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Geostatistical Assessment of Groundwater Nitrate Contamination with Reflection on DRASTIC Vulnerability Assessment: The Case of the Upper Litani Basin, Lebanon

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Abstract Groundwater constitutes the largest single source of fresh water in many parts of the world and provides a risk buffer to sustain critical water demands during cyclic and prolonged dry periods, especially in semi-arid and arid regions. However, unprecedented socio-economical growths are threatening the viability of these precious resources through fast depletion of already critically low stocks accompanied by persistent degradation of water quality due to salinization, and contamination by pesticides and fertilizers, urban sewage and industrial waste. These circumstances are particularly true of the Upper Litani Basin (ULB), which houses over 500,000 of Lebanon's 4 million population and provides the bulk of the country's agricultural output. Uncontrolled urban, agricultural and industrial growths following a prolonged civil strife and foreign occupation have resulted in the deterioration of the quality of the basin's surface water and potentially its groundwater resources. An assessment study of groundwater quality conditions in the ULB was conducted in support of efforts to manage water quality in the basin. Geostatistical analysis of groundwater nitrate levels was conducted using data collected through an extensive basin-wide water quality survey sponsored by the USAID and covered two periods representing the summer and winter periods. The results of analysis include maps of nitrate contamination and probability of exceedance of drinking-water nitrate regulatory limit. The results indicate a significant, widespread and persistent nitrates contamination of groundwater in the ULB. Nitrate levels in groundwater exceed

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standard limits for drinking water in many parts of the basin. These findings were examined with respect to those of a DRASTIC groundwater vulnerability assessment conducted by the USAID BAMAS project. Comparative analysis of the two assessments shed the light on several issues related to the application and interpretation of DRASTIC scores and the groundwater nitrate contamination process.

Keywords Water quality · Contamination · Geostatistics · Nitrate · Kriging · Groundwater · Water management · DRASTIC · Lebanon · Litani River

1 Introduction

Groundwater occupies an increasingly important role in water resources planning and management initiatives. Not only it constitutes the largest single source of fresh water, it also provides a risk buffer to sustain critical water demands during cyclic and prolonged dry periods. This is particularly true of the predominantly semi-arid and arid regions of the Middle East, where unprecedented water demands driven by fast growing populations with higher living standards are outstripping supplies and placing strenuous pressure on large yet limited and mostly fossil groundwater resources. The impact of these socio-economical changes is two-fold as they are leading to both depleting already critically low water stocks, and the deterioration of water quality due to salinization, and contamination by pesticides and fertilizers, urban sewage and industrial waste.

These circumstances equally apply to Lebanon, considered one of the most water-rich countries of the Middle East. Most of Lebanon' water resources originate from heavy winter orthographic precipitation intercepted by sharply rising mountain ranges that parallel the Mediterranean coast. The Litani River rises near the ancient city of Baalbek, 85 km east of the capital Beirut, and flows 140 km in south-westerly, southerly and westerly directions, to meet the Mediterranean north of Sour, 70 km south of Beirut. The river drains over fifth of Lebanon's total area of 10,500 km^2 and is totally contained within its border making it the country's most important water resource. In the late 1950s, a major hydroelectric system was constructed to tap the 800 m head between the Mediterranean and the river site near the town of Qaraoun, 70 km downstream from Baalbek. The development involved constructing the Qaraoun dam and diverting the river via a series of ponds and tunnels and through three hydroelectric plants to empty into the Mediterranean near Saida, 30 km north of the river's original outlet. The development has resulted in the hydrological separation between the subbasin above Qaraoun lake known as the Upper Litani Basin (ULB) and the Litani's lower reaches (see Fig. 1).

The ULB is home to over 500,000 inhabitants mostly engaged in agricultural activities, and food processing and tourism industries. Producing the bulk of Lebanon's food output, agriculture in the ULB relies on pumped water from surface water and groundwater resources during the rainless summer season. However, relentless releases of untreated domestic, industrial and agricultural wastes into the river have seriously degraded surface water quality conditions to hazardous levels. Water quality is expected to deteriorate even more rapidly if significant control measures are not implemented immediately (Assaf and Saadeh 2006).

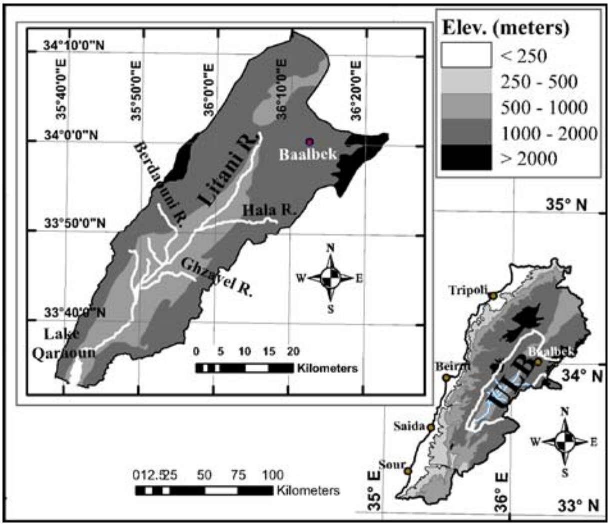


Fig. 1 The Upper Litani River Basin (ULB)

Intensive application of fertilizers, releases of untreated wastewater to open areas, ditches and septic tanks and the common practice of dumping solid waste, including animal carcasses and industrial waste, in many parts of the basin are suspected to have undermined groundwater quality conditions in the ULB.

A comprehensive study is undertaken to assess the level and extent of suspected nutrient and bacterial contamination of groundwater in the ULB to support development of policy options to manage the rising risk of contamination to human health and environment. The current paper focuses on the results from the assessment study with respect to groundwater nitrate contamination. The analysis is based on data collected through an extensive water quality survey funded by the USAID as a component of its initiative to support local government efforts to manage water quality conditions in the country (BAMAS 2005a). Prior to this survey no groundwater quality study has been conducted for the ULB. There are very few references to unpublished data that generally indicate the presence of groundwater contamination (BAMAS 2005b).

The extent of groundwater contamination was assessed using geostatistical analysis tools. The results of the analysis are presented in geo-referenced maps showing spatial distribution and probability of exceedance of groundwater nitrate concentrations for the winter and summer periods of year 2005. The maps are based on a Lambert Conformal Conic projection on a GCS Clark 1880 datum with a central meridian and latitude-of-origin of 37.35° and 34.65°, respectively. The projection has two standard parallels at 33.07333333° and 36.21638889°, and a false easting, and false northing of 300,000.00000000 m each. The results were examined in relation to those of a DRASTIC groundwater vulnerability assessment of the ULB conducted by the BAMAS project.

The aim of the present paper was to conduct an assessment study of groundwater quality conditions in the ULB in support of efforts to manage water quality in the basin, based on geostatistical analysis of sampled nitrate levels representing winter and summer seasons of year 2005, in order to investigate the significance and the spatial spread of nitrate contamination, the possible contamination sources (fertilizers, point source pollutants, etc) and whether or not the nitrate's levels meet potable water standards. Also, results from the geostatistical assessment study were compared against those from a DRASTIC vulnerability assessment conducted through the BAMAS project, aiming to provide an insight into the nitrate contamination processes and the value and limitations of the DRASTIC method.

2 Nitrate: Health Hazards and Sources

At higher levels, nitrates constitutes a serious health risk as it disintegrates in the body into nitrite, which hampers oxygen transfer by binding with haemoglobin and leading to methemoglobinemia, which is particularly life threatening to infants. Also nitrate is a precursor to the development of the genotoxic N-nitroso compounds (NOC), which are known animal carcinogens (Ward et al. 2005).

Nitrate is one of several compounds that make up the nitrogen cycle, which accompanies the larger life/death cycle in the biosphere. The nitrogen cycle is driven by several complex and interrelated processes, where atmospheric nitrogen is transformed into organic and inorganic nitrogen compounds and back into its gaseous form. These processes include fixation, ammonification, synthesis, nitrification and denitrification (Canter 1997). Through biological, atmospheric and industrial fixation, Nitrogen gas, which constitutes 79% of the atmosphere, is transformed into organic nitrogen, ammonium (NH_4), and nitrate. Organic nitrogen, mostly in the form of dead animal and plant tissues and animal fecal matter disintegrates through the process of ammonification into ammonia (NH_3) and ammonium. These inorganic nitrogen compounds along with nitrate, not readily assimilated by animals, are consumed by plants to form through synthesis protein and other organic nitrogen compounds. By feeding on plants animals derive their requirements of nitrogen, a vital building block of all life tissues.

Under aerobic conditions, ammonium is oxidized into nitrite (NO_2), which due to its instability is readily oxidized into nitrate. Known as nitrification, this process is carried out by chemoautotrophic bacteria to produce its energy needs. Nitrification is a function of several parameters including temperature, pH, ammonium concentration and microbial population.

Under anaerobic conditions, other types of bacteria use nitrate instead of oxygen to oxidize organic material. This process is known as denitrification and results in the reduction of nitrate into gaseous nitrogen. Denitrification is influenced by several factors including availability of organic substrate, temperature, moisture and pH.

The excessive application of fertilizers in agricultural section, irrigation practices and sewage contamination have dramatically increased the amount of nitrogen introduced into the soil and altered the balance of nitrogen compounds in soil and groundwater towards producing increasingly higher nitrate concentrations. Due to its solubility and weak adsorption to soil particles, nitrate can travel great distances from its source. Consequently, the impact of these human activities can have a wide geographic extent.

3 GW Nitrate Contamination in Semi-Arid regions

Conditions in semi-arid regions present particular problems that exacerbate the risk of nitrate contamination to groundwater. Under natural semi-arid conditions, low soil moisture conditions significantly retard the denitrification process leading to accumulation of nitrates in the soil over several years (Edmunds and Gaye 1997; Beller et al. 2005). Those accumulations can be flushed into the groundwater at the onset of irrigation, or during major flash flood events leading to spikes in groundwater nitrate levels.

A common practice for managing water scarcity is to resort to irrigation using treated/untreated wastewater. This practice has brought about significant benefits in terms of increasing availability of good quality water to higher priority, meeting agricultural water requirements, providing additional nutrients and reducing wastewater releases. However, several studies have shown that irrigation using treated/untreated wastewater resulted in elevated levels of nitrates in groundwater soil (Tang et al. 2004; VÁzquez et al. 2005; Kass et al. 2005; Hussain et al. 2001). Although wastewater is generally low in nitrate, it contains significant levels of ammonium compounds which convert via nitrification into nitrate, which subsequently leach into groundwater.

Under poor regulations and enforcements, farmers faced with lack of sufficient water supplies may resort to tapping into highly polluted surface or ground water. This is a common problem the ULB, especially during the long rainless seasons and drought periods (Assaf and Saadeh 2006). This practice not only increases nitrate leaching to the groundwater, it also presents a serious public health hazard as bacteria infested water may come in contact with edible vegetables.

Application of fertilizers is a common measure used to improve crop water utilization in semi-arid conditions (Zizhen and Hong 1998; Li et al. 2001). Consequently, fertilizers play an even more important role in increasing nitrate influx to the soil in semi-arid regions in comparison to more humid conditions.

4 Study Area

The ULB valley is an 850–1000 m-elevation geological depression flanked to the west by the steep Mount-Lebanon range, which rises to elevations above 2,500 m, and the less rugged Anti-Lebanon range to the east. The valley floor is mostly underlain by highly impermeable alluvial deposits that can reach over 1,000 m in thickness in the middle section of the valley. These deposits act as a natural barrier to the seepage of surface pollutants to the basin aquifers. However, a few kilometer-wide stretch of relatively porous sand/gravel deposits extend north-easterly for few kilometers in the wedge of land formed by the Litani main river and Hala River. The exposed outcrops to the west and east of the basin are composed of highly porous karstified limestones which provide minimal resistance to surface-to-groundwater contamination (see Fig. 2). No groundwater flow study was reported on the ULB, however, the groundwater can be qualitatively described to flow in the direction of the surface gradient in the upper reaches of the river, and parallel to the river system in the lower reaches (BAMAS 2005c).

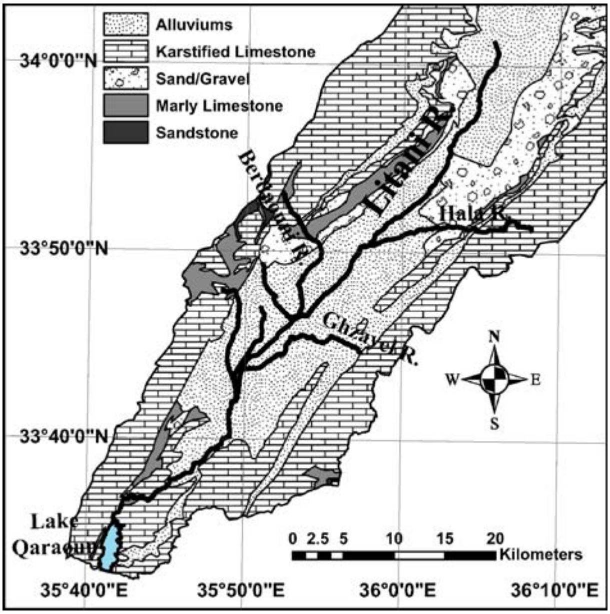


Fig. 2 Geological features of the Upper Litani Basin

The periphery of the valley is dotted by several springs that provide the bulk of the river baseflow and minimum flows during the rainless summer season. Spatially precipitation is higher on the west and west-southern slopes with much drier semi-arid conditions in the northern and eastern parts. This is characteristic of the orthographic nature of precipitation in Lebanon with most of the precipitation falling at the western and coast facing slopes. At an average of 600 mm per year, most of the precipitation falls during the November to March period, with much less during the fall months of September and October and spring months of April and May. The remaining summer months of June, July and August receive virtually no rain. As representative of average conditions in the basin, monthly rainfalls measured at the Agricultural Research and Education Center (AREC) of the American University of Beirut (33°35′N, 36°05′E, 995 m asl) and corresponding reference evapotranspiration (ETo) values are presented in Fig. 3.

The accentuated seasonality of precipitation has resulted in the reliance on irrigation through legal and illegal extractions of surface and groundwater. This is a particularly serious problem during the drier months of the year and dry years in particular, where overextractions have increased both groundwater salinity and reduced the pollution diluting capability of surface water.

A land use map for the ULB (Fig. 4) was prepared by the authors based on GIS data produced by the FAO for Lebanon (FAO 1997). The land use map clearly shows that human activity in the ULB is strongly influenced by the topo-geological features of the area, an important consideration that will be discussed later in the interpretation of vulnerability assessment results. The valley's fertile alluviums have attracted human settlement for millennia, and the area is extensively cultivated and irrigated with wide-spread, excessive and loosely controlled application of fertilizers.

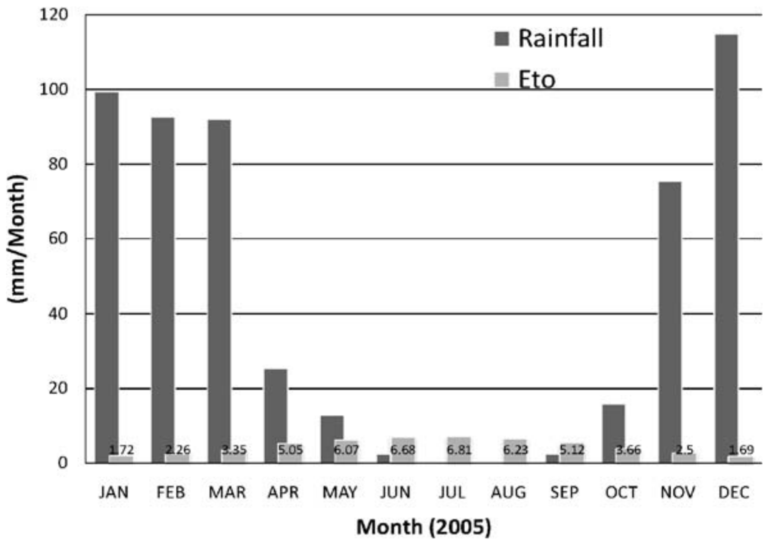
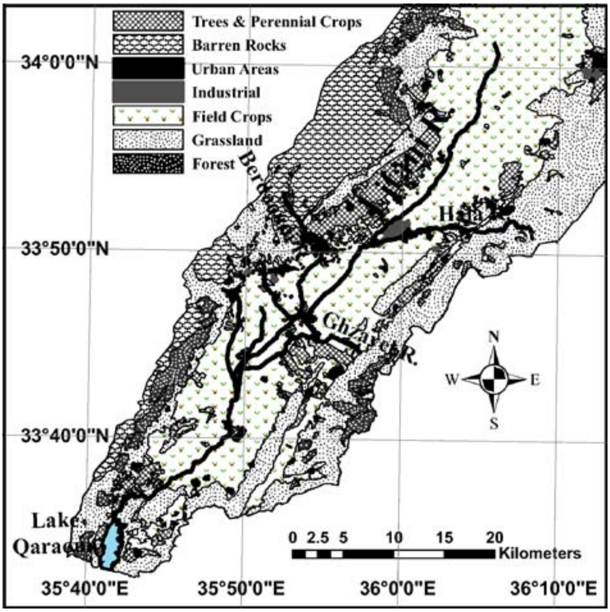


Fig. 3 Monthly rainfall and reference evapotranspiration (mm) at AREC for year 2005

Fruit trees and perennial crops are predominant in the higher and less fertile strips of lands that separate the central valley from the mountainous sides. The rugged western slopes of the basin are mostly barren rocks with patches of forest lands, while grass and forest occupy most of the lower eastern slopes.

Fig. 4 Land use map of the Upper Litani Basin



5 Materials and Methods

5.1 Data

The data includes two sets of samples representing winter (February/March) and summer (June) conditions collected in 2005 from 60 operating wells across the basin used for irrigation and drinking (Fig. 5). The majority of the wells is located in the valley and reach to depths of 70 to 100 m into the underlying alluvial aquifer. The remaining 18 wells tap into the karstified limestone aquifers in the southern part of the basin. In accordance to the standards set by the American Public Health Association, samples were collected in sterile glass bottles after running water for 15 min to ensure proper flushing. Samples were analyzed at the environmental laboratory of the American University of Beirut (AUB) (BAMAS 2005d).

The samples' nitrate contents in mg/L for the winter (February/March) and summer (June) periods are presented in Fig. 5a and b, respectively. The summary statistics of the two sets are presented in Table 1. Each measurement represents a single sample collected and handled as stated before. Nitrate levels are above the drinking health standard limit of 45 mg/l in several wells across the basin. This is particularly true for the winter period where nitrate concentration reach a maximum level of 318 mg/l. Although considered well above the health risk limit, summer concentrations are consistently lower than their winter counterparts with a mean of 48.3 mg/l in comparison to 60.3 mg/l for the winter season. Both datasets exhibit non-normal distribution which is characteristic of environmental data. Non-normality is particularly evident in the winter dataset with a strong positive skew (skewness of 2.5), and a Kurtosis of 10.2, significantly higher than the normal distribution's Kurtosis of 3. The summer dataset show much less deviation from the normal distribution with a skewness and Kurtosis of 1.5 and 5.0, respectively.

Normality is a critical condition for the application of many statistical analysis methods, including those of geostatistics. Perfect conformity to normal distribution is not expected since the process of sampling involves many uncertainties in collection, measurements and analysis. However, transformation is necessary to normalize a distinctly non-normal data, as the one considered in this study. Logarithmic transformation is a commonly used one and its application to the study's data is discussed in later sections.

5.2 Geostatistical Analysis Approach

Critical to the analysis of spatial information as the one addressed in this paper, is the ability to reliably estimate and present its spatial distribution from point data. A powerful approach to achieve this objective is the one advanced by geostatistics, where a continuous surface representing a given variable is calculated from point data based on the potential presence of correlation among data points as a function of the modulus and direction of vector separating them. Known as spatial continuity, this relationship is an important characteristic of spatial data that can provide insight into the physical nature of the phenomena under study.

Formally, geostatistics is a branch of applied statistics that deals with detection, modeling and estimation of spatial patterns (Rossi et al. 1992). It was originally

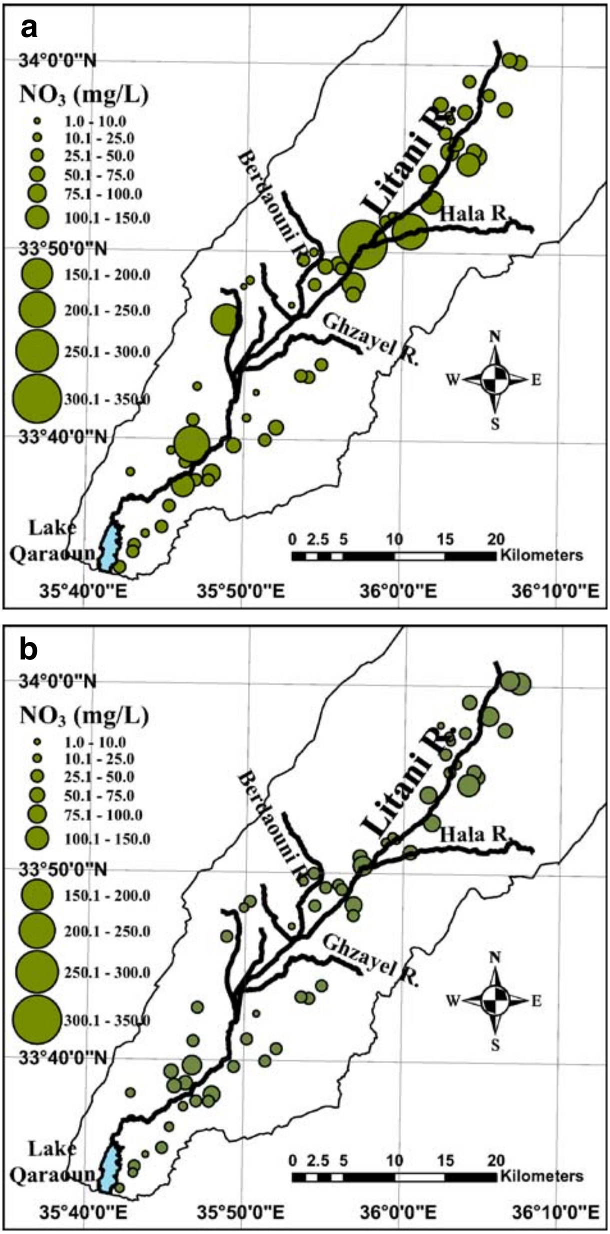


Fig. 5 Measured groundwater nitrate concentrations in the ULB: **a** winter, **b** summer

adopted by the mining industry to estimate mineral reserves based on ore samples. It was subsequently applied in a diverse range of problems including ecological studies, air pollution, climate data analysis, groundwater, surface water and soil contamination (Hossain et al. 2007; Mardikis et al. 2005; Basistha et al. 2008). The trend accelerated with the advent of increasingly powerful computer systems

Table 1 Summary statistics of the GW nitrate samples

Parameter	Winter	Summer
Count	60	60
Minimum	1.0	2.8
Maximum	318.0	170.8
Mean	60.3	48.3
Std Dev.	56.9	37.5
Coeff. of variation	0.90	0.8
Median	44.7	37.3
Quantile 25%	26.3	22.9
Quantile 75%	69.5	63.3
Skewness[a]	2.5	1.5
Kurtosis[b]	10.2	5.0

[a]Positive values indicate skewness to the right, i.e. dominance of small values, and vice versa

[b]Kurtosis is a measure of flatness of data distribution. Value > 3 indicates distribution more peaky than the normal distribution, and vice versa.

and sophisticated geostatistical analysis tools in particular those integrated within Geographic Information System (GIS) applications.

Geostatistics is based on random theory principles. Consider a given spatial medium, e.g. a groundwater contaminant plume, where n measurements, $z(x_1)$, ...,$z(x_n)$, of the variable under consideration are collected at points x_1,...,x_n. Geostatistics is based on the notion that the set of measurements represents a single realization of the random function $Z(x)$ for all possible values in the medium. Values at unmeasured locations can be best estimated based on the conditional expectation (Cooper and Istok 1988):

$$E\left[Z(x_0)|\,Z(x_1),\ \ldots,\ Z(x_n)\right] \tag{1}$$

where x_0 is a point where no measurement is available.

Geostatistics, or more specifically linear geostatistics, relies on two assumptions to solve Eq. 1 numerically. $Z(x)$ is assumed to be normally distributed, thus only two statistical moments (the mean and the variance) need to be specified. The probability distribution is also assumed to be stationary over the medium. Each measurement can be then considered an individual realization of $Z(x)$. Consequently the set of measurements can be used to calculate the mean and variance of $Z(x)$.

Kriging refers to the process of estimating variable values at unmeasured locations based on Eq. 1. Given the assumption of normality, the value at an unmeasured location, $Z(x_0)$, is estimated as a weighted average of measured values as follows:

$$Z^*(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i) \tag{2}$$

where $Z^*(x_0)$ is the kriged value at location x_0, $Z^*(x_i)$ is the known value at location x_i, λ_1,...,λ_n are a set of weights calculated based on solving the Ordinary Kriging System (OKS) designed to produce the best linear unbiased estimate (BLUE).

In order to achieve unbiased estimations in Ordinary Kriging the following set of equations should be solved simultaneously.

$$\sum_{j=1}^{n} \lambda_j \gamma \left(x_i, x_j\right) + \mu = \gamma \left(x_0, x_i\right); \quad i = 1, \ldots, n \tag{3}$$

$$\sum_{j=1}^{n} \lambda_j = 1 \tag{4}$$

$$\tilde{\sigma}_R^2 = \sum_{i=1}^{n} \lambda_i \gamma \left(x_0, x_i\right) + \mu \tag{5}$$

where

μ is the Lagrange parameter; and
$\gamma \left(x_i, x_j\right)$ is the value of the semivariogram defined as:

$$\gamma \left(\mathbf{h}\right) = 1/2E\left\{\left[Z\left(x + \mathbf{h}\right) - Z\left(x\right)\right]^2\right\} \tag{6}$$

The semivariogram is a measure of spatial continuity and depends only on the vector **h,** with origin in x_i, separating a given pair of measurements, and not the positions of these measurements. A smaller $\gamma(\mathbf{h})$ indicates a higher correlation and vice versa. Assuming isotropic conditions, i.e. ignoring **h** direction, the semivariogram is estimated by the experimental semivariogram $\gamma^*(h)$ calculated as follows:

$$\gamma^* \left(h\right) = \left[\frac{1}{2N\left(h\right)}\right] \sum_{i=1}^{N(h)} \left[z\left(x_{i+\mathbf{h}}\right) - z\left(x_i\right)\right]^2 \tag{7}$$

where $N(h)$ represents the number of pairs of measurement points separated by a distance h. $\gamma^*(h)$ is not used directly in the OKS since it is not available for all possible h values. Instead a mathematical model is fitted to the experimental semivariogram in a process known as structural analysis. Any mathematical model can be used given that it is positive definite, a property that is imposed to guarantee a unique solution of the OKS (Journel and Huijbregts 1978). Figure 6 shows the main components of a semivariogram model. $\gamma(0)$, which should theoretically be equal to zero, is known as the nugget. A nonzero nugget reflects sampling and analysis errors.

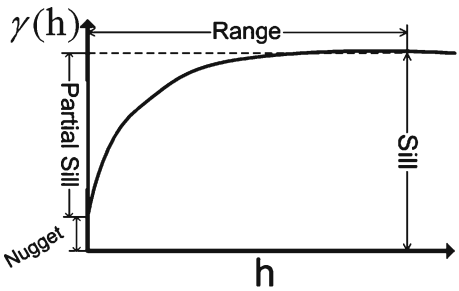


Fig. 6 A generic semivariogram model

The nugget can be attributed to measurements errors or spatial sources of variation at distances smaller than the sampling interval or both. The range is the distance beyond which γ(h) does not change significantly. A longer range indicates a stronger spatial continuity. The sill is $\gamma(\mathbf{h} = \text{range})$. The partial sill is the difference between the sill and the nugget.

The application of geostatistics involves three main steps: (1) exploration of the data to characterize its spatial continuity and assess its suitability for geostatistical analysis, also, trend analysis of the data in order to find out presence of global trends; (2) structural analysis to develop a semivariogram model, and (3) application of the OKS to produce concentration prediction surfaces and probability of exceedance maps.

5.3 DRASTIC Groundwater Vulnerability Index

In an effort to standardize methods for assessing vulnerability of groundwater to contamination, a group of prominent groundwater specialists in the USA developed together a scheme for numerical rating of groundwater contamination potential. The scheme was named DRASTIC to reflect in each letter of the name the following seven factors deemed most critical in the contamination process (Canter 1997):

D Depth to groundwater;
R Recharge rate (net);
A Aquifer media;
S Soil media;
T Topography (slope);
I Impact of the vadose zone; and
C Conductivity (hydraulic) of the aquifer.

In assessing the potential for contamination in a given area, a point rating from 1 to 10 is assigned for each factor to reflect its relative pollution potential for that area, with higher values indicating more favorable conditions for contamination. For example, smaller depths to groundwater are assigned higher ratings to indicate higher exposure to contamination. The DRASTIC index for the given area is then calculated by multiplying each factor's ratings by assigned weights that reflect the relative contribution of each factor to the contamination process in general. Two sets of weights were proposed by the DRASTIC founding group, one that pertains to all types of contaminants and the other to pesticides as presented in Table 2. Assigned weights for the generic case indicate that depth to groundwater, impact of the vadose-zone media and net recharge are the most influential in the groundwater

Table 2 DRASTIC weights (generic and pesticide)

Factor	Generic	Pesticide
Depth to groundwater (D)	5	5
Net recharge (R)	4	4
Aquifer media (A)	3	3
Soil Media (S)	2	5
Topography (T)	1	3
Impact of the vadose-zone media (I)	5	4
Hydraulic conductivity of the aquifer (C)	3	2

Table 3 Color code for DRASTIC indeed ranges

DRASTIC index range	Color
< 79	Violet
80–99	Indigo
100–119	Blue
120–139	Dark green
140–159	Light green
160–179	Yellow
180–199	Orange
> 200	Red

contamination process. This is also true for the pesticide set in addition to the soil media, which is considered to play more active role in the transmittal of pesticides to the groundwater.

DRASTIC index values can range from 26 to 226 and 29 to 256 for the generic and pesticide sets, respectively. Although no explicit characterization of DRASTIC indices was offered, a color code was proposed by the DRASTIC group to reflect the level of vulnerability as presented in Table 3, with cool colors (blue, indigo, and violet) reflecting areas with lower vulnerability and warm colors (red, orange and yellow) flagging highly vulnerable areas.

Despite its wide adoption by many agencies and researchers [see for example Hamza et al. (2006) and Fritchi et al. (2000)], the DRASTIC method is based on key notions and assumptions that may limit its application and warrants caution in the interpretation of its results. Vulnerability is a measure of the potential to contamination and not necessarily the actual level of contamination, which is also a function of pollutant loading. Also, the DRASTIC index implies vulnerability under non-point and uniform pollutant loading. Vulnerability to point-source pollution is not accounted for since pollution from point sources circumvent many of the elements that could retard contamination. However, the DRASTIC method offers a cost-effective screening process to set priorities for groundwater protection and monitoring efforts.

6 Results and Discussion

6.1 GIS Data Preprocessing

As indicated above, the analysis in this paper is based on data collected through an extensive campaign sponsored by the USAID to assess groundwater conditions in the ULB. The data was quality checked and processed into a GIS database. The GIS facilitated further validation and quality control of the data. Using ESRI ArcGIS 9.1 the GIS data was organized into layers representing different water quality parameters for the winter and summer periods. ArcGIS Geostatistical Analyst extension was then used to carry out the three-step geostatistical analysis procedure for the groundwater nitrate concentrations. The following sections present the results of this analysis.

6.2 Data Exploration

Nitrate concentrations were first checked for normality. The histogram for the winter nitrate concentrations (Fig. 7a) and the summary statistics presented in Table 1 indicate that the dataset is highly skewed and does not fit a normal distribution. Transformations can be used to make the data normally distributed and satisfy assumptions of constant variability. The Log Transformation is often used for data with a skewed distribution and a few very large values. These large values may be localized in the study area, and the log transformation will help make the variances more constant and also normalize the datasets. So, applying the logarithmic transformation, which is commonly used in geostatistics, to the dataset produced a bell-shaped histogram (Fig. 7b) that signifies that the dataset is lognormally distributed. For the logarithmic transformation, the predictions are back-transformed to the original values before a GIS map is produced.

Histogram analysis of the summer nitrate concentration dataset also indicated that the dataset is lognormally distributed. Based on these results, further geostatistical analysis was carried out on the log-transformed winter and summer nitrate concentration datasets.

Both datasets were also checked for the presence of global trends, but no significant trend was identified. Trend analysis is an important step for assessing the stationarity of the data. A global trend should be removed prior to carrying out structural analysis.

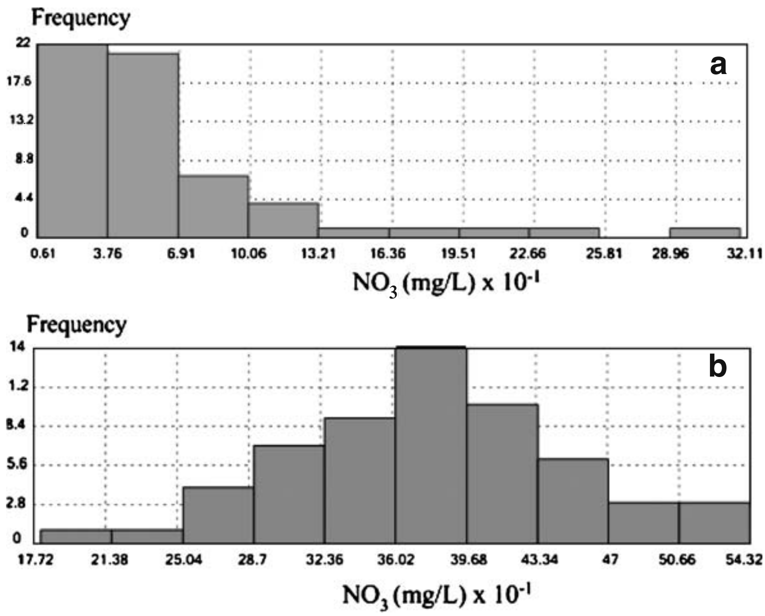


Fig. 7 Histograms for the winter groundwater nitrate concentrations: **a** untransformed, **b** logarithmic

6.3 Structural Analysis

Selecting a semivariogram model is an iterative process that involves calculating experimental semivariograms, fitting an alternative semivariogram, calculating an alternative OKS prediction surface and carrying out a cross-validation statistical analysis to assess the performance of the prediction surface in terms of unbiasedness and estimation of uncertainty. In the cross-validation process, a data point is removed from the dataset and its value is estimated from the rest of data points. The process is repeated for all data points. Two main evaluation criteria: the mean standardized prediction error (MSPE), and the root-mean-square standardized prediction error (RMSSPE) were used to assess the unbiasedness and the estimation of uncertainty, respectively. The MSPE and RMSSPE are defined as follows:

$$\mathrm{MSPE} = \frac{\sum_{i=1}^{n-1} \left(Z^*(x_i) - z(x_i)\right) / \sigma^*(x_i)}{n-1} \tag{8}$$

$$\mathrm{RMSSPE} = \sqrt{\frac{\sum_{i=1}^{n-1} \left[\left(Z^*(x_i) - z(x_i)\right) / \sigma^*(x_i)\right]^2}{n-1}} \tag{9}$$

where $Z^*(x_i)$ and $\sigma^*(x_i)$ are the estimated value and standard error of the variable at location x_i, respectively, based on the other $n-1$ data points.

In the cross-validation process, a third evaluation criteria it should be used, the average standard error (ASE). It is used in order the assessment of uncertainty, the prediction standard errors, to be valid. The OKS method gives the estimated prediction standard errors. Besides making predictions, we estimate the variability of the predictions from the measured values. It is important to get the correct variability.

If the average standard error is close to the root-mean-squared prediction error, then we are correctly assessing the variability in prediction. If the average standard error is greater than the root-mean-squared prediction error, then we are overestimating the variability of our predictions. If the average standard error is less than the root-mean-squared prediction error, then we are underestimating the variability in our predictions.

The objective of the structural analysis process is to obtain an MSPE value close to zero, which indicates unbiasedness of prediction errors, and an RMSSPE value close to one, which indicates accurate estimation of prediction variability.

Based on structural analysis, a spherical model (range = 6.08 km; sill = 0.894; nugget = 0.184) was selected for the winter semivariogram (Fig. 8a). The summer semivariogram was fitted with a spherical model (range = 6.09 km; sill = 0.759; nugget = 0.002; Fig. 8b). The spherical semivariogram model is generally defined as follows:

$$\gamma(h) = \begin{cases} \theta_p \left[\frac{3}{2}\frac{h}{\theta_r} - \frac{1}{2}\left(\frac{h}{\theta_r}\right)^3\right] + \theta_n & \text{for} \quad 0 \leq h \leq \theta_r \\ \theta_s & \text{for} \quad h > \theta_r \end{cases} \tag{10}$$

where θ_r,θ_s,θ_p and θ_n are the range, sill, partial sill and nugget, respectively.

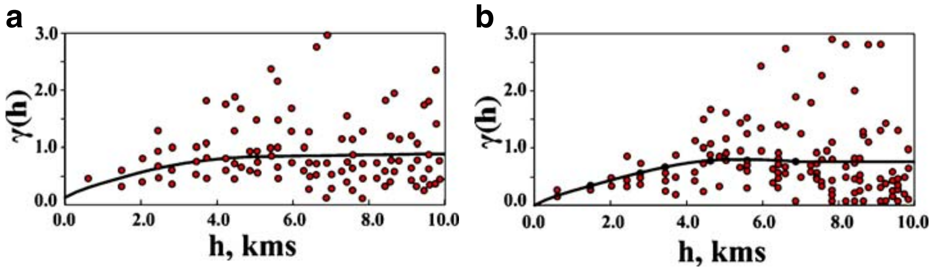


Fig. 8 Semivariogram models of nitrate ground-water levels: **a** winter, **b** summer

The semivariograms show significant spatial continuity in both winter and summer groundwater nitrate levels. This is a reflection of the high stability and mobility of nitrates in groundwater, which facilitate the migration of nitrates untransformed well beyond their source of input given the presence of highly permeable subsurface materials with adequate dissolved oxygen (Canter 1997).

6.4 OKS Estimation of Nitrate Concentration Maps

Applying the OKS to the selected semivariogram models, two prediction surfaces were calculated for the winter and summer nitrate concentrations. The prediction surfaces were limited to a partial area within the ULB (see Fig. 9a, b), which reflects the applicable range of Kriging results determined by the variogram range. This area will be referred to as the study area for the remaining part of this paper. The MSPE and RMSSPE values for the winter prediction surface are −0.067 and 1.041, respectively indicating a relatively insignificant unbiasedness and a good estimation of prediction variability. The MSPE and RMSSPE for the summer prediction surface are 0.039 and 0.625 indicating an insignificant unbiasedness, but a relatively high underestimation of prediction variability, although it is within acceptable limits set by geostatistics practitioners (Cooper and Istok 1988).

The prediction surfaces show highly variable, yet very significant and persistent nitrates contamination of groundwater throughout the basin, which is mainly attributed to leaching from heavily applied fertilizers. However, several areas have excessively high nitrate levels (>100 mg/l), indicating a possible pollution by point sources. For example the highest measured groundwater nitrate concentration value in a well in the ULB for the winter period was found downstream and very close to an industrial and an urban area in the center region of the study area.

Winter and summer contamination spatial patterns are generally similar with the exception of the northern part of the basin. Winter nitrate concentrations are generally higher than those in the summer, which reflects the lag between the application of fertilizers during the rainless season (April–August) to the time nitrates leach into the groundwater. In addition to the timing of fertilizers application, nitrates' leaching is generally affected by the soil porosity, vegetative cover, irrigation practice and rainfall intensity.

In particular, the area extending east from the confluence with the Hala River shows the highest and most extensive groundwater nitrates contamination. This can be attributed to a high agricultural-based pollution loading (see Fig. 4) over the relatively porous sand/gravel deposits that underlay most of this area (see Fig. 2). It can be also noted that maximum nitrate concentrations do no lie immediately below the porous area, but occur few kilometers south and southwest from it. This could be an indication of a nitrates migration path that follows the general south and southwesterly direction of groundwater in the ULB.

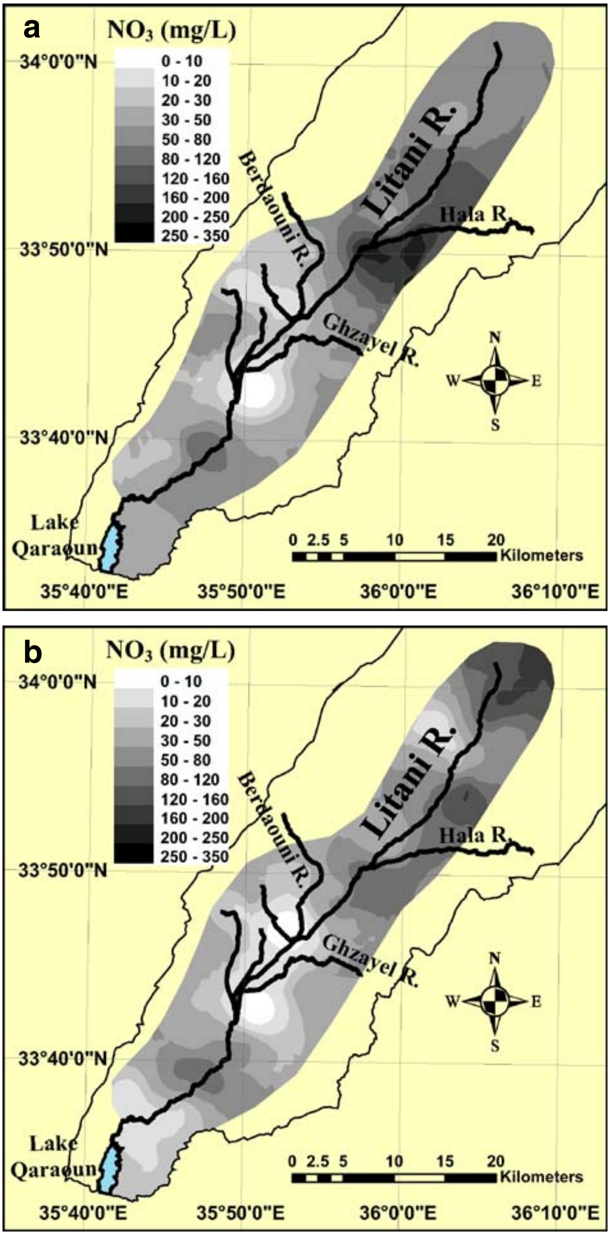


Fig. 9 Nitrate concentration in groundwater in the Upper Litani Basin: **a** winter, **b** summer

Despite extensive agricultural activity, the groundwater in the central section of the basin is the least nitrate-contaminated, which can be directly attributed to the extent and thickness of the highly impermeable alluvial deposits that effectively block the leaching of nitrates to groundwater aquifers. Also, low groundwater nitrate levels in this area can be partially attributed to the minimal agricultural activities in the neighboring upstream areas, which could otherwise contributed to nitrate pollution due to the high porosity of its surface and subsurface layers and the general downward movement of groundwater from high to lower areas.

High groundwater nitrate levels in the lower section of the basin correspond to the area that marks the transition from the alluvial deposits to the highly porous karstified limestone and is characterized by a high level of agricultural activity.

6.5 OKS Estimation of Probability of Exceedance Maps

Groundwater quality can be characterized in terms of its adherence to specific regulatory health environmental standards. In the USA, health regulations call for drinking water supplies to contain no more than 45 mg/l of nitrates. Although the validity of this figure is currently being debated by the environmental health research community (van Grinsven et al. 2006), it is still the de facto standard for drinking water in many parts of the world.

One of the advantages of using Kriging is the ability to provide assessment of the variability of estimates. Using this information, maps showing the probability of groundwater nitrate level exceeding 45 mg/l were generated for winter and summer condition (Fig. 10). In winter, groundwater is most likely unsuitable for drinking in many parts of the ULB, especially in the northern and southern parts. Quality is generally acceptable in the middle section of the basin. The situation is similar, but less extensive and more localized in the summer, with the southern bordering Qaraoun Lake and the middle section maintaining the most potable groundwater conditions.

6.6 Comparison of Geostatistical Results with a DRASTIC Vulnerability Assessment

The BAMAS project involved the development of a DRASTIC vulnerability map for the ULB to identify areas most susceptible to contamination and set priorities for groundwater quality management efforts (BAMAS 2005d). The results from the DRASTIC study are presented for the same area covered by the geostatistical study as shown in Fig. 11.

The most groundwater nitrate-contaminated area northeast of the confluence with Hala River was not clearly identified by the DRASTIC map. However, the pattern of the geostatistical map resembles that of the DRASTIC scores, with a noticeable southwesterly shift. This could indicate that nitrates may have leached into the groundwater in the northeastern section, dominated by the gravel/sand deposits characterized as moderately highly vulnerable by DRASTIC and migrated along with the southwesterly groundwater flow. A similar, but more subtle observation can be made of the southeastern section of the study area, where shift in patterns indicate nitrates migration in a northwesterly direction. These inferences point to the significance of nitrate migration in influencing the distribution of groundwater nitrate

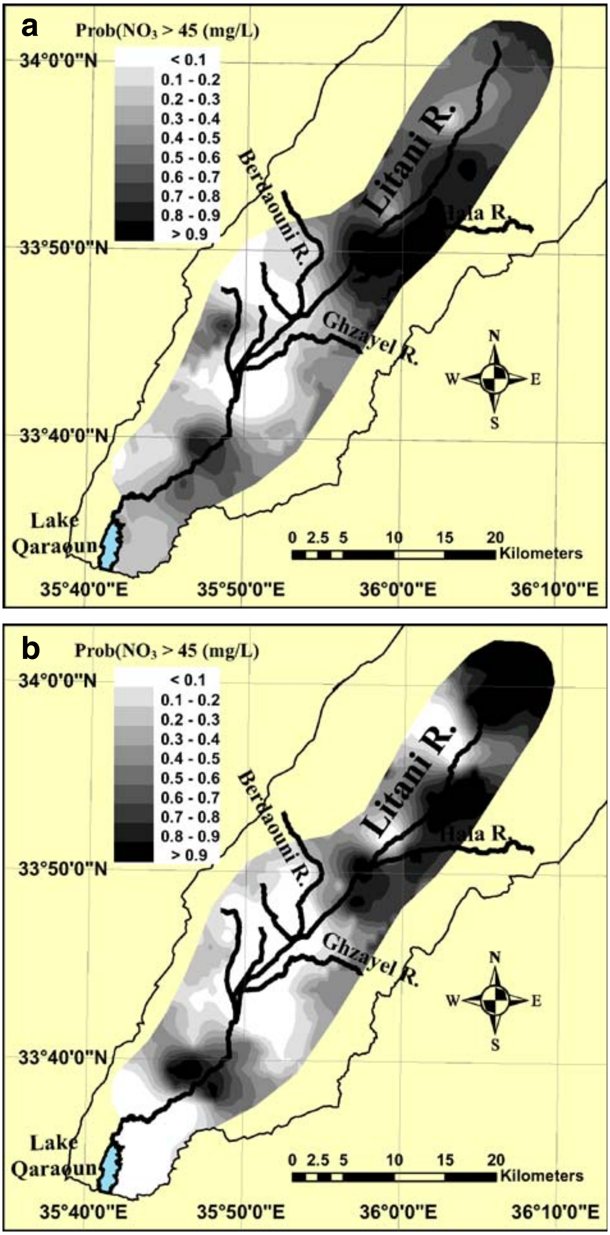


Fig. 10 Probability of exceedance maps of nitrate concentrations in groundwater in the Upper Litani Basin: **a** winter, **b** summer

contamination, whereby highly vulnerable areas, especially in the upper regions, may serve mostly as entry points of pollutants causing much higher concentrations to occur further away from the pollution loading site. These processes are not readily captured by the DRASTIC method, which is designed to identify areas with high potential of facilitating seepage of pollutants into the immediately underlying groundwater.

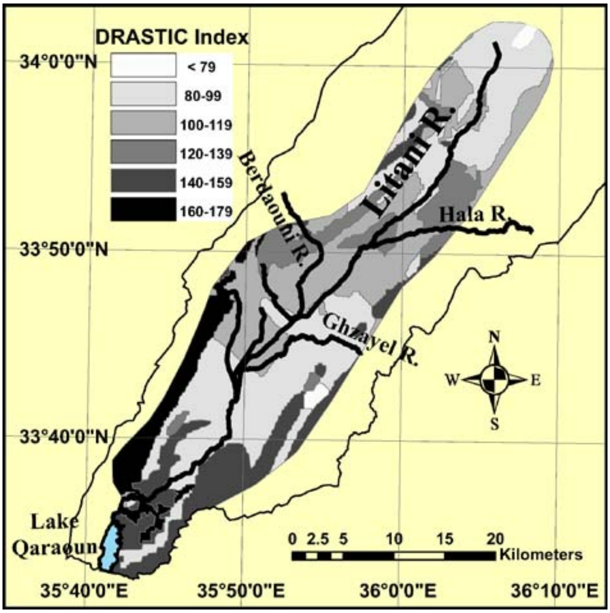


Fig. 11 DRASTIC vulnerability map of the ULB

Low DRASTIC scores for the central section of the study area correspond well with the low groundwater nitrate levels reported by the geostatistical study. This is mainly attributed to the effectiveness of the thick alluviums as a natural barrier against nitrate leaching despite the heavy agricultural activities in the area. This does not however imply that no action is required to control the excessive use of fertilizers in the area since point source pollution could provide a conduit for pollutants to contaminate the underlying groundwater.

Although the southern tip of the basin east of Qaraoun lake has been flagged by the DRASTIC index as a highly vulnerable area, it shows low levels of nitrate contamination, especially in the summer. Lower nitrate levels can be directly attributed to lower agricultural activities, mainly a consequence of unavailability of good quality soil. However, the area was assigned high DRASTIC scores since it is underlain by the highly porous karstified limestone. The same is true for the narrow band of land that extends for few kilometers at the southwestern edge of the study area. This section receives the highest DRASTIC score, yet it shows very minimal groundwater nitrate contamination. Not only does this area support few human activities, but it receives very high quality groundwater from the upper unpopulated reaches of the basin.

7 Summary and Conclusions

The paper presents an assessment of groundwater quality conditions in the Upper Litani Basin based on geostatistical analysis of sampled nitrate levels representing winter and summer seasons of year 2005. The dataset was compiled from the outcome of an extensive sampling campaign that covered 60 sites across the basin. The paper provides a summary of geostatistics principles and methodology. Ordinary Kriging, a key geostatistical tool, was used to produce georeferenced maps showing distribution of nitrate levels and probability of exceeding drinking water standards.

The results indicate significant and widespread nitrate contamination of the basin groundwater mainly attributed to leaching from excessive application of fertilizers, with a strong possibility of point source pollution. Winter nitrate levels are generally higher than summer ones signifying the lag between fertilizer application and groundwater contamination.

Groundwater is deemed unpotable for many areas in the basin, specifically in the winter and in certain sections. In contrast, groundwater in the middle section of the basin shows much lower nitrate levels, especially in the summer, which meet potable water standards.

Results from the geostatistical assessment study were compared against those from a DRASTIC vulnerability assessment conducted through the BAMAS project. Although vulnerability relates to the potential of contamination, which is conceptually distinct from the current contamination levels estimated by the geostatistical approach, the comparative analysis of the two studies provided an insight into the nitrate contamination processes and the value and limitations of the DRASTIC method, which can be summarized as follows:

The DRASTIC score of a given area is a measure of the area's potential to facilitate downward seepage of pollutants to underlying groundwater and does not consider the migration of pollutants to groundwater in other areas. This however does not negate the value of DRASTIC as a water quality management tool since mitigation measures are generally designed to reduce the potential of contamination at the entry area.

DRASTIC scores are frequently counter-correlated with existing groundwater nitrate contamination levels, since the latter are strongly associated with agricultural activities which are in turn highly dependant on soil and subsurface media types with low DRASTIC scores. Alluviums, which score low on the DRASTIC scale are the most extensively cultivated and irrigated soils due to their high fertility and water retention. In contrast leaky karstified limestones which can hardly sustain any significant agricultural activities, attain the highest DRASTIC scores.

DRASTIC approach does not account for the effect of anthropogenic effects including irrigation, change of top layers characteristics, and the formation of point pollution pathways. In particular irrigation in semi-arid parts of the world plays a critical role in facilitating leaching of nitrates and other contaminants during the drier times of the year.

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