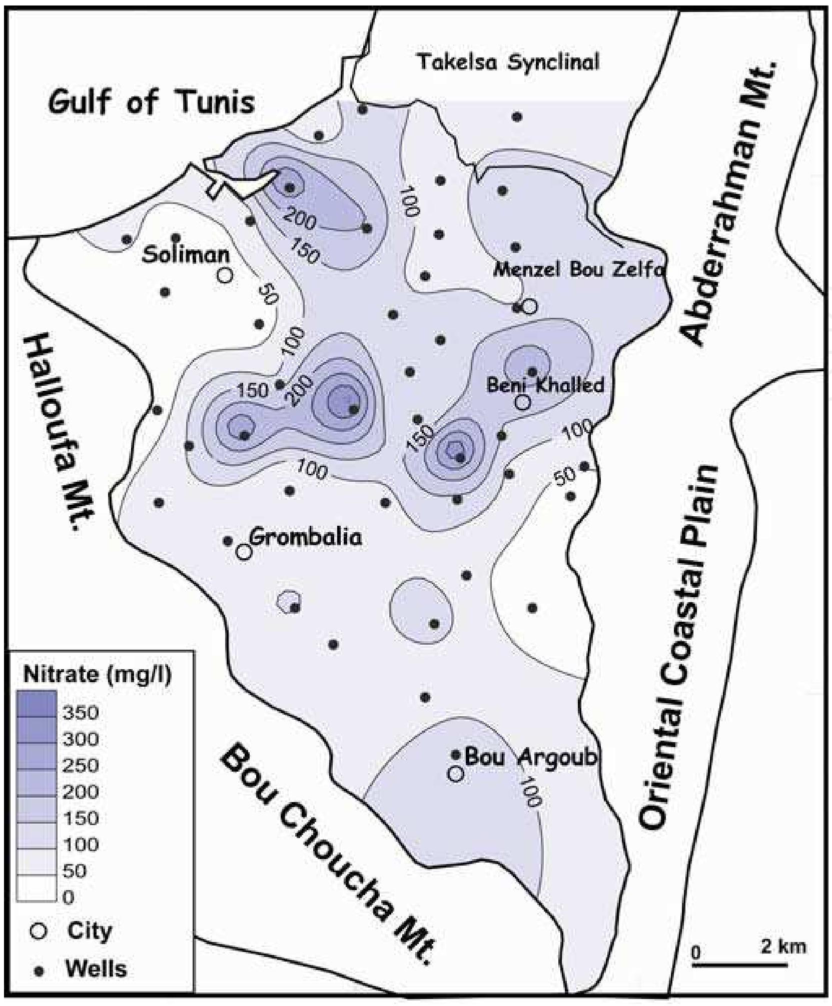


Fig. 4. Spatial distribution of nitrate

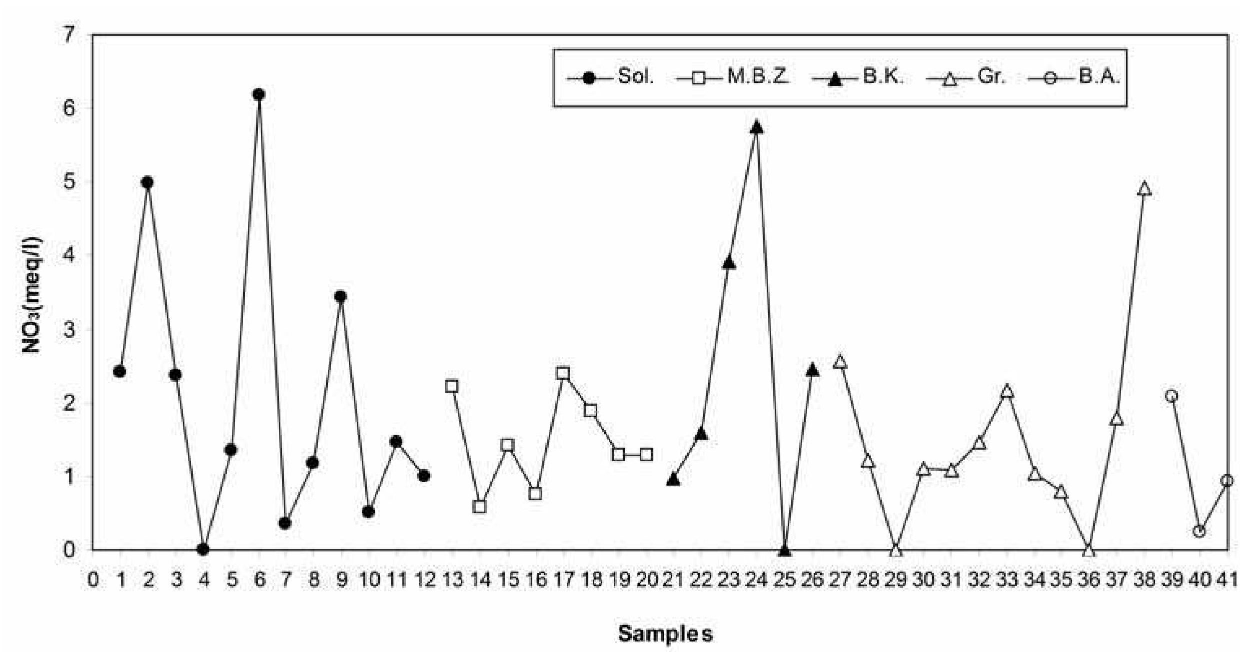


Fig. 5. Regional evolution of nitrate concentrations

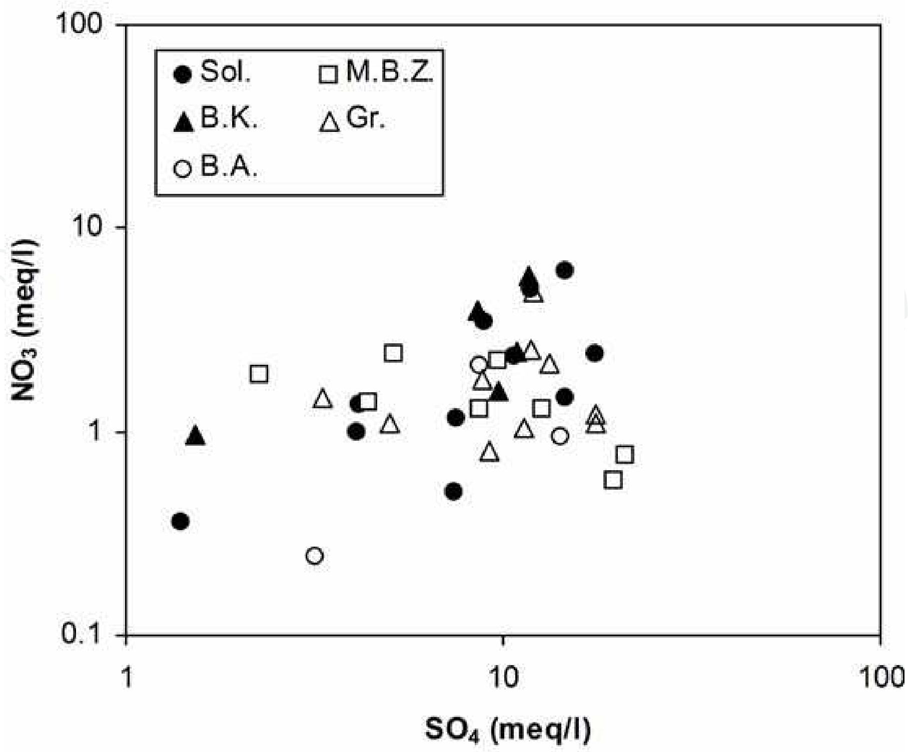


Fig. 6. Plots of SO_4 *vs*.NO_3

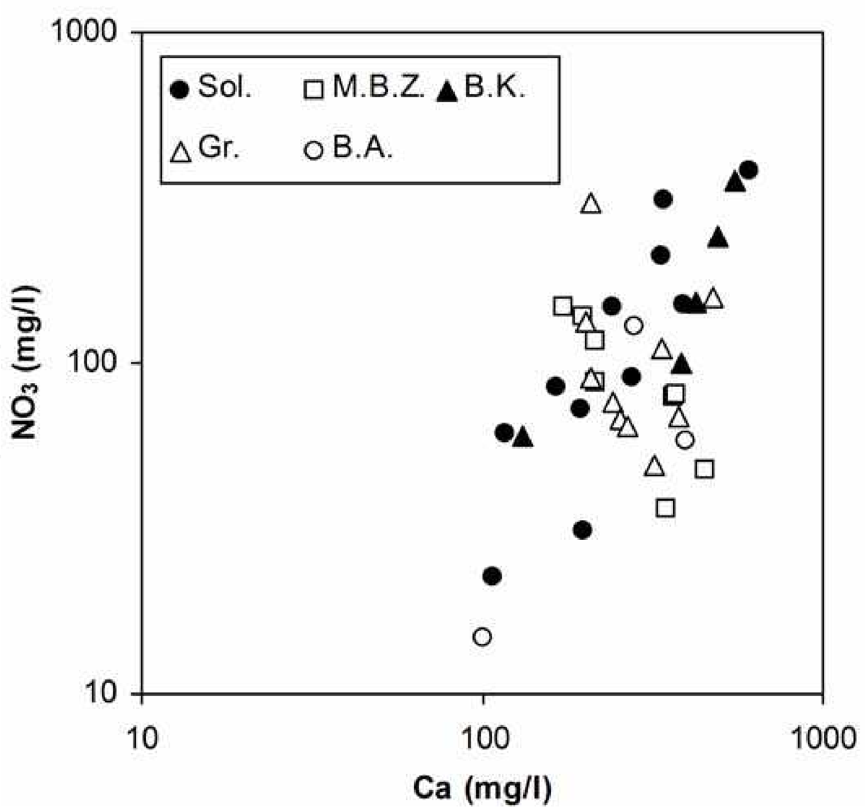


Fig. 7. Plot of Ca *vs* NO_3

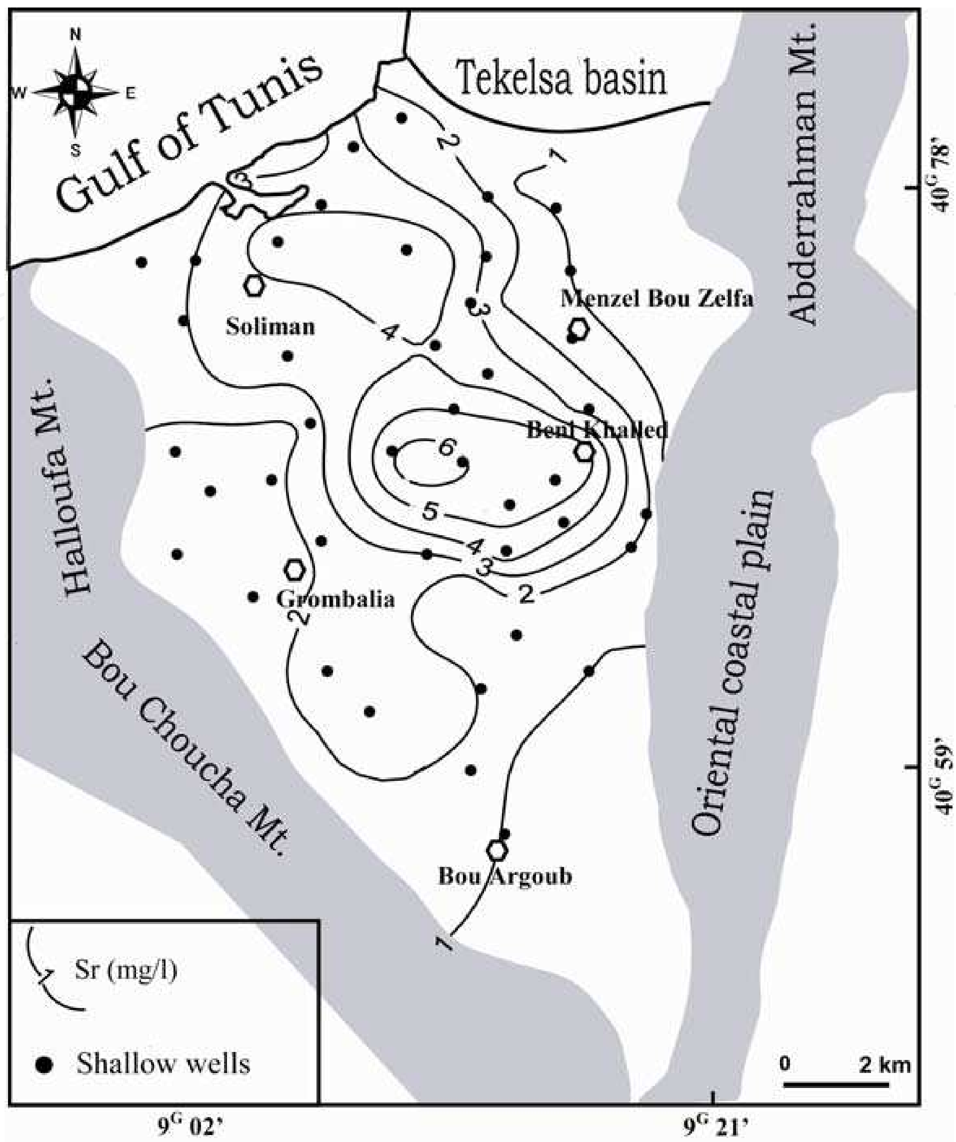


Fig. 8. Spatial distribution of stontium

The strontium concentrations in the Grombalia shallow aquifer vary within a large range from 0 to 1.5 mg/l. High strontium concentrations, exceeding 1.5 mg/l, characterize the central-western part of the basin (Fig. 8). However, moderate Sr contents are registered in Soliman and Beni Khaled regions; and relatively low contents distinguish Menzel Bou Zelfa and Bou Argoub regions (Fig. 9). High and moderate strontium concentrations, which characterize the Grombalia, Soliman and Beni Khaled regions, are mainly related to downward leakage in relation with return flow from irrigation with treated industrial waste water and, to a negligible extent, to the interaction with sulphate minerals. The correlation of SO_4 versus Sr (Fig. 10) shows a positive relationship, which indicates some Sr contribution from dissolution celestite ($SrSO_4$) associated with gypsum (Faye et al. 2005). While, the return flow is strongly suggested considering the relatively low depth of the shallow aquifer water table in the mentioned regions. On the other hand, in the Menzel Bou Zelfa and Bou Argoub zones, the ratio of strontium to sulphate is in disagreement with the celestite dissolution. In the Bou Argoub region, industrial non-treated waste waters are directly discharged into the drainage networks that may provoke high strontium contents.

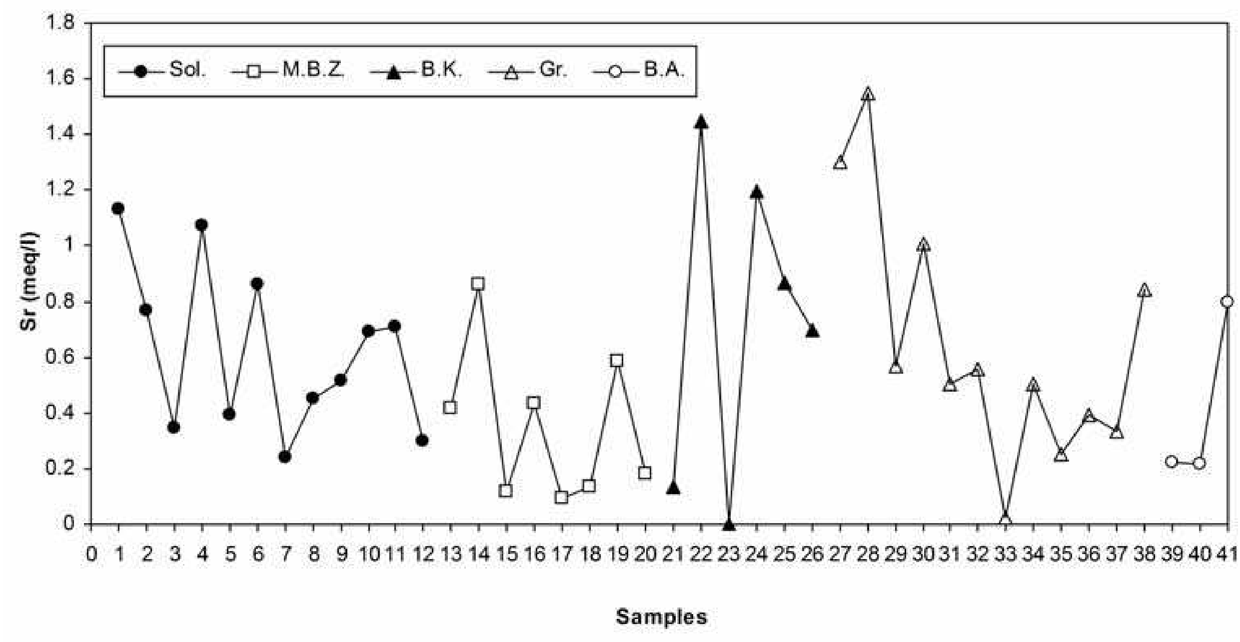


Fig. 9. Regional evolution of strontium concentrations

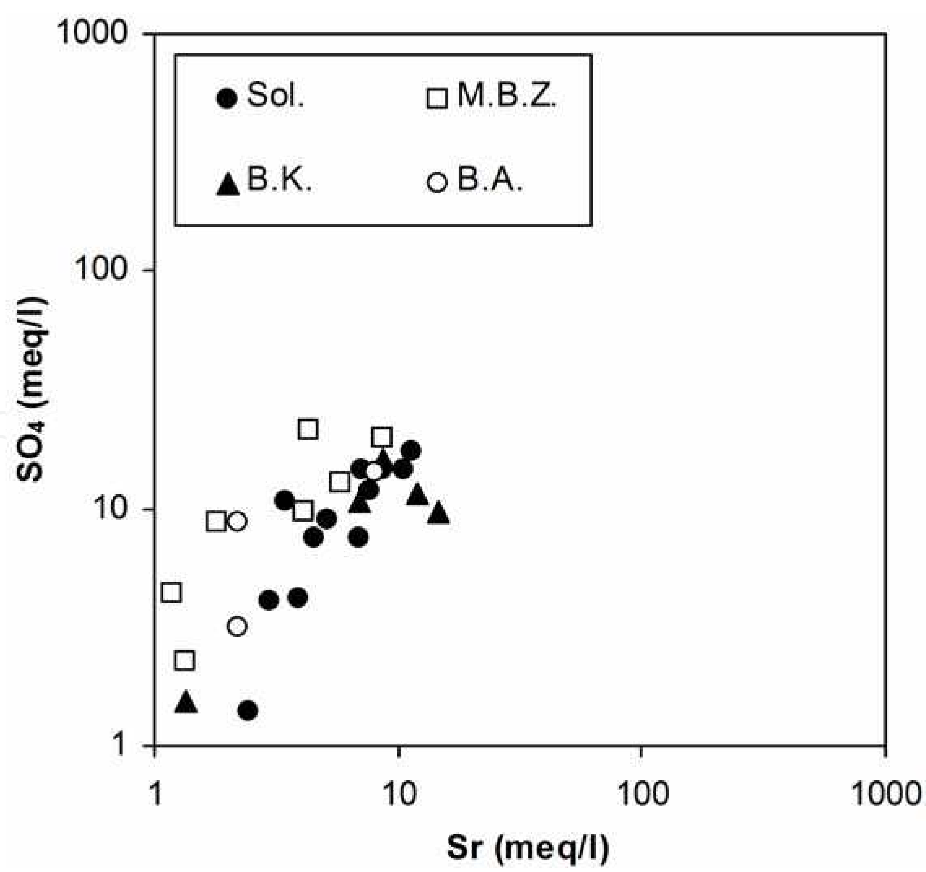


Fig. 10. Plot of Sr *vs* SO_4

Groundwater samples collected from the studied shallow aquifer show bromide contents ranging between 3.7 and 9.3 mg/l (Fig. 11). These bromides concentrations, which are above the admissible limit for drinkable waters, are too high to be derived from natural sources i.e. evaporate dissolution and marine origin of bromide. In deed, waters with high Br concentrations are localized in the central part of the basin (in Grombalia and Beni Khaled regions) but not in the Soliman costal region. This may indicate that high Br contents are so far to be related to natural sources. Consequently, these high Br concentrations are probably related the agricultural land-use patterns and lend support to the significance of the contamination by rejection of treated and non-treated waste water; and return flow from irrigation water that include high amounts of fertilizer and pesticides such as methyl bromides and other organic bromyl (Zhu et al. 2007).

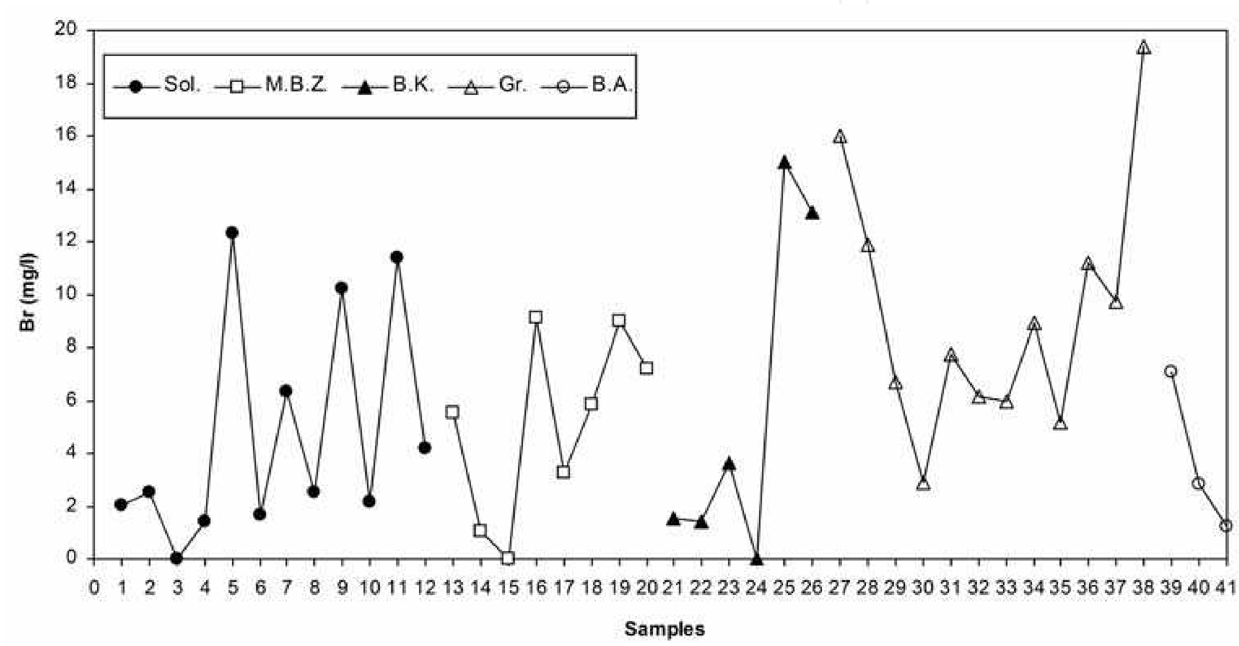


Fig. 11. Regional evolution of bromide concentrations

In addition to the anthropogenic mineralization processes mentioned above, natural processes play also a significant role in the contamination of groundwater in the Grombalia shallow aquifer.

Bivariate diagrams between ions are useful because they can point out associations between elements that can show the overall coherence of the data set. They can also indicate the participation of the individual chemical parameters in several influence factors, a fact which commonly occurred in hydrochemistry. In the plot of Na/Cl (Fig. 12), all groundwater samples fall on the 1:1 (Na:Cl) line. This well-defined correlation in conjunction with the undersaturation state with respect to the NaCl argue for the role of halite dissolution as a major process contributing to the groundwater salinization (Appelo and Postma, 1993). The dissolution of halite is verified through the general increasing trend in the Na and Cl concentrations along the groundwater flow direction (Fig. 13). The positive correlation between Ca and SO_4 (Fig. 14) and their similar spatial distribution (Fig. 15), which increase towards the discharge area, reflect that the dissolution of gypsum is another significant salinisation process. Indeed, saturation indexes show that some samples are under-saturated with respect to gypsum and anhydrite, highlighting a geochemical condition dominated by

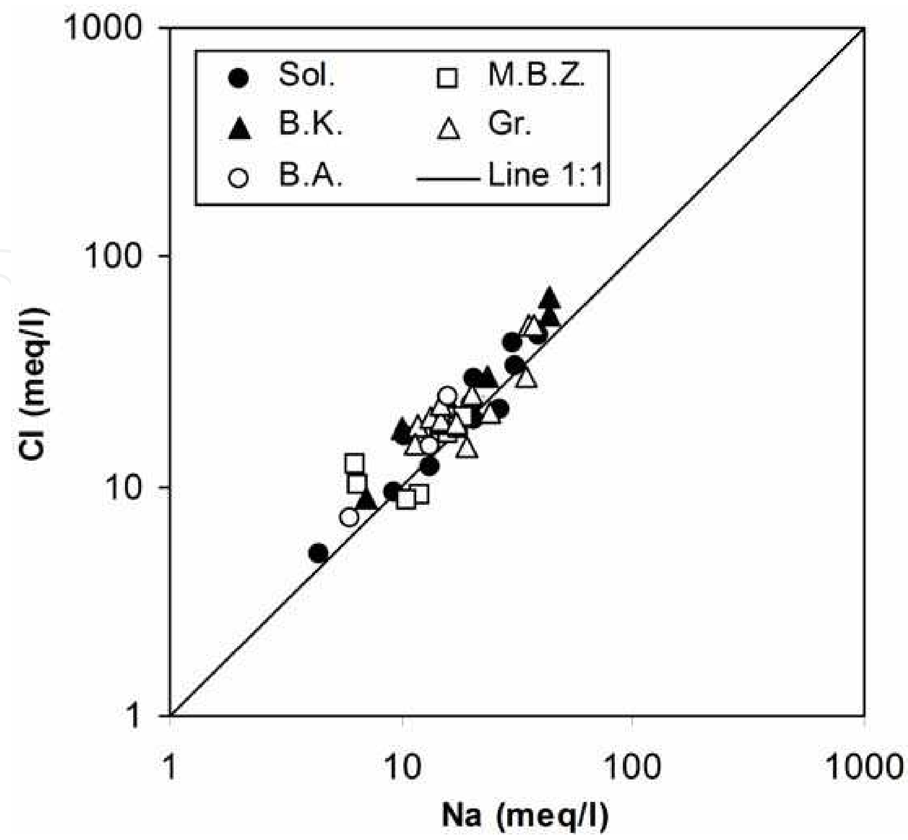


Fig. 12. Plots of Na *vs* Cl

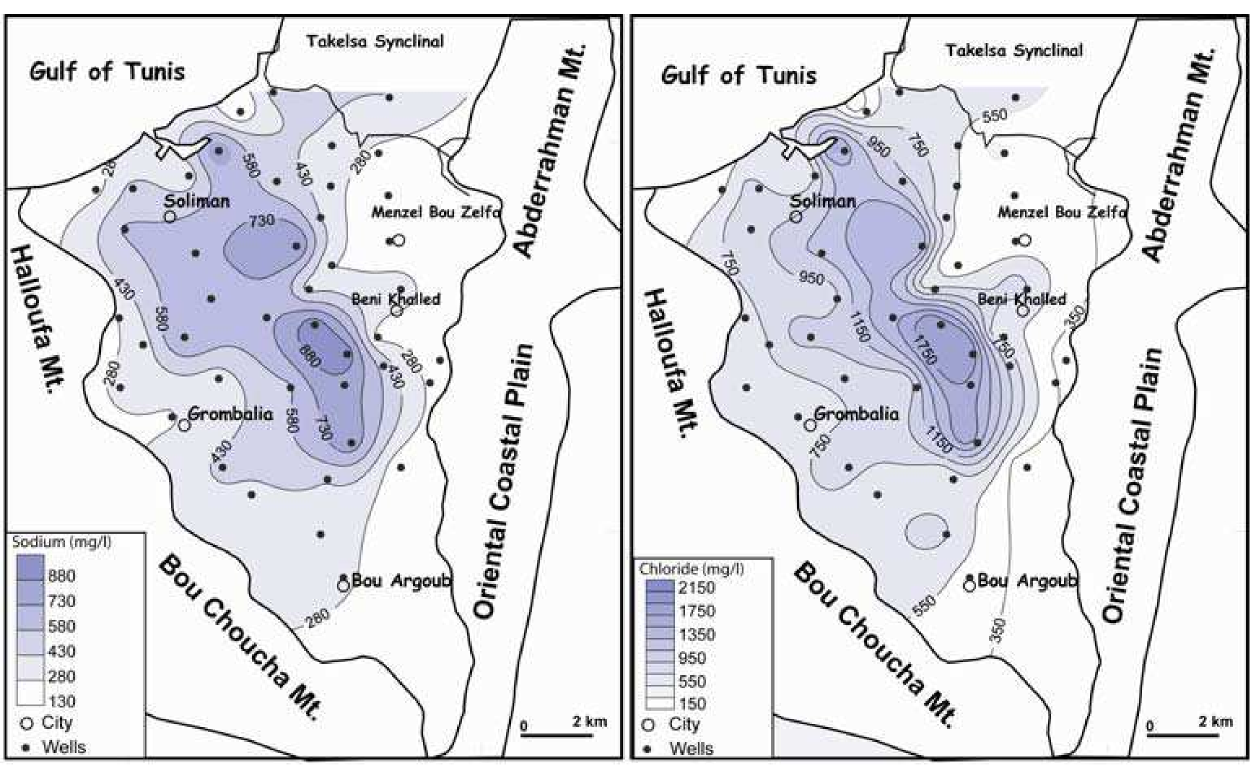


Fig. 13. Spatial distribution of Na and Cl

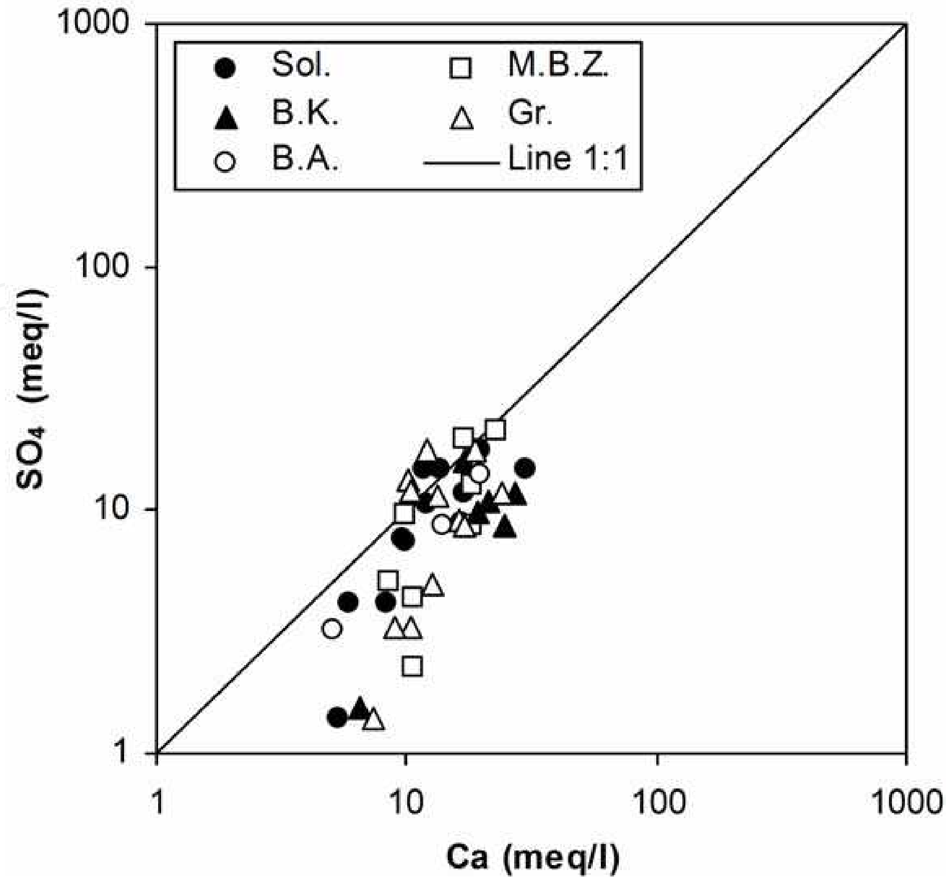


Fig. 14. Plots of Ca *vs* SO_4

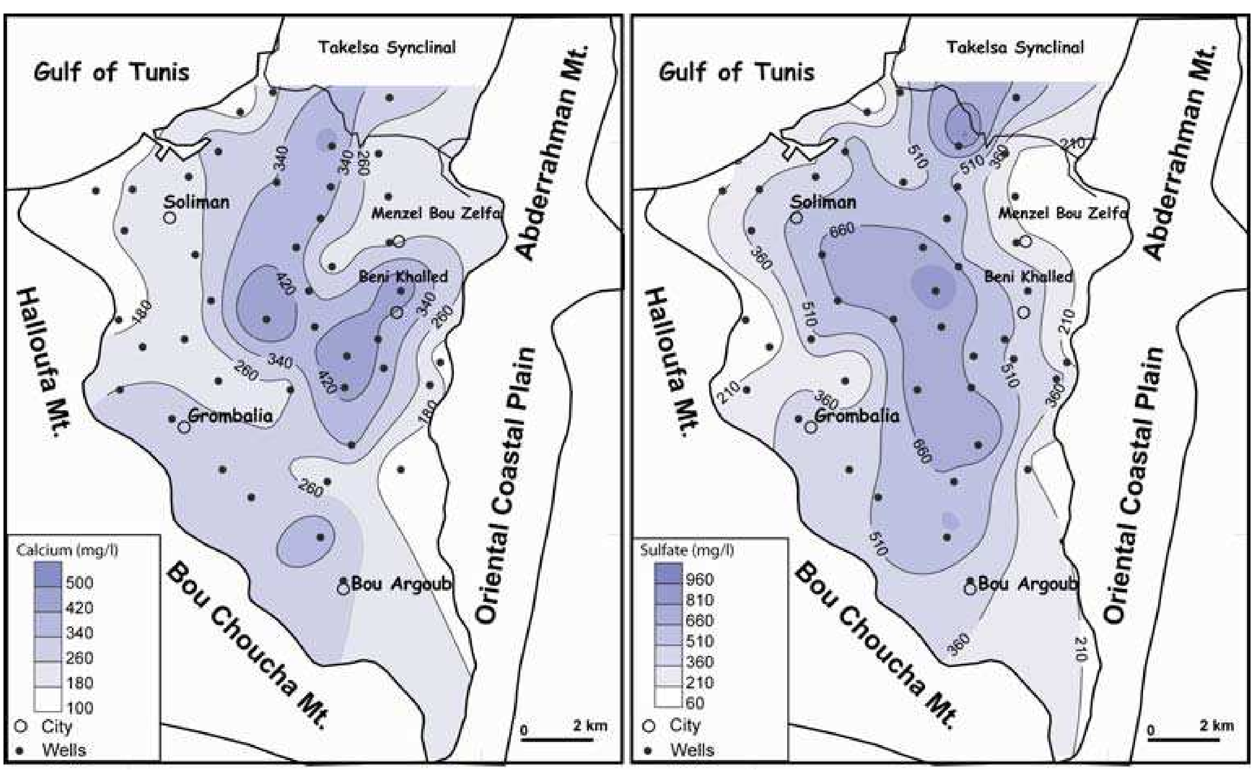


Fig. 15. Spatial distribution of Ca and SO_4

the dissolution gypsum minerals. However, some other samples display a depletion of Na *vs.* Cl that corresponds to an enrichment of Ca *vs.* SO_4, suggesting further modification by cation exchange process according to the reaction:

$$Ca\text{-}Clay(s) + 2Na^{+} \rightarrow Na_2\text{-}Clay(s) + Ca^{2+}$$

During this process, Na^{+} in the solution is exchanged with Ca^{2+} in the sediments. Moreover, the referred exchange is confirmed through the two Indices of Base Exchange (IBE), namely the Chloro-alkaline indices (CAI 1 and CAI 2) (Schoeller, 1965; Garcia et al., 2001).

$$CAI\ 1 = Cl - \frac{Na + K}{Cl}$$

$$CAI\ 2 = Cl - \frac{Na + K}{SO} + HCO_3 + CO_3 + NO_3$$

When there is an exchange between Na^{+} or K^{+} with Ca^{2+} or Mg^{2+} in the groundwater, both the above mentioned indices will be positive and if there is a reverse cation exchange prevalent then both these indices will be negative (Schoeller, 1965). All groundwater samples have positive IBE, indicating that cation exchange process became dominant in the study area and seems to occur along the groundwater flow path.

6. Conclusion

The present examination offers new, constructive, data for assessing the groundwater quality state of the Grombalia shallow aquifer, one of the most important water reservoirs in the Cap Bon peninsula. The results of this investigation lend support to the presence of both natural and anthropogenic processes that contribute to the groundwaters salinisation and may result in concentrations locally exceeding recommended limits. Elevated concentrations of NO_3, Br and Sr are ascribed to anthropogenic processes such as (i) the return flow of irrigated water enhanced by the flood irrigation practices, over-fertilization and pesticides leached downward. (ii) The intensive irrigation by the treated waste water; and (iii) the rejection of industrial non-treated waste waters in the drainage network. Furthermore, with increased water-rock interaction, the Grombalia shallow groundwaters naturally become more mineralized.

7. Acknowledgement

The author thanks the anonymous reviewers for their comments that provided substantial revision of the manuscript; all reviewers are acknowledged for their contributions.

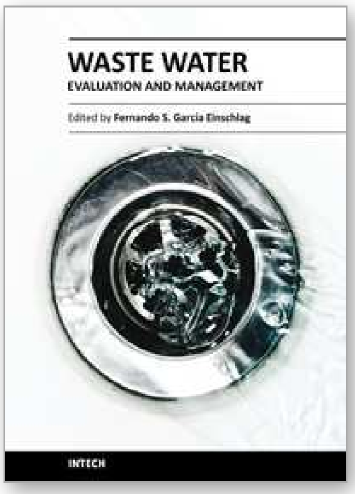
8. References

Adams S, Tredoux G, Harris C, Titus R, Pietersen K (2001) Hydrochemical characteristics of aquifers near Sutherland in the Western Karoo, South Africa. J Hydrol 241: 91– 103.

Appelo CAJ, Postma D (1993) Geochemistry, groundwater and pollution. Balkema, Rotterdam

Ball JW, Nordstrom DK (1991) WATEQ4F—User’s Manual with Revised Thermodynamic Database and Test Cases for Calculating Speciation of Major, Trace and Redox Elements in Natural Waters. United States Geological Survey, Open-File Report, 90-129 pp

Ben Ayed N (1993) Évolution tectonique de l'avant-pays de la chaîne alpine de la Tunisie du début du Mésozoïque à l'Actuel. Thèse d'État Uni. Paris-11, Orsay, Publ. Office Nat. Mines Tunis.
Ben Moussa A (2007) Caractérisation hydrogéologique hydrochimique et isotopique de nappe phréatique de Grombalia, Master, Université de Sfax, Tunisie
Ben Salem H (1995) Évolution de la péninsule du cap Bon (Tunisie orientale) au cours du Néogène, Notes Serv. Geol. Tunisie 61 : 73–84.
Blondel JAT (1991) Les séries à tendance transgressive marine du Miocène inférieur à moyen de la Tunisie centrale [Trangressive series of the Lower and middle Miocene in central Tunisia]. PhD Thesis, University of Genova, Italy
Bohike JK, Smith RL, Hannon JE (2007) Isotopic analysis of N and O in nitrite and nitrate by sequential selective bacterial reduction to N2O. Anal Chem 79(384):5888–5895
Burollet PF (1956) Contribution à l'étude stratigraphique de la Tunisie centrale. Annale des mines et de la géologie, 345 p
Chihi L (1995) Les fossés néogènes à quaternaires de la Tunisie et de la mer Pélagienne : une étude structurale et une signification dans le cadre géodynamique de la Méditerranée centrale. Thèse d'État, Uni. de Tunis II.
Colleuil B (1976) Etude stratigraphique et néotectonique des formations néogènes et quaternaires de la région de Hammamet-Nabeul (Cap Bon) D.E.S, Université de Nice
DGRE (Direction Générale des Ressources en Eau) (2005) Annuaire de l'exploitation des nappes phréatique de la Tunisie. DGRE, Tunis, Tunisie
Elmejdoub N, Jedoui Y (2009) Pleistocene raised marine deposits of the Cap Bon peninsula (N–E Tunisia): Records of sea-level highstands, climatic changes and coastal uplift. Geomorph 112: 179–189
Faye S, Maloszewskib P, Stichlerb W, Trimbornb P, Fayea SC, Gaye ChB (2005) Groundwater salinization in the Saloum (Senegal) delta aquifer: minor elements and isotopic indicators. Sci Tot Enviro 343: 243– 259
Garcia MG, Del Hidalgo M, Blesa MA (2001) Geochemistry of groundwater in the alluvial plain of Tucuman province. Argentina. J Hydrol 9: 597-610.
Piper AM (1944) A graphic procedure in the geochemical interpretation of water-analyses. *Trans Am Geophys. Union* 25: 914-923.
Hadj Sassi M, Zouari H, Jallouli C (2006) Contribution de la gravimétrie et de la sismique réflexion pour une nouvelle interprètation géodynamique des fossés d'effondrement en Tunisie : exemple du fossé de Grombalia. Compt Rend Géosc 338: 751-756
Rightmire CT (1978) Seasonal variation in pCO2 and 13C content of soil atmosphere. Wat Resou Res 14: 691
Schoeller H (1939) Le Quaternaire du Golfe ancien de Grombalia, Tunisie, 14-30 pp
Schoeller H (1965) Hydrodynamique lans le karst. Actes du Colloque de Dubrovnik, IAHS/ UNESCO, 3–20pp
Stigter TY, Carvalho AMM, Ribeiro L, Reis E (2006) A Impact of the shift from groundwater to surface water irrigation on aquifer dynamics and hydrochemistry in a semi-arid region in the south of Portugal. Agricultural water management 85: 121–132
Zhu a GF, Li ab ZZ, Su c YH, Ma d JZ, Zhang b YY (2007) Hydrogeochemical and isotope evidence of groundwater evolution and recharge in Minqin Basin, Northwest China, J Hydrol 333: 239– 251.



Waste Water - Evaluation and Management

Edited by Prof. Fernando SebastiÃ¡n GarcÃa Einschlag

ISBN 978-953-307-233-3
Hard cover, 470 pages
Publisher InTech
Published online 01, April, 2011
Published in print edition April, 2011

Fresh water resources are under serious stress throughout the globe. Water supply and water quality degradation are global concerns. Many natural water bodies receive a varied range of waste water from point and/or non point sources. Hence, there is an increasing need for better tools to asses the effects of pollution sources and prevent the contamination of aquatic ecosystems. The book covers a wide spectrum of issues related to waste water monitoring, the evaluation of waste water effect on different natural environments and the management of water resources.