ORIGINAL ARTICLE

Assessment of nitrate contamination in unsaturated zone of urban areas: The case study of Tehran, Iran

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Abstract Modeling fate of nitrogen in unsaturated and saturated zone is a complex process, which requires detailed geochemical data. Complexities of the process as well as data insufficiencies are two major issues, which make quantitative assessment of the problem more complicated. In this work, a lumped-parameter model (LPM) is proposed that has been evaluated for a data-limited case to study temporal and steady-state behavior of Nitrate and Ammonium in unsaturated zone. The concentration of components in the model are assumed as the depth-averaged concentrations, and dispersive fluxes have been neglected. The case study area is Tehran City aquifer, which is highly contaminated by domestic wastewater discharge into the groundwater. Three sources for Nitrogen contamination have been studied, namely domestic wastewater, park/recreational applications, and wet deposition. Results show that Nitrate production in the first few meters (<5 m) is quite large. To compare the model results with the measurements, error estimation analysis based on Vornoi map has been fulfilled. Finally, it is shown that there is a fairly good correlation coefficient between simulation and measurements, which approves the validity of the LPM.

Keywords Nitrate · Unsaturated zone · Lumped-parameter model · Wastewater · GIS · Tehran

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Introduction

In recent decades, water shortage has become a severe problem in arid and semi-arid countries. Because of the importance of groundwater in supplying drinking water, its environmental aspects such as contamination transport in groundwater have been significantly studied. Many researches have focused on contamination of groundwater due to anthropogenic sources mainly by agricultural activates and domestic wastewater. Nitrate contamination of groundwater is one of the main subjects in many of these studies (e.g., Lagerstedt et al. 1994; D'Agostino et al. 1998; DeSimone and Howes 1998; Abu Maila et al. 2004; Schilling and Wolter 2007). According to Tesoriero and Voss (1997), a proper prediction of NO_3–N leaching in the unsaturated zone is essential for the assessment of groundwater contamination and ultimately for development of a nutrient management protocol. The World Health Organisation (1996) has established maximum permissible limits for Nitrate in water used for drinking purposes at 10 mg/L NO_3–N. Ingestion of Nitrate by infants can cause low oxygen level in blood and a potentially fatal condition (Spalding and Exner 1993; Nolan 2001).

To have a reliable tool for quantitative management of pollution problems, researchers have developed several models for different applications. These models can be classified under two large groups; qualitative assessment tools and quantitative assessment tools. To predict Nitrate contamination risks and fates in large areas, different methods such as vulnerability assessment index, mass balance, and lumped-parameter models (LPMs) have been developed. DeSimone and Howes (1998) determined the percentages of different processes of Nitrogen fate such as sorption, nitrification, volatilization, etc., in a large area. Wakida and Lerner (2005) and Groffman et al. (2004) have

measured total Nitrogen loadings in large-scale urban areas. Ju et al. (2006) has studied the annual Nitrogen budget and groundwater Nitrate concentrations in three major intensive cropping systems in north of China. Nolan (2001) has also investigated relationship among precipitation, population, and Nitrate concentration in groundwater. Joekar-Niasar (2003) and Joekar-Niasar and Ataie-Ashtiani (2003) have suggested an assessment approach based on the modified DRASTIC (Aller et al. 1987) for domestic wastewater source in urban areas. Since large-scale studies of groundwater contamination cover mostly qualitative aspects of problem (Osborn et al. 1998, Rupert 2001), it is necessary to define an approach for quantitative assessment of contamination.

Existing quantitative models are mostly based on soil–plant systems. Antonopoulos and Wyseure (1998) developed WANISIM model for modeling fate and transport of Nitrogen in agricultural applications. Hutson and Wagenet (1991) developed LEACHN to simulate transport of Nitrogen in soil using Richard's equation. Kaluarachchi and Parker (1998) developed a three-dimensional finite-element model for simulation of transport and transformation of Nitrogen in unsaturated zone. There are a large number of accurate numerical methods and models, available for solute transport equation with reaction term (e.g., Ataie-Ashtiani and Hossaini 2005a, b; Ataie-Ashtiani et al. 1999). One of the few models for nonagricultural applications was developed by MacQuarrie et al. (2001). They developed a detailed model for simulating fate and transport of Nitrogen components in a septic tank system in saturated and unsaturated zones. This model also includes detailed geochemical, physical, and biochemical processes. However, involved complexities in these models make their applicability limited to small areas. Although many numerical models have been developed for simulating Nitrogen fate, it is difficult to employ them in large scale due to the limited available field data. Hence, analytical methods, simple models, and LPMs are of interest in such cases. For instance, Saâdi et al. (2003) developed a simple model for a large-scale study of Nitrate contamination in the unsaturated zone for agricultural fields of the Mnasra with area of 500 km^2. They developed a simple unsaturated zone model to describe Nitrogen dynamics in the field. They have estimated quantitatively seasonal Nitrate concentrations at different observation wells within a large area. All the aforementioned modeling tools are based on detailed geochemical input data of the porous media, which makes it difficult to apply in large-scale cases. For cases with insufficient data, LPMs are of great value. LPMs were introduced for the first time in 1950s and 1960s for interpretation of environmental radioisotope data in groundwater hydrology (Ling and El-Kadi 1998). In the recent decade, various analytical models have been developed using the first-order kinetic and linear isotherm equations to estimate pesticide contamination of groundwater. Ling and El-Kadi (1998) developed a LPM for Nitrogen transformation in the unsaturated zone for a soil–plant system. Since there are very few models developed for large urban areas with continuous discharge of wastewater that can explain temporal and spatial behavior of Ammonium and Nitrate in unsaturated zone, we have modified and applied a LPM based on Ling and El-Kadi (1998) in a geographic information system (GIS). This model needs less geochemical data compared with the abovementioned models. We have studied temporal and spatial contamination of Nitrate and Ammonium in unsaturated zone. Effect of depth on groundwater in retarding the discharged contamination in groundwater has been illustrated. In addition, the required time for reaching steady-state condition in unsaturated zone and the spatial distribution of contamination level has been studied.

Geochemical processes

Figure 1 shows major concepts of Nitrogen transformations associated with the soil–groundwater environment in cesspools or septic tanks. Bulk ratio of Nitrogen in wastewater at the cesspool is in form of urea, organic Nitrogen, and aqueous Ammonium. Urea can be hydrolyzed under anaerobic conditions, and Ammonium anion is produced (Wilhelm et al. 1994). Ammonium anion can be immobilized geochemically by adsorption to the soil. Nitrification process is fulfilled in two stages. At the first stage, in the presence of oxygen, Ammonia may be rapidly oxidized to Nitrite (NO_2^-) by the autotrophic Ammonia-oxidizing bacteria (*Nitrosomonas*). In the second stage, the autotrophic Nitrite-oxidizing bacteria oxidize Nitrite to Nitrate. Nitrite is a rather unstable Nitrogen species, which will generally be reduced or oxidized. However, Nitrate is quite soluble in water, and is not significantly adsorbed by clay-rich soils, since it is an anion. Usually, nitrification occurs mostly in the aerobic unsaturated zone, and it is thought generally that it is an oxic process. In some cases, Ammonia oxidizers are able to oxidize ammonia under anoxic conditions as explained by Wilhelm et al. (1994). Below the groundwater table, Nitrate can be reduced to Nitrogen gas. This process is called denitrification. It occurs primarily in anoxic conditions, and involves heterotrophic bacteria (*Paracoccus*, *Pseudomonas*). Additionally, in case of Nitrogen gas saturation in the groundwater, it tends to migrate out of the saturated zone. In spite of the fact that denitrification takes place in saturated zone under anoxic conditions, oxic denitrification has been also observed (Lee et al. 2006). In this case study,

because of continuous discharge of wastewater for several decades, physical properties of this soil are different from a soil sample in an undisturbed area. In addition, due to the assumption of depth-averaged processes, nitrification and denitrification processes can be both considered in the same zone.

Model description

Concept of proposed LPM is shown in Fig. 2. Dispersive fluxes are neglected because of gravity effect and spatial setup of the model. Simplified equation of mass conservation for average concentration of contaminant in soil column is considered as follows:

$$\partial(\theta c)/\partial t = -\partial(qc)/\partial z \pm (\text{Sink/Source}) \tag{1}$$

where θ is the soil water content within depth (cm^3/cm^3), q is the water flux (cm/day), c is the solute concentration in solution (mg/cm^3), and z is the depth to groundwater (cm).

By integrating Eq. 1 over depth to groundwater we can write:

$$\int_0^L \partial(\theta c)/\partial t\, dz = -\int_0^L \partial(qc)/\partial z \pm \phi \tag{2}$$

in which ϕ is a source/sink term. It can be assumed that depth (L) is not dependent on time. This assumption is valid if groundwater table is not changing significantly. Based on this concept, average concentration in depth is of interest. Depth-averaged values of variables θ, c, and (θc) at a given time are defined as follows:

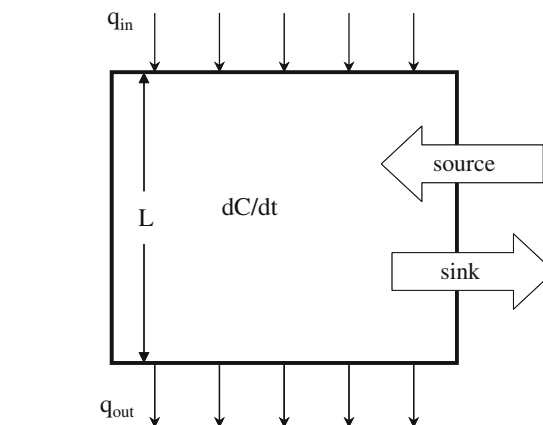Fig. 1 Basic processes of nitrogen compounds in saturated and unsaturated zone

Fig. 2 Schematic of mass balance box

$$\langle \theta \rangle = 1/L \int_0^L \theta(z,t) dz \tag{3}$$

$$\langle c \rangle = 1/L \int_0^L c(z,t) dz \tag{4}$$

$$\langle \theta c \rangle = 1/L \int_0^L \theta(z,t) c(z,t) dz \tag{5}$$

Rewriting Eq. 2 results:

$$L\langle \partial(\theta c)/\partial t \rangle = c_{in} q_{in} - c_t q_t \pm \phi \tag{6}$$

in which c_t is the concentration in solution below the depth of interest (mg/cm^3), c_{in} is the dissolved concentration of contaminant applied to the top of depth of interest (mg/cm^3), q_{in} is the inflow recharge per unit area (cm/day), q_t is the outflow from the depth of interest per unit area (cm/day), and ϕ is the sink or source term over the depth.

To quantify the involved terms in such a large-scale problem in which temporal variation of variables θ and c is not abrupt, an approximation to the left side of Eq. 6 is made, although mathematically it is not correct.

$$L\langle \partial(\theta c)/\partial t \rangle \approx L\langle \theta \rangle \partial \langle c \rangle/\partial t + L\langle c \rangle \partial \langle \theta \rangle/\partial t \tag{7}$$

Based on the mass balance principle, change of the average water content equals the inflows minus outflows from the soil column.

$$L\partial \langle \theta \rangle/\partial t = q|_{z=0} - q|_{z=L} = P + I_{ww} - q_t \tag{8}$$

where P is the precipitation (cm/day) and I_{ww} is the wastewater inflow rate (cm/day).

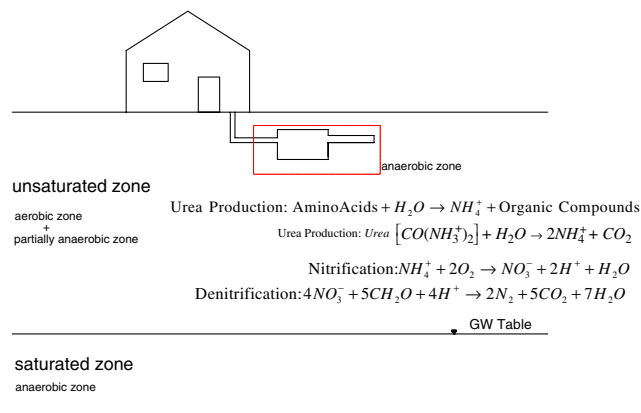By inserting Eqs. 8 and 7 into Eq. 6, Eq. 9 will be obtained as follows:

$$(L\langle\theta\rangle)\mathrm{d}\langle c\rangle/\mathrm{d}t + (P + I_{ww})\langle c\rangle + (c_t - \langle c\rangle)q_t$$
$$= c_{in}q_{in} \pm \phi(t) \tag{9}$$

It is assumed that the average concentration in the soil column is equal to the concentration at the bottom of soil column. Since urea is hydrolyzed to Ammonium rapidly in septic tanks and cesspools, the amount of urea in contrast to Ammonium is negligible. Considered processes in model include transformation of Ammonium to Nitrate (nitrification) with k_1 (day^{-1}) rate, transformation of Nitrate to Nitrogen (denitrification) with k_2 (day^{-1}) rate, soil adsorption, and volatilization of Ammonium to Ammoniac gas (Fig. 3). Finally, following set of equations are obtained:

$$q_o = P + I_{ww} \tag{10}$$

$$(L\bar{\theta})\mathrm{d}A/\mathrm{d}t + q_o A = q_{in}A_{in} - L(\rho_b K_{dA} + \varepsilon K_H)\mathrm{d}A/\mathrm{d}t$$
$$- k_1(L\bar{\theta}A) \tag{11}$$

$$(L\bar{\theta})\mathrm{d}N/\mathrm{d}t + q_o N = q_{in}N_{in} + k_1(L\bar{\theta}A) - (L\rho_b K_{dN})\mathrm{d}N/\mathrm{d}t$$
$$- k_2(L\bar{\theta}N) \tag{12}$$

where K_{dA} and K_{dN} are the distribution coefficients (cm^3/g) of Ammonium and Nitrate, respectively. Attenuation rates for the transport of Ammonium and Nitrate are defined as λ_1 and λ_2, respectively, which are given as follows:

$$\lambda_1 = (1/R_{FA})(k_1 + q_{in}/L\bar{\theta}) \tag{13}$$

$$\lambda_2 = (1/R_{FN})(k_2 + q_{in}/L\bar{\theta}) \tag{14}$$

Solution of ordinary differential equations, Eqs. 11 and 12, will be as follows:

$$A = (q_{in}A_{in}/(LR_{FA}\bar{\theta}\lambda_1))(1 - \exp(-\lambda_1 t)) + A_o \exp(-\lambda_1 t) \tag{15}$$

$$R_{FA} = 1 + \rho_b K_{dA}/\bar{\theta} + \varepsilon K_H/\bar{\theta} \tag{16}$$

$$R_{FN} = 1 + \rho_b K_{dN}/\bar{\theta} \tag{17}$$

where R_{FA} is the retardation factor of Ammonium (–), A_o is the initial concentration of Ammonium in soil (mg/cm^3), and R_{FN} is the retardation factor of Nitrate (–).

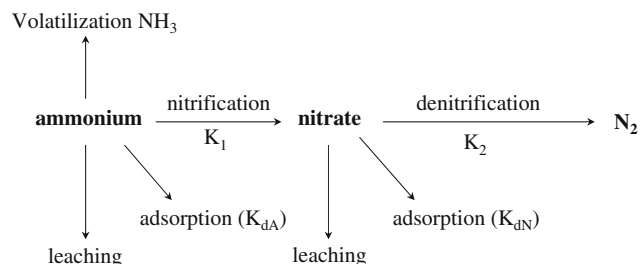Finally, solution of Eq. 12 will be as follows:

Fig. 3 Considered nitrogen transformations in LPM

$$N = q_{in}/(L\bar{\theta}\lambda_2 R_{FN})(N_{in} + k_1 A_{in}/(R_{FA}\lambda_1))$$
$$(1 - \exp(-\lambda_2 t)) + k_1/(R_{FN}(\lambda_2 - \lambda_1))$$
$$(A_0 - q_{in}A_{in}/(LR_{FA}\bar{\theta}\lambda_1)) \times (\exp(-\lambda_1 t) - \exp(-\lambda_2 t))$$
$$+ N_o \exp(-\lambda_2 t) \tag{18}$$

where N_o is the initial concentration of Nitrate in soil (mg/cm^3), t is the time (day), and ρ_b is the soil bulk density (g/cm^3).

Description of the case study

Tehran City has a population of more than 6.8 millions with a high dependency on the groundwater resources for drinking water (JICA and CEST 2000). About 35–55% of water demand of Tehran is supplied by groundwater resource that is contaminated by individual traditional cesspools and septic tanks for many years (Mahmoudi 2001). The study area covers more than 500 km^2 consisting of 20 municipal districts (Fig. 4). Constructing traditional cesspools and septic tanks is the conventional way for wastewater disposal, although in very few small areas there are wastewater disposal networks. Thus, wastewater is directly discharged into the subsurface. Because of the dense building construction, ground surface is almost covered by buildings, streets, and other impermeable surfaces. There are some limited park/recreational applications in the study area. Thus, major Nitrogen contamination sources can be considered as wastewater discharge, park and recreational spots, and air deposition.

Figure 5 shows spatial distribution of depth to groundwater as well as measurement points within the study area. Groundwater level has been measured in 87 points in three periods: March 2000, August 2000, and March 2001(Regional Water Authority of Tehran 2001). Observations show that groundwater level is not changing significantly during the measurement period. Since Tehran is located in southern domain of Elborz mountain chain, there is a moderate slope from north to south, and depth to groundwater table varies from 10 to 180 m. Surface slope in southern parts is less than that in northern parts, and groundwater flow direction is from north to south. Mean annual precipitation varies between 250 and 350 mm decreasing towards south, which shows semiarid condition of the study area.

LPM model setup

Inflow data

As mentioned earlier, three main sources for Nitrogen in the study area are considered as follows:

(a) Domestic wastewater: spatial distribution of waste-water quantity has been estimated using population projection. Japan International Cooperation Agency (JICA) and Centre for Earthquake and Environmental Studies of Tehran (CEST) (2000) have reported in details spatial distribution of demographic information in a GIS framework. We should note that Tehran population has increased dramatically during past two decades. Figure 6 shows trend of population increase in Tehran during the past century (Ohadi 2000; ISC 2008). Obviously rate of increase has decreased during recent years. According to TWWC (2000)
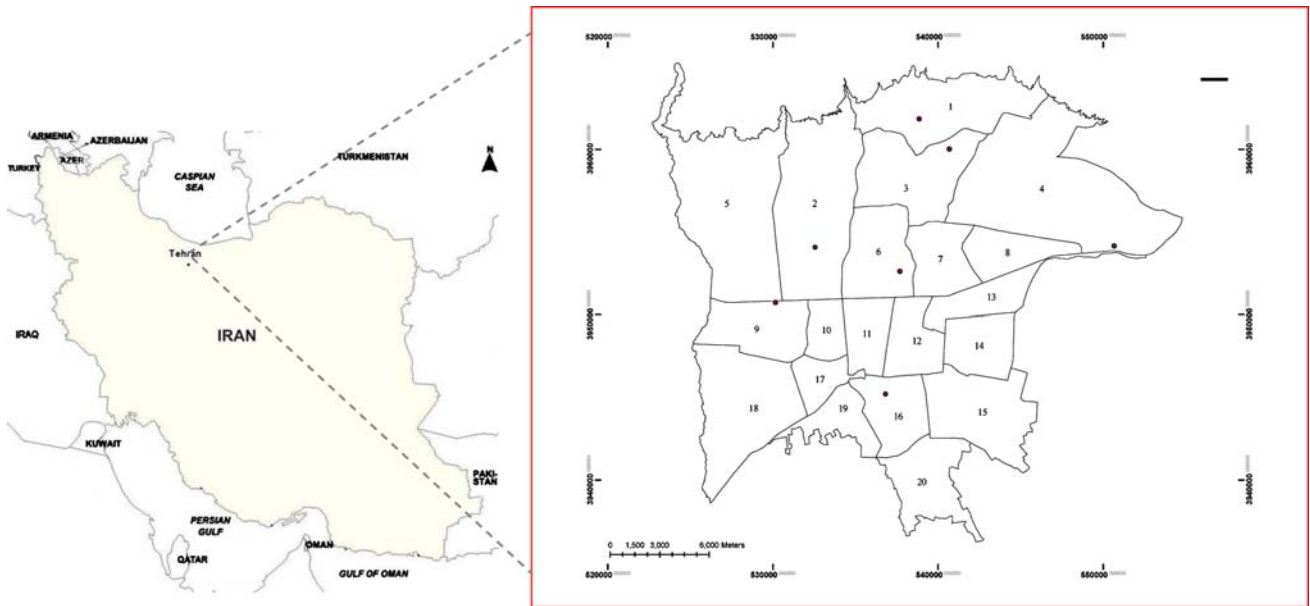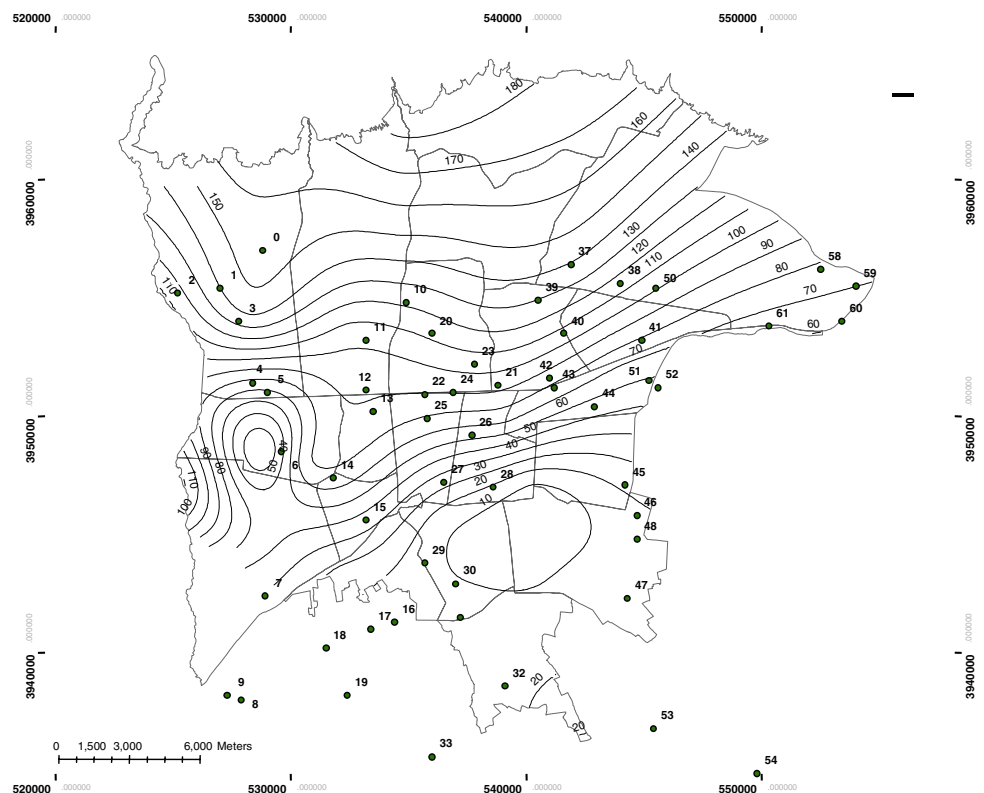

Fig. 4 Case study location and air quality control stations

Fig. 5 Spatial distribution of depth to groundwater (m) and location of measurement wells (2000–2001)
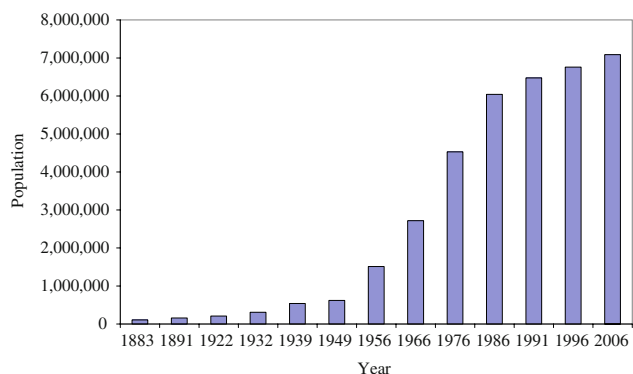
Table 2 Average air N-pollutant concentration in Tehran (ppm) (2000–2001)

Station	X (UTM)	Y (UTM)	NOx	NO$_2$	NO
Tajrish	538,853	3,961,851	0.0960	0.0487	0.0473
Villa	537,687	3,952,603	0.2931	0.0807	0.2123
Sorkh-Hesar	550,643	3,954,147	0.0220	0.0163	0.0056
Pardisan	532,556	3,954,062	0.1348	0.0728	0.0804
Azadi	530,156	3,950,726	0.1910	0.0409	0.1500
Gholhak	540,668	3,960,011	0.2465	0.0858	0.1565
Bahman	536,813	3,945,206	0.2887	0.1705	0.1219

wastewater discharge rate in Tehran is estimated about 162 L/day per capita. Annually average of wastewater quality is also presented in Table 1. Based on the population projection in the study area and wastewater discharge rate, estimated annual Nitrogen loading is ranging from 270 to 305 kg N ha^{-1} year^{-1}. Wakida and Lerner (2005) have reviewed various studies about non-agricultural sources of groundwater Nitrogen. Reported range of Nitrogen contamination from leaky sewers is about 3–123 kg N ha^{-1} year^{-1} in their review which is much smaller than loading level in this study.

(b) Atmospheric deposition: nitrogen compounds in atmosphere can be in oxidized or reduced forms. The oxidized compounds are generated by cars and industry. Reduced compounds are mainly released from agriculture and intensive feed stock rearing. To have a primary assessment of the importance of this source in contrast to the wastewater, wet deposition has been estimated roughly. Spatial distributions of atmospheric Nitrogen compounds and precipitation have been prepared based on seven air-quality control stations and four meteorological stations. Air N-pollutant concentration have been measured in three stages with 6-month intervals in 2000 and 2001. Average air N-pollutant concentrations have been shown in Table 2. Estimated average wet deposition of Nitrogen is about 16.5 mg N m^{-2} year^{-1} (about 0.2 kg N ha^{-1} year^{-1}). The highest reported value of atmospheric deposition is between 10 and 20 kg N

ha^{-1} year^{-1} in an industrial area covered with permeable surfaces under high range of precipitation (Wakida and Lerner 2005). Groffman et al. (2004) have measured Nitrogen loading for three successive years in an urban area. The highest amount of total Nitrogen loading is about 11.2 kg N ha^{-1} year^{-1}. In both mentioned studies, run-off is discharged into the groundwater and contamination potential is much higher. Because of the physical features of the case study, which is covered mostly by impermeable surfaces as well as small amount of precipitation, amount of wet deposition compared to wastewater contamination potential can be neglected.

(c) Fertilizers: according to the standards, normally Nitrogen loading in park/recreational applications is about 200 kg N ha^{-1} year^{-1} (Lerner 2000). Based on the existing land-use map of the case study, covered surface by parks and grasslands has been estimated. Estimated total Nitrogen loading within the case study is estimated about 900 tons per year.

Comparing different aforementioned contamination sources, it is estimated that urban wastewater includes almost 95.5% of total nitrogen loading source. Parks/recreational applications and wet air deposition, which include 4.5% of total nitrogen loading source, are negligible compared to urban wastewater loading.

Outflow data

Concentration of Nitrogen compounds near to groundwater table is regarded as outflow. Groundwater quality has been

Table 1 Inflow wastewater quality at different wastewater treatment plants in Tehran (TWWC 2000) (mg/L of N)

Treatment plant	Jonoub	Ekbatan	Shoush	Saheb-gharanieh	Mahalati	Gheitarieh	Zargandeh
Ammonium	32.95	29.43	60.45	29.88	38.19	35.37	39.43
Nitrate	0.54	1.53	0.86	3.22	1.70	2.84	2.23
Nitrite	29.96	27.14	54.92	28.17	35.1195	32.99	36.44

measured in 65 stations heterogeneously distributed in the study area. Regional Water Authority of Tehran (2001) has reported measurements of NH_3, NO_3, and NO_2 in three periods in 2000 and 2001. Average concentration of these compounds over this period has been shown in Table 3 in Appendix.

Model parameters and variables

Because of the scarcity of geochemical data in the case study, model parameters have been determined based on literature, and they have been optimized based on available Nitrate concentration in groundwater for three successive periods.

Since the model structure is based on one-dimensional averaging in depth, the results are very sensitive to k_1 and k_2 values. In this case study, due to the physical specifications of the area such as continuous discharge of wastewater for several decades, range of variation of soil moisture is not wide and hence, soil–water content values are determined based on the data available from few geotechnical boreholes. In addition, MacQuarrie et al. (2001) has determined 0.4 for sandy aquifer under effect of septic tanks. Soil water content for gravel media is determined to be about 0.44. In our study, average water content in soil media is about 0.40. ε and Henry coefficient are assumed to be equal to 0.15 and 2, respectively (Ling and El-Kadi,1998). Ammonium and Nitrate distribution coefficients are assumed equal to be 3.5

and 0.001, respectively (Tillotson and Wagenet 1982). In this model, concentration is calculated as a mean value in depth that is considered fixed within depth. Hence, with increase of depth, error occurrence possibility for k_1 and k_2 increases. To solve this problem, a parametric model for these coefficients has been developed for different depths in which coefficients have been determined based on depth to groundwater. Figure 7 shows variation trend of coefficients in different depths. This method for determination of coefficients can solve partially the lack of field data.

Results

Spatial and temporal aspects of contamination

In this section, spatial and temporal behavior of Nitrate contamination is studied. In addition, steady-state condition of Nitrate in the study area is discussed. To get a better insight into the dynamics of Ammonium and Nitrate, typical breakthrough curves of these components are shown in Fig. 8. As mentioned earlier, constant flux has been assumed for boundary condition. In Fig. 8a, constant flux is applied for time less than 1,000 days, but in Fig. 8b, constant flux is applied for the whole simulation. Thus, a peak concentration in Fig. 8a and a steady-state condition in Fig. 8b are expected. In Fig. 8a, it is clear that there is a delay time between peak concentration of Ammonium and Nitrate, due to the fact that Nitrate is produced after
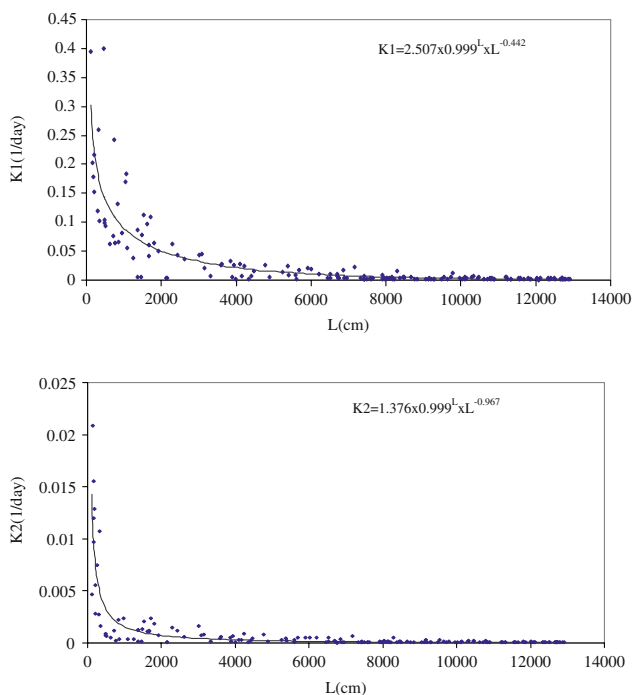
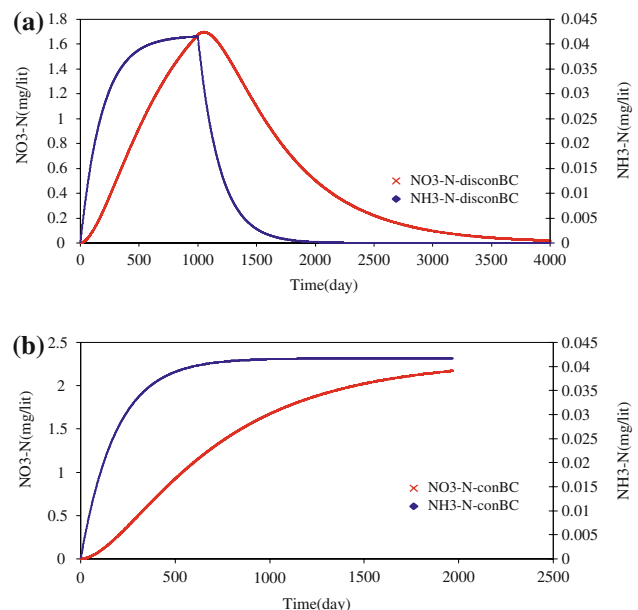**Fig. 7** Relationship between k_1 (day^{-1}), k_2 (day^{-1}), and depth in LPM model

Fig. 8 Typical breakthrough curve of Nitrate and Ammonium in a soil column under (**a**) constant influx for $t < 1,000$ days and under (**b**) constant influx for all t
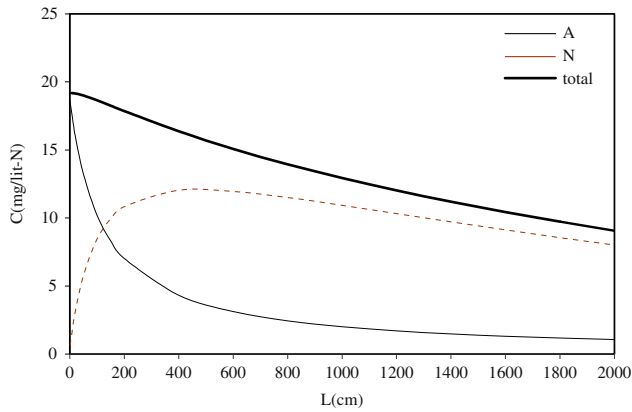
Fig. 9 Ammonium and Nitrate and total nitrogen concentration in different depths

Ammonium nitrification. Figure 8b shows that Ammonium requires less time to reach the steady state, since it is a prime substance. Nitrate has much smaller absorption and transformation rates, and is a product of Ammonium transformation (nitrification). In addition, Fig. 9 shows concentration distributions of Nitrate and Ammonium and total nitrogen in depth. It shows that with increase of depth, total nitrogen discharged to the groundwater decreases due to transformation and adsorption. However, a peak concentration is observed for Nitrate, which is dependent on the sharp decrease of Ammonium. In depths lower than 5

m, highest amount of Nitrate concentration is expected, which is in a good agreement with other studies (Foster et al. 1982; Antonakos and Lambrakis 2000). Since in the LPM concentrations are averaged in total depth of unsaturated zone, required time to reach the steady-state condition is highly dependent on the depth to groundwater and also on the boundary condition. We have assumed a constant depth to groundwater during our simulations. However, population distribution, which determines discharge to groundwater, has been normalized by population in 1996. Discharge has been updated during simulation with population in 1986, 1991, and 1996. Population after 2005 has been assumed to be constant. Based on these assumptions, Fig. 10 shows spatial distribution of the steady-state time in the study area. As it can be observed, depending on the depth to groundwater and local influx conditions, 2.5–946 years are required to reach the local steady-state condition. Southern parts of the study area that have smaller depth to groundwater compared to the northern parts can reach the steady-state conditions much faster. It is estimated that almost 50% of the study area will be in steady-state condition in 100 years considering existing demographic condition as the initial condition of the model. Because of the temporal evolution of concentration in the unsaturated zone, and also demographic development of Tehran, we compare model result in snapshot of 25th year with measurement data. Figure 11 shows

Fig. 10 Spatial distribution of time to reach steady-state condition for nitrogen components
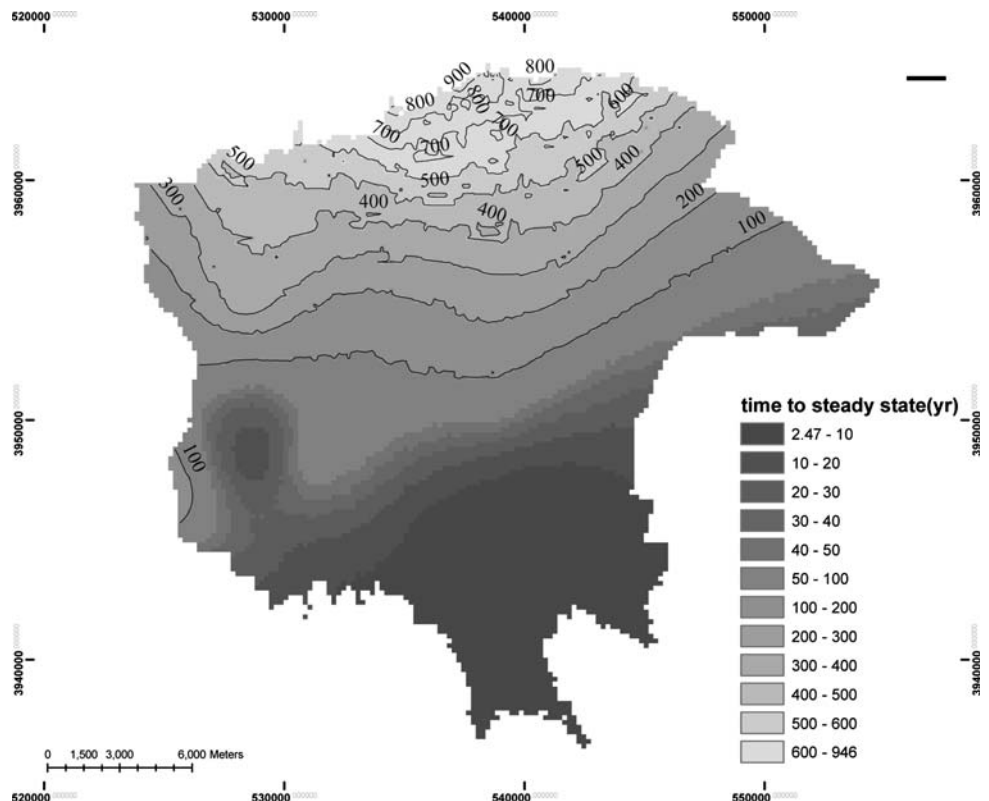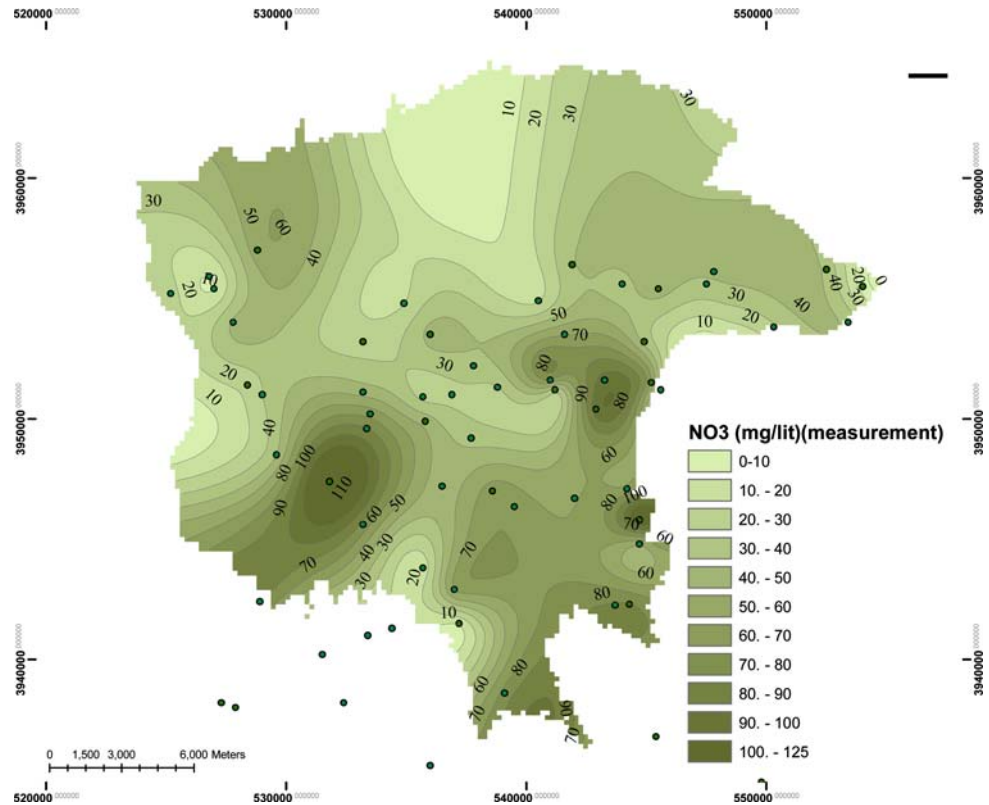
Fig. 11 Spatial distribution of Nitrate concentration (mg/L) based on measurements (2000–2001)

the spatial distribution of Nitrate concentration within 2000–2001. Maximum observed concentration of Nitrate in the measurement points is about 110 mg/L. Figure 12a, b shows concentration of Nitrate in 25th year and at steady-state condition, respectively. As it can be observed, contaminations in southern parts in both figures are similar, because they can reach the steady-state condition in less than 25 years. In addition, in northern parts, we have not observed high Nitrate contamination level in the measurements. However, if boundary conditions and wastewater disposal system do not change, northern parts will also suffer from high level of Nitrate contamination in future. It has been observed that subsurface contamination is directly controlled by wastewater discharge to groundwater.

Model results analysis

For comparing model results with field measurements, zonal analysis has been used. Thus, domain discritization has been applied by Vornoi diagram. Using Vornoi diagram, each measurement point will be representative for its region. Thus, higher density of data points will result in smaller region elements. Figure 13 shows the Vornoi map in the study area. As it can be seen in north or south-west of the study area, density of data points is much less than the central parts, which results in larger region (polygon)

elements. We have compared averaged results of model (Fig. 12a) and measurement data (Fig. 11) per each (region) polygon element as shown in Fig. 14. Correlation coefficient between model results and measurement is about 0.73, which is in an acceptable range. To identify in which zones higher disagreement between model and measurement is observed, relative error in each zone has been estimated. Relative error, Er, estimated for the simulated χ and measured value, $\langle \chi \rangle$, is defined as follows:

$$\text{Er} = \frac{|\chi - \langle \chi \rangle|}{\langle \chi \rangle} \qquad (19)$$

Figure 15 shows the relative error based on the Vornoi map. According to Fig. 15, in those region (polygon) elements, which are located in margins, larger relative error has been observed. Because of the lack of measurement points for groundwater quality outside the study area, we have to extrapolate the measurements. These extrapolated data are considered as the benchmark for comparing with model results. Thus, uncertainty increases not only due to the modeling procedure, but also due to bench mark definition for comparing with model results. Figure 15 shows that simulation results in majority of zones are in acceptable range with low relative errors (less than 20%). Larger differences between the model results and the measurements are generally due to the uncertainty in field data extrapolation. However, the selected extrapolation strategy

Fig. 12 Spatial distribution of Nitrate concentration (mg/L) based on simulation (**a**) at year 25 and (**b**) at steady-state condition
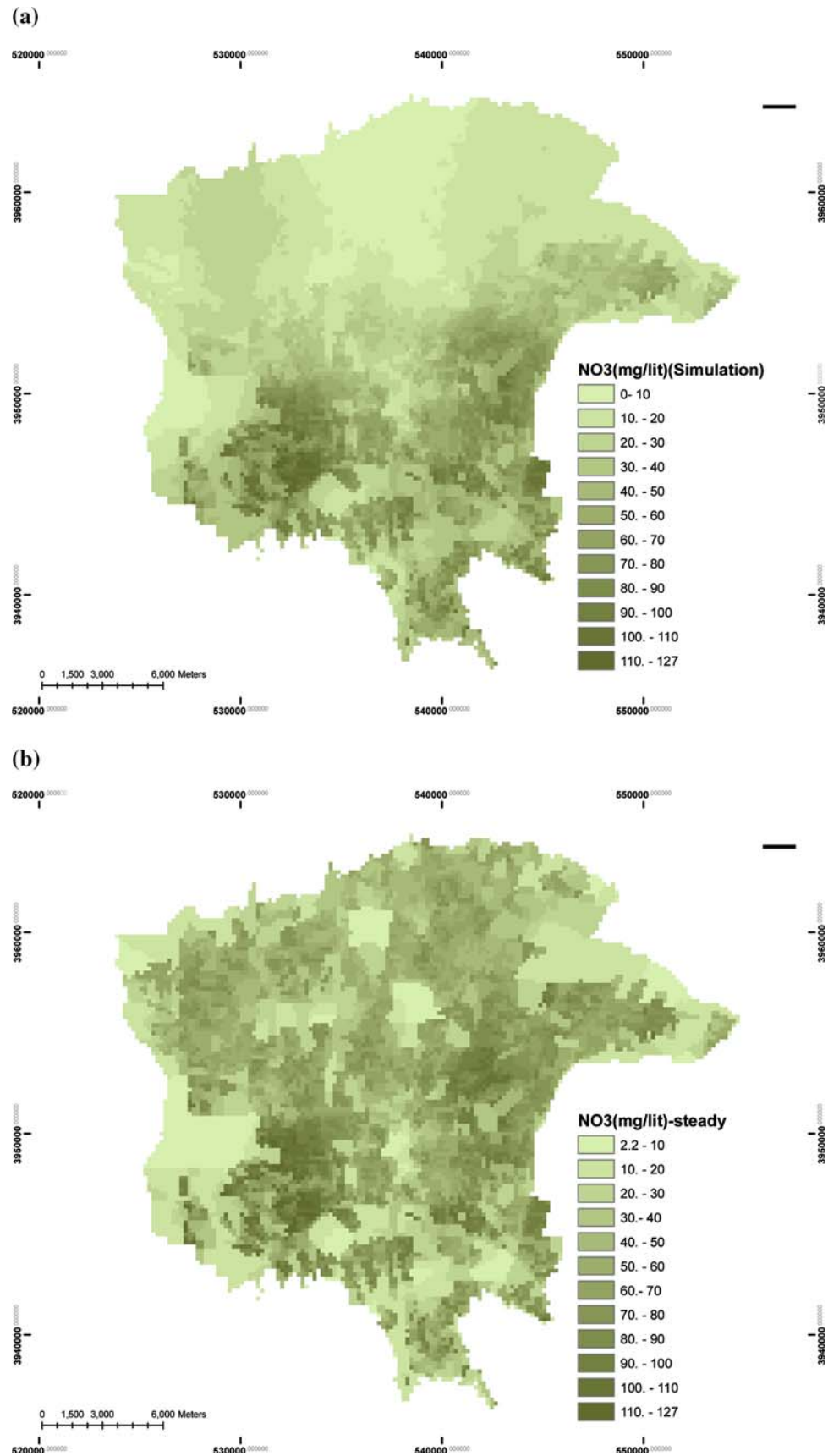
has been chosen so that minimum relative error between measurement and simulations occurs.

Summary and remarks

Large-scale modeling of Nitrate contamination in data-limited cases is a challenging task. In addition, involved processes in nitrogen fate in porous media are complicated. Furthermore, there are few studies related to large-scale modeling of Nitrate contamination due to the domestic wastewater. We have developed a LPM for modeling Nitrate and Ammonium fate in unsaturated zone neglecting dispersive fluxes to model nitrogen fate in unsaturated zone under the effect of continuous domestic wastewater discharge. We have applied this model in Large Tehran City (>500 km^2) as a case study, which is highly contaminated by domestic wastewater discharge. Wastewater discharge, wet deposition, and parks/recreational applications have been assumed as Nitrogen sources. Using detailed demographic and landuse data in a GIS framework, total nitrogen loading from different sources has been assessed. More than 95% of nitrogen loading in Tehran City is discharged from domestic cesspools. LPM results show that in first few meters where nitrification occurs, highest Nitrate concentration level in depth can be observed. Simulations show that existing condition of Nitrate contamination in
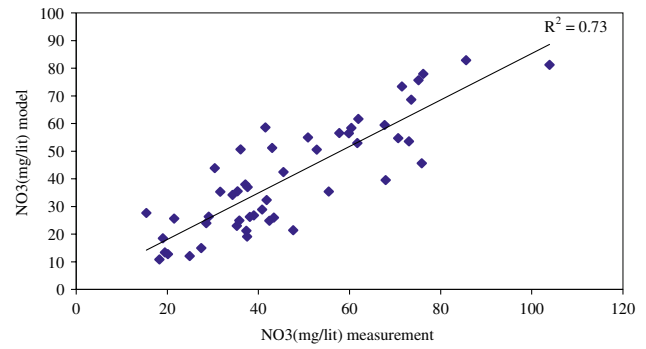
Fig. 14 Comparison between zonal mean of concentration resulted from simulation and field data for each Vornoi polygon

Tehran is in temporal condition. Since depth to groundwater controls the dynamics of N-pollution, it takes more time to reach the steady-state condition in deeper locations. In deeper depths, amount of contamination for both components decreases and required time to reach the steady-state condition for N-contamination is nonlinearly proportional to the inverse of depth to groundwater. Spatial distribution of steady-state Nitrate concentration shows high risks in northern parts of study area in future. This result can be considered in groundwater quality management protocols in Tehran. Results analysis showed that in those locations in which more data points are available, smaller relative error has been observed. In spite of

Fig. 13 Vornoi diagram based on data points of groundwater quality measurements
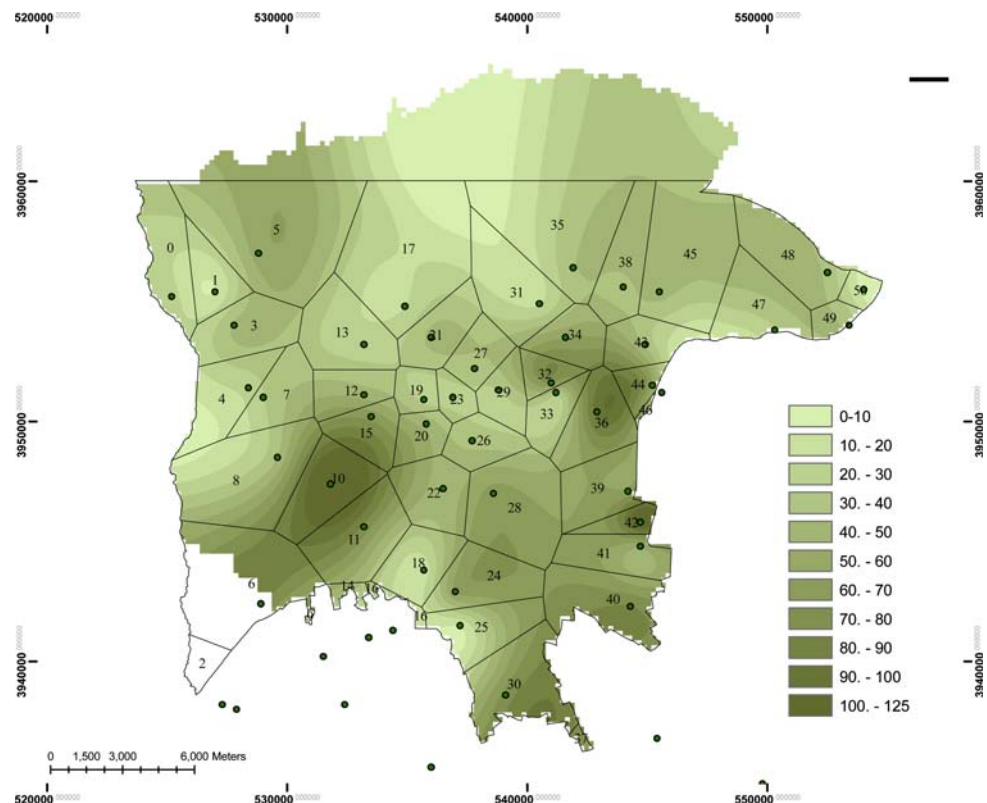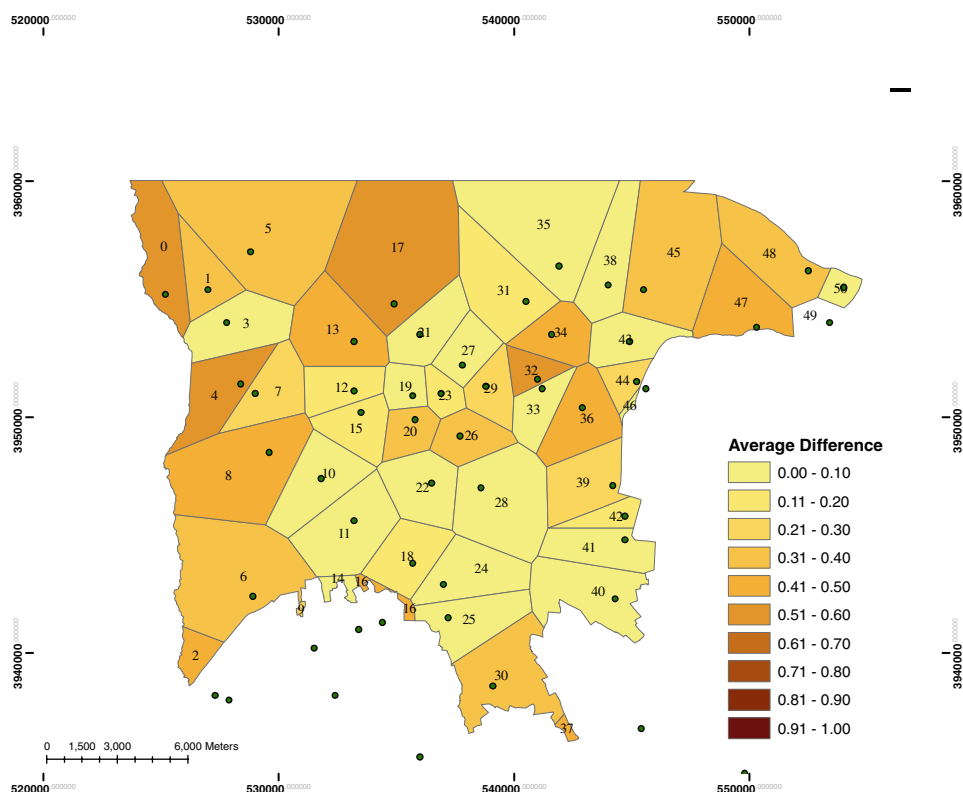
Fig. 15 Relative error of simulation result compared to measurements at each Vornoi polygon element

increased uncertainties due to the field data extrapolation, there is still acceptable agreement between LPM results and measurements with correlation coefficient of 0.73.

Appendix

See Table 3.

Table 3 Average concentration of Nitrogen components in groundwater (m/L) (2000–2001)

No.	X (UTM)	Y (UTM)	NO$_2$	NO$_3$	NH$_3$
0	528,800	3,957,000	0.028	55.100	0.346
1	527,000	3,955,400	0.004	9.800	0.244
2	525,200	3,955,200	0.006	23.000	0.257
3	527,800	3,954,000	0.004	41.620	0.294
4	528,400	3,951,400	0.002	23.600	0.306
5	529,000	3,951,000	0.013	29.800	0.266

Table 3 continued

No.	X (UTM)	Y (UTM)	NO$_2$	NO$_3$	NH$_3$
6	529,600	3,948,500	0.014	39.900	0.210
7	528,900	3,942,400	0.005	80.300	0.450
8	527,900	3,938,000	0.009	2.900	0.427
9	527,300	3,938,200	0.014	25.700	0.534
10	534,900	3,954,800	0.008	19.600	0.665
11	533,200	3,953,200	0.001	25.400	0.382
12	533,200	3,951,100	0.009	46.100	0.500
13	533,500	3,950,200	0.002	66.400	0.260
14	531,800	3,947,400	0.005	124.800	0.300
15	533,200	3,945,600	0.007	77.000	0.633
16	534,400	3,941,300	0.016	22.100	0.435
17	533,400	3,941,000	0.006	16.900	0.270
18	531,500	3,940,200	0.040	9.100	0.311
19	532,400	3,938,200	0.002	36.400	0.353
20	536,000	3,953,500	0.010	42.900	0.680
21	538,800	3,951,300	0.007	29.500	0.330
22	535,700	3,950,900	0.031	27.400	0.487
23	537,800	3,952,200	0.006	36.700	0.360
24	536,900	3,951,000	0.004	27.600	0.473
25	535,800	3,949,900	0.015	46.100	0.360
26	537,700	3,949,200	0.005	36.400	0.540
27	536,500	3,947,200	0.085	45.200	0.420
28	538,600	3,947,000	0.080	64.200	0.550
29	535,700	3,943,800	0.006	14.500	0.260

Table 3 continued

No.	X (UTM)	Y (UTM)	NO_2	NO_3	NH_3
30	537,000	3,942,900	0.022	60.500	0.366
31	537,200	3,941,500	0.006	11.200	0.300
32	539,100	3,938,600	0.031	74.000	0.390
33	536,000	3,935,600	0.014	54.400	0.480
34	536,400	3,933,400	0.003	23.500	0.321
35	535,300	3,930,100	0.006	26.500	0.333
36	538,800	3,928,300	0.007	25.200	0.403
37	541,900	3,956,400	0.005	38.900	0.260
38	544,000	3,955,600	0.002	37.400	0.284
39	540,500	3,954,900	0.001	18.900	0.330
40	541,600	3,953,500	0.003	59.200	0.448
41	544,900	3,953,200	0.004	37.500	0.340
42	541,000	3,951,600	0.034	70.700	0.393
43	541,200	3,951,200	0.007	34.200	0.320
44	542,900	3,950,400	0.008	95.200	0.270
45	544,200	3,947,100	0.008	62.400	0.240
46	544,700	3,945,800	0.001	111.000	0.340
47	544,300	3,942,300	0.023	80.700	0.359
48	544,700	3,944,800	0.001	51.200	0.684
49	543,750	3,934,600	0.005	45.700	0.511
50	545,500	3,955,400	0.004	44.400	0.404
51	545,200	3,951,500	0.005	59.400	0.270
52	545,600	3,951,200	0.005	15.400	0.404
53	545,400	3,936,800	0.030	31.900	0.444
54	549,800	3,934,900	0.004	64.100	0.600
55	549,800	3,934,400	0.012	84.900	0.540
56	548,500	3,929,000	0.019	17.900	0.390
57	547,100	3,928,000	0.003	29.800	0.540
58	552,500	3,956,200	0.004	37.000	0.300
59	554,000	3,955,500	0.005	5.500	0.403
60	553,400	3,954,000	0.007	36.600	0.280
61	550,300	3,953,800	0.008	28.200	0.430
62	553,200	3,934,000	0.013	24.600	0.550
63	550,950	3,926,700	0.006	28.200	0.661

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