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ORIGINAL ARTICLE

Vulnerability assessment of urban groundwater resources to nitrate: the case study of Mashhad, Iran

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Abstract Groundwater vulnerability assessment of urban areas is a challenging task in the fast trend of urbanization around the globe. This study introduces a new approach for modifying well-known parameters of common vulnerability indexes to adjust them for urban areas. The approach is independent of a specific weighting system. The aquifer of Mashhad city, contaminated by domestic wastewater, is selected as a case in this study. In order to evaluate the aquifer vulnerability due to anthropogenic activities, at first, parameters of depth to groundwater, recharge, land use, and soil are modified based on their basic concepts and their influences on contamination attenuation. Then, the modified parameters are used simultaneously in several index methods to investigate the capability of the modified parameters to increase correlation coefficient of all employed index methods with the measured nitrate concentration. Accuracy of the modified methods is evaluated by Spearman nonparametric correlation. It is shown that considering the wastewater discharge into recharge parameter leads to an increase of 20% in correlation coefficient. Also, level difference technique shows that more than 70% of the vulnerable areas are predicted correctly in all utilized methods. The accurate prediction in all employed methods indicates that these modifications are independent of the type of index method. Moreover, sensitivity analysis reveals that the recharge and the land use are both the most significant parameters for evaluating the vulnerability.

Keywords Vulnerability mapping · DRASTIC · Geographic information systems (GIS) · Nitrate contamination

Introduction

In arid and semiarid regions, the major part of drinking water is supplied by groundwater resources. Due to the high dependency on groundwater, degradation of groundwater quality is a serious concern in many parts of the world (Li and Merchant 2013; Kazemi 2011). Groundwater is susceptible to contamination from land use, anthropogenic impacts and other surface sources (Sener et al. 2009). Thus, the prevention of the groundwater contamination (Huan et al. 2012) and delineation of the vulnerable regions (Brindha and Elango 2015) are essential for protecting these vital resources.

Groundwater vulnerability is referred to the tendency or likelihood for contamination to reach a specific position in groundwater after introducing in uppermost of the aquifer (Thirumalaivasan and Karmegam 2001), and it calculates the sensitivity of the groundwater quality to an imposed contaminant load which is considered as a fundamental aspect of groundwater management (Raju et al. 2014). It is classified into intrinsic, which depends on the hydrogeological characteristics of the aquifer (Frind et al. 2006), and specific, which studies the vulnerability to particular contaminant or a group of pollutants (Zwahlen 2004).

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There are three general categories for assessing the groundwater vulnerability and contamination: statistical methods, process-based simulation models, and overlay index methods (Dixon 2004). The overlay index methods are relatively simple methods which can be applied from regional to global scale (Brindha and Elango 2015). They are based on the aquifer's characteristics such as hydrogeological characteristics that are dominant in groundwater contamination. Nitrate contamination of groundwater is one of the main sources of groundwater contamination in particular by agricultural activates and domestic wastewater (Joekar-Niasar and Ataie-Ashtiani 2009). The correlation of measured nitrate and index method has been regarded as an indicator for assessing the groundwater vulnerability methods (Javadi et al. 2011) since nitrate is not generally present in groundwater under the natural condition.

Specific and intrinsic aquifer vulnerability has been studied in various researches using different index methods such as DRASTIC, pesticide DRASTIC, modified DRASTIC, modified pesticide DRASTIC, susceptibility index (SI) (Leal and Castillo 2003; Ahmed et al. 2015; Neshat et al. 2014; Brindha and Elango 2015; Assaf and Saadeh 2009; Ahmed 2009). DRASTIC method, which evaluates intrinsic vulnerability, is more popular than other methods (Almasri 2008) as it is capable to compatible with various aquifer types such as fractured bedrock (Denny et al. 2007), karstic, sedimentary, carbonate (Brindha and Elango 2015). Joekar-Niasar and Ataie-Ashtiani (2003) proposed an assessment approach based on the modified DRASTIC (Aller et al. 1987) for domestic wastewater source in urban areas. However, recently groundwater specific vulnerability is become more meaningful than intrinsic vulnerability, as the extensive human activates may change some of the effective factors of the intrinsic vulnerability (Huan et al. 2012). Saidi et al. (2011) assessed the vulnerability and risk of groundwater contamination and modified the conventional weighting system by conducting sensitivity analysis. Huan et al. (2012) rebuilt the index system by correlating the parameters of the model to nitrate concentration and then assessed the groundwater vulnerability with modified model which incorporates the land use. Brindha and Elango (2015) indicated that sensitivity analysis of vulnerability index maps reveals the importance of one parameter over other parameters.

Generally, the researchers in the previous studies first selected a particular index and then tried to modify it by changing the rates and weights of each parameter to obtain better correlation with measured nitrate. However, this issue highly depends on the type of index they select and may not be consistent with other index methods. The main objective of this study is to propose a new perspective for modifying well-known parameters of common indexes to adjust them for urban areas, regardless of the weighting system that is applied.

Study area

Mashhad, the capital city of Khorasan-e-Razavi Province, is the second most populous city in Iran. It is divided into 13 municipal districts or 45 municipal sub-districts (Lashkaripour et al. 2014). The population of Mashhad is 3,131,586, and its area is 280 km^2 (Planning and Development Department of the Mashhad Municipality 2014). It is a holy city and is best known for its pilgrimage shrine of Imam Reza. It is estimated that over 20 million pilgrims visit the tomb of Imam Reza each year (Tandise 2013). The Mashhad plain, located in the northeastern part of Iran (Fig. 1), covers an area of 6131 km^2, extending from 35°59′–37°04′N and 58°22′–60° 07′E and including Mashhad City. The elevation of the plain varies from 900 to 1500 m with an average of 1200 m above mean see level (Tandise 2013). The average elevation of the Mashhad City is 980 m above sea level. The south, west, and southwest parts of Mashhad have higher elevation than other parts.

The main river of Mashhad plain is Kashaf-rud River which once flowed from northwest to the southeast. It also crosses the northern border of Mashhad city. The river is dry now, and water flow only in small parts of the downstream of the river which are distant from Mashhad city. The direction of the groundwater flow is mainly from northwest to southeast. Further, in the southern high elevations, the groundwater flow direction is targeted to the southeast and northeast. Generally, the groundwater depth increases with the decrease in distance from Kashaf-rud (which is the thalweg of the Mashhad plain) toward high elevation.

The average annual precipitation is 219.35 mm in the arid and semiarid climate of Mashhad. There are some limited parks and recreational applications in the city. Mashhad city is developed over alluvial fans which are good sources of groundwater; however, rapid urban development, over 20 million visit by pilgrims, and lack of effective sewer collection network deteriorate the groundwater quality (Kazemi 2011). In 2001, water consumption per capita was 210 L, 70% of which was turn into wastewater. Municipal districts have not had sewer collection network and have used septic tanks and cesspits, similar to many other large cities in Iran (e.g., Joekar-Niasar and Ataie-Ashtiani 2009), except for new municipal districts such as western and some parts of eastern districts which recently have been equipped with sewer collection network.

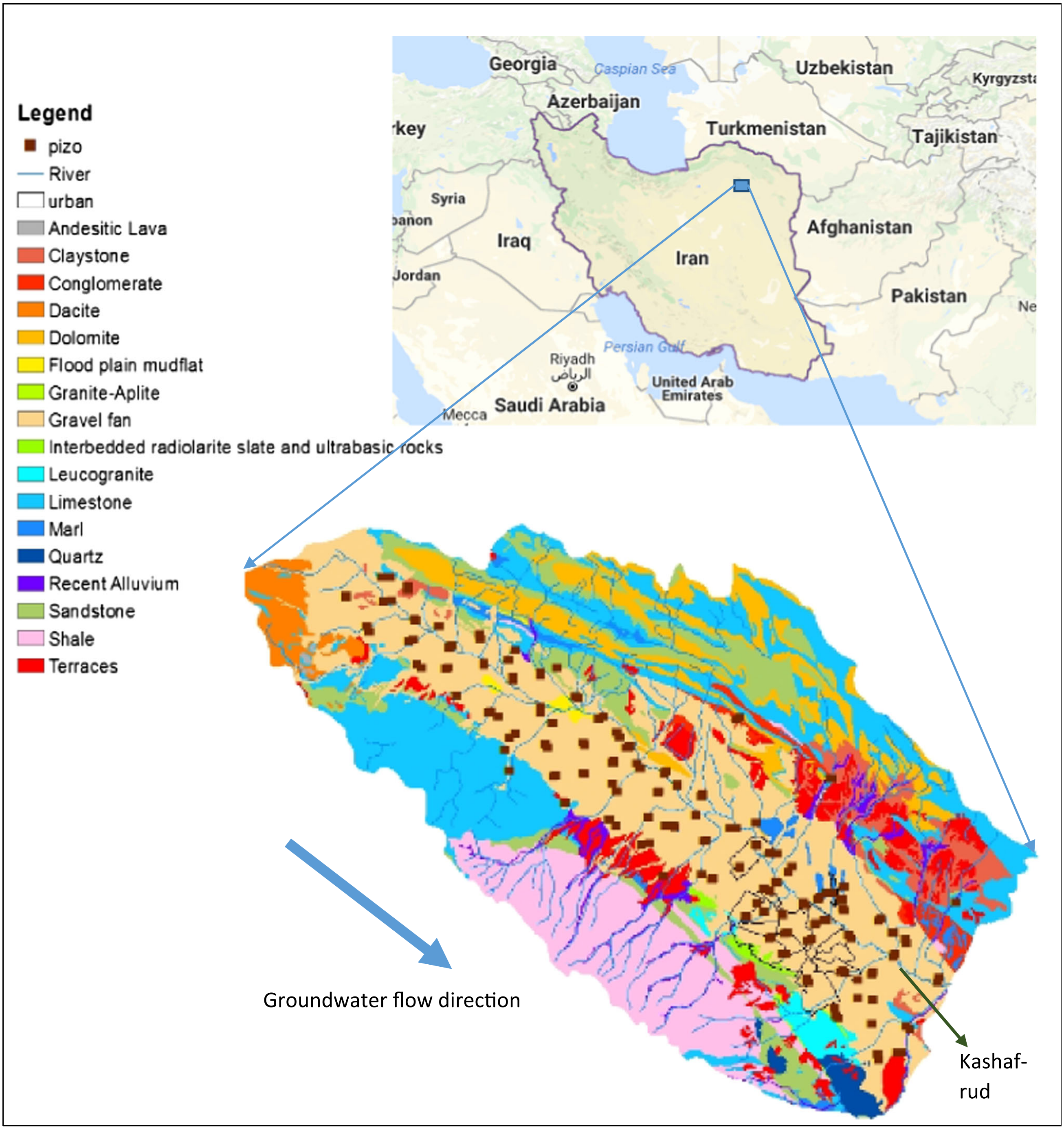


Fig. 1 Location of study area and monitoring points (piezometers) in Mashhad plain

Methodology

A number of groundwater contamination vulnerability methods are utilized in this section. A key attention in this study is to modify recharge, land use, and soil parameters based on their concepts and their influences on contamination attenuation to yield improvement in all of the employed index methods, independent from weighting system. Then, the modified parameters are used simultaneously in several index methods to investigate the capability of the modified parameters to increase the correlation coefficient of all index methods with measured nitrate. After that, level difference is used to classify indexes and finally sensitivity analysis is applied to designate the contribution of the important parameters in groundwater contamination.

DRASTIC methods and modified DRASTIC method

One of the most common overlay index methods for evaluating groundwater contamination is the DRASTIC method which considers three major elements: rate, range, and weight (Aller et al. 1987). DRASTIC model identifies vulnerable zones based on the seven parameters representing hydrogeological features of the aquifer including: depth to groundwater (*D*), recharge (*R*), aquifer media (*A*), soil media (*S*), topography (*T*), impact of vadose zone (*I*), and hydraulic conductivity of the aquifer (*C*). The corresponding ratings for parameters ranges (*r*) are multiplied by the weight of each parameter (*w*) in GIS framework, and they finally added up according to Eq. (1) to create the DRASTIC vulnerability index:

$$\text{DRASTIC index} = D_rD_w + R_rR_w + A_rA_w + S_rS_w + T_rT_w + I_rI_w + C_rC_w \tag{1}$$

Values of ‘*w*’ range from 1 to 5; 5 is assigned to most significant parameters, whereas 1 is assigned to least significant parameters. Similarly, the values of ‘*r*’ range from 1 to 10 depending on the vulnerability potential. There are two types of DRASTIC: Generic DRASTIC (Aller et al. 1987) is applied in normal condition, and pesticide DRASTIC (Aller et al. 1987) is applied to consider the effect of pesticides on groundwater. Both are calculated using Eq. 1. The only difference between DRASTIC models is the values of ‘*w*’. The modified index (Secunda et al. 1998) is calculated using Eq. 2 to consider the effect of anthropogenic activities on groundwater. Tables 1 and 2 show the values of ‘*r*’ and ‘*w*’ which are used to obtain each indexes.

$$\text{Modified DRASTIC index} = \mathit{DRASTIC}\text{index} + \text{LU}_r\text{LU}_w \tag{2}$$

where LU is the land use parameter. The calculated index represents the relative measure of the groundwater vulnerability. The higher index attributed to each region shows the more tendency to contamination.

Susceptibility index (SI) method

The main differences between the SI method defined by (Ribeiro 2000) and DRASTIC index are the elimination of vadose zone, hydraulic conductivity, and soil type and the inclusion of land use. Land use is employed in SI method to show the anthropogenic activities which is an important factor in groundwater contamination. SI identifies the vulnerable zones based on five parameters including: depth to groundwater (*D*), recharge due to rainfall (*R*), aquifer media (*A*), topography (*T*), and land use (LU). SI is obtained as follow:

$$\text{Susceptibility index} = D_rD_w + R_rR_w + A_rA_w + T_rT_w + LU_rLU_w \tag{3}$$

Tables 1 and 2 present the values of ‘*w*’ and ‘*r*,’ respectively. For generating the layers and calculating the final index, the same steps as in the DRASTIC index are implemented.

Sensitivity analysis

A type of sensitivity analysis is employed to designate the contribution of important parameters in groundwater contamination. In this section, sensitivity analyses are conducted on DRASTIC, pesticide DRASTIC, modified DRASTIC, and SI by map removal sensitivity analysis and single parameter techniques.

Map removal sensitivity analysis

In this step, reaction of the system due to the change in an input parameter is evaluated and the importance of using each parameter in generating the vulnerability index maps is determined. Equation 4 (Lodwick et al. 1990) calculates map removal sensitivity analysis:

$$S = \left| \frac{\left(\frac{V}{N}\right) - \left(\frac{v}{n}\right)}{V} \right| \times 100 \tag{4}$$

where *S* is the sensitivity measure expressed in terms of variation index, *V* is the unperturbed vulnerability index,

Table 1 Parameters and weightage used for models (Aller et al. 1987; Ribeiro 2000)

Parameter	DRASTIC	Pesticide DRASTIC	SI	Modified DRASTIC
Depth to groundwater (*D*)	5	5	0.186	5
Net recharge (R)	4	4	0.212	4
Aquifer media (*A*)	3	3	0.259	3
Soil media (*S*)	2	5		2
Topography (*T*)	1	3	0.121	1
Impact of vadose zone (*I*)	5	4		5
Hydraulic conductivity (*C*)	3	1		3
Land use (L)			0.222	5

Table 2 Rates which are used to obtain indexes

Depth to groundwater (*D*)		Recharge (*R*)		Aquifer media (*A*)	
Range (m)	Rate	Piscopo rate	Rate	Range	Rate
>30	1	3–5	1	Massive shale	2
22.5–30	2	5–7	3	Thin bedded sandstone limestone	3–4
15.2–22.5	3	7–9	5	Massive sandstone	6–7
9.1–15.2	5	9–11	8	Sand and gravel	8
4.6–9.1	7	11–13	10		
1.5–4.6	9				
0–1.5	10				

Soil (*S*)		Topography (*T*)		Vadose zone (*I*)	
Range	Rate	Range (%)	Rate	Range	Rate
Asphalt pavements, thoroughfares	1	>18	1	Clay/silt	1
Peat	8	12–18	3	Shale	3
Building roofs	10	6–12	5	Sand and gravel with significant silt and clay	5
		2–6	9	Sandstone	6
		0–2	10	Sand and gravel	8

Hydraulic conductivity (*c*)		Modified land use	
Range (m/day)	Rate	Range	Rate
0–4.1	1		
4.1–12.2	2	New districts that have been included in city borders since 2005	3
12.2–28.5	4	The districts populated from 1951 to 2005 which have lower pilgrim density	5–8
28.5–40.7	6		
40.7–81.5	8		
>81.5	10	Original core, old district with no sewer system	10

Aller's rates were used for rating of depth to groundwater (*D*), aquifer media (*A*), topography (*T*), vadose zone (*I*), and hydraulic conductivity (*C*), and other parameters were rated based on modifications in this study

v is the perturbed vulnerability index, N is the number of data layers used to compute V, and n is the number of data layers used to compute v. Unperturbed is an index that incorporates all parameters. Perturbed vulnerability index has lower number of parameters than unperturbed vulnerability.

Single parameter sensitivity

Using single parameter sensitivity, the theoretical weight assigned in the model is compared to the effective weight of each parameter since the weights used to compute the vulnerability index can be differed depending on the properties of the study area of interest (Babiker et al. 2005). Also, impact of each parameter on the groundwater vulnerability index is assessed based on the single parameter sensitivity analysis (Napolitano and Fabbri 1996) as follows:

$$W = \frac{(Pr \times Pw)}{V} \times 100 \tag{5}$$

where W is the effective weight of each parameter, Pr is the rating value of parameter, Pw is its weight, and V is the overall vulnerability index.

In this work, DRASTIC method is used because it considers all hydrological parameters which are important for assessing the intrinsic vulnerability. Pesticide DRASTIC is used to model the vulnerability due to the large amount of fertilizers and pesticides used for artificial parks and green spaces. SI and modified DRASTIC are modeled to determine the impact of anthropogenic activities, especially the land use. Furthermore, the indexes are validated with measured nitrate to investigate the goodness of the correlation of these methods with measured data. Finally, sensitivity analyses are performed on aforementioned models to determine influential parameters.

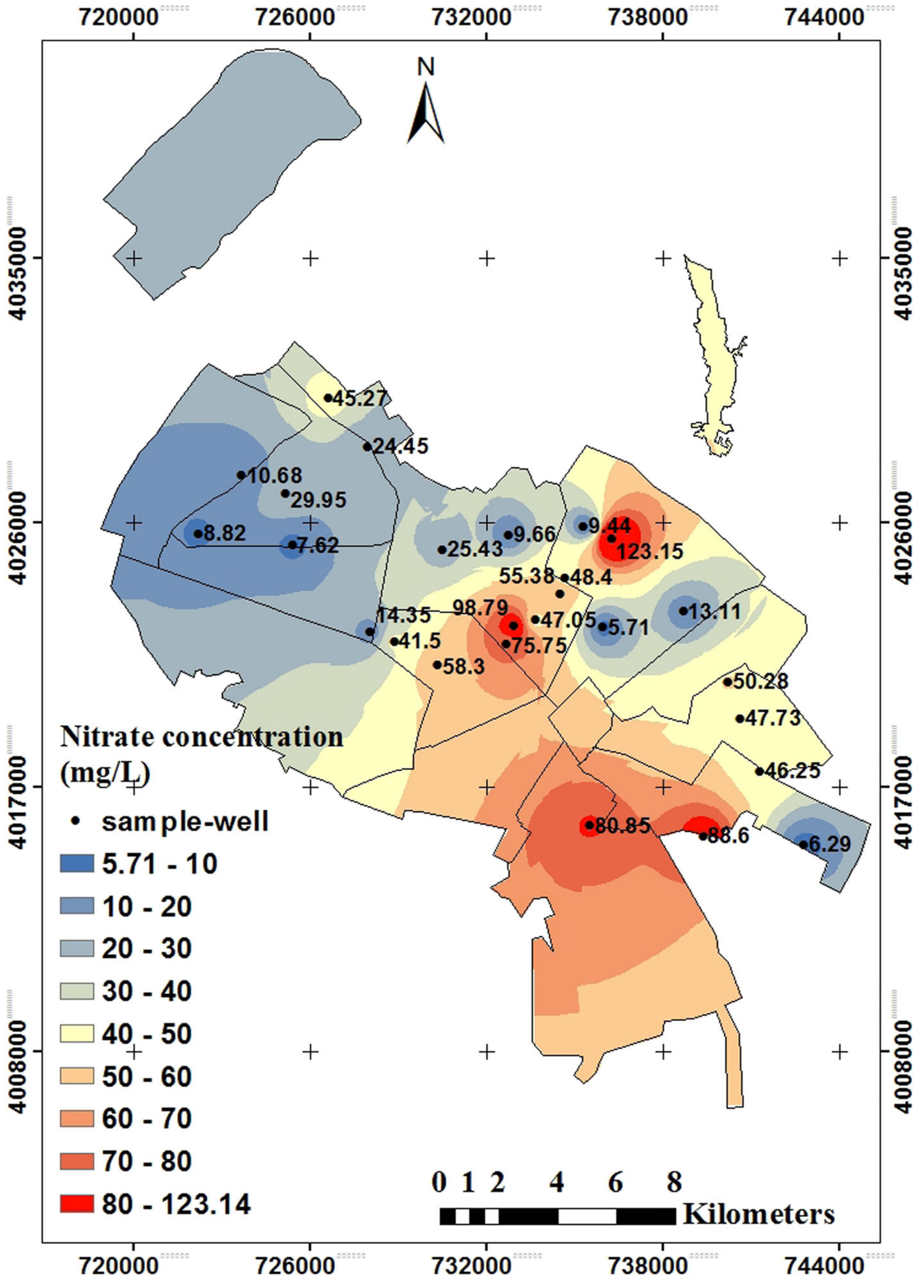


Fig. 2 Nitrate sampling wells and the values of nitrate concentration data (mg/l). *The numbers indicate nitrate concentration data

Results and discussion

Preparation of various maps

In this section, the collected nitrate concentration data and rating of each parameter used in index methods are described.

Nitrate concentration map

Nitrate concentration data of Mashhad collected during 2001 was obtained from (Research Committee of Regional Water Authority of Khorasan 2004; Dolati 2010). The location of sample wells and nitrate concentration values are shown in Fig. 2. The nitrate concentrations were interpolated over entire area with the inverse distance weighting (IDW) method. The obtained layer was divided into five category: 5—high (50–123 mg/l); 4—moderate high (40–50 mg/l); 3—Moderate (20–40 mg/l); 2—moderate low (10–20 mg/l); 1—low (5.7–10 mg/l). The maximum nitrate concentration was observed in central and some parts of northern district, and the least contaminated districts were located in the northwest. Maximum permissible limit for nitrate in drinking water is 10 mg/L NO_3–N (the World Health Organization).

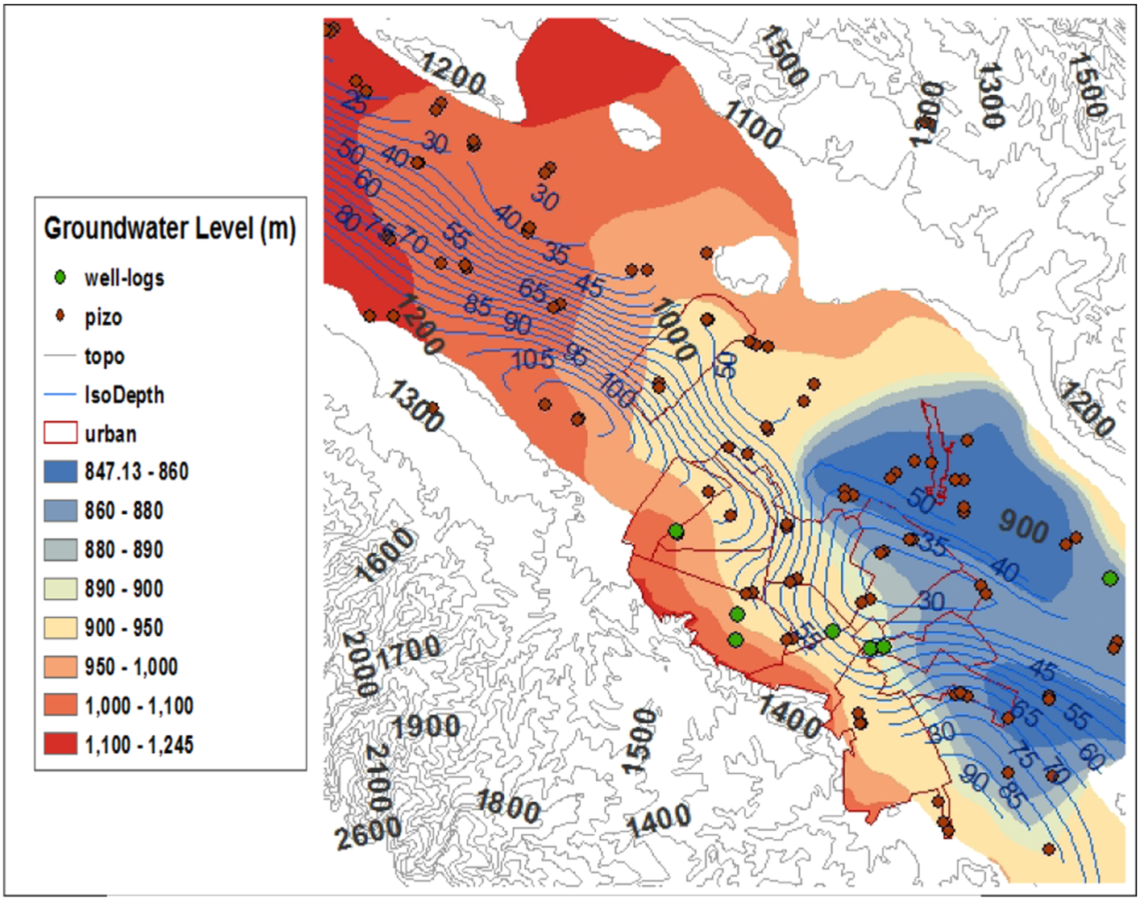


Fig. 3 Groundwater level and iso-depth contours (m), well logs, and topographic contours (m)

Depth to groundwater

Depth to groundwater refers to distance from ground surface to the groundwater table (Aller et al. 1987). Depth to groundwater is an important parameter for assessing groundwater contamination because an increase in travel time led to contaminant attenuation (Aller et al. 1987). In this study, 80 wells (Fig. 3) in Mashhad plain were monitored and water table data were collected by Regional Water Authority of Khorasan (2001), and finally depth to groundwater layer was generated by inverse distance weighting (IDW) interpolation method. Generally, in Mashhad, depths to groundwater are deep, and approximately in all parts of the study area it has the values of more than 30 m. The lowest values of the depth to groundwater (26–30 m) were found in the northeast, and the highest values (95–107 m) were located in some parts of the northwest and the south. Depth to groundwater layer is shown in Fig. 4a. The ratings 1 and 2 were assigned to depth to groundwater according to the Aller's rates which are presented in Table 2. However, in urban areas the most amount of recharge penetrate from septic tanks, so it is preferable to consider distance of septics to groundwater instead of depth to groundwater, as suggested by Joekar-Niasar and Ataie-Ashtiani (2009) in the case of nitrate contamination in unsaturated zone of urban areas in Tehran, Iran. In this case study, because most of the area have deep groundwater table (more than 30 m), subtracting the depth of septics from depth to groundwater do not affect the rate of this parameter. Figure 4b shows the rates of reduced depth to groundwater; conversely, in shallow aquifer small change in depth to groundwater may change the rate of this parameter. It is recommended that this subtraction be considered in shallow aquifers.

Net recharge

The amount of water penetrated into aquifer is presented by the net recharge parameter (Aller et al. 1987). It is important because it carries the contaminant vertically into the groundwater (Aller et al. 1987). Since artificial recharges add significant volume of water, they should be considered in evaluating net recharge parameter. In this regard, wastewater discharge is considered using information of population, areas, spatial distribution of population (Planning and Development Department of the Mashhad

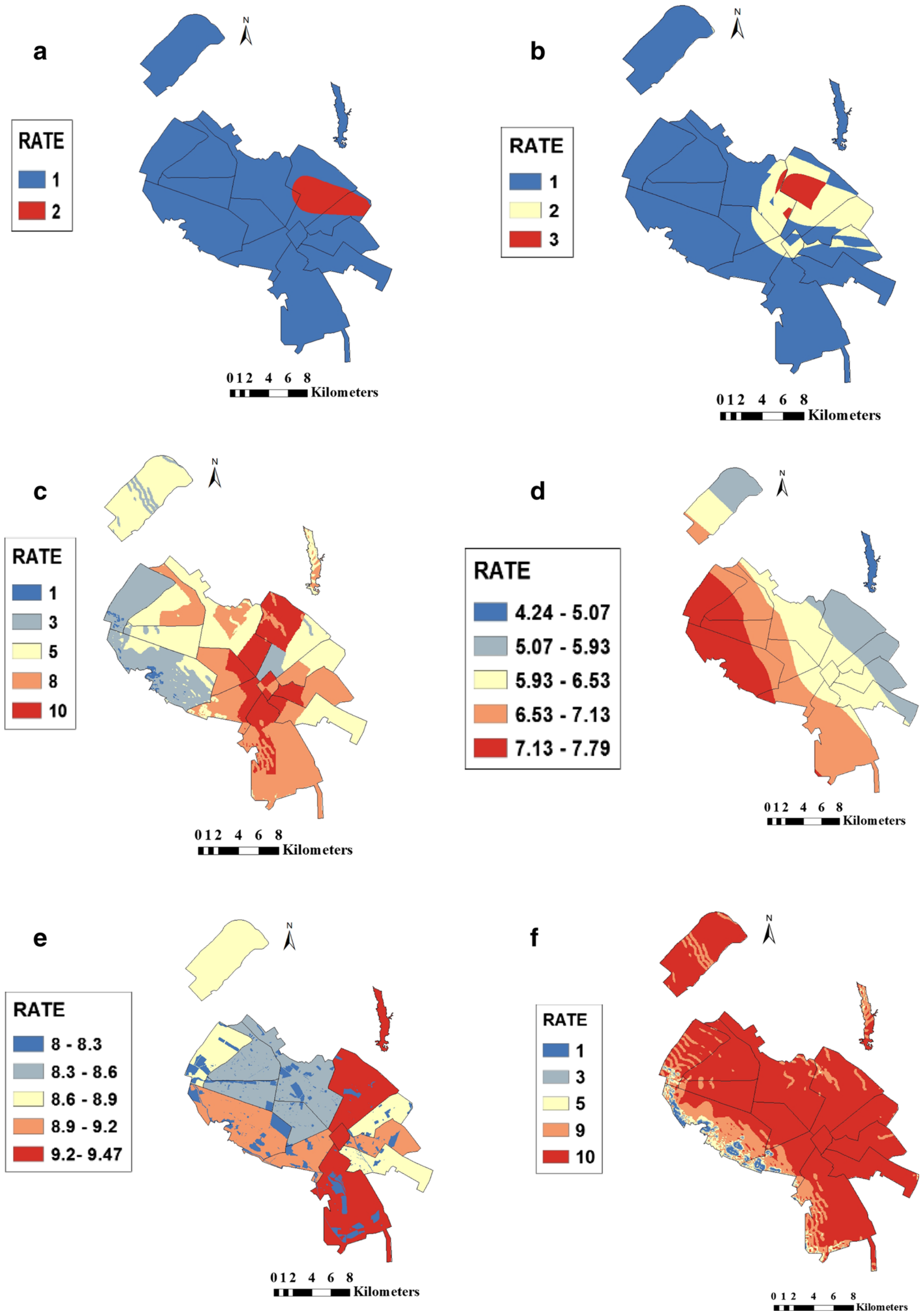
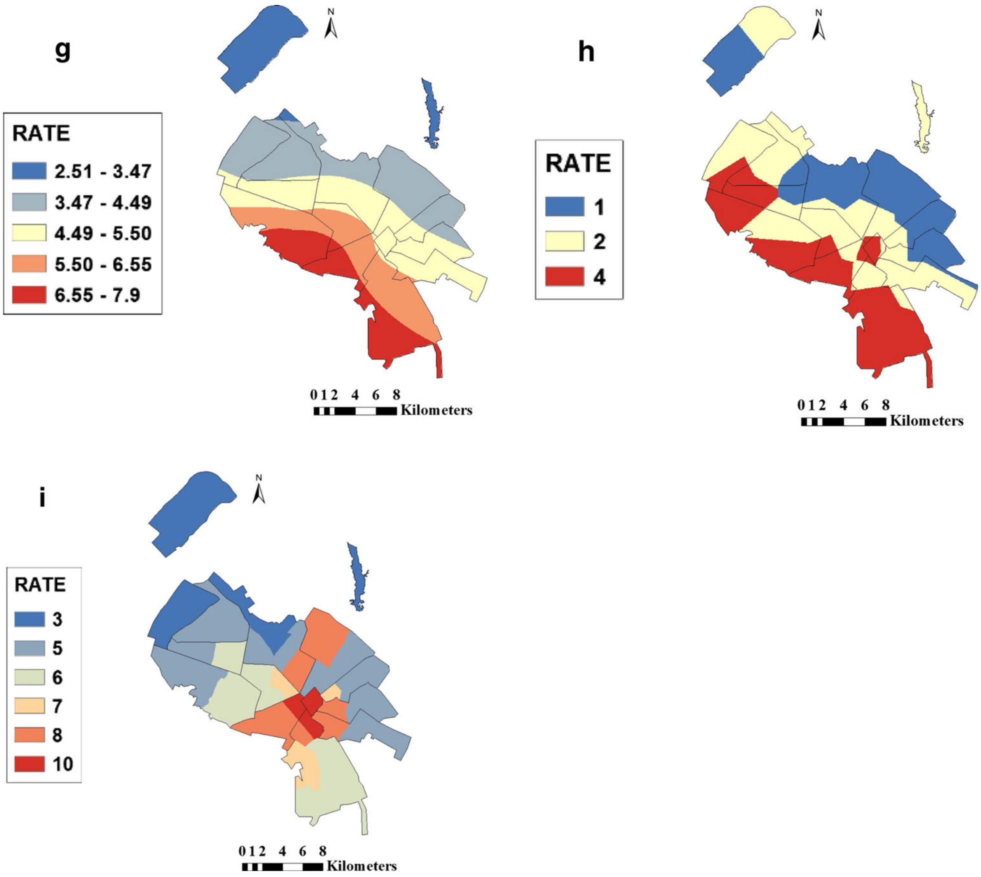


Fig. 4 Assigned rates; **a** depth to groundwater, **b** reduced depth to groundwater, **c** net recharge, **d** aquifer media, **e** soil media, **f** topography, **g** vadose zone, **h** hydraulic conductivity, and **i** land use

Municipality 2014), and wastewater generation rate per capita (Regional Water Authority of Khorasan 2001); also, the recharge by rain water was considered in parks, green spaces, and building roofs. In each municipal district, coverage rate is obtained using weighted average technique which is explained in 'Soil media' section. Then, to obtain the amount of water rainfall, coverage rate was multiplied by rainfall layer generated using Kriging interpolation with data of Regional Water Authority of Khorasan (2001).

The net recharge for each municipal district was calculated using Piscopo method (Piscopo 2001). The unitless values of rainfall and wastewater discharge were assigned 1–4. The central and some northern parts have highest values due to excess wastewater discharge. Similarly, the topographic unitless values varying from 1 to 4 were assigned. Soil permeability was classified into five groups ranging from 'very low' to 'high' (1–5). According to ranges of Piscopo, unitless values were assigned to each of

Fig. 4 continued



three parameters based on their ability to increase the recharge value (RV) potential. Finally, recharge value layer was achieved by the following equation:

$$\mathrm{RV} = \mathrm{RA} + T + \mathrm{SP} \tag{6}$$

where RA is the rainfall and wastewater discharge unitless value, T is the topographic unitless value, and SP is soil permeability unitless value. The ratings of 1–10 were obtained for net recharge which are presented in Fig. 4c. The southern and south western parts have the lowest rating (1 and 3), and the central and eastern parts have the highest net recharge.

Aquifer media

Aquifer media refer to the soils with generally high permeability such as sand and gravel aquifers (Aller et al. 1987). In this work, DRASTIC layer of aquifer media was generated using the map of Mashhad aquifer (Lashkaripour et al. 2014) and Kriging interpolation of the well logs data obtained from Regional Water Authority of Khorasan-e-Razavi (2012). The location of wells is shown in Fig. 3. Mashhad alluvial aquifer is unconfined. Lithologically, the aquifer gradation changes gradually from coarse in western and southern parts to fine in eastern and northern parts. Clay is the main constitution of lithology in the eastern and northern well logs, while in the southern and southwestern parts the main constitution of lithology is sand with little amount of clay. According to Table 2, relatively high DRASTIC rates (6–8) were assigned to the southern, western, and southwestern parts. However, toward east, the DRASTIC rates decrease such that the lowest value (the rate of 4) was assigned to the eastern parts (Fig. 4d).

Soil media

Soil media refer to top level of the vadose zone. The purpose of using soil parameter in the DRASTIC method was to consider the ability for absorption, storage, and penetration of water into deeper depth. In fact, the main goal of using this parameter is related to storage capability and ability of conducting water into the groundwater.

Because the study area is urban and surface soil is covered by buildings, streets, sidewalk, etc., the conventional rating system according to soil types is not realistic, and it needs to take the urban texture into account. In this study, this layer was created considering that which part of the area is capable of collecting water and which part is capable of conveying it as runoff (such as asphalt pavements, thoroughfares, streets). So, the urban area was divided into two main parts using the maps provided in Planning and Development Department of the Mashhad Municipality (2014).The first part includes streets and building roofs, while the second part includes parks and green spaces. Because streets are assumed impermeable, the rate of 1 was assigned to them. Moreover, the rate of 10 was assigned to the building roofs because they act like funnels conveying water into cesspits, abruptly. Using weighted average technique (in terms of area covered by streets and roofs), the rates of DRASTIC were obtained (coverage rate). In second part, the soil types considered to be peat for parks and green spaces. Hence, the rate of 8 was assigned to this part (Fig. 4e).

Topography

Topography refers to the slope of the region, which influences the time period for infiltration. Lower slopes provide a more opportunity for contaminant to infiltrate. Thus, higher rating values were assigned to them. Slope layer was generated using contour layer obtained from Regional Water Authority of Khorasan-e-Razavi (2012). The rates (Aller et al. 1987) were assigned to slope layer based on Table 2. Almost all parts of the study area were assigned the rate of 10 (Fig. 4f).

Vadose zone

Vadose zone refers to the above horizon of groundwater table which is generally unsaturated (Aller et al. 1987). To generate vadose zone layer, the map of Mashhad vadose zone (Lashkaripour et al. 2014) and the data of well logs (which are presented in Fig. 3) obtained from Regional Water Authority of Khorasan-e-Razavi (2012) were used and rated (Table 2) according to (Aller et al. 1987). Vadose zone media change gradually from coarse aggregate in west and south to fine in east and north. Therefore, the DRASTIC rates vary between 2 and 8. The rate of 8 was assigned to the most vulnerable areas (western parts) and vice versa (Fig. 4g).

Hydraulic conductivity

Hydraulic conductivity is the ability of an aquifer to convey water (Aller et al. 1987). So, it determines the velocity of contaminant movement through the aquifer. The reliability of this parameter is very small because of its high spatial variability. Hydraulic conductivity was generated by comparing and using maps in Tandise (2013) and Environmental Research Center of Khorasan-e-Razavi (2007). The hydraulic conductivity of the study area includes three parts (Fig. 4h): less than 4.1 m/day (with a rating of 1), between 4.1 and 12.2 m/day (with a rating of 2), and between 12.2 to 28.5 m/day (with a rating of 4).

Modified land use

Land use is one of the most crucial factors that can negatively affect groundwater quality through anthropogenic activities (Ribeiro 2000; Lavoie et al. 2015). In conventional methods such as SI, one rate is assigned to entire urban land use types (the rate of 75 is assigned to continuous urban areas, airports, harbors, roads (rail), areas with industrial or commercial activity, laid out green spaces). This is valid when the study area is large scale and includes urban, agriculture, and natural areas. However, when the study area is small scale, the conventional rating system cannot show the complex human activities in urbanized regions. Hence, a more accurate rating system for the land use is needed.

In this regard, the map and information of Mashhad borders as well as its development presented in Planning and Development Department of the Mashhad Municipality (2014) (which contains old urban texture map, last version of urban boundary, and information of Mashhad) and Dolati's study (2010) (which contains urban area boundary from 1951 to 2005) were employed to modify the land use. The rate of 10 was assigned to original core and old texture of the city district as it has not equipped with sewer system yet. Also, high number of pilgrims travel to this district regularly due to the presence of holy shrine. The rate of 8–5 was assigned for the districts populated from 1951 to 2005 because they are relatively newer districts and the pilgrim density is lower. The rate of 3 was assigned to new districts since they have included in city borders after 2005 (Fig. 4i).

Application and classification of vulnerability assessment models

Vulnerability map indexes were obtained by multiplying the rated layers by individual weighting factor and summing the results according to Eqs. 1, 2, and 3. As shown in Fig. 5a, DRASTIC indexes were obtained in the range of 74–142. Relatively low vulnerable indexes were located in some parts of north, northeast, and northwest where the aquifer and vadose zone were rich in fine aggregate resulting in high pollutant attenuation capacity. Higher vulnerable indexes were located in south, southeast, and center where the aquifer and vadose zone are constituted of coarse aggregates resulting in low pollutant attenuation capacity.

As shown in Fig. 5b, pesticide DRASTIC index varies between 96 and 179. The relatively low vulnerable indexes were located in northwest, some parts of southwest, and

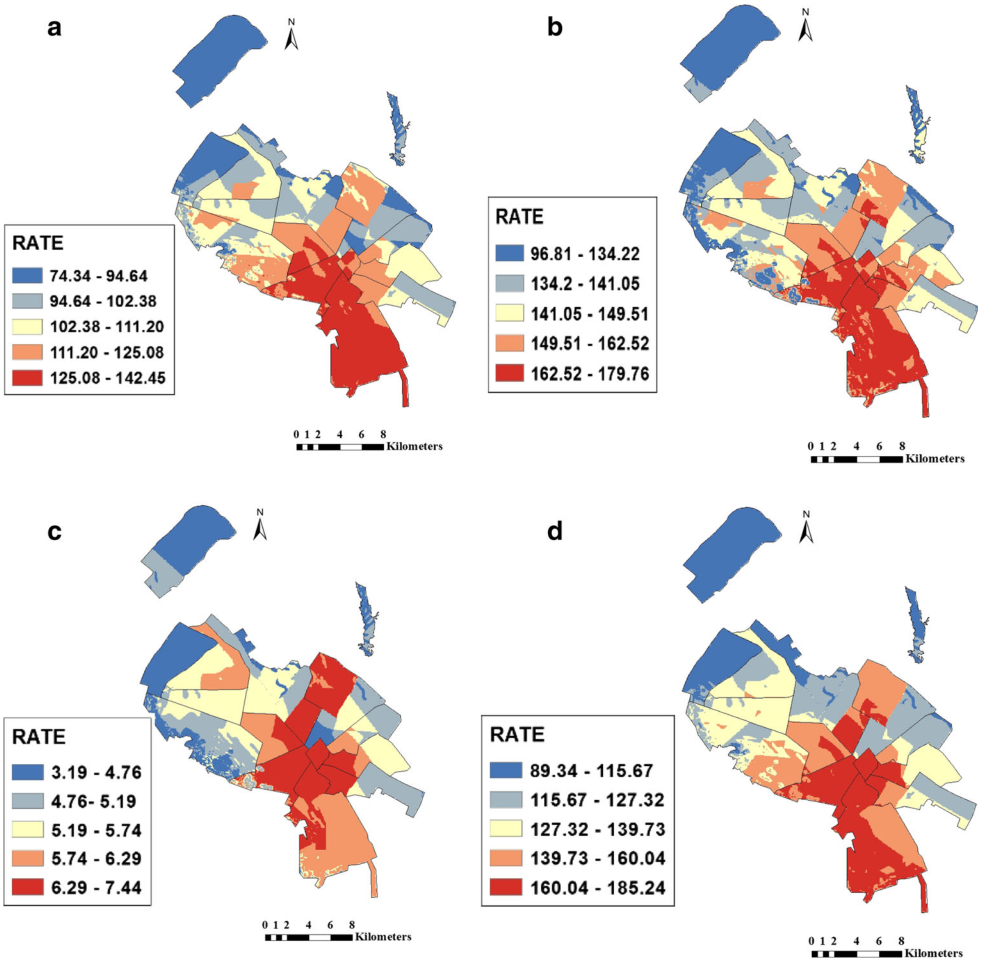


Fig. 5 **a** DRASTIC index, **b** pesticide DRASTIC index, **c** SI, and **d** modified DRASTIC index

Table 3 Results of assessment of index methods (percentage of study area)

Model	Overestimate (%)	Underestimate (%)	Correct (%)
DRASTIC	1.48	23.61	74.91
Pesticide DRASTIC	1.8	23.47	74.73
Modified DRASTIC	0.89	22.77	76.34
SI	1.66	23.58	74.76

small parts of north. High vulnerability was in south, center, and some parts of north. The SI (Fig. 5c) varies between 3.1 and 7.4. The center and some parts of north have high vulnerability and west and northwest have low vulnerability. Also, modified DRASTIC index (Fig. 5d) varies between 89.34 and 185.23. The relatively low vulnerable indexes were located in northwest and small parts of north. High vulnerability was located in south, center, and some parts of north. This is because they are the old and main cores of the city which has high land use value. Also, they are densely populated and most of the pilgrims resident there due to hotels and proximity to holy shrine. Moreover, because these areas are flat, the topographic values are high. The results of SI and modified DRASTIC are similar which indicates the effect of modified land use.

Quantile classification method was used to classify the indexes (Fig. 5a–d). It is selected as the most appropriate method (Sener et al. 2009; Yin et al. 2013). The quantile classification method distributes index values into groups containing an equal number of values. Each of the vulnerability indexes has been classified into five groups. The group 5 was assigned to high vulnerable zone, and the group 1 was assigned to low vulnerable zone; for instance, for DRASTIC index, the groups are: 5—high (125.08–142.44); 4—moderate high (102.38–125.08); 3—moderate (102.38–111.2); 2—moderate low (94.64–102.38); 1—low (74.34–94.64).

Also, for verifying the goodness of classification, level difference between each of indexes and nitrate concentration was implemented. As mentioned before, the index and the nitrate concentration were classified into the 5 aforementioned groups. The goodness of classification was obtained by subtracting the number of index's class from the number of nitrate concentration's class. If the value was between −1 and 1, the classification was considered correct, while it is considered overestimated and extensively overestimated when the values were obtained −2 or −3 and −4 or −5, respectively. Moreover, the corresponding positive values were considered underestimated and extensively underestimated, respectively. According to the results of the level difference (Table 3), 74.91, 74.73, 74.76, and 76.34% of the area in DRASTIC, pesticide DRASTIC, SI, and modified DRASTIC, respectively, are assessed correctly. Table 3 presents the values of the overestimations and underestimations for each method.

Table 4 Results of map removal sensitivity analysis

Parameter removed	Min	Max	Mean	SD
DRASTIC				
D	0.48	1.7	1.54	0.23
R	0	3.95	1.52	0.92
A	0	2.65	0.65	0.45
S	0	1.59	0.39	0.32
T	0.45	2.24	0.89	0.3
I	0	4.23	1.37	0.69
C	0.03	1.96	1.33	0.47
Pesticide DRASTIC				
D	1.08	1.9	1.76	0.15
R	0	2.58	0.755	0.58
A	0	1.63	0.29	0.18
S	1.47	4.622	2.64	0.46
T	0.032	2.03	0.97	0.33
I	0	2.26	0.41	0.32
C	1.1	2.1	1.8	0.255
Modified DRASTIC				
D	0.52	1.4	1.21	0.16
R	0	2.37	0.929	0.53
A	0	1.82	0.37	0.32
S	0	1.053	0.25	0.21
T	0.38	1.69	0.75	0.23
I	0	2.58	0.79	0.45
C	0.07	1.52	1.06	0.33
LU	0	3.15	1.02	0.54
SI				
D	2.98	4.37	4.08	0.24
R	0	4.47	1.42	0.93
A	0.014	10.75	2.71	1.48
T	0	4.45	0.8	0.66
LU	0	4.49	0.97	0.69

Table 5 Results of map removal sensitivity analysis by using Eq. 4 without absolute sign

Parameter removed	Min	Max	Mean	SD
DRASTIC				
D	−1.79	−0.488	−1.55	0.23
R	−2.044	3.97	1.36	1.13
A	−0.2	2.65	0.65	0.456
S	−0.49	1.59	0.67	0.36
T	−2.47	−0.45	−0.899	0.303
I	−0.12	4.23	1.37	0.69
C	−1.97	−0.042	−1.34	0.47

Validation of groundwater vulnerability to nitrate model

The models were validated by correlating indexes to nitrate concentration. The Spearman rank correlation factor was used to verify the effectiveness of the generated vulnerability maps. If domestic wastewater discharge were considered into the recharge parameter, the correlation of DRASTIC index, pesticide DRASTIC index, SI (susceptibility index), and modified DRASTIC index with nitrate concentration would be obtained 0.52, 0.57, 0.64, and 0.61, respectively, which all of them are significant at the 0.01 level (Condition 1). If the domestic wastewater discharge were not considered in recharge parameters, the above correlations would be less than 0.25, 0.35, and 0.42 for DRASTICs, modified DRASTIC, and SI, respectively (Condition 2).

In condition 2, because the contamination loads are not considered in DRASTICs, they can only calculate vulnerability potential. As a result, the indexes do not correspond well with the nitrate concentration data. In the other word, it would be possible that the vulnerability potential of a region to be high, but it has not been contaminated because of the absence of contamination source and vice versa. Thus, the correlation of DRASTIC and pesticide DRASTIC models in condition 2 was obtained lower than that of their corresponding values in condition 1 in which the contamination loads were considered.

The correlation of SI and modified DRASTIC methods is higher than that of the DRASTICs for both conditions because they take into account the land use layer which indirectly related to the contamination source. Also, the correlation of the SI and modified DRASTIC is significant at the 0.05 level for condition 2. According to the results, generally, human activities are the main reason for groundwater contamination in Mashhad City.

Table 6 Results of the analysis of R.D.

Parameter and method	Theoretical weight (%)	Effective weight (%)			
		Min	Max	Mean	SD
DRASTIC					
D	22	3.51	11.35	4.98	1.39
R	17	3.85	36.53	22.51	6.8
A	13	13.08	30.23	18.19	2.74
S	9	11.34	23.93	16.45	2.18
T	4	0.8	11.48	8.88	1.822
I	22	13.54	39.7	22.52	4.18
C	13	2.45	14.07	6.21	2.84
Pesticide DRASTIC					
D	19	2.78	7.75	3.64	0.92
R	15	3.09	26.89	16.63	5.22
A	12	9.07	24.1	13.37	1.91
S	19	23.14	42.09	30.17	2.8
T	12	2.08	23.84	19.46	3.31
I	15	7.5	27.86	13.37	3.07
C	8	1.21	7.64	3.1	1.53
Modified DRASTIC					
D	18	2.69	8.81	4	1.14
R	14	2.98	29.15	17.99	5.14
A	11	10.27	25.31	14.66	2.65
S	7	8.91	19.87	13.26	2.17
T	4	0.61	9.8	7.16	1.63
I	18	11.74	30.56	18.059	3.22
C	11	1.85	11.97	5	2.31
LU	18	11.8	34.59	19.6	3.81
SI					
D	0.186	2.5	8.4	3.61	0.98
R	0.212	4.93	35.07	23.03	6.11
A	0.259	20.68	63.01	30.87	5.95
T	0.121	2.177	27.71	20.89	4.1
LU	0.222	12.03	37.96	21.31	4.62

Sensitivity analysis

Results of map removal sensitivity analysis calculated by Eq. 4 are shown in Table 4. Interestingly, it can be seen that the depth to groundwater has low average rate, but has relatively high map removal sensitivity mean. It is not logical because high map removal sensitivity represents significant contribution of the layer in vulnerability index maps. This contradictory result led to use of Eq. 4 without absolute sign.

By recalculating the sensitivity analysis without absolute sign (Table 5), it revealed that some parameters such as *D* and *C* had negative average that expresses the negative effect of these parameters in indexes, while each parameter rationally increases the indexes. The reason is that the unperturbed index is divided by N and the perturbed index is divided by n. For instance, in DRASTIC model (which has 7 parameters), depth to groundwater has low rate (1 is assigned to approximately entire area), and its removal has no significant effect on the index which results in little difference between unperturbed (7 parameters) and perturbed (6 parameters) index. Considering Eq. 4, the difference of dividing unperturbed index by 7 and perturbed index by 6 may lead to negative result when there is no significant difference between unperturbed and perturbed index (as in the case of depth to groundwater). By using absolute sign, this problem may not be detected, and it leads to misunderstanding that the higher average indicates the more significant contribution of parameter.

To the authors' point of view, for better evaluation, it is appropriate to use relative difference which, technically, is the effective weight formula (Eq. 5) as follows:

$$\text{R.D.} = \frac{\text{ID} - \text{RID}}{\text{ID}} \times 100 \quad (7)$$

where R.D. is relative difference, ID is the index that is created using all parameters, and RID is the index created by removal of the parameter of interest.

Using Eq. 7, the role of each parameter in index generation can be designated (Table 6). For DRASTIC index, the effective weight of *I*, *R*, *A*, and *S* are, respectively, highest which are compatible to their theoretical weight sequential, but *D* and *C* has the lowest effective weights which are not compatible to their theoretical weight sequential. For other three methods, effective weight of all parameters follows their own theoretical weight sequential except for *C* and *D*, like DRASTIC method. Although the results of sensitivity analyses show that *D* has low effective weight, it cannot be inferred that this parameter is low priority. Comparing Figs. 2 and 3 reveals that for almost all places having lower depth to groundwater, the nitrate contamination is higher and vice versa. The reason of low mean effective weight is high depth to groundwater which leads to lower rates.

In the SI method, the contribution of LU is high of the order of 21%, showing the significant role of LU in specific vulnerability generation. Also, in modified DRASTIC in which all parameters are used to generate vulnerability index, LU has the most effective weight confirming the significance role of the land use. Moreover, the results of analysis show that *R* parameter is very important in all methods.

Conclusion

This study presented a new approach for modifying well-known parameters of common vulnerability indexes to adjust them for urban areas. The method is independent of the weighting system in modifying the parameters and provides a better estimation accuracy for each method.

The results of the study show that considering wastewater discharge into recharge parameter increases the correlation with measured nitrate concentration to more than 20% in all methods. A higher correlation of SI and modified DRASTIC with respect to other two DRASTIC models demonstrates the importance of the modified land use parameter. As the study area is an urban aquifer and the modified recharge and modified land use parameters are directly related to the anthropogenic activities, they have additional contributions to the higher correlation of indexes with nitrate concentration data among other parameters.

As most of the area have deep groundwater table, subtracting the depth of septics from depth to groundwater has not influenced the rate of this parameter. However, in shallow aquifers small changes in depth to groundwater may change the rate of this parameter. It is recommended that this subtraction be considered for shallow aquifers.

The results of sensitivity analysis show that map removal analysis for evaluating the overlay index methods is not appropriate. Hence, relative difference was used instead of map removal technique which shows that except for *D* and *C*; for all used index methods, the effective weight for all parameters follows their own theoretical weight sequential. Comparing figures of nitrate concentration and depth to groundwater map reveals that for almost all places having lower depth to groundwater, the nitrate contamination is higher and vice versa. The reason that weight sequential does not conform to its theoretical weight sequential is the high depth to groundwater that leads to lower rates. In fact, the role of *D* parameter is not well considered in Mashhad aquifer. It is suggested that the ranges of *D* parameter be changed by measuring depth to groundwater and corresponding nitrate concentrations for several periods. The same is true for hydraulic conductivity.

Level difference technique showed that more than 70% of vulnerability of study area were predicted correctly in all used methods. This indicates that these modifications are independent of the type of index method.

The results of the modified indexes show that the central, southern, and small part of northern districts have highest contamination potential and western and northwestern districts have the lowest contamination potential. Because the SI and modified DRASTIC have good correlation with measured nitrate, and also they consider the land use parameter, they are suitable for managing the land use planning.

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