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Modeling nitrate contamination of groundwater in agricultural watersheds

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Summary This paper presents and implements a framework for modeling the impact of land use practices and protection alternatives on nitrate pollution of groundwater in agricultural watersheds. The framework utilizes the national land cover database (NLCD) of the United State Geological Survey (USGS) grid and a geographic information system (GIS) to account for the spatial distribution of on-ground nitrogen sources and corresponding loadings. The framework employs a soil nitrogen dynamic model to estimate nitrate leaching to groundwater. These estimates were used in developing a groundwater nitrate fate and transport model. The framework considers both point and non-point sources of nitrogen across different land use classes. The methodology was applied for the Sumas–Blaine aquifer of Washington State, US, where heavy dairy industry and berry plantations are concentrated. Simulations were carried out using the developed framework to evaluate the overall impacts of current land use practices and the efficiency of proposed protection alternatives on nitrate pollution in the aquifer.

Introduction

Agricultural activities are probably the most significant anthropogenic sources of nitrate contamination in groundwater (Carey and Lloyd, 1985; DeSimone and Howes, 1998; Gusman and Mariño, 1999; Birkinshaw and Ewen, 2000; McLay et al., 2001; Ledoux et al., 2007; Oyarzun et al., 2007). Elevated nitrate concentrations in drinking water can cause *methemoglobinemia* in infants and stomach cancer in adults (Lee et al., 1991; Wolfe and Patz, 2002). As such, the US Environmental Protection Agency (US EPA) has established a maximum contaminant level (MCL) of 10 mg/l NO_3-N (US EPA, 1995). Nitrogen is a vital nutrient to enhance plant growth. This fact has motivated the intensive use of nitrogen-based fertilizers to boost up the productivity of crops in many regions of the world (see for instance Laftouhi et al., 2003). Nevertheless, when nitrogen-rich fertilizer application exceeds the plant demand and the

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denitrification capacity of the soil, nitrogen can leach to groundwater usually in the form of nitrate which is highly mobile with little sorption (Meisinger and Randall, 1991; Birkinshaw and Ewen, 2000; Shamrukh et al., 2001). Many practices result in non-point source pollution of groundwater and the effects of these practices accumulate over time (Schilling and Wolter, 2001). These sources include fertilizer and manure applications, dissolved nitrogen in precipitation, irrigation flows, and dry atmospheric deposition. Point sources of nitrogen are shown to contribute to nitrate pollution of groundwater. The major point sources include septic tanks and dairy lagoons and many studies have shown strong correlation between high concentrations of nitrate and these sources (Erickson, 1992; Arnade, 1999; MacQuarrie et al., 2001).

Many studies in the literature have developed management options for protecting groundwater quality from nitrate contamination. Yadav and Wall (1998) examined the costs of obtaining acceptable nitrate levels in the drinking water of Garvin Brook area in Winona County, Minnesota. In this area, an average of 34% of the sampled domestic wells had nitrate in excess of the MCL. The protection alternatives implemented in the area included the maintenance of selected septic systems, reducing the overall nitrogen application rate, split applications of fertilizers, and the proper crediting of nutrients available in the soil. Since fate and transport models were not utilized in their study, it was not clear if the nitrate concentration of 10 mg/l NO_3-N or less was reached. Additionally, the lag time between the adoption of the protection alternatives and groundwater restoration was unknown. Bernardo et al. (1993) developed a modeling framework for assessing the environmental and economic consequences for protecting groundwater quality. The framework consists of three stages: (i) a crop simulation and chemical transport model, (ii) an optimization model, and (iii) a groundwater flow model. The output from the framework provides optimal practices across the study area. The main shortcoming of this study is that nitrate concentration in the aquifer is controlled through constraints of nitrate leaching from the soil. Therefore the aquifer's ability to naturally attenuate nitrate was not considered. Kim et al. (1993), Kim et al. (1996), and Lee and Kim (2002) developed a procedure to determine the optimal fertilizer use considering the occurrences of nitrate in groundwater. They assumed that a fixed proportion of the fertilizers applied will ultimately leach to groundwater and that the time period between application and entrance into the aquifer is represented by a constant time lag. In groundwater, nitrate was assumed to be decayed at a specific rate. Based on these assumptions, an equation was developed to estimate nitrate concentration in groundwater as a function of the on-ground nitrogen loading from fertilizers. They derived an optimal tax rate on nitrogen fertilizer use, which would lead to the optimal fertilizer use and the maximum net benefits subject to nitrate concentration equivalent to MCL. Since these studies did not account for nitrogen mass in the soil prior fertilization and due to the assumption that nitrate in the groundwater exclusively comes from fertilizers, optimal nitrogen fertilizer application rates may be overestimated. This overestimation verily leads to ultimate nitrate concentrations in the aquifer beyond the MCL.

Previous studies that were involved in the modeling of nitrate fate and transport in groundwater and in developing management options to minimize nitrate concentration in groundwater can be classified into the following two broad categories (according to Fig. 1 which conceptually depicts the interacting processes that govern nitrate occurrences in groundwater): (i) studies that incorporated soil transformation models to determine nitrate leaching to groundwater (Refsgaard et al., 1999; Lasserre et al., 1999; Birkinshaw and Ewen, 2000; Ledoux et al., 2007) and (ii) studies that did not encompass soil transformation models in the development of nitrate fate and transport models of groundwater (Mercado, 1976; Carey and Lloyd, 1985; Shamrukh et al., 2001).

In the first group of these studies, a wide range of soil models were used and incorporated. These models were readily available from the literature such as PRZM (Carsel et al., 1985), LEACHP (Wagenet and Huston, 1987), GLEAMS (Leonard et al., 1987) and NLEAP (Shaffer et al., 1991), or were developed specifically to cope with a site of interest and to address certain objectives with a particular format of output (see for instance Almasri and Kaluarachchi, 2004a) or simply to reduce the amount of data needed to crank up the model as proposed by Ling and El-Kadi (1998) who developed a simple lumped-parameter analytical model of soil transformations of nitrogen.

The development of a conceptual model that best accounts for the different parameters influencing nitrate fate and transport in groundwater is ultimately the key to a successful simulation of nitrate concentration in groundwater. The conceptual model of nitrate fate and transport in groundwater integrates generally the following components (Refsgaard et al., 1999; Lasserre et al., 1999; Gusman and Mariño, 1999; Birkinshaw and Ewen, 2000; Nolan et al., 2002; Almasri and Kaluarachchi, 2004a; Ledoux et al., 2007; Almasri, 2007): (i) watershed hydrology; (ii) land use cover to compute the spatial distribution of on-ground nitrogen loadings; (iii) detailed assessment of all nitrogen sources in the study area and their allocation to the appropriate land cover classes; (iv) approximate description of the nitrogen dynamics in the unsaturated zone (including both soil and vadose zones); (v) realistic estimation of nitrate leaching to groundwater; (vi) understanding the groundwater flow system; (vii) accounting for groundwater–surface water interactions with the proper characterization of *N*-transformations in surface water bodies; and (viii) detailed description of nitrate fate and transport processes in groundwater.

Characterization of nitrogen sources and identification of areas with heavy nitrogen loadings from point and non-point sources is important for land use planners, environmental regulators, and is essential for developing fate and transport models. Once such high-risk areas have been identified, preventative measures can be implemented to minimize the risk of nitrate leaching to groundwater (Lee, 1992; Lee et al., 1994; Tesoriero and Voss, 1997; Ramanarayanan et al., 1998). Accurate quantification of nitrate leaching to groundwater is difficult due to the complex interaction between land use practices, on-ground nitrogen loading, groundwater recharge, soil nitrogen dynamics, and soil characteristics. This complex interaction is conceptually illustrated in Fig. 1. When conducting a regional-scale

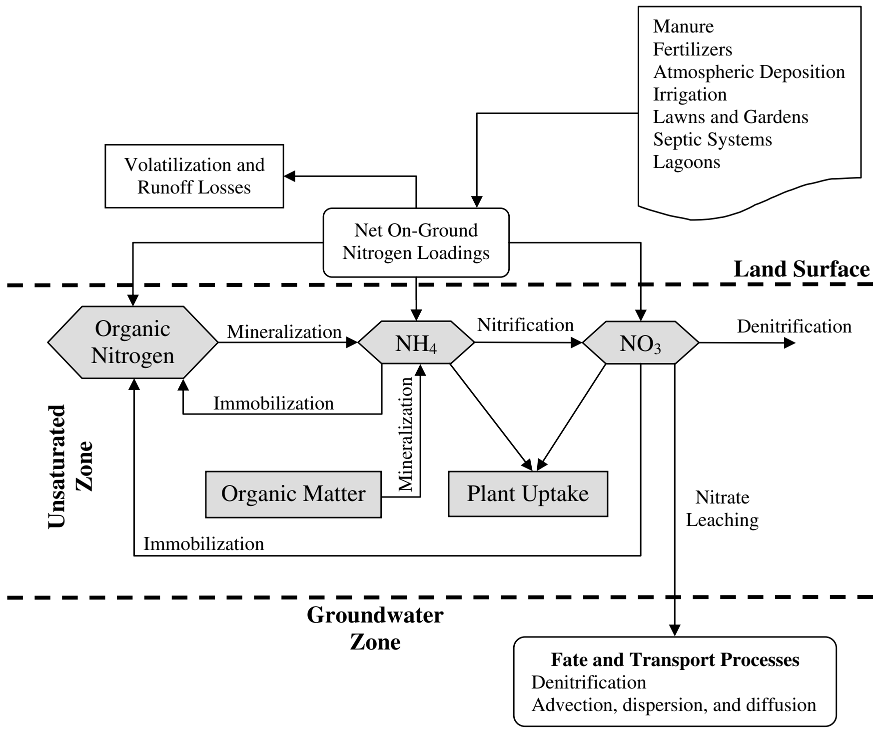

Figure 1 A schematic representation of the integrated three-zone approach to conceptualize the interacting processes that govern nitrate occurrences in groundwater. Note that nitrate concentration in groundwater is ultimately a function of on-ground nitrogen loading.

analysis and modeling, it is important to understand the interaction of the aforementioned factors to account for the transient and spatially variable nitrate leaching to groundwater. It is thus essential to use a soil nitrogen model. In turn, groundwater fate and transport models are vital in simulating the impact of proposed protection alternative measures that protect groundwater quality and reduce the level of contamination.

The very objective of this paper is to develop a conceptual modeling framework that integrates the on-ground nitrogen loadings, nitrogen soil dynamics, and nitrate fate and transport in groundwater. The modeling framework accounts for point and non-point sources of nitrogen. This integration is of great importance to realistically account for the different processes that nitrogen undergoes and in order to arrive at rational estimates of nitrate concentrations in groundwater. To demonstrate the applicability of the framework, Sumas—Blaine aquifer of Whatcom County, Washington State, US was considered.

Modeling framework

Overall description

Fig. 2 depicts a pictorial representation of the proposed framework for modeling the impact of land use on nitrate contamination of groundwater (Almasri, 2007). The framework is a simplification to the itemized conception presented earlier in the introduction of this manuscript. The framework incorporates the identification of the spatial distribution of the on-ground nitrogen sources and corresponding loadings, the simulation of soil nitrogen dynamics, and the modeling of the groundwater flow system and the nitrate fate and transport processes (Almasri and Kaluarachchi, 2004a).

In order to better comprehend the issue of linking the different components of the modeling framework as presented in Fig. 2, Fig. 3 depicts these linkages along with the different models as used in this study. First of all, the soil nitrogen model was developed earlier for the site presented later in this work (see Almasri and Kaluarachchi, 2004a for more details). In addition, the modeling framework relies on MODFLOW (Harbaugh and McDonald, 1996) for the simulation of the groundwater flow model and on MT3D (Zheng and Wang, 1999) to simulate the nitrate fate and transport processes in groundwater. Both, MODFLOW and MT3D use the same finite-difference grid.

It is worth mentioning that there are different mechanisms that control the fate and transport of nitrogen in the soil and groundwater zones. In addition, the models utilized in the framework connote different levels of complexities among them. It is however very important to keep in mind that these models and components ought to be executed in a sequential manner as depicted in Fig. 3. These linkages and steps are summarized as follows:

1. On ground nitrogen loading is computed. Thereafter, all surface losses of nitrogen are accounted for. The net loading is then considered as net input of nitrogen to the soil zone. Spatiality of the on-ground nitrogen loadings is maintained by using a land use map for nitrogen source allocation;

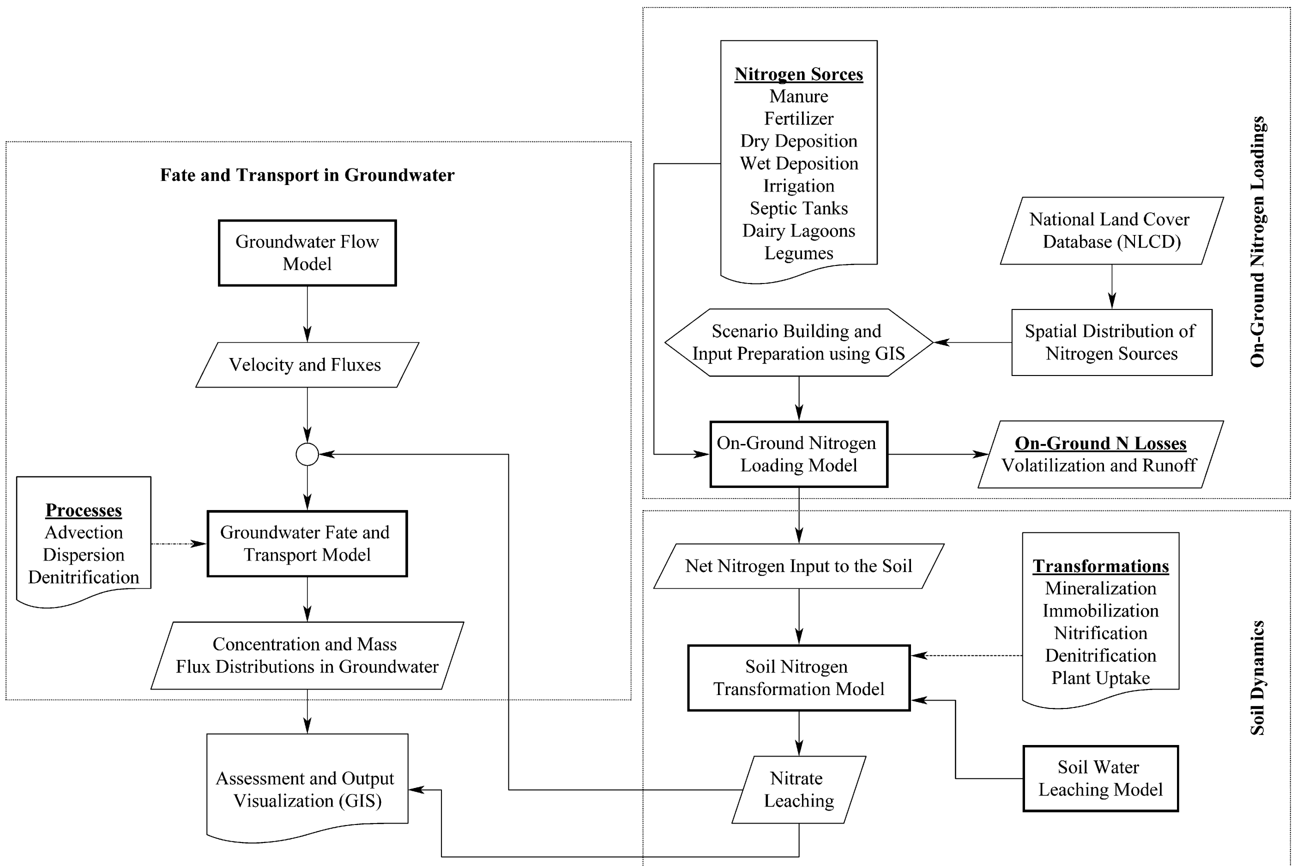

Figure 2 Schematic describing the modeling framework for the assessment of nitrate occurrences in groundwater for different input parameters and management scenarios.

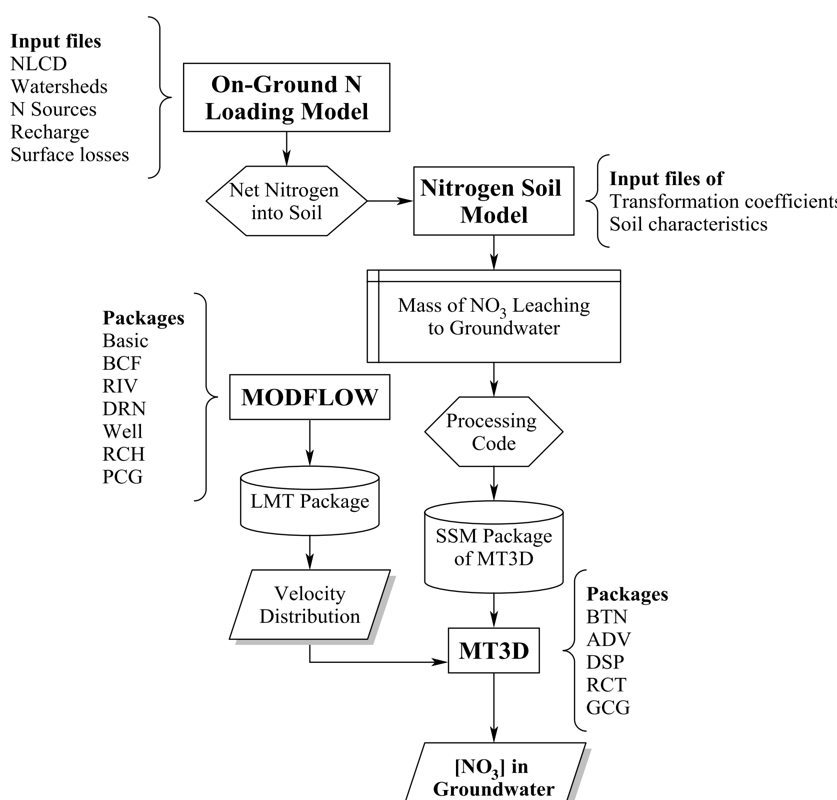

Figure 3 A schematic of the linkages between the models of on-ground N loading, soil N transformations, MODFLOW and MT3D.

2. This nitrogen input is subject to different transformations and plant uptake in the soil zone as shown in Fig. 1. The outcome of this would leach to groundwater as NO_3. Again, the NO_3 that leaches to the groundwater is dealt with spatially where it is written into the sink and source mixing (SSM) input file (supported by MT3D). This file contains all the information about the concentrations (or mass distribution) of NO_3 that enter the aquifer corresponding to the point and non-point sources. Generally, the SSM file is immense in terms of its size. This is due to the fact that at each time step, you ought to specify for each cell of the model domain the corresponding mass of NO_3 leaching to groundwater. To assure efficiency in framework implementation, it is better to develop the SSM file automatically. This feature would enhance the implementation of the modeling framework in highly distributed fine resolution situations;
3. Once the SSM file is developed automatically using an intermediate processing code, MT3D can be executed after the development of the necessary input files;
4. There is one important file to consider which is the FTL file (generated by MODFLOW for MT3D using the LMT package). In this file, MODFLOW stores important information that enables the MT3D to compute the velocity field. Needless to mention that the velocity field is necessary to account for the advection process of NO_3 in groundwater.
5. Stream—aquifer interaction is addressed roughly using the RIV package of MODFLOW. Both FTL and SSM files contain the related information to the RIV package along with other relevant packages.

Since this modeling framework is intended for regional analysis that entails large areas, fine time steps were avoided. Monthly time steps were considered for the soil and MT3D models while MODFLOW was developed under steady-state conditions and consequent assumptions. A transient groundwater flow model would capture better many of the dynamics of the drivers that ultimately dictate the transport of NO_3 in groundwater and hence the concentration distribution. Nevertheless, a transient model would imply that all input data to be variable with time which was unavailable for the study under consideration.

On-ground nitrogen loadings

The first step for the development of the modeling framework is the characterization of the spatial variability of the on-ground nitrogen sources and the estimation of the corresponding spatial and temporal distribution of the nitrogen loadings (see Figs. 1 and 2). The spatiality of the on-ground nitrogen sources can be characterized using the National Land Cover Database (NLCD) as prepared by the United States Geological Survey (see for instance Nolan et al., 2002; Almasri and Kaluarachchi, 2004a,b). The NLCD is accessible and processable by GIS and thus GIS can be conveniently utilized in utilizing the on-ground nitrogen loadings from the different point and non-point sources (see for instance Almasri and Kaluarachchi, 2003). The NLCD grid is comprised of 21 different land use classes that describe the entire US. The main land use classes of the NLCD include agriculture, industrial, residential, and surface water bodies. Table 1 shows the different nitrogen sources that

Table 1 The allocation of nitrogen from the different sources according to the NLCD classes

NLCD class	Dairy manure	Wet deposition	Dry deposition (regional)	Dry deposition (dairy)	Irrigation	Fertilizer	Lawns	Legumes
Open water								
Perennial ice/snow								
Low intensity residential		√	√				√	
High intensity residential		√	√				√	
Commercial/industrial/transportation								
Bare rock/sand/clay		√	√					
Quarries/strip mines/gravel pits		√	√					
Transitional		√	√		√	√		
Deciduous forest		√	√					
Evergreen forest		√	√					
Mixed forest		√	√					
Shrubland		√	√					
Orchards/vineyards/other		√	√		√	√		
Grasslands/herbaceous		√	√		√	√		
Pasture/hay		√	√		√	√		√
Row crops		√	√		√	√		
Small grains		√	√		√	√		
Fallow		√	√		√	√		
Urban/recreational/grasses		√	√				√	
Dairy farms	√	√	√	√	√			
Woody wetlands		√	√					
Emergent herbaceous wetlands		√	√					

concurrently contribute to each NLCD class. It should be noted that we chose the NLCD merely to demonstrate the procedure of allotting the loadings since the categories of the NLCD are wide and comprehensive. These categories can be generalized to cover different land use classifications espoused at different places.

Soil nitrogen dynamics

Once nitrogen enters the soil, it undergoes several biochemical transformations before leaching to groundwater mostly as nitrate (see Figs. 1 and 2). Many models are available to simulate soil nitrogen transformations. Detailed illustration of available models can be found in Ma and Shaffer (2001) and McGechan and Wu (2001). The main reactions and pathways that the nitrogen undergoes include mineralization, immobilization, nitrification, denitrification, volatilization, crop uptake, and leaching from the soil zone. The final output from the soil nitrogen models is the spatial and temporal nitrate leaching to groundwater at specified time intervals. Such models can be customized to provide the output for the different NLCD classes across the study area of interest. Nitrate available for leaching, NAL, (kg/month) for each NLCD class is calculated from the total nitrate budget as follows:

$$\mathrm{NAL} = \mathrm{NAL}_0 + \mathrm{NO}_3^{\mathrm{So}} - \mathrm{NO}_3^{\mathrm{Si}} \tag{1}$$

where NAL_0 is nitrate available for leaching at the beginning of each time step (month) and $\mathrm{NO}_3^{\mathrm{So}}$ and $\mathrm{NO}_3^{\mathrm{Si}}$ are the summations of all the monthly sources and sinks of nitrate, respectively. $\mathrm{NO}_3^{\mathrm{So}}$ includes nitrate that enters the soil from the ground surface, nitrate from nitrification, and the initial nitrate mass. $\mathrm{NO}_3^{\mathrm{Si}}$ includes nitrate losses in runoff, immobilization, denitrification, and plant uptake. The monthly flux of nitrate leaching (kg/month), NL, is computed using the following exponential relationship as presented by Shaffer et al. (1991) and Pierce et al. (1991):

$$\mathrm{NL} = \mathrm{NAL} \times \left[1 - \exp\left(\frac{-K \times \mathrm{WAL}}{\omega}\right)\right] \tag{2}$$

where K is the leaching coefficient (L^0) and equals 1.2 as inferred from Pierce et al. (1991, p. 280); WAL is the water available for leaching (m^3); and ω is the volume of voids of the soil (m^3) which can be determined using the following equation (Pierce et al., 1991):

$$\omega = \left[1 - \frac{\mathrm{BD}}{\mathrm{PD}}\right] \times \text{soil depth} \times \text{surface area} \tag{3}$$

where BD is the bulk density ($\mathrm{kg/m}^3$) and PD is the particle density ($\mathrm{kg/m}^3$). The value of K in Eq. (2) depends largely on soil characteristics and can be altered during the process of calibration if needed. The motivation for using Eq. (2) in simulating the amount of nitrate leaching is its simplicity. In addition, Eq. (2) is used in the NLEAP model which is one of the most popular models for the simulation of nitrate leaching (see Section ''Soil nitrogen dynamics''). Mathematical derivation of an equation similar to Eq. (2) is given in Williams and Kissel (1991).

Groundwater flow and nitrate fate and transport

The last major step in this framework is the development of the nitrate fate and transport model in groundwater (see Fig. 2). The partial differential equation that governs the three-dimensional transport of a single chemical constituent in groundwater, considering advection, dispersion, fluid sinks/sources, equilibrium-controlled sorption, and first-order irreversible rate reactions is described in the following (Zheng and Bennett, 1995):

$$R\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{\theta}C_s - \lambda\left(C + \frac{\rho_b}{\theta}\overline{C}\right) \tag{4}$$

where C is the dissolved concentration (ML^{-3}); $\overline{C}$ is the adsorbed concentration (MM^{-1}); t is time (T); D_{ij} is the hydrodynamic dispersion coefficient tensor ($\mathrm{L}^2\mathrm{T}^{-1}$); v_i is the pore water velocity (LT^{-1}); q_s is the volumetric flow rate per unit volume of aquifer and represents fluid sources and sinks (T^{-1}); C_s is the concentration of the fluid source or sink flux (ML^{-3}); λ is the reaction rate constant (T^{-1}); R is the retardation factor (L^0); ρ_b is the bulk density of the porous medium (ML^{-3}); and θ is the porosity (L^0).

As can be concluded from Eq. (4), the nitrate fate and transport model requires the velocity of the groundwater flow. In our case, the FTL file of the LMT package (supported by MODFLOW) contains all the necessary information for MT3D to compute the velocity field. As such, it is necessary to develop a groundwater flow model to obtain the velocity field. The following governing equation of the three-dimensional groundwater flow has to be solved and the head distribution and subsequently the velocity are obtained and computed (Schwartz and Zhang, 2003):

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right) - W = S_S\frac{\partial h}{\partial t} \tag{5}$$

where K_{xx}, K_{yy} and K_{zz} are values of hydraulic conductivity (LT^{-1}) along x-, y-, and z-coordinate axes; h is the hydraulic head, W is a flux term that accounts for pumping (LT^{-1}), recharge, or other sources and sinks; S_s is the specific storage (L^{-1}); and t is time (T). The solution to Eq. (5) provides a transient prediction of hydraulic head in a three-dimensional domain for an anisotropic hydraulic-conductivity field (Schwartz and Zhang, 2003).

Coefficients of hydrodynamic dispersion (see Eq. (4)) are given by the following equations:

$$D_\mathrm{L} = \alpha_\mathrm{L} v_i + D^* \tag{6}$$

$$D_\mathrm{T} = \alpha_\mathrm{T} v_i + D^* \tag{7}$$

where D_L and D_T are the longitudinal and transverse hydrodynamic dispersion coefficients, respectively; D^* is the effective diffusion coefficient ($\mathrm{L}^2\mathrm{T}^{-1}$); and α_L and α_T are the longitudinal and transverse dispersivities (L), respectively. To estimate the longitudinal dispersivity, the following relationship can be used (Xu and Eckstein, 1995):

$$\alpha_\mathrm{L} = 0.83 \times [\log(L)]^{2.414} \tag{8}$$

where L is the spatial scale of the groundwater flow (m) and α_L is the longitudinal dispersivity (m). The ratio of transverse to longitudinal dispersivity was taken as 0.1 (Gelhar et al., 1992). Molecular diffusion for nitrate equals

$5 \times 10^{-5}\,m^2/d$ (Frind et al., 1990). Denitrification is the dominant chemical reaction that affects nitrate concentration in the groundwater under anaerobic conditions (Frind et al., 1990; Hantush and Mariño, 2001; Shamrukh et al., 2001). The first-order decay coefficient, λ, is related to the half-life time, $t_{1/2}$, as follows:

$$\lambda = \frac{0.693}{t_{1/2}} \tag{9}$$

The half-life time of nitrate is in the range of 1–2.3 years (Frind et al., 1990). However, this range cannot be generalized since the half-life time of nitrate depends on aquifer typology. Nitrate is a highly mobile species with little sorption on the solid matrix. Hence, sorption is neglected and the retardation coefficient is assumed to be one (Shamrukh et al., 2001). Initial conditions represent nitrate concentration at the beginning of simulation. Sinks and sources are considered as boundary conditions and they are classified as areally distributed or as points. Examples of point sinks or sources include wells, drains, and rivers. It is necessary to specify the concentration of nitrate for sources. Nitrate leaching to groundwater from the soil was taken in the units of mass per month (kg/month) over model cells. For sinks, nitrate concentration equals the concentration of the groundwater at the sink location.

Application of the modeling framework

To show framework applicability, it was implemented for the extended Sumas–Blaine aquifer located in an agricultural watershed, Whatcom County, Washington State, US.

Description of the study area

Sumas–Blaine aquifer (see Fig. 4) is the principal surficial aquifer in the study area and is located in the Nooksack Watershed in Whatcom County in the northwest corner of Washington State, US. Sumas–Blaine aquifer is used for domestic, agricultural, and industrial purposes and occupies an area of about 388 km^2 (Tooley and Erickson, 1996). Most of the soils in the study area are categorized as well drained. The water table is shallow, typically less than 3 m, but exceptions occur near the City of Sumas where the depth to the water table exceeds 17 m and depths exceed 8 m near the eastern part of the aquifer (Tooley and Erickson, 1996). Annual precipitation ranges between 1500 mm in the northern uplands to about 1000 mm in the lowlands. Recharge to the aquifer is largely due to the infiltration of precipitation and irrigation. Evapotranspiration is highest during June-to-August period (Cox and Kahle, 1999). The study area under consideration is larger than the boundaries of Sumas–Blaine aquifer and includes parts of Canada.

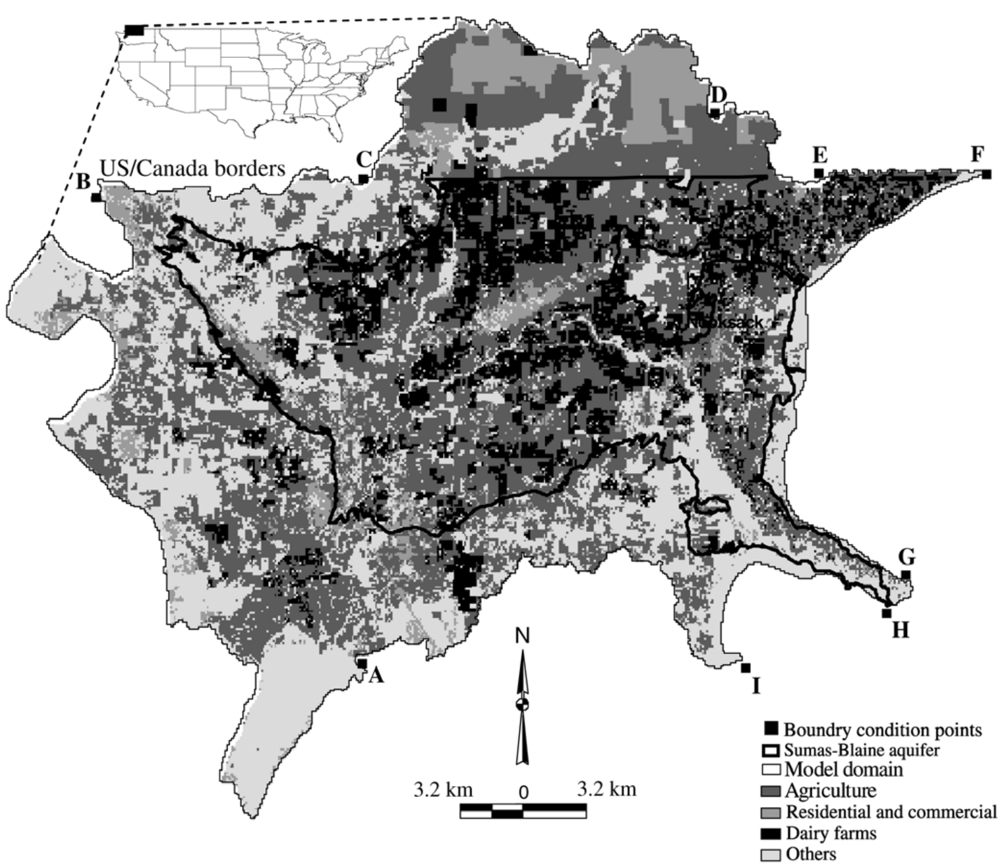

Figure 4 Layout of the model domain consisting of the extended Sumas–Blaine aquifer, locations of boundary conditions, and land use classes as of 1992 after merging the dairy farm areas. It should be noted that there are 21 land use classes considered in the analysis and for a better visualization, these classes are condensed to four classes in this figure.

One reason for this larger area is that there is a substantial manure application on berry plantations located in the Canadian side. Since the groundwater flow is from north to south towards the Nooksack River, the nitrogen-rich manure application in the Canadian side has major influence on groundwater quality in the south (Stasney, 2000; Nanus, 2000;Mitchell et al., 2003). In addition, the extended area supports a more realistic boundary conditions that suite the groundwater flow model. The total area of the extended aquifer region is approximately 973 km^2 and is shown in Fig. 4. From then on, the model domain or the study area will refer to the extended Sumas–Blaine aquifer. There are 39 drainages representing the extended aquifer regions.

Due to the intensive agricultural activities in the study area (see Fig. 4 for the land cover distribution), groundwater quality in the aquifer has been continuously degrading and nitrate concentrations are increasing (Erickson, 1998; Kaluarachchi et al., 2002). The study area is the second in Washington State and the eighth in the US for dairy production (Stasney, 2000). The persistent elevated nitrate concentrations in the groundwater of the study area are found close to the locations of dairies (Morgan, 1999). The study area produces more than 59% of the US red raspberries ranking fifth in world raspberry production (Stasney, 2000). The aquifer readily interacts with surface water and serves as an important source of summer streamflows for the rivers and creeks in the study area (Tooley and Erickson, 1996). The study area supports a variety of fish species important to the cultural heritage, economy, and the ecology of the area (Blake and Peterson, 2001). Since the role of nitrate in *eutrophication* is well recognized (Wolfe and Patz, 2002), nitrate contamination of the surface water of the study area is a concern as it greatly affects the fish habitat. In general, the transport of nitrate to surface water occurs mainly via discharge of groundwater during baseflow conditions (Hubbard and Sheridan, 1994; Devlin et al., 2000; Schilling and Wolter, 2001; Bachman et al., 2002). Therefore, the prevention of groundwater contamination from nitrate also protects surface water quality.

Nitrogen sources and loadings

As originally developed by the USGS, the NLCD grid does not include the dairy farm class. Nevertheless, the dairy farm sector is a major industry in the study area. To integrate the dairy farm areas within the NLCD grid, a GIS polygon shapefile of the spatial distribution of the dairy farms was obtained and merged with the NLCD. The nitrogen sources in the study area include dairy and poultry manure, dairy lagoons, application of nitrogen-based fertilizers on agricultural fields and lawns, atmospheric deposition, irrigation with nitrogen-contaminated groundwater, septic tanks, and nitrogen fixed by legumes.

To calculate the on-ground nitrogen loadings from manure and dairy lagoons, a GIS point shapefile of the spatial locations of the dairy farms was utilized. The number of dairy farms in the study area exceeds 200 with a total of more than 51,000 milking cows; 7500 dry cows; 10,000 heifers; and 9000 calves. To compute nitrogen loading from dairy manure, the numbers of animals for each drainage was determined using the GIS point shapefile that contains the spatial distribution of the dairy farms along with the key data. Thereafter, the numbers of animals for each drainage were multiplied by the corresponding annual nitrogen production (Meisinger and Randall, 1991). This loading was allotted to the dairy farm class as shown in Table 1. The average annual nitrogen leaching from a dairy lagoon was estimated as 850 kg of N for the study area (Cox and Kahle, 1999). This amount was multiplied by the number of lagoons per drainage to obtain the nitrogen loading from dairy lagoons.

Nitrogen from agricultural fertilizers is obtained by multiplying the fertilizer application rate for each crop with the corresponding fertilized area for each drainage using the information from Cox and Kahle (1999), Blake and Peterson (2001), and Almasri and Kaluarachchi (2004a). As depicted in Table 1, this amount of nitrogen was then distributed uniformly over the agricultural NLCD classes located in each drainage. Those classes include for instance, *orchards*, *grasslands/herbaceous*, *row crops*, *fallow*, *pasture/hay*, and *small grains*. In addition, inorganic fertilizers are used for the lawns and gardens of the study area. The annual lawn fertilizer application rate equals 148 kg/ha (Kaluarachchi and Almasri, 2004). We used the *urban/recreational/grasses* and *residential* classes of the NLCD to approximate the area of lawns and gardens. Clovers are nitrogen fixing leguminous plants that are common in the study area. Cox and Kahle (1999) reported an annual contribution of 5.5 kg/hectare of nitrate from legumes. This loading from legumes was assigned to the *pasture/hay* NLCD class.

Atmospheric deposition of nitrogen corresponds to nitrogen dissolved in precipitation and dry deposition (Schepers and Mosier, 1991). The average nitrogen concentration in rainfall in western Washington is 0.26 mg/l (Cox and Kahle, 1999). Nitrogen loading from precipitation is calculated by multiplying this concentration with precipitation amount. Dry deposition of nitrogen includes particulate fallout and sorption of gaseous materials. Following Cox and Kahle (1999), the regional nitrogen deposition was about 46% of wet deposition for western Washington or 1.12 kg/ha and this amount was allocated for the entire study area. The annual rate of dry redeposition of nitrogen volatilized from dairy manure was taken as 17 kg/hectare and allocated to the dairy farm class.

To estimate the nitrogen loading from irrigation, the mean drainage concentrations of nitrate, ammonium, and organic-N in irrigation water were estimated from the database compiled by Kaluarachchi et al. (2002) using GIS. For each drainage, the monthly irrigation volume was then multiplied by these concentrations to obtain the nitrogen loading due to irrigation. The per capita annual nitrogen loading from septic tanks equals 4.5 kg (Cox and Kahle, 1999). A GIS point shapefile of the spatial distribution of the septic tanks was used to assign the corresponding nitrogen loadings. The GIS shapefile provides the number of bedrooms connected with each septic tank. It was assumed that a bedroom serves one person.

Soil nitrogen dynamics

Shaffer et al. (1991) developed the *Nitrate Leaching and Economic Analysis Package* (NLEAP), which is widely used in many field sites as evident from the literature (see for instance Khakural and Robert, 1993; Shaffer et al., 1994; Follett et al., 1994; Wylie et al., 1994; Wylie et al., 1995; Follett, 1995; Shaffer et al., 1995; Delgado et al., 1998; Xu et al., 1998; Delgado, 1999; Delgado et al., 2000; Ersahin, 2001; Ersahin and Rüstü Karaman, 2001; Rimski-Korsakov et al., 2004). NLEAP is a field-scale model that determines the mass of nitrate leaching to groundwater due to agricultural practices. In this work, the soil nitrogen model that was developed by Almasri and Kaluarachchi (2004a) was used. This model follows the framework outlined in the NLEAP model and others (Shaffer et al., 1991; Williams and Kissel, 1991; Schepers and Mosier, 1991; Pierce et al., 1991). The motivations for developing a soil nitrogen model are (Almasri and Kaluarachchi, 2004a): (i) to incorporate agricultural, domestic, and natural sources of nitrogen; (ii) ease of data manipulation using the NLCD grid and the flexible output processing using GIS; and (iii) ability to integrate the overall model with the fate and transport model of nitrate in groundwater.

WAL (in Eq. (2)) is approximated as the recharge to groundwater. A GIS polygon shapefile of groundwater recharge coverage for the study area was obtained from Vaccaro et al. (1998) and processed for the study area. Vaccaro et al. (1998) estimated recharge values for Puget Sound aquifer system, which encompasses the study area. They used liner regression between precipitation and groundwater recharge. Data for estimating the regression equations were obtained from precipitation and recharge estimates of 26 small basins within the Puget Sound aquifer. The recharge estimates were obtained from previous studies in the area that used a deep percolation model and the Hydrogeological Simulation Program-FORTRAN (HSPF). The annual recharge estimates were then adjusted based on land use and land cover.

A detailed illustration about the development, application, and verification of the soil nitrogen model is provided in Kaluarachchi and Almasri (2004) and Almasri and Kaluarachchi (2004a).

Groundwater flow model

The geology of the study area is such that there are three major geologic layers and two confining units. The major layers are Sumas layer, Everson-Vashon fine-grained unit, and finally the Everson-Vashon coarse-grained unit (Kemblowski and Asefa, 2003b). Sumas layer is the main productive layer and the most vulnerable to nitrate contamination (Morgan, 1999). Much of the groundwater extraction and nitrate contamination occur in this layer. This layer is composed mainly of stratified sand and gravel outwash and the coarse-grained alluvium of the Nooksack and Sumas Rivers. Sumas layer covers most of the model domain except in the northwestern, southwestern, and central eastern parts. The Everson-Vashon fine-grained layer is a semi-confining unit composed of thick accumulation of unsorted clay and sandy silt with some local coarse-grained lenses. Typically, this layer is more than 33 m thick and restricts the hydraulic connectivity between the overlying Sumas layer and the underlying Everson-Vashon coarse-grained layer. Tesoriero et al. (2000) modeled the groundwater flow for a portion

Table 2 Description of boundary conditions used in the development of the groundwater flow and nitrate fate and transport models (see Fig. 4)

Segment	Flow[a]	Transport
AB	Constant head	Type-1 with zero concentration
BC	No-flow	Zero-dispersive
CD	No-flow	Zero-dispersive
DE	No-flow	Zero-dispersive
EF	Constant flux	Type-1 with concentration of 3 mg/L
FG	No-flow	Zero-dispersive
GH	Constant head	Type-1 with variable concentrations
HI	No-flow	Zero-dispersive
IJ	No-flow	Zero-dispersive

[a] Adapted from Kemblowski and Asefa (2003a).

of the study area and assumed a no-flow boundary for the bottom of Sumas layer. Therefore, a single-layer model was developed corresponding to Sumas layer and the groundwater flow model is a vertically integrated two-dimensional areal model. This means that the 3-D general groundwater flow equation (see Eq. (5)) reduces to 2-D. The boundary conditions stipulated for the model domain given in Fig. 4 are summarized in Table 2 (Kemblowski and Asefa, 2003b).

Nooksack and Sumas rivers are the two major rivers that drain the study area along with several creeks and ditches. The RIVER package of MODFLOW was used to simulate the stream–aquifer interaction. Ditches are modeled using the DRAIN package of MODFLOW. Locations of rivers and ditches were obtained from an existing GIS coverage and levels were approximated from the digital elevation model grid. The transmissivity distribution was obtained for Sumas layer following the analysis of the pumping test data (Cox and Kahle, 1999; Kemblowski and Asefa, 2003b). The model domain was uniformly discretized into a finite-difference grid of $100 \times 100\ m^2$ cells. Model calibration was conducted by altering the transmissivity values until the simulated potentiometric heads matched closely the observed ones. A detailed illustration regarding the development of the groundwater flow model can be found in Kemblowski and Asefa (2003a).

Nitrate fate and transport model

As mentioned earlier, MT3D was used in developing the nitrate fate and transport model using the same finite-difference grid as in MODFLOW. MT3D interfaces directly with MODFLOW. It retrieves the saturated thickness for each cell, fluxes across cell interfaces in all directions, and the locations of flow rates of the various sources and sinks. This information is generated and saved by MODFLOW in an unformatted flow-transport link file (the FTL file). As in the flow model, the nitrate fate and transport model is a vertically integrated two-dimensional areal model with a variable cell thickness. For temporal discretization, each year was divided into 12 stress periods where each stress period corresponds to one month during which all inputs are constant. The initial conditions are set as the background concentration of nitrate for the entire model domain to predict the semi-equilibrium conditions. The boundary conditions stipulated for the model domain given in Fig. 4 are summarized in Table 2.

For the study area, denitrification was considered as the sole dominant chemical reaction that affects nitrate concentration in the aquifer. Tesoriero et al. (2000) carried out a study on the mechanism and rate of denitrification in the aquifer. They concluded that significant denitrification occurs as facilitated by anaerobic conditions and due to the dramatic increase in excess N_2 concentrations coupled with a decline in nitrate levels in groundwater immediately downgradient from the nitrate plume. The low levels of dissolved oxygen along the deep groundwater flow path and the presence of nitrite in the water samples from the deep wells suggest that denitrification is occurring in the aquifer.

Calibration

The purpose of calibrating the mathematical model of nitrate fate and transport is to update the critical input parameters such that the simulated nitrate concentrations are in close agreement with the field observed concentrations (Zheng and Bennett, 1995). In the following, calibration data and related parameters, calibration approach, assessment measures, and results of model calibration and verification are given.

Calibration data

Kaluarachchi et al. (2002) compiled the nitrate concentration data of the groundwater of the study area in a composite GIS-based database. The nitrate concentration data used in the calibration and verification of MT3D were obtained mainly from four agencies, USGS, Whatcom County Department of Health, Washington State Department of Health, and Washington State Department of Ecology. All available data were assembled into a single composite database. There are 3831 wells with 9842 measurements of nitrate from 1990 to 2000. A GIS point shapefile of well spatial locations and corresponding data was developed and used. All the wells tap Sumas–Blaine aquifer. Since the developed model of nitrate fate and transport in groundwater is a single-layer model, no differentiation was made between the wells in terms of well sampling depth.

The database was assessed to determine its suitability for calibration. The analysis of the database showed that the nitrate concentrations of 1990 and 1991 are the best in terms of the spatial and temporal distributions. The data of 1997 are spatially distributed, but concentrated in the months of March and April. The data of 1998 are better in terms of the monthly distribution when compared to 1997 data, but lack the spatiality. As such, observations from 1990 and 1991 and observations from 1997 and 1998 were utilized in model calibration and verification, respectively. It is worth mentioning that the concentration data is time averaged. Fig. 5 depicts the spatial distribution of model calibration and verification receptors.

Calibration parameters

The most critical and uncertain parameters should be calibrated. In order to designate the parameters that mostly influence the simulated nitrate concentrations at the calibration receptors, a preliminary sensitivity analysis was conducted. The following input parameters were chosen;

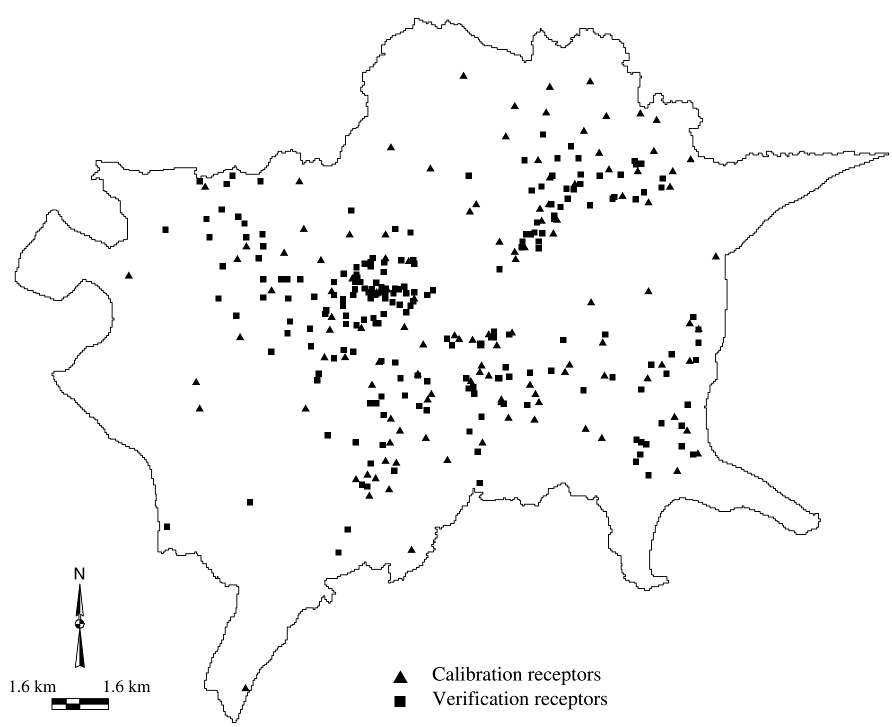

Figure 5 The spatial distribution of the nitrate receptors used for model calibration and verification.

groundwater denitrification rate, longitudinal dispersivity, initial concentration, river nitrate concentration, soil mineralization rate, soil nitrification rate, soil denitrification rate, on-ground manure loading, on-ground fertilizer loading, atmospheric deposition, percentage of runoff losses, and rate of surface volatilization. Relative sensitivities were calculated using the following relationship (McCuen and Snyder, 1986):

$$\upsilon_{\Re} = \frac{\partial M_O / M_O}{\partial M_I / M_I} \quad (10)$$

where $\upsilon_{\Re}$ is the relative sensitivity coefficient of model output parameter M_O with respect to the model input parameter M_I. Model output includes a multitude of parameters depending on the purpose of the analysis. For instance, the output parameter could be nitrate leaching to groundwater or nitrate concentration. $\upsilon_{\Re}$ is convenient for comparing sensitivity coefficients for different parameters of different physical units. The values of the root mean squared error (RMSE) of the observed versus simulated nitrate concentrations at the calibration receptors were calculated for the abovementioned input parameters and the corresponding relative sensitivity coefficients were computed (by the end of the 10 year period) after increasing the parameters by 50%. Such increase is in concordant with many studies in the literature (see for instance Anderson and Woessner, 1992). Fig. 6 depicts the relative sensitivity coefficients for the different input parameters. As can be concluded from this figure, groundwater denitrification rate has the highest influence followed by manure loading, fertilizer loading, soil denitrification rate, runoff losses, and soil nitrification rate.

Since dispersion dictates to some extent nitrate mass distribution in the groundwater, it has a noticeable effect on RMSE. The effects of soil mineralization rate and surface water nitrate concentration distribution are insignificant with regard to the calibration receptors. Fig. 6 provides a genesis guess of the direction of parameter change in order to improve model calibration results. For instance, Fig. 6 suggests a decrease in groundwater denitrification rate in order to decrease the RMSE while an increase in the fertilizer application rate is preferable since it decreases the RMSE. As such, the calibration parameters are the groundwater denitrification rate and the soil nitrification and denitrification rates. However, on-ground nitrogen loadings from manure and fertilizers were kept constant through the calibration process since these loadings are known to an acceptable level of certainty.

Calibration approach

Since the current land use practices have been occurring in the study area for a long time except for small changes, nitrogen buildup in the soil and the transport of nitrate in the aquifer are expected to be in a quasi-steady state. That is, the annual mean value of nitrate concentration at a given location may be in a steady state and that the transient variation of nitrate concentration over a year at a given location may be approximately repeated every year. Therefore, the model at a specific location produces twelve dissimilar monthly nitrate concentration values every year and after reaching the quasi-steady state it repeats them on yearly basis. In order for the model to be in this quasi-steady state, it was run for a long time period using a nitrate baseline concentration of 0.1 mg/l as the initial concentration for the entire model domain. Afterward, the model was calibrated for the above mentioned calibration parameters via the trial-and-error approach for the 1990 and 1991 time averaged nitrate concentration data.

Calibration and verification assessment measures

In general, correlation-based and error-based measures have been widely used to evaluate the goodness-of-fit of the hydrologic models (Legates and McCabe, 1999). The

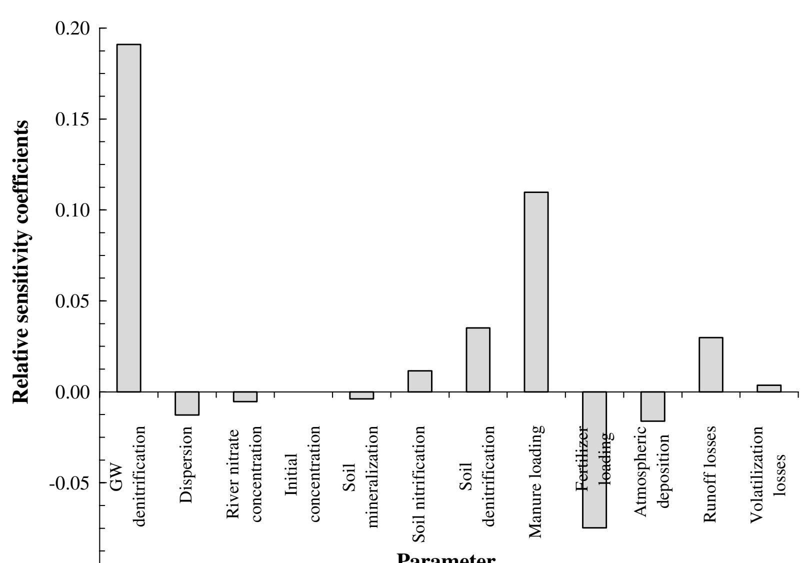

Figure 6 Relative sensitivity coefficients of the root mean square error between the observed and simulated nitrate concentrations at the calibration receptors with respect to different input parameters. Input parameters were increased by 50%.

correlation-based measures considered in this work include the correlation coefficient, r, index of agreement, and coefficient of efficiency. The index of agreement is given in the following equation (Legates and McCabe, 1999):

$$d = 1 - \frac{\sum_{i=1}^{n}(O_i - S_i)^2}{\sum_{i=1}^{n}(|S_i - \bar{O}| + |O_i - \bar{O}|)^2} \tag{11}$$

where d is the index of agreement (L^0); O_i and S_i are the observed and simulated nitrate concentrations at receptor i (mg/l); $\bar{O}$ is the average observed nitrate concentration; and n is the number of receptors. The index of agreement varies from 0 to 1 with higher values indicating better agreement between the simulated and observed concentrations. The coefficient of efficiency (E) is given in the following relationship (Legates and McCabe, 1999):

$$E = 1 - \frac{\sum_{i=1}^{n}(O_i - S_i)^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2} \tag{12}$$

The coefficient of efficiency is a dimensionless measure, which ranges from $-\infty$ to 1 with higher values denoting better agreement. However, Legates and McCabe (1999) suggested the use of other dimensionless coefficients that are not inflated by squared values such as the modified index of agreement (d_1), and the modified coefficient of efficiency (E_1), as defined in the following equations:

$$d_1 = 1 - \frac{\sum_{i=1}^{n}|O_i - S_i|}{\sum_{i=1}^{n}(|S_i - \bar{O}| + |O_i - \bar{O}|)} \tag{13}$$

and

$$E_1 = 1 - \frac{\sum_{i=1}^{n}|O_i - S_i|}{\sum_{i=1}^{n}|O_i - \bar{O}|} \tag{14}$$

The error-based measures include the root mean squared error (RMSE), the mean absolute error (MAE), and the mean relative error (MRE). These measures can be computed using the following formulas (Anderson and Woessner, 1992; Legates and McCabe, 1999):

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i}^{n}(O_i - S_i)^2}{n}} \tag{15}$$

$$\mathrm{MAE} = \frac{\sum_{i}^{n}|O_i - S_i|}{n} \tag{16}$$

$$\mathrm{MRE} = \frac{\mathrm{RMSE}}{\Delta} \tag{17}$$

where Δ is the concentration range and equals the difference between the maximum and minimum observed nitrate concentrations. MRE is an important measure since both RMSE and MAE do not provide a relative indication in reference to the actual data.

Calibration and verification results

Calibration was carried out via the trial-and-error approach, though; automated calibration was sought at the outset. It turned out that automated calibration codes would require a whole lot of model runs to figure out the sensitivity of calibration receptors to the calibration parameters at the different designated zones. As such, a uniform value of groundwater denitrification rate was first assigned to the entire model domain and equaled 8.25×10^{-3} day^{-1} corresponding to a nitrate half-life of 2.3 years (Frind et al., 1990). This value of the denitrification rate was considered as a reference value. Through the course of calibration, denitrification rates were spatially altered from the reference value until the simulated nitrate concentrations at the calibration receptors matched closely the observed values. At receptors where simulated nitrate concentrations were largely different from the observed ones; soil nitrification and denitrification rates were altered.

Fig. 7 depicts the scatterplot of the observed versus simulated nitrate concentrations at the calibration receptors

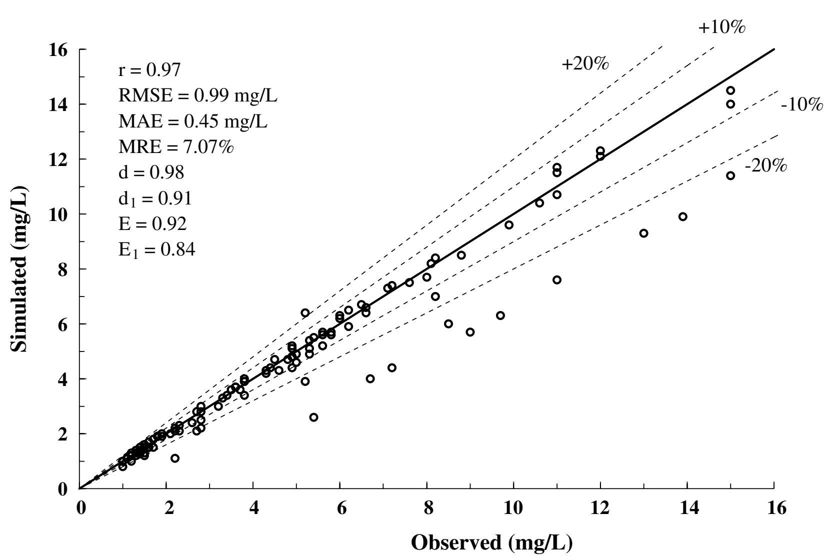

Figure 7 Scatterplot of the observed versus simulated monthly nitrate concentrations at the calibration receptors. The solid line represents the 45° line and the dashed lines represent the ±10% and ±20% error bounds. The symbols are: correlation coefficient (r), root mean squared error (RMSE), mean average error (MAE), mean relative error (MRE), index of agreement (d), modified index of agreement (d_1), coefficient of efficiency (E), and modified coefficient of efficiency (E_1).

(shown in Fig. 5). To facilitate the assessment of the calibration results, error bounds were provided as shown in Fig. 7. Error bounds were calculated by adding (and subtracting) the percentage of error to the simulated and observed values and then drawing the corresponding upper and lower lines that go through. The majority of the points are within the ±10% error bounds. It is worthwhile to mention that there are few outliers below the 45° line. These outliers signify that the model underestimates the concentrations at these receptors and that higher nitrate leaching might be needed. Likewise, Fig. 8 depicts the scatterplot of the observed versus simulated nitrate concentrations at the verification receptors (shown in Fig. 5). Fig. 8 shows that the model performance in the verification phase is slightly poor when compared to the calibration results. Nevertheless, a large number of data points fall within the ±20% error bounds.

Assessment measures of model calibration and verification are summarized in Figs. 7 and 8. High values of correlation coefficients, indices of agreement, and coefficients of efficiency suggest a good match between observed and simulated nitrate concentrations. Although the modified index of agreement and the modified coefficient of efficiency show lower values as expected, they still denote a good calibration results and to a less extent acceptable verification results. The mean relative error signifies low relative errors in the calibration and verification simulations. Further analysis showed that 80% and 60% of the simulated concentrations were within an error margin of 10% for calibration and verification, respectively.

To further verify the outcome of the calibrated model, the total yearly nitrate mass estimates in the groundwater of the drainages of the study area were calculated from the observed and simulated nitrate concentrations. We examined the scatterplot (not shown here) of the total annual nitrate mass in the groundwater of the drainages of the model domain as estimated from the nitrate observation receptors and the model simulation results. The results signify a contrast of 15%. The relationship between average annual on-ground nitrogen loading rate and the average annual simulated nitrate concentrations for model domain drainages was examined. This relationship confirms in a broad sense the existence of a distinct relationship with a 0.77 correlation coefficient. The few outliers (not shown in the manuscript) signify the possible interference of specific explanatory parameters such as soil type, groundwater recharge, soil permeability, nitrogen constituents, and the groundwater fate and transport processes. Finally, Fig. 9 depicts the spatial distribution of nitrate concentration after reaching the quasi-steady state at the end of the simulation period. Results show a high correlation between elevated nitrate concentrations and agricultural areas including dairy farms.

Sensitivity analysis

In general, a sensitivity analysis is carried out to test the overall responsiveness of the model to a certain input parameter (Zheng and Bennett, 1995; Oyarzun et al., 2007). The sensitivity analysis points out the critical parameters that need to be investigated and scrutinized via field studies and data gathering. Additionally, sensitivity analysis can be viewed as a way to assess the uncertainty effect of the input parameters on the model output.

A set of the input parameters was chosen and Eq. (10) was utilized to compute the relative sensitivity coefficients to these input parameters for the frequency of MCL violations for the entire study area for ±50% change in each input parameter. Fig. 10 depicts the results of the sensitivity analysis where groundwater denitrification rate and the on-ground manure loading have the highest impact on the frequency of MCL violations followed by fertilizer loading and atmospheric deposition. Fig. 10 shows clearly that the

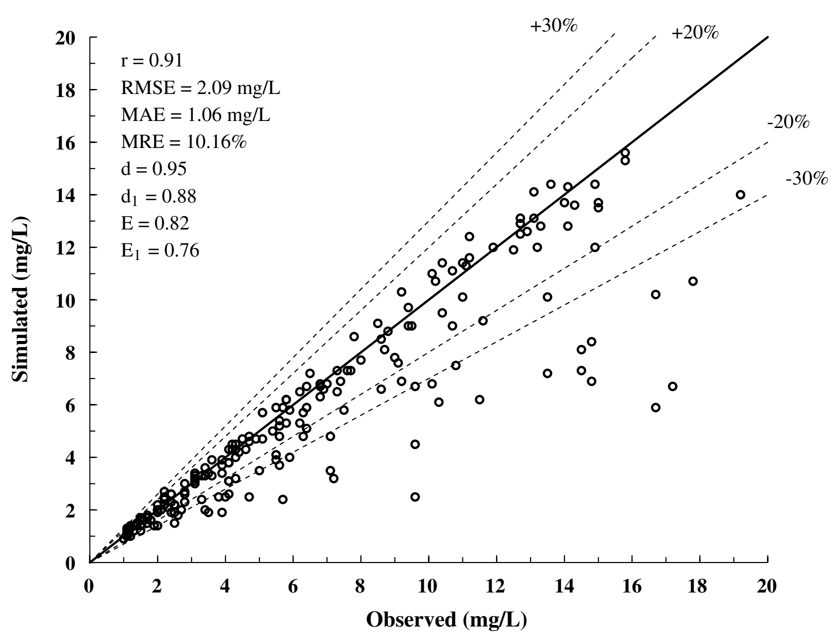

Figure 8 Scatterplot of the observed versus simulated monthly nitrate concentrations at the verification receptors. The solid line represents the 45° line and the dashed lines represent the ±20% and ±30% error bounds.

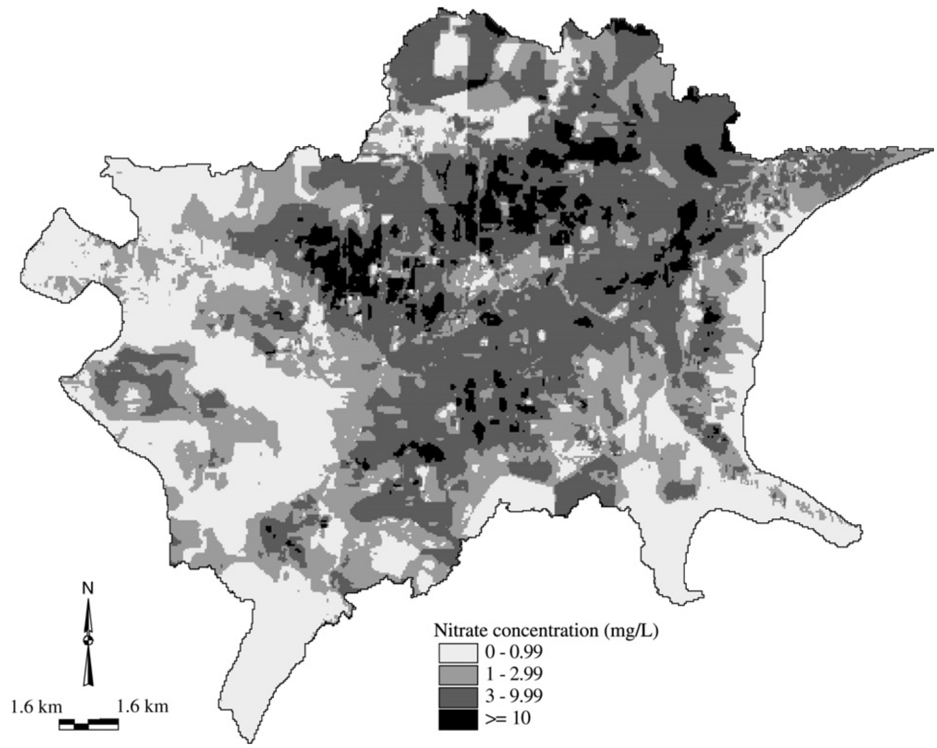

Figure 9 The spatial distribution of nitrate concentration at the end of the simulation period.

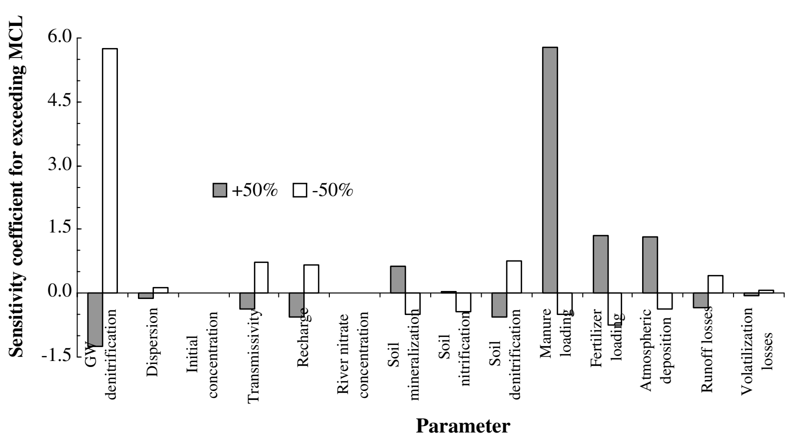

Figure 10 Relative sensitivity coefficients of the frequency of nitrate concentrations exceeding the MCL with respect to different parameters for a ±50% change in each parameter.

denitrification process in groundwater has a higher impact on reducing the nitrate mass in the groundwater when compared to advection (transmissivity) and mechanical dispersion. Further analysis was conducted to evaluate the sensitivity of nitrate mass in the groundwater to individual changes in groundwater denitrification rates. A [−100%, +100%] range of changes in groundwater denitrification rates was considered. Fig. 11 depicts the sensitivity of nitrate mass in the groundwater at the end of the simulation period to different change percentages in the calibrated groundwater denitrification rates. Apparently, the sensitivity of nitrate mass is extremely high to reductions in denitrification rates as compared to the same increase percentages. This behavior, depicted in Fig. 11, is attributed to the exponential relationship between nitrate concentration and denitrification rate when keeping all other fate and transport processes unchanged. Although not shown here, by increasing the denitrification rate, less time is required to attain the quasi-steady state. It should be mentioned that the pre-calibration analysis was not meant to be comprehensive and just selected parameters were considered in the analysis.

Simulation of the protection alternatives

Dairy manure and fertilizers are the main sources of nitrogen in the study area (Stasney, 2000; Nanus, 2000; Mitchell

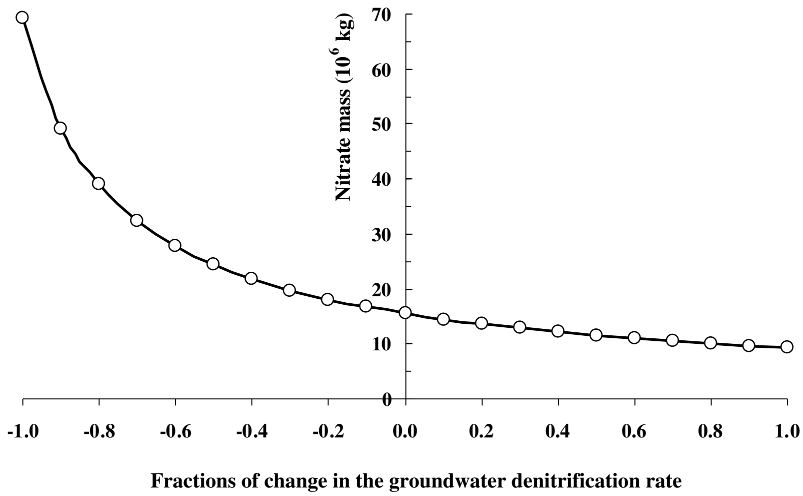

Figure 11 Sensitivity of the total annual nitrate mass in the groundwater of the study area at the end of the simulation period to different multiplication coefficients of the groundwater denitrification rates.

et al., 2003; Almasri and Kaluarachchi, 2004a,b). One of the biggest problems associated with an increasing dairy herd size is that dairy acreage often does not increase. The application of increasing quantities of dairy manure to the same land area may result in water quality problems and inverse environmental consequences. The reduction of manure loading is expected to lower nitrate leaching and nitrate occurrences in the groundwater. If it turns out that the land base is insufficient for manure application, then protection alternatives should be introduced. Such alternatives may consider reducing herd size, manure composting/exporting, or implementing feeding strategies to reduce nutrient content in the excrement (Davis et al, 1999). Since fertilizer application on agricultural areas has been recognized as a main source of nitrate contamination of groundwater, reduction in nitrogen fertilizer application rates is an efficient option (Mercado, 1976; Yadav and Wall, 1998). Puckett et al. (1999) cited many studies that estimated a fertilizer application rate that is 24–38% higher than the crop demand. A 40% reduction in manure and fertilizer application rates was considered and the developed framework was used to evaluate the outcome correspondingly. Fig. 12 depicts the time series of nitrate mass in the groundwater for the do-nothing alternative and for the manure and fertilizer reduction alternatives. In addition, the effectiveness of the combination of these scenarios is shown in Fig. 12. It can be concluded that reducing the manure loading yields more reduction in the total nitrate mass in the groundwater as compared to the reduction in fertilizer application. Combining both alternatives shows improved results. It is worth mentioning that NO_3 mass in the aquifer for the do-nothing alternative shows an increasing trend until reaching the quasi-steady state conditions in almost the last three years. Apparently, the time needed for reaching the quasi-steady state varies from location to location.

The impact of the protection alternatives on nitrate concentration time series was analyzed. Fig. 13 shows the nitrate concentration time series for a receptor located in a dairy farm area. Obviously, reducing manure loading had a considerable impact on nitrate concentration at this

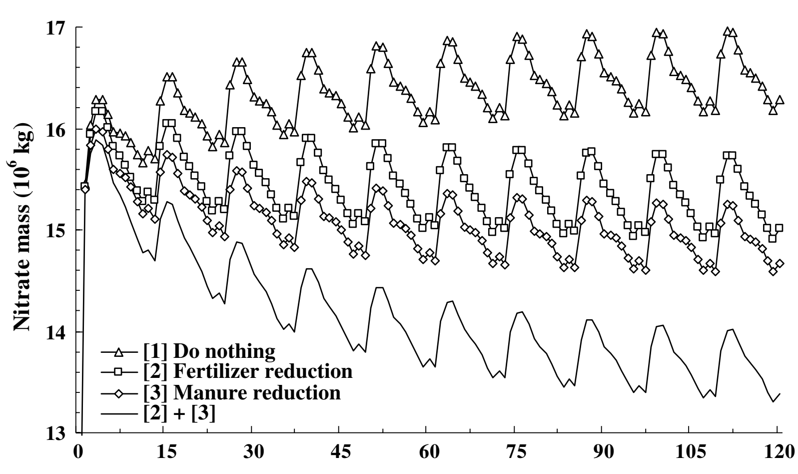

Figure 12 Total nitrate mass in the groundwater of the study area for different protection alternatives.

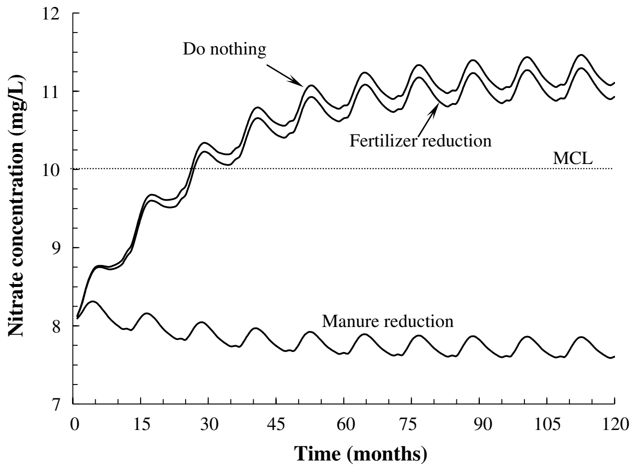

Figure 13 Impact of protection alternatives on time series of nitrate concentrations at a receptor located in a dairy farm area.

receptor while a reduction in the fertilizer loading is mostly insignificant. This signifies the fact that different protection alternatives might be needed to reduce the nitrate concentration based on the location of the receptor since specific alternatives may not be efficient at particular locations. This differentiation between the outcomes of the different protection alternatives and the corresponding efficiencies is possible only by using the modeling framework.

Finally, it should be noted that the protection alternatives discussed here were based on the goal of reducing the nitrate mass in the subsurface from the on-ground nitrogen sources. None of these protection alternatives addressed potential economic implications to the local economy. A sound decision analysis framework should not only consider management alternatives to reduce nitrate loading to the subsurface, but also the potential economic implications of the decisions and the long-term environmental gains.

Capabilities and advantages

The modeling framework performs the following: (i) develops a better understanding and quantification of fate and transport of nitrate in groundwater; (ii) simulates the long-term nitrate concentrations due to the existing land use practices and proposed management scenarios; (iii) determines the spatial and temporal nitrate concentrations in the groundwater; (iv) computes the nitrate mass flux between surface and groundwater at critical stream segments; (v) estimates the spatial and temporal distribution of on-ground nitrogen loadings and corresponding nitrate leaching to groundwater; (vi) estimates the nitrogen buildup in the soil; and (vii) determines the natural attenuation potential of different sub-areas.

In addition, the framework can accommodate the following management scenarios: (i) change of land use classes at fine spatial resolution; (ii) change of land use practices within one or more land use class; e.g., dairy farm practices, fertilizer applications, types of fertilizers used, and maintenance of dairy lagoons and septic tanks; and (iii) the use of nitrification inhibitors to hold up the formation of nitrate in the soil from ammonium.

The potential remedial alternatives that can be assessed by the modeling framework are: (i) the change in land use classes to satisfy groundwater quality; (ii) the change in land use practices within given land use classes; (iii) the potential need for removal/changes of drinking water sources under a given management alternative to satisfy groundwater quality needs; and (iv) the selection of alternative drinking water sources under a potential threat from a proposed management scenario.

The key advantages of this modeling framework are: (i) it addresses site-specific management issues; (ii) it can be readily used to assist in developing data gathering and field monitoring networks; (iii) it is a tool to determine if time-consuming and expensive field investigations such as pilot studies are needed; (iv) if pilot studies are needed, the model can be readily used to select sensitive locations and design pilot studies at such areas; and (v) it provides an easy tool for mapping aquifer vulnerability, if needed.

Summary and conclusions

In this work, a modeling framework was developed to model the impact of land use on nitrate pollution of groundwater in agriculture-dominated watersheds. Applicability of this framework was demonstrated for the extended Sumas—Blaine aquifer. The framework utilizes the NLCD grid of the USGS and GIS to account for the spatial distribution of on-ground nitrogen sources and corresponding loadings and employs a soil nitrogen dynamic model to estimate the corresponding nitrate leaching to groundwater. Thereafter, the estimates of nitrate leaching were utilized in developing the nitrate fate and transport model (using MT3D) after being linked to the groundwater flow model (using MODFLOW). The framework considers both point and non-point sources of nitrogen across 21 different land use classes and the calculations are transient at monthly intervals. The nitrate fate and transport model was calibrated and verified and sensitivity analysis was conducted. A number of simulations were carried out to evaluate the overall impacts of current land use practices and the efficiency of proposed management options to protect groundwater quality from nitrate pollution. The following conclusions were made based on the outcome of this work:

1. Proper estimation of on-ground nitrogen loadings and nitrate leaching to groundwater is necessary to develop the nitrate fate and transport models in groundwater. A reliable prediction should consider details of on-ground nitrogen loadings as well as soil nitrogen kinetics;
2. For Sumas—Blaine aquifer, groundwater denitrification rates as well as the on-ground manure loadings have the highest impact on the frequency of MCL violations followed by fertilizer loading and atmospheric deposition. Results show that the denitrification process in groundwater has a higher impact on reducing nitrate mass in groundwater when compared to advection and mechanical dispersion. With increasing the groundwater denitrification rate, less time is required to attain the quasi-steady state. However, the occurrence of denitrifi-

cation in groundwater is site specific. In fact, denitrification may differ from location to location in an aquifer based on the prevailing conditions;
3. In areas dominated by dairy farms, the reduction of manure loading has a high impact on reducing nitrate mass buildup in the aquifer compared to fertilizer loading reduction;
4. Combining different management options such as manure and fertilizer loading reduction proved to be a successful approach for reducing nitrate pollution of groundwater. However, the economic aspects should be considered when designing such alternatives; and
5. The implementation of the modeling framework showed that not all management options would be efficient in reducing nitrate concentration. For instance, reduction of fertilizer loading was not efficient compared to manure loading reduction. Thus, management options should not be subjectively applied before being assessed by the model.

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