ORIGINAL ARTICLE

# Hydrochemical, isotopic and statistical characteristics of groundwater nitrate pollution in Damascus Oasis (Syria)

**Boulos Abou Zakhem · Rania Hafez**

**Abstract** A multi approach methodology using hydrochemistry, environmental stable isotopes and multivariate statistical analysis, were carried out to identify the sources and distributions of groundwater nitrate pollution. Based on the spatial distribution of nitrate concentrations, nitrate pollution occurs mainly in the central part of the study area. Thus, the irrigated areas are likely to be the most affected by this pollution. More than 51.8 % of the sampled wells exceed the maximum contaminant level of 50 mg/L for drinking water. High nitrate levels are associated with isotopic enrichment of $\delta^{18}O$ values, clearly indicating that evaporation of irrigation water during infiltration and groundwater contamination. $\delta^{18}O–NO_3^-$ trends suggest isotopic distinct, non-point source origins which vary spatially and temporally, due to different degrees of evaporation, irrigation return flow and the intensive use of mineral and organic fertilizers and wastewater seepage. However, the anomalies of nitrates in the vicinities of Kabbass tannery are considered as point pollution by dumping of industrial wastewater into drainage network, without treatment. PCA showed the existence of four significant PCs that explain 70 % of the variance. FI represents the nitrates pollution of groundwater. FII exhibits the mineralization processes by interaction between groundwater and the host rocks. FIII and FIV indicate anthropogenic contamination by heavy metal. The proposed approaches have successfully illustrated and assessed the groundwater nitrate pollution.

## Introduction

Due to the scarcity of surface water in many regions around the world and the rapid increase in the population, there has been sharp increase in the potable water demand. Groundwater is becoming an important source of drinking water supply. The value of groundwater depends not only on its availability but also on its consistent good quality. Groundwater contamination is one of the most important environmental problems in the present world.

Many previous studies on groundwater quality have shown that nitrate is derived from various point and non-point sources of pollution, such as agricultural, urban and industrial activities. The application of nitrogen-based fertilizers is the most extensive human source of $NO_3^-$ in shallow groundwater systems. The amount of nitrate leached from agricultural lands is strongly influenced by factors inherent in nature such as soil type, groundwater depth and climate conditions (Mikkelsen 1992). In groundwater and pore water that is strongly oxidizing, $NO_3^-$ is the stable form of dissolved nitrogen. It moves with the groundwater and experiences no chemical transformation and little or no retardation. Very shallow groundwater in highly permeable sediment commonly contains considerable amounts of dissolved oxygen. It is in these hydrogeological environments that $NO_3^-$ migrates large distances from its input areas (Shimojima and Sharma 1995).

Groundwater nitrate pollution has become a widespread problem which affects all countries. It reduces the potential

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of available freshwater resources, generates health problems, especially in rural areas and put at risk the socioeconomic development of the country (Colleen 1993; Aghzar et al. 2002; Berdai et al. 2002). Such situations may become worse in arid and semi-arid areas, where water resources are limited and evaporation rates are high with flood irrigation type. Mineral fertilizers, septic systems, cattle manure and organic matters used in agriculture, which contain nitrogenous compounds derived by the effect of anthropogenic activities, lead to the increase of nitrate pollution (Lake et al. 2003; Widory et al. 2004; Liu et al. 2005; Rao 2006).

In many groundwater basins, urbanization has created a growing demand for drinking water, while long histories of agricultural activity have left aquifers potentially at risk from nitrate. Water agencies and regulators can develop more effective management strategies when nitrate sources are well understood. Nitrate concentrations approaching and greater than the maximum contaminant level (MCL) are impairing the viability of many groundwater basins as drinking water sources.

The present paper aims, therefore, to determine the hydrochemical characteristics of alluvial aquifer in Damascus Oasis, where the nitrate pollution of groundwater is increasing along the last decades. A multi-approach methodology using hydrochemistry, environmental stable isotopes and principal components analysis (PCA), was carried out to identify the sources and distribution of this pollutant. The information provided in this paper would be useful for the development of sustainable groundwater management and appropriate protection planning. It is generally recommended to be applied in similar environments especially in arid and semi-arid areas.

## Study area

Damascus Oasis lies between latitudes 33°24′ to 33°37′N and longitudes 36°15′ to 36°38′E with an area of about 1200 Km$^2$ and altitude ranged between 550 and 750 m a.s.l. The Oasis represents the lower part of Barada and Awaj Basin, where Oteibeh and Hijaneh lakes are located in the eastern part representing the natural drainage system of surface water. Damascus city is located in the western part of the Oasis. The drainage pattern is controlled by Barada and Awaj Rivers which are the main rivers of the hydrographic network in the basin. Barada River is fed by both Barada spring with an average discharge of 3.12 m$^3$/s and the Cretaceous Karistic Figeh Spring which has an average discharge of 7.7 m$^3$/s (Selkhozpromexport 1986). The climate is Mediterranean type, which is characterized by rainy cold winter and hot dry summer (Soumi and Chayeb 1989). The mean annual rainfall is 221 and

136 mm measured in Mazzeh and Damascus airport meteoric stations, respectively (Homsi et al. 1989).

Quaternary sediments of Damascus depression in the western part are composed of pebble, gravel and conglomerates. While, fine sand and silty soils are encountered in the central zone, and consisting of loamy and clayey lacustrine deposits in the eastern part (Ponikarov 1966). Quaternary alluvial aquifer system consists of pebble, gravel, sand, silt and clay which have 400–450 m thickness. This aquifer compiles several sub-aquifers (multi layers) that differ in their lithological characteristics. The aquifer is generally unconfined but in some places becomes semi-confined by clay lenses. The upper part (10–20 m) of this aquifer is mostly made up of alluvial-proluvial materials, mainly of loam and clays. The hydraulic conductivity varies sharply from 3.7 to 142 m/day, and thus the transmissivity (165–3700 m$^2$/day) (Selkhozpromexport 1986). The water quality is generally good (TDS < 0.9 g/l), but the aquifer system is severely being exploited throughout many wells (>25,000) for irrigation and drinking purposes. Groundwater flow direction is from west to east in parallel with the flow direction of Barada River. The hydraulic head changes from 660 m a.s.l. near Damascus City, to less than 530 m a.s.l. in the vicinity of Oteibeh Lake that corresponds to 0.004 ± 0.002 of hydraulic gradient.

## Socioeconomic activities

The total population in Damascus Oasis is about 5 million, accounting for approximately 20 % of the total population of Syria. Thus, various socioeconomic activities take place in this area such as urbanization, industry and agriculture. There are more than 12,000 factories ranged from microscale to large-scale belong to private and public sectors. The number of chemical, metal, and textile manufactures constitutes 40 % approximately of total factories but they produce huge load of heavy metals generated mainly from leather processing, metal calving and battery production. While, the main sources of lead are smelting and processing of lead (World Bank Group 1998). The most highly contaminated area that worth to be mentioned is the Kabbass (DMKB) tannery located in the eastern suburb and H. Balss (DMHB) industrial zone in the southern suburb of Damascus city. This area comprises several types of industries, but the most critical is the large cluster of tanneries. Leather processing is carried out approximately by around 164 tanneries.

The first sewage water treatment plant in Damascus Oasis started operation in 1998. It is located in Adra area, 20 km northeast of the city. The plant has good biological treatment but there is no special treatment for inorganic matters specially heavy metals. The wastewater treatment

plant is designed for 2.25 million of the population and it works only to 60 % of its capacity leaving about 73 % of the total domestic wastewater without treatment (Ministry of Housing 2000). Both, the treated and untreated wastewater are used for irrigation transmitting massive amount of nitrogen components and heavy metals to the soil and finally to the groundwater.

## Materials and methods

### Sampling and analysis

Twenty-seven groundwater samples were collected from pumping wells used for municipal drinking water supply in Damascus Oasis during May and November 2001 representing high and low seasons, respectively. However, our study is completely based on the data of low water season. The sampling locations were selected according to the distribution of land use pattern, including industrial and agriculture zones (Fig. 1). As such the data reasonably represents the hydrochemical characteristics of the aquifers in the study area. Physical parameters including pH, temperature, electrical conductivity (EC), total alkalinity and dissolved oxygen (DO) were measured in the field. Chemical analyses of major ions as $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$ and $NO_3^-$ were analyzed using Chromatograph (Dionex 120). Overall precision of the analysis is within ±5 %. Heavy metal concentrations (Pb, Cd, Cu and Zn) were measured using the anodic stripping voltammetric (ASV) method (Montero Alvarez et al. 2007; Sonthalia et al. 2004) with (693 VA) processor, Metrohm (Swiss made). The isotopic analysis ($\delta^{18}O$ and $\delta^2H$) was measured by Finnigan Mat Mass Spectrometer DELTA plus, following the standard method of $CO_2$ water equilibration (Epstein and Mayeda 1953) with accuracy of (±0.1 ‰) and (±1 ‰), respectively. Chemical and isotopic analyses were performed in the laboratories of the Atomic Energy Commission of Syria (AECS) under the control of National Quality Control Program and in cooperation with International Atomic Energy Agency (IAEA).

### Principal component analysis (PCA)

PCA is a multivariate technique that analyzes a data table in which observations are described by several inter-correlated quantitative dependent variables. Its goal is to extract the important information from the table, to represent it as a set of new orthogonal variables called principal components (PC) which compress the size of the data set by keeping only this important information, to simplify the description of the data set and analyze the structure of the observations and the variables (Abdi and Williams 2010).

Standardization of the raw data tends to eliminate the impact of different measurement units, and renders the data dimensionless as follows:

$$Z = (X_i - \mu)/\sigma \qquad (1)$$

where $Z$ is standardized value, $X_i$ indicates the original value of the measured parameter $i$, $\mu$ is the mean and $\sigma$ is the standard deviation of the set (Davis 1986; Hamzaoui-Azaza et al. 2009).

The linear correlations between variables are determined by coefficients in the $(-1, 1)$ interval in the correlation matrix. The relationship between two parameters is more significant when the coefficient approaches the extreme values of $-1$ and 1. A positive coefficient suggests a commonality between the correlated elements, such as similar evolutionary patterns. A negative coefficient indicates that the variables in question are evolving in opposite directions (Hamzaoui-Azaza et al. 2009).

## Results and discussion

### Groundwater hydrochemistry

Groundwater chemistry is the main factor determining its suitability for drinking, domestic, agricultural and industrial purposes. The analytical results of physical and chemical parameters of groundwater were compared with the standard guideline values as recommended by the World Health Organization (WHO 2004) and with the Syrian standard (Ministry of Environment 1994) for drinking and public health purposes.

Groundwater temperature varies from 14 to 27.7 °C with mean and standard deviation values of 20.2 and 2.9 °C, respectively. The small range of values shows the uniformity of groundwater temperatures inside the Quaternary aquifer in Damascus Oasis. The maximum value was measured in Oteibeh (DOT) well which is probably connected to deep groundwater zone. The pH values of groundwater range from 6.9 to 8.3 which show that the groundwater samples of Quaternary aquifer are neutral and very homogeneous. According to the WHO, the range of desirable pH values of water prescribed for drinking purposes is 6.5–8.5 (WHO 2004).

Physical and chemical parameters including summary statistics, such as mean, minimum, maximum, range and standard deviation, are reported in Table 1. The abundance of the major ions in groundwater is in the following order: $Ca^{2+} > Na^+ > Mg^{2+} > K^+ = HCO_3^- > SO_4^{2-} \geq Cl^-$.

In all groundwater samples, the highest concentrations of cations and anions are below the maximum acceptable level. Whereas, in Oteibeh well (DOT) the concentrations of cations and anions such as $Na^+$, and $SO_4^{2-}$, are above
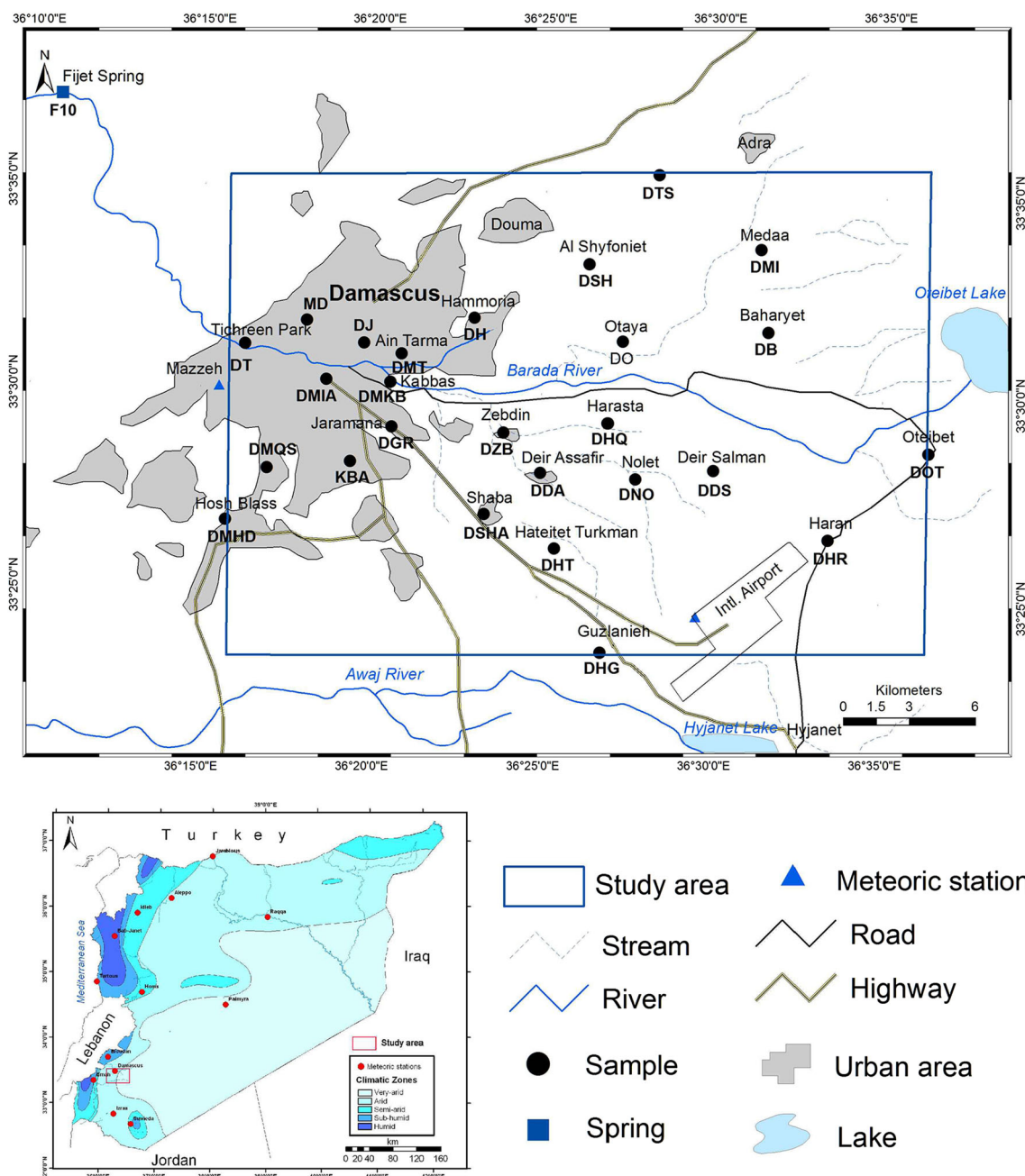
**Fig. 1** Study area and sample location map (Abou Zakhem and Hafez 2014)

the maximum acceptable level for dinking waters (323.2 and 994.7 mg/l, respectively) (WHO 2004).

*Water type*

Major element concentration (meq/l) of groundwater samples were plotted on a piper diagram (Fig. 2), the results show that there are three groups of water type: The first group is represented by Figeh Karistic spring (F10) and samples from the western part of the Oasis (Teshreen park DT). This group has a calcium bicarbonate composition (Ca–HCO$_3$ type). The EC ranges from 302 µS/cm in (F10) to 623 µS/cm in (DT). The second group is represented by Babila (KBA), Jobar (DJ), Nola (DNO) and Zebdin (DZB) located in the center of Oasis. The diagram shows that the water facies are mainly calcium or magnesium bicarbonate (Ca–Mg–HCO$_3$ type), and gradually changes to become sodium chloride type (Na–Cl type) towards the east. The highest measured EC (1027 µS/cm) is found in DZB. The third group is characterized by the highest concentrations of sodium, chloride or sodium sulfate (Na–SO$_4$ or Na–Cl type) which found in Oteibeh and

**Table 1** Summary statistics of chemical parameters in groundwater samples

| Parameter | Mean | Mini. | Maxi. | Range | SD | WHO | Syr. |
|---|---|---|---|---|---|---|---|
| $T$ (°C) | 20.2 | **14** | 27.7 | 13.7 | 2.9 | | |
| pH | 7.4 | **6.9** | 8.3 | 1.4 | 0.3 | 6.5–8.5 | 6.5–8.5 |
| EC ($\mu$S/cm) | 1049.9 | **302** | 2850 | 2548 | 487.8 | | |
| DO (mg/l) | 5.8 | **3.5** | 8.8 | 5.3 | 1.6 | | |
| $HCO_3^-$ (mg/l) | 299.9 | **75.6** | 481.9 | 406.3 | 110.3 | | |
| $Na^+$ (mg/l) | 48.4 | **1.6** | 323.2 | 321.6 | 61.7 | 200 | 200 |
| $K^+$ (mg/l) | 2.7 | **0.3** | 10.0 | 9.7 | 2.5 | | |
| $Mg^{2+}$ (mg/l) | 25.7 | **4.8** | 73.8 | 69.0 | 16.9 | | |
| $Ca^{2+}$ (mg/l) | 100.7 | **29.7** | 205.3 | 175.6 | 42.9 | | |
| $Cl^-$ (mg/l) | 76.5 | **19.8** | 214.2 | 194.4 | 52.4 | 250 | 250 |
| $NO_3^-$ (mg/l) | 44.5 | **0.1** | 157.4 | 157.3 | 36.1 | 50 | 50 |
| $SO_4^{2-}$ (mg/l) | 83.2 | **16.0** | 994.7 | 978.7 | 189.5 | 250 | 250 |
| SI vs. Calcite | 0.28 | **−0.24** | 0.63 | 0.87 | 0.17 | | |
| $rCa/rMg$ | 4.78 | **0.17** | 9.71 | 9.54 | 2.57 | | |
| Pb ($\mu$g/L) | 1.53 | **1.00** | 4.80 | 3.80 | 0.87 | 10 | 10 |
| Cd ($\mu$g/L) | 0.27 | **0.25** | 0.40 | 0.15 | 0.05 | 3 | 5 |
| Cu ($\mu$g/L) | 4.10 | **0.10** | 18.90 | 18.80 | 4.50 | 2000 | 1000 |
| Zn ($\mu$g/L) | 25.51 | **5.00** | 93.00 | 88.00 | 27.47 | 3000 | 3000 |

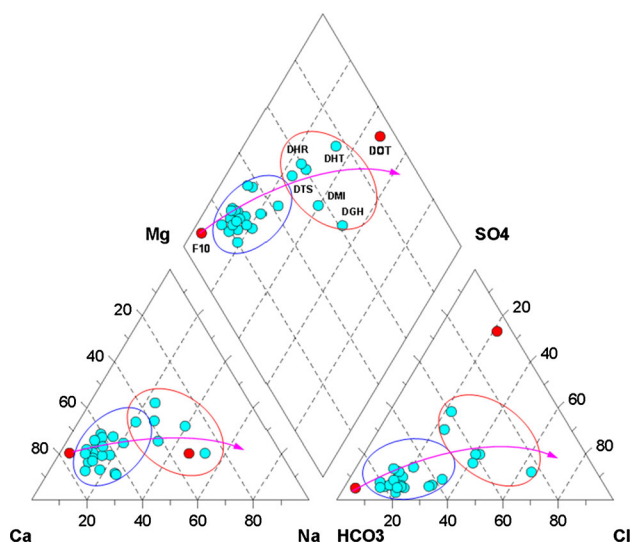*WHO*, *Syr* guideline and Syrian standard for drinking water



**Fig. 2** Piper diagram showing water types, *arrows* indicate salinity increases

its surrounding areas. In DOT the EC is 2850 $\mu$S/cm and the concentrations of $SO_4^{-2}$ is 994.6 mg/l. Generally, the salinity is gradually increasing along the groundwater flow path from west to east of the study area, as indicated by arrows (Fig. 2).

### Chloride variations

Chloride concentration map shows the spatial distribution of dissolved salts (Fig. 3), where the lowest $Cl^-$ concentration is found in the west and northwest and increases towards southeast and northeast. The general direction of groundwater flow lines is perpendicular to chloride concentration contours. Maximum chloride concentrations are observed along the principle axis of aquifer discharge. It is worth mentioning the occurrence of high chloride concentration (125 mg/l) at DMKB where tannery factories are located and therefore it is considered as industrial point of pollution (Abou Zakhem and Hafez 2009).

### $rHCO_3^-/rCl^-$ variations

Figure 4 shows the iso-ratio contours map of the $rHCO_3^-/rCl^-$ ($r$ in meq/l) which, clearly exhibits the hydraulic relationship between the shallow aquifer and the carbonate aquifer (Antonakos and Lambrakis 2000). Increased values of the $rHCO_3^-$ to $rCl^-$ ratio, mainly around the tributary of Barada River (from 3 to 6), involve increased $rHCO_3^-$ concentrations which result from dissolution of the carbonate rocks. For example, in an open system as karstic aquifer, a mole of calcite or dolomite gives 2 or 4 mol of bicarbonate during their dissolution in groundwater (Appelo and Postma 1993). Decreased values of the $rHCO_3^-$ to $rCl^-$ ratio (below 3), generally along the groundwater flow path, suggest increased $rCl^-$ concentrations. Combination of the two maps (Figs. 3 and 4) confirms that the aquifer is recharged from the west and northwest, the western recharge being eventually related to the karstic limestone aquifer and Barada water originated from karstic springs. It is worth to mention that the high value of chloride (125 mg/l) at DMKB tannery industrial zone, has contributed to decrease of $rHCO_3^-/rCl^-$ value showing point of anthropogenic pollution.
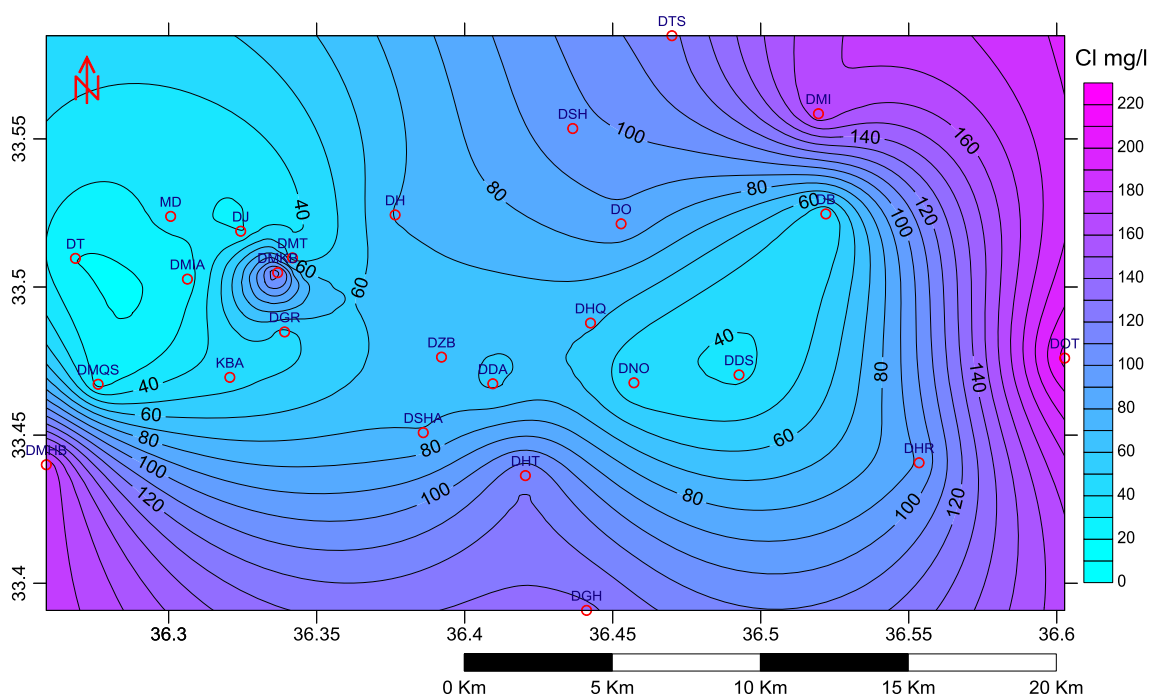
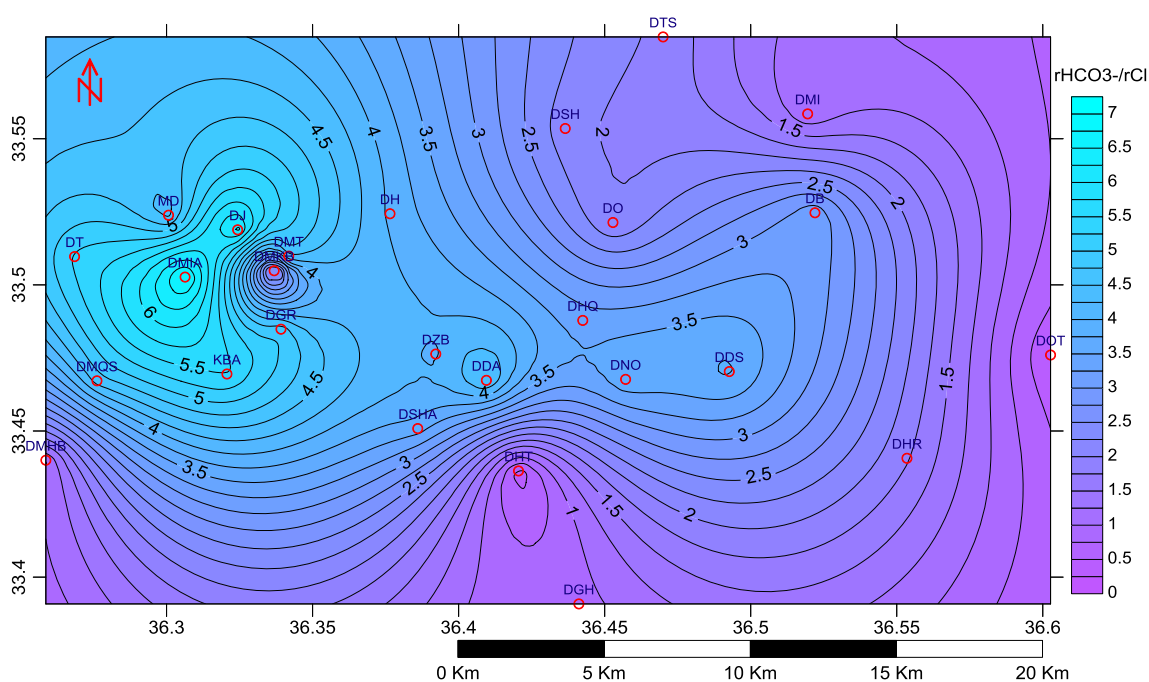**Fig. 3** Cl⁻ distribution map of groundwater samples in the study area



**Fig. 4** $r$HCO$_3$⁻/$r$Cl⁻ distribution map of groundwater samples in the study area

### Saturation index SI

Interactions between groundwater and surrounding host rocks are considered to be the main processes which control the observed chemical characteristics of groundwater in the aquifer. The mineral reaction processes (dissolution or precipitation) is measured by the saturation index for each mineral (Deutsch 1997). The saturation index (SI) describe quantitatively the deviation of water from equilibrium with respect to dissolved minerals and are expressed as S.I. = Log (IAP/$K_t$), where IAP is the ion activity product and $K_t$ is the equilibrium solubility

constant. If the solution is in equilibrium with respect a mineral, the $SI = 0$. Generally, equilibrium is taken to be between $SI = -0.1$ to $0.1$. An error of $\pm 0.05$ pH unit leads to an uncertainty of $\pm 0.05$ units in the SI of minerals and in view of the uncertainties in the Ca, Mg and $HCO_3$ analysis, the total uncertainties are of the order of $\pm 0.1$ units of SI (Adams, et al. 2001). If $SI \geq 0.1$ indicating over saturation and the mineral would tend to precipitate, if $SI \leq -0.1$, they indicate under saturation and the solution would tend to dissolve the mineral (Subyani 2005; Cidu et al. 2009; Hamzaoui-Azaza et al. 2009).

The calculated values of saturation index with respect to calcite (SI vs. Cal.) of the groundwater samples ranges from $-0.24$ to $0.63$ with an average value of $0.28$ and standard deviation of $0.17$. The results of SI indicate that 7 % of samples are in equilibrium. Approximately 82 % of the groundwater samples, the SI vs. Cal. values are between $0.2$ and $0.4$ and 11 % are between $0.5$ and $0.7$ of the water samples. The groundwater is therefore developing from a state close to saturation toward oversaturated with respect to calcite. Thus, precipitation of calcite is expected with increasing of saturation index.

### Sulfate variation

Distribution map of $SO_4^{2-}$ concentrations in groundwater shows that major part of the studied area is below 100 mg/l (Fig. 5). Sulfate concentration increases gradually exceeding 200 mg/l in the east (DHR) to reach 994.6 mg/l in Oteibeh area (DOT). This value is above the maximum acceptable level (250 mg/l) of the WHO's drinking water guideline (WHO 2004) and Syrian standard (Ministry of Environment 1994). The sulfate origin is probably derived from the dissolution of evaporite minerals such as gypsum and anhydrite along the upward flow path from deep groundwater through the Neogene's evaporate formations (Kattan 2006).

### Dissolved oxygen (DO)

Dissolved oxygen in groundwater plays a major role in the occurrence of nitrate. The nitrification process involves oxidation of organic nitrogen and ammonia $NH_3$ to nitrite $NO_2^-$ and nitrate $NO_3^-$. Groundwater with a high level of DO such as might be found in shallow, fast-moving, and/or more permeable zones would facilitate the nitrification process when nitrogen is present. Likewise, low DO levels would inhibit nitrification. However, note that other factors including presence of certain bacteria also influence nitrification (Ann Soule and Hg 2011). In this study the range of DO was between 3.5 and 8.8 mg/L, with a mean of

5.8 mg/L. The wells of high DO above 7 mg/L are found in western part of the study area, related to the fresh water from Figeh spring and Barada River recharge zone. The wells of highest nitrate concentrations are located near industrial zones and urban areas which are characterized by DO between 4 and 7 mg/l. Generally, this DO concentrations exhibit oxidizing conditions where nitrification process is dominant. Note that DO levels cannot be used to predict high nitrates since there may not be a source of nitrogen. As expected, there were no wells with low DO and nitrates above background. Denitrification processes occur only when dissolved oxygen falls below a certain level (<3 mg/l) (Rivett et al. 2008). The lowest concentration of DO (3.5 mg/l) is measured in (DHT) having nitrate concentration of 11.3 mg/l, where the unsaturated zone soils are dominated by clay and groundwater level which become deeper toward the east prevailing reduction conditions.

### Groundwater Nitrate pollution

The nitrate concentrations ($NO_3^-$) of groundwater samples range between 0.1 and 157.4 mg/L with an average of 45.4 mg/L (Table 1). Box plot shows that, median, 25th and 75th percentiles are 52.8, 11.3 and 60 mg/l, respectively. The frequency distribution of the sampled wells of nitrate concentration classes (Fig. 6) indicates that about 75 % of samples $NO_3^- > 11.3$ mg/l. 50 % of samples $NO_3^- > 52.8$ mg/l and 25 % of samples $NO_3^- > 60$ mg/l. About 51.8 % of samples exceed the highest permissible limit of 50 mg/L in drinking water of Syrian standards (Ministry of Environment 1994) and World Health Organization standards (WHO 2004). Therefore, groundwater chemistry shows that the quality of drinking water taken from the aquifer is problematic.

The examination of the spatial distribution of nitrate concentrations (Fig. 7) shows that the highest nitrate concentrations are observed in the eastern, parts of Damascus city. The upstream part of Damascus aquifer seemed to be spared by nitrate contamination. Nitrate concentration in groundwater increases from Teshreen (DT) (20.7 mg/l) pumping station located in the western part of Damascus city, exceeding the Syrian maximum concentration level (MCL) for drinking water (50 mg/l) in DJ, Kadam (DMQS), DZB, Hamorieh (DH), KBA and Jaramana (DGR). This polluted zone located in the eastern part of Damascus metropolitan is vulnerable to urban pollution. Furthermore, this map demonstrates clearly that very high levels of nitrate (e.g. >100 mg/L) are situated within the irrigated areas in Shifonieh (DSH), where agricultural activities involving nitrogen compounds are intensively used.
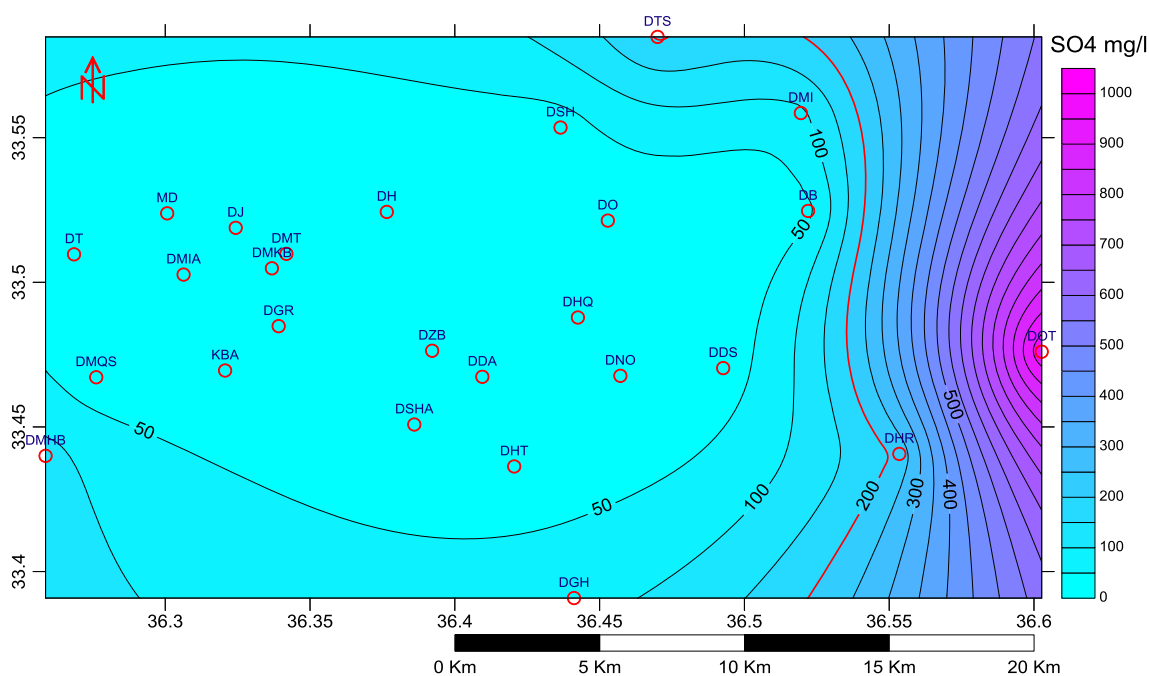
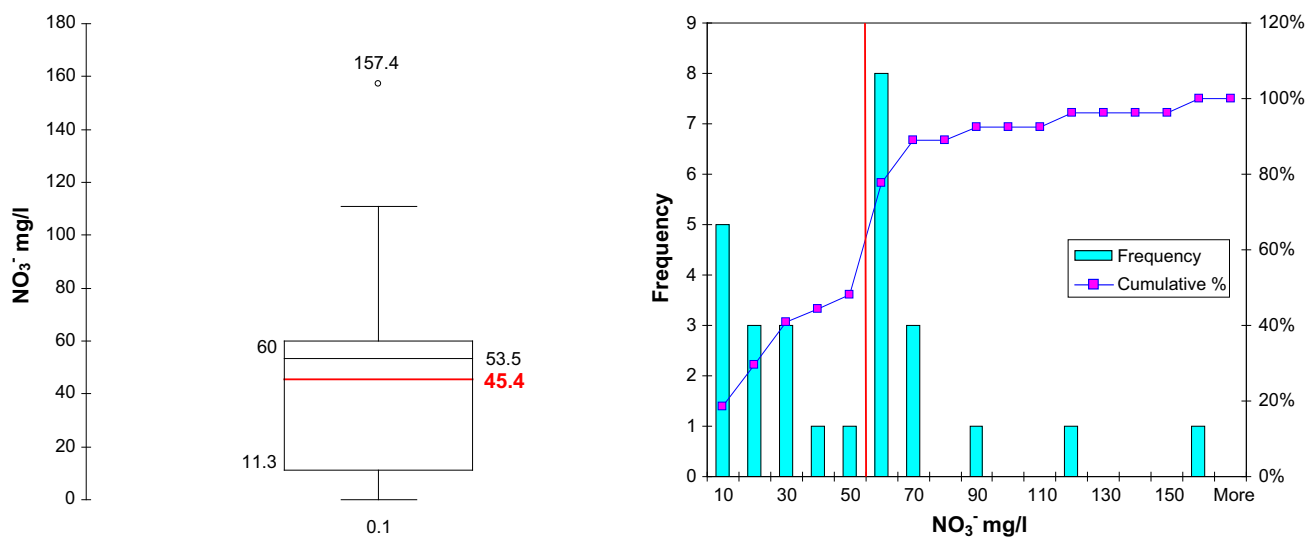**Fig. 5** SO$_4^{2-}$ distribution map of groundwater samples in the study area



**Fig. 6** *Box plots* and frequency distribution of nitrate concentrations in groundwater

The irrigation with untreated and treated wastewater discharged from the treatment plant located in Adraa city, where 73 % of the total domestic wastewater is without treatment so far (Ministry of Housing 2000).

Abou Zakhem and Hafez (2001) found that nitrate concentrations are accumulating in the upper part (above 2 m depth) of the unsaturated zone, trapped by clay and fine sediments. Since the water table is greater than 5 m depth, the groundwater is protected against nitrate concentrations. Whereas, nitrate leaches through sandy unsaturated zone reaching the aquifer and contaminates the groundwater in this area.

*NO$_3^-$ and Cl$^-$ relationship*

In the scatter of NO$_3^-$ and Cl$^-$ (Fig. 8), groundwater samples are distributed around tow lines. First line is parallel to Cl$^-$ concentration with no or minor NO$_3^-$ variations and NO$_3^-$ concentration is below 10 mg/l, where the dissolution processes are dominant in the deep zone of the aquifer. The second line demonstrate a proportional increases of NO$_3^-$ with increasing Cl$^-$, where evaporation processes is the main factor controlling the groundwater mineralization under aerobic condition leading to nitrification of organic matters and groundwater contamination.
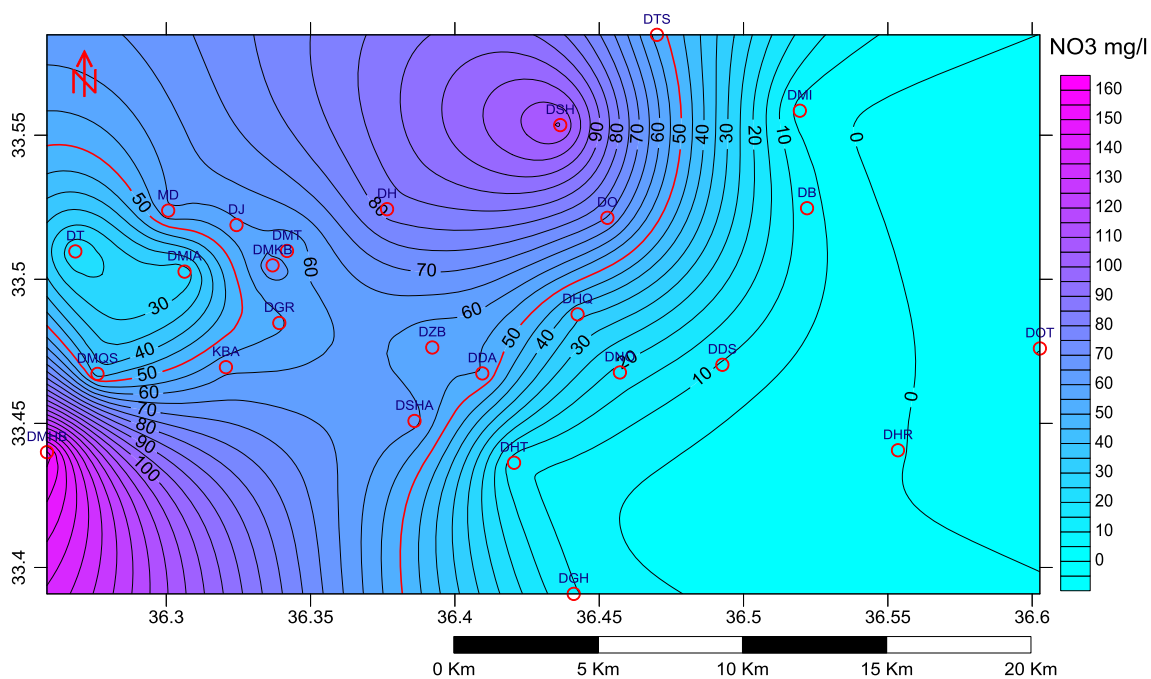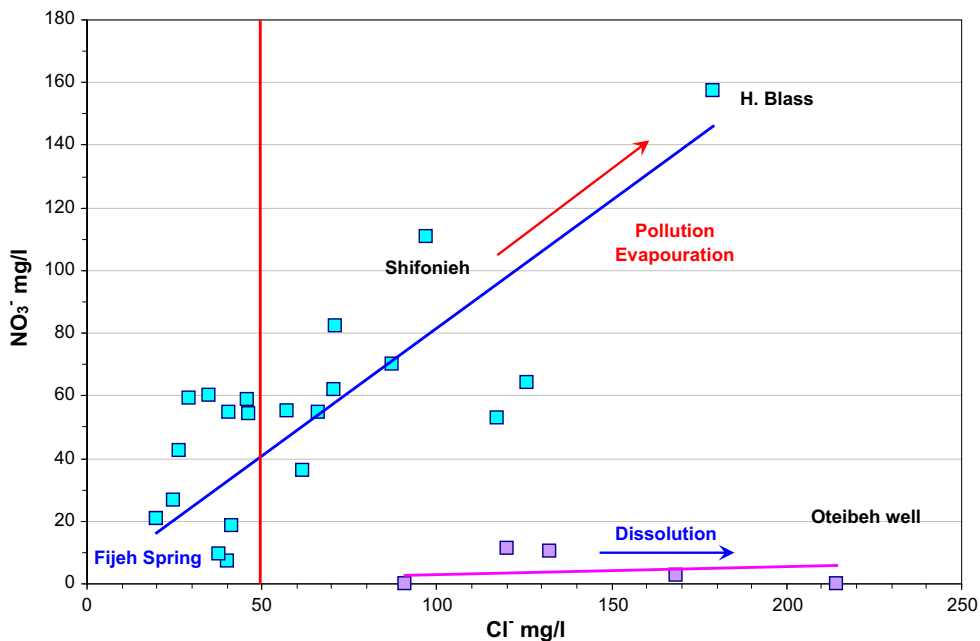
**Fig. 7** $NO_3^-$ distribution map of groundwater samples in the study area

**Fig. 8** $NO_3^-$ and $Cl^-$ relationship in groundwater samples



Isotopic composition

*Isotope contents in groundwater*

The frequency distribution of $\delta^{18}O$ content in groundwater (Fig. 9) shows that $\delta^{18}O$ varies between −6.5 and −9.5 ‰ with an average value of −8.25 ‰. In Figeh spring the $\delta^{18}O$ is more depleted where it is ranged between −8.5 and

−9.5 ‰ with an average value of −9 ‰, which represents the main recharge source of groundwater. The mean altitude of recharge zone of Figeh spring is about 2000 m a.s.l. computed by the Altitude effect equation: $\delta^{18}O = 0.0014\ Alt. − 6.3$ (Abou Zakhem and Hafez 2010). Whereas, the groundwater is more enriched by stable isotopes towards the eastern part of Damascus Oasis (Oteibeh Lake), indicating to evaporation conditions.

**Fig. 9** Frequency distribution of $\delta^{18}O$ contents in groundwater
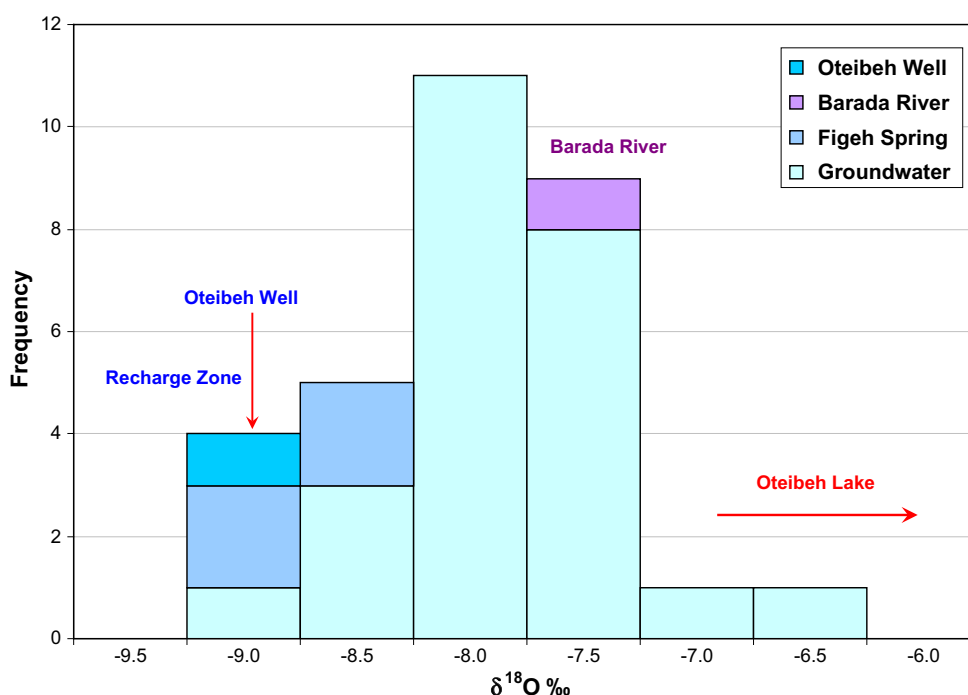


It is shown from Fig. 9 that the recharge zone of shallow groundwater in Damascus Oasis is mainly related to that of Figeh Spring and Barada River.

## $\delta^2H$ and $\delta^{18}O$ relationship

Groundwater samples are distributed between the global meteoric water line with d-excess = +10 ‰ (Craig 1961) and the Mediterranean Meteoric Water Line (MMWL) with d-excess = +22 ‰ (Nir 1967). This indicates that groundwater recharge is mainly from Mediterranean precipitation origin. The main recharge zone is located in Anti-Lebanon Mountain which is characterized by d-excess between 17 and 22 ‰ (Gat and Carmi 1970; Abou Zakhem and Hafez 2010). These values are similar to those found in other areas of the Mediterranean (Clark and Fritz 1997). The intercept between the groundwater samples line with Mediterranean Meteoric Water Line represent the isotopic composition of precipitation that recharge the aquifer systems before any evaporation process. This point is $\delta^{18}O = -9$ and $\delta^2H = -51$ ‰. The correlation between $\delta^2H$ and $\delta^{18}O$ fits the sample points with the relation as follow (Fig. 10):

$$\delta^2H = 6.1\delta^{18}O + 2.6 R^2 = 0.76 \qquad (2)$$

Furthermore, the figure shows that points corresponding to wells sampled in Damascus Oasis region are $\delta^{18}O$ enriched relative to those of Figeh Spring and they are plotted under the MMWL. These waters have undergone evaporation process to varying degrees from Damascus city

in the west to Oteibeh Lake in the east, where the groundwater is more enriched with stable isotopes. Therefore, an evaporation trend can be delineated (Fig. 10) and presents a slope of 6.1, distinctly less than the slope of the MMWL of 8. Barada River isotopic index is −7.9 ‰ and −44 ‰ for $\delta^{18}O$ and $\delta^2H$, respectively, which exhibit a relative isotopic enrichment. Consequently, the recharge zones is close to that of Figeh Spring, which is believed to be located in the Anti-Lebanon mountain chain rather than direct infiltration of local rain water. Barada River catchments are located in the same recharge areas and it contributes in shallow groundwater recharge. Whereas, Oteibeh well exhibit unexpected depleted stable isotope values, which may be explained by the hydraulic connection with deep Cretaceous aquifer (Kattan 2006).

## Scatter of $\delta^{18}O$ vs. $NO_3^-$ in groundwater

Considering the data points as a single group and excluding groundwater samples with low nitrate content (<50 mg/L), the high nitrate levels in groundwater are associated with high $\delta^{18}O$ content (Fig. 11). Thus, significant evaporation processes of irrigation water marked with isotopic and nitrate enrichment infiltrate into the groundwater system. Similar observations were reported in Sacramento Valley, California, USA and in Souss-Massa Basin, Morocco, (Davisson and Criss 1993; Criss and Davisson 1996; Tagma et al. 2009). In fact, a combination of nitrate concentration and oxygen or hydrogen isotope data indicates that isotopic enrichment of the irrigation water with high

loading of $NO_3^-$ is recharging the aquifer. This further indicates that there is an imbalance between plant uptake and nitrate availability. For example, due to application of fertilizer at a time when it cannot be taken up by plants. Alternatively, the plant density is too low to fully utilize the nitrate produced naturally in the soil. The positive relationship between $NO_3^-$ and $\delta^{18}O$ (Fig. 11) also suggests that groundwater originates from two or more isotopic distinct non-point sources, which vary spatially as well as temporally, due to different degrees of evaporation and different amounts of excessive nitrate and thus show deviation of points from the main central trend.

## Principal component analysis (PCA)

PCA allows reducing a large number of variables (measured physical and chemical parameters), to smaller number of factors by explaining the correlation matrix, without losing much information (Jakson 1991; Meglen 1992;
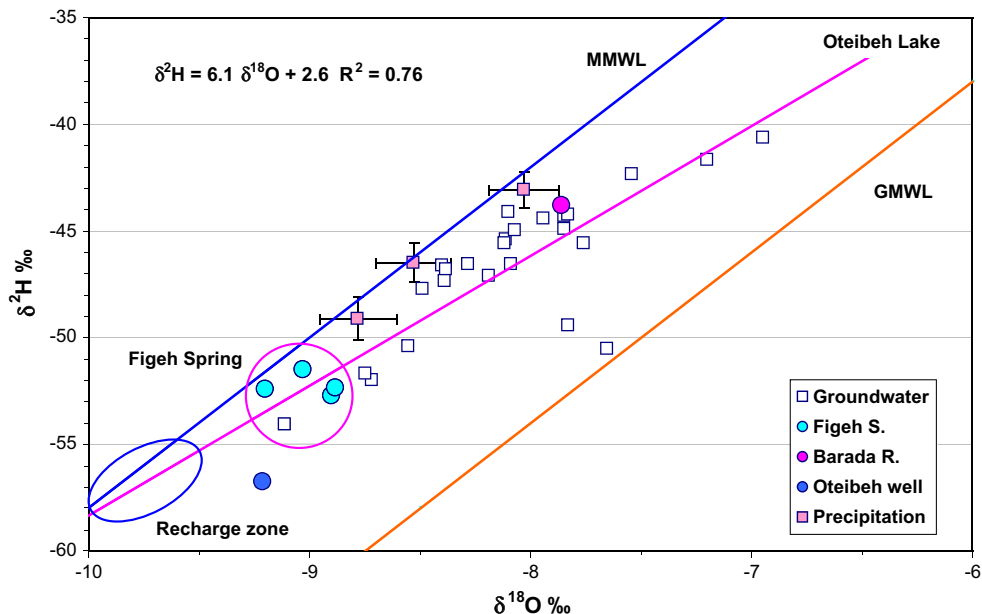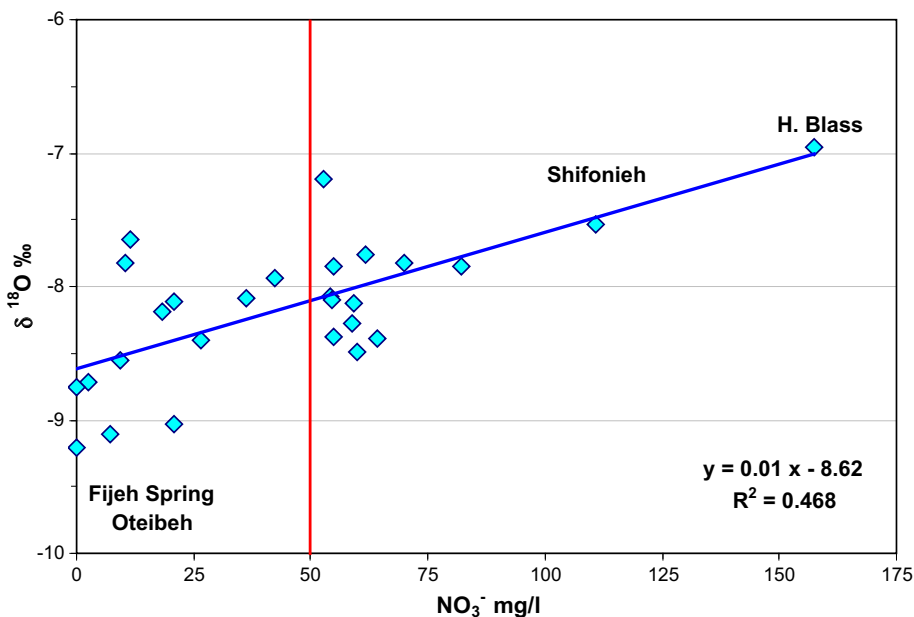
**Fig. 10** $\delta^2H$ and $\delta^{18}O$ relationship in groundwater samples

**Fig. 11** $\delta^{18}O$ and $NO_3^-$ relationship in groundwater samples

Cloutier et al. 2008). The varimax rotation was applied to increase the participation of higher contribution variables and reduce the lesser contribution variables. PCA allows defining eigen vectors of a variance covariance or a correlation matrix from a data set corresponding to a raw matrix of I rows of observations by J columns of variables (Hamzaoui-Azaza et al. 2009; Davis 1986).

In our study, PCA was applied to chemical data of 27 groundwater samples (observations), from shallow aquifer systems to extract the principal factors corresponding to the different processes that control water chemistry and sources of variation in the data. Thus, the 17 original variables are transformed into 17 uncorrelated ones (orthogonal) called PC. The participation of the original variables in the PC is given by loading and the transformed observations are called scores. This method was widely applied in water quality studies (Helena et al. 2000; Adams et al. 2001; Stamatis et al. 2011). The statistical software (STATISTICA) was used, the 17 variables are Pb, Cd, Zn, Cu, Na, K, Mg, Ca, Cl, $NO_3$, $SO_4$, pH, EC, T, $HCO_3$, $rCa/rMg$ and SI-Calcite.

PCA provides a correlation matrix between variables (Table 2), taking into consideration all variables (multi correlation). Significant correlation coefficient ($r$) is defined as 0.5, thus, all variables with r value higher than this correlation have been considered and highlighted in Table 2. A strong and positive correlation is observed in bicarbonate and calcium ($r = 0.73$), magnesium and sulfate ($r = 0.76$), sodium and chloride gives ($r = 0.87$) and sodium and sulfate ($r = 0.73$). The positive and high correlation between EC and the other major elements such as Ca, Mg, Na, Cl and $SO_4$ is normal. These correlations reflect the chemical characteristic of the aquifer. However, $NO_3$ and EC have ($r = 0.7$), $NO_3$ and Ca have ($r = 0.85$) and $NO_3$ and pH have ($r = -64$) these high correlations could be explained by anthropogenic pollution.

Four factors were selected according to the computed percentage of total cumulative variance of more than 70 % and the loadings of 17 variables on these factors are shown in Table 3. FI explains 29.9 % of the variance and have positive correlations with variables: Ca, $NO_3$, $HCO_3$ and EC, and negatively correlated with pH and Zn. This factor represents the nitrates pollution of groundwater associated with high Ca, $HCO_3$ and EC concentrations with relatively low pH. Whereas, FII explains 21.9 % of the variance and related to the variables: Na, Cl, Mg, $SO_4$ and EC, and negatively with $rCa/rMg$. This factor exhibits the mineralization by dissolution of aquifer materials. Thus, the increasing of Na, Cl, Mg and $SO_4$ concentrations is associated with increase of EC and decrease of $rCa/rMg$ values. FIII explains 10.3 % of the variance and contributed by the variables such as K, Cu and SI-Cal. This factor reveals the saturation index versus calcite, high

concentrations of K and Cu. FIV explains 8.4 % of the variance and involves variables as Pb and Cd. This factor divulges the Pb and Cd contamination (Table 3).

Figure 12 illustrates the main factors related to the anthropogenic pollution (F I and F III).

Factor score of groundwater samples related to FI and FIII contains three groups (Fig. 13):

Group 1 is negatively correlated to FI and involves samples from F10, DT DGH, DMI, DDS, DB, DHT, and DNO. This group represents the freshwater which is characterized by high pH, low EC, $NO_3$, Ca and $HCO_3$ concentrations. It is located in western part of Damascus Oasis. The water is Ca–$HCO_3$ type.

Group 2 is positively correlated to FI and presented by the samples located in the eastern part of Damascus city toward the centre of Oasis, from H. Blass to Shifonieh (DO, DTS, KBA, DJ, DSHA, DZB, DDA, DSH, DH and DMHB). It is characterized by high $NO_3$, Ca, $HCO_3$ concentrations, high EC and low pH values. Nitrate pollution is probably the result of the agricultural activities and irrigation with treated and non treated wastewater. The water is Ca-$HCO_3$ type.

Group 3 is positively correlated to FIII and involving DMKB, DGR, DMIA, DMQS groundwater samples. These samples are located in the vicinities of Kabbass tannery (DMKB), which represent industrial point pollution. This group has high concentrations of K, $rCa/rMg$, SI-Cal. and Cu.

## Discussion about nitrate pollution

Contamination of the groundwater can occur if input of $NO_3^-$ into soil exceeds the consumption by plants and denitrification (Mcclain et al. 1994). The excess of $NO_3^-$ in the groundwater occurred as a result of $NO_3^-$ leaching from irrigation, wastewater septic tanks, sewage sludge, animal manure and synthetic fertilizers (Thorburn et al. 2003). In the unsaturated zone, during nitrification process, bacteria oxidize ammonia from organic matter to nitrite and nitrate as shown in the following redox reaction equations (Antonakos and Lambrakis 2000):

$$2NH_4^+ + 3O_2 \leftrightarrow 2NO_2^- + 2H_2O + 4H^+ \qquad (3)$$

$$2NO_2^- + O_2 \leftrightarrow 2NO3^- \qquad (4)$$
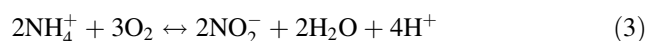
$NO_3^-$ containing compounds in the soil are generally soluble and readily migrate into groundwater (Wakida and Lerner 2002).

In Damascus Oasis, nitrate pollution can be separated into two categories: non point diffuse pollution and point pollution. Diffuse pollution is related to agricultural activities. To increase yields, farmers sometimes exceed required fertilizer application. The irrigation with wastewater

**Table 2** Correlation matrix of 17 physico-chemical variables in groundwater samples

| Variables | Pb | Cd | Zn | Cu | Na | K | Mg | Ca | Cl | NO$_3$ | SO$_4$ | pH | EC | T | HCO$_3$ | rCa/rMg | SI-Cal. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pb | 1 | | | | | | | | | | | | | | | | |
| Cd | 0.31 | 1 | | | | | | | | | | | | | | | |
| Zn | −0.24 | 0.19 | 1 | | | | | | | | | | | | | | |
| Cu | 0.13 | 0.16 | −0.16 | 1 | | | | | | | | | | | | | |
| Na | 0.04 | 0.17 | −0.02 | −0.05 | 1 | | | | | | | | | | | | |
| K | 0.01 | −0.40 | −0.25 | 0.18 | 0.16 | 1 | | | | | | | | | | | |
| Mg | 0.23 | 0.06 | −0.11 | −0.20 | **0.55** | −0.01 | 1 | | | | | | | | | | |
| Ca | −0.06 | −0.18 | −0.38 | −0.03 | 0.15 | 0.19 | 0.17 | 1 | | | | | | | | | |
| Cl | 0.11 | 0.13 | −0.01 | −0.02 | **0.87** | 0.11 | **0.52** | 0.35 | 1 | | | | | | | | |
| NO$_3$ | 0.12 | −0.05 | −0.44 | −0.12 | 0.18 | −0.00 | 0.29 | **0.85** | 0.35 | 1 | | | | | | | |
| SO$_4$ | 0.25 | 0.18 | −0.07 | −0.11 | **0.73** | 0.10 | **0.76** | 0.09 | **0.57** | 0.31 | 1 | | | | | | |
| pH | −0.11 | 0.22 | 0.21 | 0.21 | −0.10 | −0.13 | −0.33 | **−0.79** | −0.21 | **−0.64** | −0.12 | 1 | | | | | |
| EC | 0.13 | 0.01 | −0.30 | −0.10 | **0.68** | 0.15 | **0.72** | **0.70** | **0.79** | **0.70** | **0.64** | **−0.61** | 1 | | | | |
| T | 0.21 | 0.25 | 0.28 | 0.04 | **0.55** | 0.00 | 0.26 | −0.24 | 0.46 | −0.07 | **0.52** | 0.10 | 0.17 | 1 | | | |
| HCO$_3$ | −0.10 | −0.35 | −0.34 | −0.09 | 0.07 | 0.31 | 0.38 | **0.73** | 0.11 | 0.48 | 0.04 | **−0.78** | **0.56** | −0.34 | 1 | | |
| rCa/rMg | −0.37 | −0.25 | −0.17 | 0.18 | −0.31 | 0.35 | **−0.65** | 0.42 | −0.23 | 0.23 | −0.38 | −0.14 | −0.11 | −0.47 | 0.10 | 1 | |
| SI vs. Cal | −0.29 | −0.10 | −0.21 | 0.34 | 0.00 | 0.32 | 0.00 | 0.24 | −0.04 | 0.11 | −0.07 | 0.17 | 0.10 | −0.21 | 0.36 | 0.19 | 1 |

The bold entries highlight coefficient significance above 0.5

is rendering groundwater at high risk of pollution. This leaching process increases in magnitude when the soil texture is coarse (Cosserat et al. 1990; Vinten et al. 1994; Pixie and Dennis 1995; Kim et al. 2004). In the central sector of the study area, the soil is composed of more than 60 % of sand with a low percentage of clay. Such a

**Table 3** Loadings of 17 physico-chemical variables of groundwater samples

| Variables | F I | F II | F III | F IV |
|---|---|---|---|---|
| Pb | 0.112 | 0.127 | −0.079 | **0.832** |
| Cd | −0.251 | 0.172 | −0.111 | **0.603** |
| Zn | **−0.524** | 0.106 | −0.419 | −0.324 |
| Cu | −0.179 | −0.090 | **0.718** | 0.346 |
| Na | 0.046 | **0.925** | 0.108 | −0.056 |
| K | 0.139 | 0.128 | **0.635** | −0.285 |
| Mg | 0.339 | **0.722** | −0.199 | 0.195 |
| Ca | **0.911** | 0.067 | 0.183 | −0.133 |
| Cl | 0.208 | **0.844** | 0.077 | −0.018 |
| NO$_3$ | **0.831** | 0.167 | 0.041 | 0.117 |
| SO$_4$ | 0.125 | **0.836** | −0.028 | 0.176 |
| pH | **−0.868** | −0.083 | 0.200 | 0.081 |
| EC | **0.687** | **0.690** | 0.068 | 0.015 |
| $T$ | −0.351 | **0.684** | −0.085 | 0.151 |
| HCO3 | **0.813** | 0.039 | 0.131 | −0.247 |
| $r$Ca/$r$Mg | 0.246 | **−0.500** | 0.439 | −0.353 |
| SI vs. Cal. | 0.087 | −0.011 | **0.715** | −0.197 |
| Total variance (%) | 29.94 | 21.91 | 10.29 | 8.42 |
| Cumulative variance (%) | **29.94** | **51.85** | **62.14** | **70.56** |

The bold entries highlight coefficient significance above 0.5

composition would favorite nitrification processes. In Damascus plain, flood irrigation covers 85 % of the total irrigated areas, whereas drip and sprinkler irrigation represents only 15 %. Flood irrigation has low efficiency and does not offer groundwater enough protection against pollution. Consequently, significant amounts of nitrates may reach the groundwater. This finding is supported by $NO_3^-$ and $\delta^{18}O$ relationship. High nitrate levels in groundwater are associated with isotopic enrichment of $\delta^{18}O$ values, clearly indicating that evaporation of irrigation water along with infiltration and nitrate contamination of groundwater system.

Accordingly, the main factors which effectively contribute to shallow groundwater nitrates pollution process are soil texture, unsaturated zone thickness, irrigation type and irrigation return flows. Nevertheless, the localized anomalies of nitrates in the vicinities of Kabbass tannery might be explained by industrial point pollution.

## Conclusion

The investigation carried out to identify the sources and distributions of groundwater nitrate pollution, provide the following conclusions:

Groundwater samples are classified in three major types:

(a) Fresh water with low EC value of calcium bicarbonate type (Ca–HCO$_3$) from the western part of the Oasis.

(b) Transitional zone in the center of studied area with calcium or magnesium bicarbonate type (Ca–Mg-HCO$_3$).



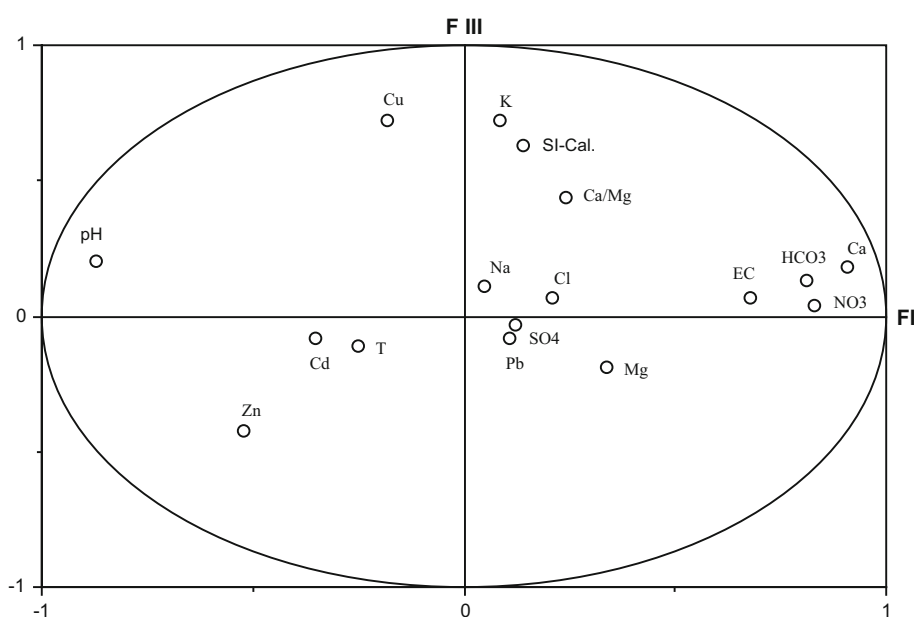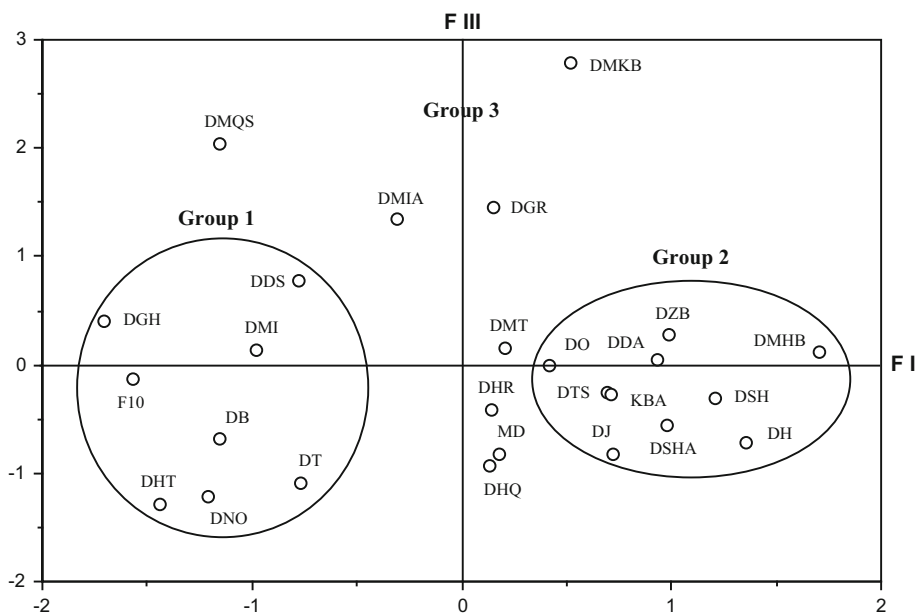**Fig. 12** Factor loading of 17 Variables (F I and F III)

**Fig. 13** Factor score (samples) F I and F III

According to the spatial distribution of nitrate concentrations, the pollution occurs mainly in the central part of the study area. Thus the irrigated areas are likely to be the most affected by nitrate pollution. More than 51.8 % of the water samples exceed the maximum contaminant level (MCL) of 50 mg/l of Syrian standard for drinking water.

Generally, the DO concentrations exhibit oxidizing conditions where nitrification process is dominant. High nitrate levels in groundwater are associated with isotopic enrichment of $\delta^{18}O$ contents, clearly indicating that evaporation of irrigation water along the infiltration and nitrate contamination of groundwater system. Nitrate pollution of groundwater can be separated into two categories: non point diffuse pollution and point pollution. Diffuse pollution is related to agricultural activities, where the main origin of nitrate is mineral fertilizers and wastewater. The main factors which effectively contribute to shallow groundwater nitrates pollution process are soil texture, unsaturated zone thickness, irrigation type and irrigation return flows. Nevertheless, the localized anomalies of nitrates in the vicinities of Kabbass tannery might be explained by industrial point pollution.

PCA showed the existence of four significant PCs that explain 70 % of the total variance. FI (29.9 %) represents the nitrates pollution of groundwater. FII (21.9 %) exhibits the mineralization processes by interaction between groundwater and the host rocks. FIII (10.3 %) and FIV (8.4 %) indicate anthropogenic contamination by heavy metal.

The combined use of hydrochemical, isotopic and statistical approaches in the groundwater investigation is highly informative and essential for the assessment of groundwater quality. Consequently, it is generally recommended to be applied in arid and semi-arid regions, environment.

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