



ELSEVIER

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Research papers

Global sensitivity analysis for identifying important parameters of nitrogen nitrification and denitrification under model uncertainty and scenario uncertainty

Zhuwei Chen^a, Liangsheng Shi^{a,*}, Ming Ye^b, Yan Zhu^a, Jinzhong Yang^a

^a State Key Laboratory of Water Resources and Hydropower Engineering Sciences, Wuhan University, Wuhan, Hubei 430072, China

^b Department of Scientific Computing, Florida State University, Tallahassee, FL, USA

ARTICLE INFO

This manuscript was handled by “G. Syme”
Editor-in-Chief

Keywords:

Nitrification and denitrification
Reduction function
Model averaging
Scenario averaging
Sobol' method of sensitivity analysis

ABSTRACT

Nitrogen reactive transport modeling is subject to uncertainty in model parameters, structures, and scenarios. By using a new variance-based global sensitivity analysis method, this paper identifies important parameters for nitrogen reactive transport with simultaneous consideration of these three uncertainties. A combination of three scenarios of soil temperature and two scenarios of soil moisture creates a total of six scenarios. Four alternative models describing the effect of soil temperature and moisture content are used to evaluate the reduction functions used for calculating actual reaction rates. The results show that for nitrogen reactive transport problem, parameter importance varies substantially among different models and scenarios. Denitrification and nitrification process is sensitive to soil moisture content status rather than to the moisture function parameter. Nitrification process becomes more important at low moisture content and low temperature. However, the changing importance of nitrification activity with respect to temperature change highly relies on the selected model. Model-averaging is suggested to assess the nitrification (or denitrification) contribution by reducing the possible model error. Despite the introduction of biochemical heterogeneity or not, fairly consistent parameter importance rank is obtained in this study: optimal denitrification rate (K_{den}) is the most important parameter; reference temperature (T_r) is more important than temperature coefficient (Q_{10}); empirical constant in moisture response function (m) is the least important one. Vertical distribution of soil moisture but not temperature plays predominant role controlling nitrogen reaction. This study provides insight into the nitrogen reactive transport modeling and demonstrates an effective strategy of selecting the important parameters when future temperature and soil moisture carry uncertainties or when modelers face with multiple ways of establishing nitrogen models.

1. Introduction

The nitrogen cycle, together with the carbon cycle, plays an important role in sustaining subsurface and terrestrial environments and ecosystems (European Environment Agency (EEA), 2000; Galloway et al., 2004; Rivett et al., 2007). In subsurface hydrology, nitrogen reactive transport modeling is a vital tool for simulating nitrogen transformation and for estimating the amount of nitrogen transport within and between soil and groundwater. Nitrogen reactive transport modeling is complicated for the fact that nitrogen transport is controlled by a large number of physical, chemical, and biological processes and their associated parameters. It is important to identify the important parameters that control nitrogen reactive transport so that limited resources can be used to better characterize the important parameters to improve the accuracy of model predictions. The identification of important

parameters is nontrivial due, in part, to the following three challenges: (1) the parameters vary substantially in space and time, and it is uncertain which parameter values should be used for the identification of important parameters; (2) the parameters may be used by a number of alternative models, and the parameter importance may vary between different models; (3) the scenarios of future system conditions under which model predictions are made are uncertain, and the scenario uncertainty may affect the parameter importance. While existing methods of global sensitivity analysis are able to identify important parameters under parametric uncertainty (Griensven et al., 2006; Mishra et al., 2009; Saltelli et al., 2010; Rakovec et al., 2014; Zhang et al., 2013; Razavi and Gupta, 2015, 2016a,b; Song et al., 2015; Wainwright et al., 2014), there has been few study that identifies important parameters under model and scenario uncertainty for nitrogen reactive transport modeling.

* Corresponding author.

E-mail address: liangshs@whu.edu.cn (L. Shi).

Model uncertainty and scenario uncertainty are prevalent in nitrogen reactive transport modeling. With respect to model uncertainty, various models have been developed based on different conceptual and mathematical descriptions of nitrogen reactive transport. Hansen et al. (1995) compared five alternative models (ANIMO, SOILN, OMNI, NLEAP, and DAISY), and Heinen (2006) reviewed more than fifty models. Frolking et al. (1998) described four models (CENTURY, DNDC, Expert-N, and NASA-CASA) for simulating nitrous oxide (N₂O) emissions. Wu and McGechan (1998) compared four soil nitrogen dynamics models (ANIMO, SUNDIAL, SOILN, and DAISY). Rodrigo et al. (1997) discussed nine models that have been developed for simulating the effects of temperature and water content on carbon and nitrogen transformation in soils. Following Meyer et al. (2014), a scenario is defined as a future state or condition under which the models are simulated. With respect to scenario uncertainty, it is always uncertain under what future temperature and precipitation conditions nitrogen reactive transport predictions are made, and there is also no consensus on how scenarios influence model predictions. For example, Heinen (2006) found that moisture content is important to denitrification; Wang et al. (2005) reported that temperature is a controlling factor of denitrification; Pohlert et al. (2007) pointed out that pH is important to nitrogen cycling. McIntyre et al. (2005) and Wang et al. (2013) considered impacts of spatial variability of model parameters (e.g., hydraulic conductivity) on nitrogen transport. These studies indicate that the nitrogen reactive transport models are diverse, and that these models are used under different future system conditions.

This study is focused on identifying the important parameters that control nitrification and denitrification, which play an important role in the nitrogen cycle. Particularly speaking, the model uncertainty considered in this study are related to various reduction functions used in literature for estimating actual nitrification and denitrification rates. The rates are evaluated by multiplying potential rates (the maximum rates under optimal conditions) with reduction functions that depend on various factors, such as nitrate concentration, moisture content, temperature, and pH of soils (see the review article of Heinen (2006) and references therein). Since the factors affect nitrification and denitrification in different ways, a number of reduction functions have been developed, and it is often uncertain which function should be used. Taking denitrification as an example, according to Heinen (2006), "... reduction by soil conditions is site-specific, and, therefore, a universal, simple process model for denitrification does not seem to exist". For all the reduction functions, they heavily depend on soil temperature and moisture, which affect microbial processes in soils (Rodrigo et al., 1997). The two factors usually vary substantially in space and time, and the variation leads to scenario uncertainty. It is necessary to identify important parameters for a range of future temperature and precipitation, rather than for fixed (e.g., present-day) temperature and precipitation values. There are some other factors (such as pH and soil organic carbon) that may affect nitrogen reactive transport, but they are ignored in this study.

With the consideration of parametric uncertainty, model uncertainty, and scenario uncertainty, the following three questions are raised immediately for identifying important parameters in nitrogen reactive transport problem: (1) Are the parameters important to one model also important to another model? (2) Are parameters important under one prediction condition still important under another prediction condition? (3) How scenario affects the performance of model prediction? This study answers the above three questions in the field of nitrogen reactive transport modeling by using a method recently developed by Dai and Ye (2015). Different from existing methods of global sensitivity that can be used only for a single model and a single modeling scenario, this method considers multiple models and multiple scenarios in the context of model averaging and scenario averaging. Rather than choosing a single model and define a single scenario, model, and scenario averaging method is introduced to alleviate the disparity of sensitivity analysis between different models and scenarios.

Although this study is focused on the nitrification and denitrification processes, the method of global sensitivity analysis is mathematically general and can be applied to other reactive transport processes of nitrogen and other contaminants. It is hoped that this study can provide a framework and an example of using global sensitivity analysis to select important parameters in nitrogen modeling (and reactive transport modeling in a broad sense) under the uncertainty of model parameters, structures, and scenarios. To the best of our knowledge, such an example is unprecedented.

In the rest of this paper, Section 2 describes the new method for variance-based global sensitivity analysis under parametric, model, and scenario uncertainties. Section 3 presents the details of nitrogen reactive transport modeling at the lysimeter scale as well as the six modeling scenarios, four models, and the parameter distributions. The results of sensitivity analysis are listed in Section 4. In Section 5, we discussed the necessity of consideration of models and scenarios in sensitivity analysis and the impact of scenarios on nitrogen processes. The conclusions of this study are given in Section 6.

2. Methodology

This section gives a brief description of the sensitivity indices defined by Dai and Ye (2015) for the following three situations: (1) for a single model and a single scenario, (2) for multiple models but a single scenario, and (3) for multiple models and multiple scenarios. The details of deriving the indices are referred to Dai and Ye (2015).

For a single model M and a single scenario S , $Y = f(\mathbf{X}, M, S)$, where Y is a scalar model output and $\mathbf{X} = \{X_1, X_2, \dots, X_k\}$ denotes a vector of random model parameters. When considering model and scenario uncertainty, the model output can be written as $Y = f(\mathbf{X}, \mathbf{M}, S)$, where \mathbf{M} denotes a model set with multiple models, $\mathbf{M} = \{M_1, M_2, \dots, M_j\}$, and S denotes a scenario set with multiple scenarios, $S = \{S_1, S_2, \dots, S_i\}$, respectively. Since parameters are different in different models, \mathbf{X} is the union of parameters in each model, $\mathbf{X} = \mathbf{X}^{(1)} \cup \mathbf{X}^{(2)} \dots \cup \mathbf{X}^{(j)}$, where $\mathbf{X}^{(j)}$ is the parameters of model M_j . By using the law of total variance and the law of total expectation, the predictive variance of Y can be decomposed as (Dai and Ye, 2015)

$$V(Y) = E_S E_{\mathbf{M}|S} E_{\mathbf{X}|\mathbf{M},S} V(Y|\mathbf{X}, \mathbf{M}, S) + E_S E_{\mathbf{M}|S} V_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, \mathbf{M}, S) + E_S V_{\mathbf{M}|S} E_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, \mathbf{M}, S) + V_S E_{\mathbf{M}|S} E_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, \mathbf{M}, S) \quad (1)$$

where $\mathbf{M}|S$ and $\mathbf{X}|\mathbf{M},S$ indicate the hierarchical relations that models are conditioned on scenarios and that parameters are conditioned on models and scenarios. Note that the total uncertainty consists of three parts, i.e., parameter, model, and scenario uncertainty, while the interactions between them are ignored.

The four terms at the right-hand side of Eq. (1) represent data uncertainty, $E_S E_{\mathbf{M}|S} E_{\mathbf{X}|\mathbf{M},S} V(Y|\mathbf{X}, \mathbf{M}, S)$, parametric uncertainty, $E_S E_{\mathbf{M}|S} V_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, \mathbf{M}, S)$, model uncertainty, $E_S V_{\mathbf{M}|S} E_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, \mathbf{M}, S)$, and scenario uncertainty, $V_S E_{\mathbf{M}|S} E_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, \mathbf{M}, S)$. The data uncertainty here is treated as the variance of measurement error, and it is assumed to be a constant and thus not involved in sensitivity analysis. The model uncertainty is caused by different mean predictions given by different models (also known as between-model uncertainty). Similarly, the term of scenario uncertainty is caused by different mean predictions under different scenarios (also known as between-scenario uncertainty). The parametric uncertainty is not limited to a single model, but for multiple models and under different model scenarios. Therefore, $E_S E_{\mathbf{M}|S} V_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, \mathbf{M}, S)$ is used in this paper as the basis of global sensitivity analysis under parametric, model, and scenario uncertainties.

For a single model, M , and a single scenario, S , the mean operations over models and scenarios disappear, and the $E_S E_{\mathbf{M}|S} V_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, \mathbf{M}, S)$ term becomes

$$E_S E_{\mathbf{M}|S} V_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, \mathbf{M}, S) = V_{\mathbf{X}|\mathbf{M},S} E(Y|\mathbf{X}, M, S) \quad (2)$$

Based on this equation and in the same manner of Sobol’ sensitivity analysis (Saltelli et al., 2010), the first-order sensitivity index is defined as

$$S_i = \frac{V_{X_i|M,S} E_{X_{-i}|M,S}(E(Y|X,M,S)|X_i)}{V_{X|M,S} E(Y|X,M,S)}, \tag{3}$$

and the total-effect sensitivity index is defined as:

$$S_{T_i} = \frac{E_{X_{-i}|M,S} V_{X_i|M,S}(E(Y|X,M,S)|X_{-i})}{V_{X|M,S} E(Y|X,M,S)} = 1 - \frac{V_{X_{-i}|M,S} E_{X_i|M,S}(E(Y|X,M,S)|X_{-i})}{V_{X|M,S} E(Y|X,M,S)} \tag{4}$$

where X_i is the i -th parameter, and X_{-i} denotes all other parameters but X_i . The mean and variance can be evaluated using the Monte Carlo (MC) method of Saltelli et al. (2010).

Imagine there have two independent sampling matrices **A** and **B**, with $k \times N$ as dimensions, where k is the number of factors, N is the number of simulations. Now introduce matrix $\mathbf{A}_B^{(i)}$ ($\mathbf{B}_A^{(i)}$) where all columns are from **A** (**B**) except the i -th column which is from **B** (**A**). Saltelli et al. (2010) compared several practices for the simultaneous computation of Sobol’s sensitivity indices and suggested an improved computation for S_i , where the numerator is proposed for a fixed model and scenario:

$$V_{X_i|M,S} E_{X_{-i}|M,S}(E(Y|X,M,S)|X_i) = V_{X_i}(E_{X_{-i}}(Y|X_i)) = \frac{1}{N} \sum_{j=1}^N f(\mathbf{B})_j - f(\mathbf{A}_B^{(i)})_j - f(\mathbf{A})_j \tag{5}$$

where $(\mathbf{B})_j$ denotes the j -th row of matrix **B**.

The computation of S_{T_i} proceeds from Eq. (4), where the numerator is obtained from:

$$E_{X_{-i}|M,S} V_{X_i|M,S}(E(Y|X,M,S)|X_{-i}) = E_{X_{-i}}(V_{X_i}(Y|X_{-i})) = \frac{1}{2N} \sum_{j=1}^N (f(\mathbf{A})_j - f(\mathbf{A}_B^{(i)})_j)^2 \tag{6}$$

A total of $2N$ simulations are needed to compute Y corresponding to sampling matrices **A** and **B**, while $k \cdot N$ simulations are required to compute Y from matrices $\mathbf{A}_B^{(i)}$ for all factors.

When considering multiple models, **M**, but a single scenario, S , the mean operation over scenarios disappears, and the $E_S E_{M|S} V_{X|M,S} E(Y|X,M,S)$ term becomes

$$E_S E_{M|S} V_{X|M,S} E(Y|X,M,S) = E_{M|S} V_{X|M,S} E(Y|X,M,S). \tag{7}$$

The corresponding first-order and total-effect sensitivity indices for the multiple models but the single scenario are defined as

$$S_i^M = \frac{E_{M|S} V_{X_i|M,S} E_{X_{-i}|M,S}(E(Y|X,M,S)|X_i)}{E_{M|S} V_{X|M,S} E(Y|X,M,S)} \tag{8}$$

and

$$S_{T_i}^M = \frac{E_{M|S} E_{X_{-i}|M,S} V_{X_i|M,S}(E(Y|X,M,S)|X_{-i})}{E_{M|S} V_{X|M,S} E(Y|X,M,S)} \tag{9}$$

The mean of multiple models, $E_{M|S}(\cdot)$, in Eqs. (8) and (9), is evaluated by using the model averaging method $E_{M|S}(\cdot) = \sum_K P(M_k|S)(\cdot)$, where $P(M_k|S)$ is the probability of model M_k under scenario S and satisfies $\sum_K P(M_k|S) = 1$. The computation here are under a hierarchical structure. Taking the denominator of the right hand side of Eq. (8) as an example, the first mean is with respect to the models postulated for scenario S , and the variance, $V_{X|M,S} E(Y|X,M,S)$, is the variance of inner expectation, $E(Y|X,M,S)$, calculated over all the changing values of the parameters under the model set **M** and scenario S . Here is the difference between the new method and the conventional method such as the Sobol’ sensitivity analysis. Unlike the model averaging output that is the weighted average of individual models, the index, S_i^M ,

is not a weighted averaging of S_{T_i} of individual models. Instead, model averaging is conducted for the denominator and numerator separately, and the ratio of the weighted averages is used for evaluating the sensitivity index.

When considering multiple models, **M**, and multiple scenarios, **S**, the first-order and total-effect sensitivity indices for the multiple models and the multiple scenarios are defined as

$$S_i^{MS} = \frac{E_S E_{M|S} V_{X_i|M,S} E_{X_{-i}|M,S}(E(Y|X,M,S)|X_i)}{E_S E_{M|S} V_{X|M,S} E(Y|X,M,S)} = \frac{\sum_S \sum_M P(S)P(M|S) V_{X_i|M,S} E_{X_{-i}|M,S}(E(Y|X,M,S)|X_i)}{\sum_S \sum_M P(S)P(M|S) V_{X|M,S} E(Y|X,M,S)} \tag{10}$$

and

$$S_{T_i}^{MS} = \frac{E_S E_{M|S} E_{X_{-i}|M,S} V_{X_i|M,S}(E(Y|X,M,S)|X_{-i})}{E_S E_{M|S} V_{X|M,S} E(Y|X,M,S)} = \frac{\sum_S \sum_M P(S)P(M|S) E_{X_{-i}|M,S} V_{X_i|M,S}(E(Y|X,M,S)|X_{-i})}{\sum_S \sum_M P(S)P(M|S) V_{X|M,S} E(Y|X,M,S)} \tag{11}$$

The mean of multiple scenarios, $E_S(\cdot)$, in Eqs. (10) and (11), is evaluated by using the scenario averaging method $E_S(\cdot) = \sum_L P(S_l)(\cdot)$, where $P(S_l)$ is the probability of scenario S_l and satisfies $\sum_L P(S_l) = 1$. The computation are similar to Eqs. (6) and (7).

3. Nitrogen reactive transport modeling and associated uncertainty

This section first describes the numerical modeling for simulating unsaturated flow and nitrogen transport at the lysimeter scale. We consider six scenarios and four models for modeling nitrogen nitrification and denitrification, and identify important parameters related to the scenarios and models. The different models in this study are established based on different responses to environmental factors and the scenarios are designed by setting the possible future states of environmental factors. The mathematical functions evaluating nitrification and denitrification processes considered in this study are widely used in nitrogen modeling. Therefore, the numerical modeling of this study presents a case in which model parameters, structures, and structures are tangled together to render the identification of important parameters sophisticated.

3.1. Lysimeter-scale nitrogen reactive transport modeling

As shown in Fig. 1, the lysimeter domain is 3 m in length. The soil texture is clay loam., The soil water characteristic curve and unsaturated hydraulic conductivity are described by the van Genuchten model (van Genuchten, 1980) with the following parameter values: residual soil-water content $\theta_r = 0.095$, saturated soil-water content $\theta_s = 0.41$, $\alpha = 1.9 \text{ m}^{-1}$, $n = 1.31$, and saturated hydraulic conductivity $K_s = 0.6 \text{ md}^{-1}$ (Simunek et al., 2005). The initial averaging volumetric water content is 0.31. The top boundary is subject to an atmospheric boundary condition, and the bottom and lateral boundaries are prescribed as the no-flow boundary condition. The horizontal flow is not considered in the domain. The finite-element mesh with 36 triangular elements and 38 nodes is used in modeling. The time step is automatically adjusted with an initial time step of 0.01 day and a maximum time step of 0.05 day. The total simulation period is 100 days. The initial concentrations of ammonium and nitrate are uniform over the whole domain, with the values of 5 mg/L and 20 mg/L, respectively. The flow and solute transport equations are solved by ORTHOMIN method (Mendoza et al., 1991). Soil temperature and moisture are the environmental factors which influence reactive nitrogen transport in

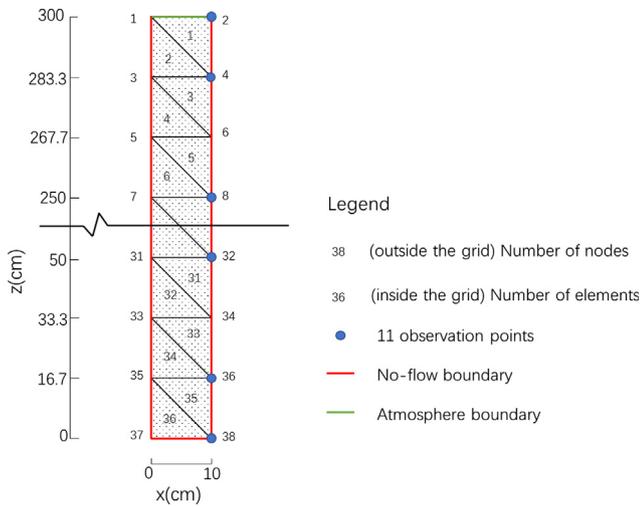


Fig. 1. Diagram of the modeling domain, boundary conditions, and locations of observation points.

this study, which are given in Section 3.3.

3.2. Unsaturated flow and nitrogen transport modeling

Nitrogen-2D, developed by Yang et al. (2008) is used for the numerical modeling. The numerical model involves a two-dimensional, variably unsaturated flow and nitrogen transport with consideration of nitrification and denitrification. The flow model is governed by the Richards' equation,

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i} \left(K_{ij} \frac{\partial h}{\partial x_j} \right) - \frac{\partial K_{i2}}{\partial x_i} - S \quad (12)$$

where θ is volumetric water content, h is pressure head, S is a sink/source term, x_i the spatial coordinates with x_1 in the horizontal and x_2 in the vertical directions, K_{ij} represents the components of the unsaturated soil conductivity tensor.

The transport of ammonium and nitrate in the soil is governed by the conventional advection-dispersion equation. The governing equation of ammonium transport is

$$\frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_{NH4}}{\partial x_j} \right) - q_i \frac{\partial C_{NH4}}{\partial x_i} - \theta \frac{\partial C_{NH4}}{\partial t} = -R_{nit} \quad (13)$$

where D_{ij} denotes the components of the dispersion coefficient tensor, q_i is the magnitude of Darcy flux, C_{NH4} is ammonium concentration, R_{nit} is the actual nitrification rate. The governing equation of nitrate transport is:

$$\frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_{NO3}}{\partial x_j} \right) - q_i \frac{\partial C_{NO3}}{\partial x_i} - \theta \frac{\partial C_{NO3}}{\partial t} = R_{nit} - R_{den} \quad (14)$$

where C_{NO3} is the nitrate solution concentration, and R_{den} is the actual denitrification rate. The details of modeling nitrification and denitrification are given in Section 3.4, where the alternative functions for evaluating actual nitrification and denitrification rates are discussed.

3.3. Six scenarios of temperature and precipitation

The six scenarios considered in this study are a combination of three scenarios of future soil temperature and two scenarios of future precipitation. The three temperature scenarios correspond to three different yearly-average temperatures of 15, 5, and 25 °C, and the scenarios are denoted as S15, S5, and S25, respectively. For each of the three temperature scenarios, the temperature profile, $T(z,t)$, at depth z of the soil and a given time, t , is calculated from the empirical equation

of Rijtema and Kroes (1991),

$$T(z,t) = T_a + A_0 \exp\left(-\frac{z}{D_m}\right) \cos\left(\omega t + \varphi - \frac{z}{D_m}\right) \quad (15)$$

where T_a is the yearly-average temperature (°C), A_0 is the amplitude of temperature wave (°C), D_m is damping depth (m), ω is the frequency of temperature wave, φ is a phase shift. Except T_a , the parameter values are the same under the three scenarios, and they are $A_0 = 5$, $D_m = 3$, $\omega = 0.017214$, and $\varphi = 2.388$. Eq. (15) indicates that the temperature profiles (in depth) have the same shape under the three scenarios, but have different values due to the different T_a values. When calculating the response of nitrogen process to temperature (discussed in Section 3.4), the reference temperature was suggested within the range of 15–35 °C (Heinen, 2006). Our design of the temperature scenario was based on this suggestion, while the yearly-average temperature in the base scenario is 15 °C (denoted as S15). Under scenario S5, the yearly average temperature is designed at 5 °C, and the lowest temperature in the domain is 0 °C, under which the biofilm is inactive. For scenario S25, the largest temperature in the domain is 30 °C, as it has been reported that the optimal temperature for nitrification and denitrification is around 25° to 30 °C (Rysgaard et al., 2004; Saad and Conrad, 1993). Therefore, nitrification and denitrification may respond differently under the three temperature scenarios, which is discussed in Section 3.4 below. The two precipitation scenarios are the present-day scenario with the precipitation of 13 mm and the wet scenarios with the increased precipitation of 26 mm during the whole simulation period. Under the two precipitation scenarios, the averaging soil moisture in this domain ranges from 0.3 to 0.33 and 0.3 to 0.37. The nitrification rate may respond differently to the soil moisture, which is discussed in Section 3.4. By applying these two designed precipitation scenarios, the impact of soil moisture on nitrogen reactive models and parameters is presented in the next part.

Combining the three temperature scenarios and the two precipitation scenarios leads to a total of six scenarios that are denoted as S15P, S5P, S25P, S15W, S5W, and S25W, for which the letter S stands for scenario, the numbers for soil temperature, and the letters of P and W for precipitation. The scenarios have substantial impacts on the unsaturated flow and nitrogen transport. The precipitation scenarios also affect the simulations of nitrogen concentration, because moisture content affects the actual rates of nitrification and denitrification, as discussed in Section 3.4 below.

3.4. Four reduction functions and their random parameters

Following Yang et al. (2008), nitrification is modeled as the first-order process,

$$R_{nit} = \frac{\partial \theta N}{\partial t} = -K_{nit}(\theta + \rho K_d) f_m f_T N, \quad (16)$$

and denitrification as the Michaelis-Menten process,

$$R_{den} \frac{\partial \theta N}{\partial t} = -K_{den} f_m f_T \frac{(\theta + \rho K_d) N}{(\theta + \rho K_d) N + K_C}, \quad (17)$$

where N is the ammonium or nitrate concentration in the soil solution, K_{nit} the optimal nitrification rate, K_d the distribution coefficient for adsorbing solute, ρ is soil bulk density, K_{den} is the optimal denitrification rate, K_C the half-saturation coefficient, and f_m and f_T are the reduction factors of the soil moisture and soil temperature, respectively. In this study, the reduction factors (f_m and f_T) are evaluated using alternative models given in SOILN (Johnsson et al., 1987) and DAISY (Hansen et al., 1993), two software that have been widely used for nitrogen modeling (e.g., de Neergaard et al., 2002; Eckersten et al., 2007; Liang et al., 2014; Yang et al., 2008).

Table 1 lists the four alternative models used for the nitrification process and the other four models for the denitrification process. Two alternative functions (denoted as T1 and T2) are used for modeling the

Table 1
Alternative models used to evaluate reduction factors f_m and f_T for calculating actual nitrification and denitrification rates. Functions T1 and M1 are adopted from model SOILN, and T2 and M2 from DAISY. The explanation of abbreviations are given follows.

	Nitrification	Denitrification
T1	$f_T = Q_{10}^{(T-T_r)/10}$	$f_T = Q_{10}^{(T-T_r)/10}$
T2	$f_T = \begin{cases} 0, (T \leq 2) \\ 0.15(T-2), (2 < T \leq 6) \\ 0.1T, (6 < T \leq 20) \\ e^{(0.47-0.027T+0.00193T^2)}, (20 < T \leq 40) \end{cases}$	$f_T = 1$
M1	$f_m = \begin{cases} (\frac{\theta - \theta_w}{\theta_{lo} - \theta_w})^m, \theta_w \leq \theta < \theta_{lo} \\ 1, \theta_{lo} \leq \theta < \theta_{hi} \\ e_s + (1-e_s)(\frac{\theta_s - \theta}{\theta_s - \theta_{hi}})^m, \theta_{hi} \leq \theta < \theta_s \end{cases}$	$f_m = \begin{cases} 0, \theta \leq \theta_d \\ (\frac{\theta - \theta_d}{\theta_s - \theta_d})^{d1}, \theta > \theta_d \end{cases}$
M2	$f_m = \begin{cases} \frac{pF}{1.5}, pF < 1.5 \\ 1, 1.5 \leq pF < 2.5 \\ 2 - \frac{2pF}{5}, 2.5 \leq pF < 5 \\ 0, pF > 5 \end{cases}$	$f_m = \begin{cases} 0, x_w < 0.8 \\ 2(x_w - 0.8), 0.8 < x_w \leq 0.9 \\ 0.2 + 8(x_w - 0.9), 0.9 < x_w \leq 1 \end{cases}$

impacts of soil temperature on nitrification and denitrification. Function T1, adopted from SOILN and used for both nitrification and denitrification processes, is based on the Arrhenius or van't Hoff laws (Rodrigo et al., 1997). T is the soil temperature evaluated using Eq. (15). T_r is the reference temperature for which $f_T = 1$. Q_{10} is the response to a 10 °C soil temperature change. Q_{10} and T_r are treated as random variables and discussed below. Function T2 (used in DAISY) of nitrification is based on the understanding that the nitrification process is controlled by different types of microbes in different temperature ranges, and takes the form of the piecewise function. The T2 function of denitrification (also used in DAISY) does not consider the temperature impacts, and uses the constant value of one for any temperature.

Two alternative functions (denoted as M1 and M2) are used for modeling the impacts of moisture content on nitrification and denitrification. Function M1 of nitrification (used in SOILN) simulates the impacts of moisture content on actual nitrification rate, where θ_s is the saturated moisture content, θ_{hi} and θ_{lo} are the high and low water content, respectively, within which the reduction function is one, and θ_w is the minimum water content for process activity, and m is an empirical constant. For the soil used in this study and based on literatures (Johnsson et al., 1987; Wu and McGechan, 1998), the suggested values of the parameters are $\theta_s = 0.41$, $\theta_{hi} = 0.33$, $\theta_{lo} = 0.3$, $\theta_w = 0.17$, and $e_s = 0.6$. Parameter m is treated as a random variable and discussed below. In function M1 of denitrification (used in SOILN), θ_d is the threshold moisture content for denitrification, and its value is taken as 0.17 (Wu and McGechan, 1998).

Function M2 of nitrification (used in DAISY) is a function of soil matric potential, pF (the 10-base logarithm of the soil water tension in cm water). Function M2 of denitrification (used in DAISY) is a function of the degree of water saturation x_w (the ratio of moisture content to saturated moisture content). Since matric potential and the degree of saturation are simulated by the flow model (Eq. (12)), M2 does not have its specific parameters.

A combination of the two reduction functions of soil temperature and the two reduction functions of moisture content gives a total of four alternative models: T1M1, T1M2, T2M1, and T2M2, representing a variety of ways of evaluating the reduction functions. Integrating these models into the nitrogen transport models described in Section 3.2 leads to four alternative models of nitrogen reactive transport. For the four models, because of the diversity of substrates, environmental conditions, and temperature ranges, the following five parameters related to nitrification and denitrification processes are considered as random variables: K_{nit} (the optimal rate of nitrification), K_{den} (the optimal rate of denitrification), Q_{10} and T_r used in function T1, and m used

in function M1. Based on literature search (Korom, 1992; Bengtsson et al., 2003; Heinen, 2006), the following uniform distributions are assumed for the parameters: $K_{nit} \sim U(0.0001, 0.1)$, $K_{den} \sim U(0.0001, 0.1)$, $Q_{10} \sim U(1.01, 3.5)$, $T_r \sim U(10, 30)$, and $m \sim U(0.5, 2.5)$.

3.5. Case with stratified biochemical heterogeneity

The above case considered one very simple situation. However, nitrogen transport and reaction may face a much more complex situation in a real-world application. For example, the biomass species varies along the vertical direction, which leads to a stratified distribution of biotic reaction activity. Thus, the model parameters would be spatially stratified at the field site. To simplify, the spatial stratified heterogeneity is defined as between strata variance in this study, which means model parameters are different between strata. We further investigate nitrogen reactive transport in a vertical stratified domain which is equally divided into two layers. The hydraulic parameters in both layers are same with those discussed in Section 3.1, while the five reactive parameters are set differently in two layers. The same four models, six scenarios and parameter distributions are applied in this case. Thus, the sensitivity analysis of a total of ten parameters is evaluated. Results and discussion of this two-layer case will be presented in Section 5.4.

4. Results

This section presents the results of the global sensitivity index evaluated for individual models and scenarios, for multiple models (after model averaging) but individual scenarios, and for multiple models and multiple scenarios (after scenario averaging). Although both the first-order and total sensitivity indices defined in Section 2 are calculated, only the results of total sensitivity index are presented, because it considers the impacts of parameter interaction on model outputs, which is not considered by the first-order sensitivity index. In addition, only the sensitivity analysis results regarding to nitrate concentration are presented. The total sensitivity index is evaluated at the 11 observation points shown in Fig. 1, and the average index value of each 11 index values is calculated and used for the plotting and discussion below. Without loss of generality, equal probability of scenarios and models (i.e., the probability of each of the six scenarios is 1/6 and the probability of each of the four models is 1/4) are used for evaluating the sensitivity indices below. While the impacts of the probability on the sensitivity results were found by Dai and Ye (2015), discussing the impacts is beyond the scope of this study.

Fig. 2 plots the probability density functions (PDFs) of nitrate

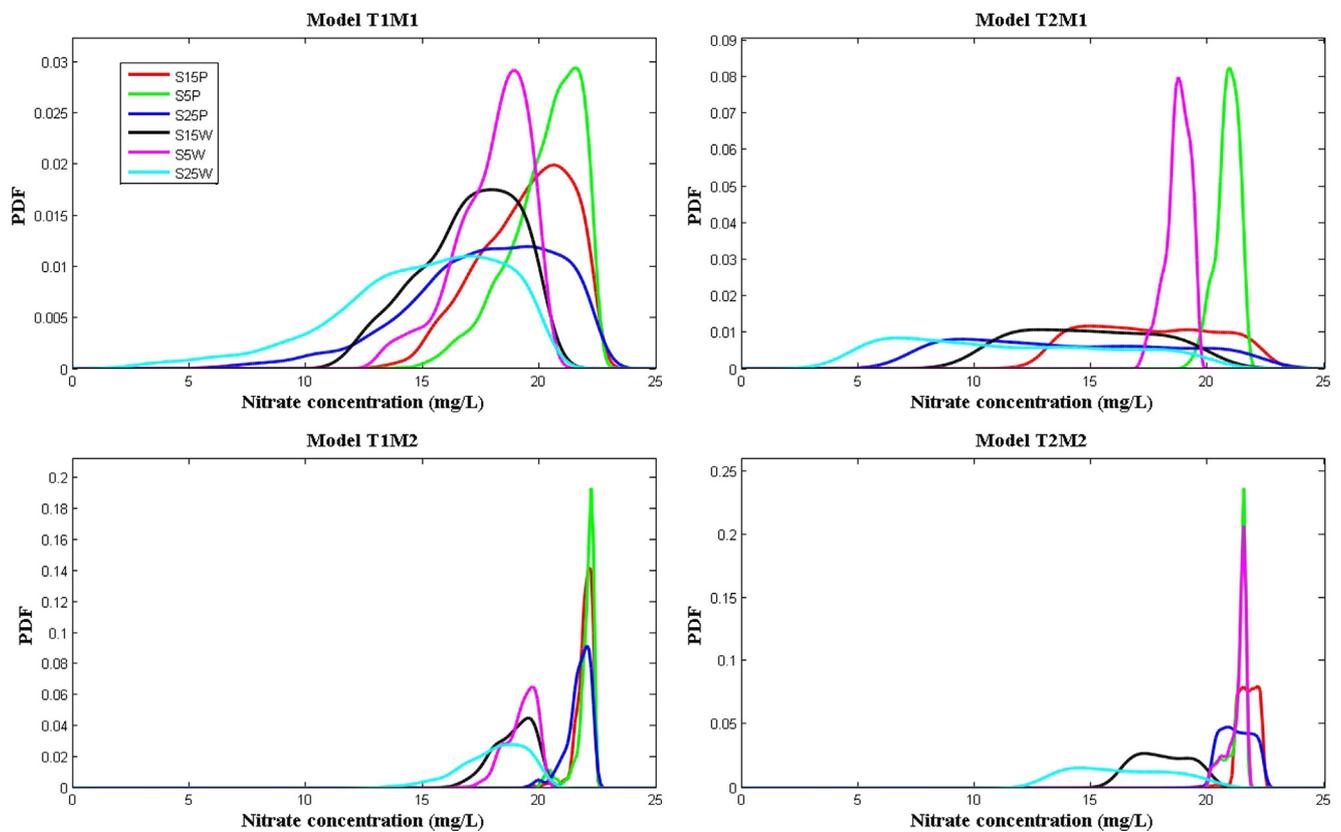


Fig. 2. Probability density function (PDF) of average nitrate concentration simulated at 100 day for each model and scenario.

concentration (averaged over the eleven observation points shown in Fig. 1) simulated using different models under different scenarios at the simulation time of 100 day as an example (the PDFs of other simulation times are similar to those shown in Fig. 2 and thus not shown). The figure shows that the variability of simulated nitrate concentration is substantially different for different models and scenarios. Since the variance of simulated nitrate concentration is the denominator of the sensitivity index (Eqs. (3) and (4)) for a single model and scenario, the importance of parameters under different models and scenarios are not directly comparable. It is, therefore, necessary to use the method described in Section 2 to evaluate the sensitivity index for multiple models and scenarios.

Table 2 lists the total sensitivity index (%) (averaged over the eleven

observation points shown in Fig. 1) of the five parameters evaluated using the individual models and scenarios for nitrate concentration at the simulation time of 100 days. If a parameter is not used in a model, the index value of the parameter is set to zero for the model. For example, since parameters Q_{10} and T_r are not used in the models related only to T2, the sensitivity index values of the two parameters are zero for all the models associated with T2.

Table 3 lists the total sensitivity index (averaged over the eleven observation points shown in Fig. 1) evaluated for the four models but every single scenario. As indicated by Eqs. (8) and (9), the multi-model sensitivity index of a parameter is not the arithmetic mean of the parameter's sensitivity index of the four models, but the ratio between the model-averaged variance of the specific parameter and the model-

Table 2

Average total sensitivity index (%) of the nitrate concentration at simulation time of 100 days evaluated for individual models and scenarios.

	Scenario 1 (S15P)		Scenario 2 (S5P)				Scenario 3 (S25P)					
	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2
	M1	M1	M2	M2	M1	M1	M2	M2	M1	M1	M2	M2
K_{den}	75.86	98.25	53.53	88.52	62.59	43.46	26.05	4.80	75.89	99.03	68.63	98.42
K_{nit}	4.68	1.49	34.46	12.08	10.92	57.93	62.75	95.51	1.18	0.35	9.10	2.24
T_r	23.16	0.00	17.78	0.00	10.23	0.00	9.59	0.00	27.88	0.00	29.00	0.00
Q_{10}	8.31	0.00	7.08	0.00	30.49	0.00	19.70	0.00	9.19	0.00	10.27	0.00
m	0.01	0.00	0.00	0.00	0.03	0.08	0.00	0.00	0.00	0.00	0.00	0.00
	Scenario 4 (S15W)		Scenario 5 (S5W)				Scenario 6 (S25W)					
	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2
	M1	M1	M2	M2	M1	M1	M2	M2	M1	M1	M2	M2
K_{den}	77.30	98.37	73.70	99.06	64.29	48.28	55.13	16.60	75.11	99.03	74.97	99.76
K_{nit}	3.54	1.18	8.92	2.25	8.53	53.32	23.95	85.07	1.07	0.30	1.94	0.43
T_r	21.64	0.00	20.95	0.00	10.37	0.00	9.25	0.00	27.34	0.00	29.63	0.00
Q_{10}	8.55	0.00	8.29	0.00	31.10	0.00	26.79	0.00	8.79	0.00	9.76	0.00
m	0.01	0.00	0.00	0.00	0.02	0.06	0.00	0.00	0.04	0.00	0.00	0.00

Table 3

Average total sensitivity index (%) of the nitrate concentration at simulation time of 100 days evaluated for multiples models but individual scenarios (columns 2–7) and for multiple models and multiple scenarios (the last column).

	S15P	S5P	S25P	S15W	S5W	S25W	S
K_{den}	89.51	52.50	90.91	90.96	58.30	91.01	88.48
K_{nit}	3.89	28.00	0.91	2.56	20.24	0.65	2.90
T_r	7.78	8.12	9.57	7.39	8.53	9.48	8.92
Q_{10}	2.81	23.34	3.17	2.92	25.39	3.07	4.46
m	0.01	0.03	0.00	0.00	0.02	0.01	0.01

averaged variance of all the parameters. In other words, the results listed Table 3 are not simply the arithmetic mean of the results listed in Table 2. Taking Scenario S5P as an example, the sensitivity index value of Q_{10} in Table 3 is 23.34%, significantly larger than the arithmetic mean (12.55%) of the four index values (30.49%, 0%, 19.7%, and 0%) listed in Table 2. The multi-model sensitivity index is more informative than the arithmetic average, because the former better reflects the contribution of the variance caused by a parameter to the variance caused by all the parameters in the model-averaging sense.

In the last column of Table 3, the total sensitivity index of each parameter for multiple models and multiple scenarios are listed. This index is the composite parametric sensitivity by simultaneously considering uncertainty in model parameters, structures, and scenarios. The table shows that parameter K_{den} is the most important parameter for the simulated nitrate concentration under the multiple models and scenarios considered in this study. The second most important parameter is parameter T_r , followed by parameters Q_{10} and then K_{nit} ; parameter m is the least important parameter.

5. Discussion

This section discusses the results presented in the last section to understand why the parameter importance varies or remains invariant for different models and scenarios, why the concepts of model uncertainty and scenario uncertainty help understand conflicting results of parameter importance reported in literature, and why the new parameter sensitivity indices (with consideration of model uncertainty and scenario uncertainty) help identify the parameters important to nitrification and denitrification.

5.1. Important nitrogen parameters vary among different individual functions and scenarios

Table 2 shows that the values of sensitivity index of model parameters (except m) vary substantially for different models and scenarios. For example, under scenario S5P, the total sensitivity index of parameter K_{den} changes from 62.59% for model T1M1 to 4.80% for model T2M2; taking model T2M2 as an example, the index changes from 4.8% under Scenario S5P to 99.76% under Scenario S25W. These results indicate that, without considering model and scenario uncertainties, identifying important parameters based on a single model and a single scenario may lead to incorrect identification.

The substantial variation of important parameters across different models and scenarios is not surprising, because model simulations vary substantially under different models and scenarios. More specifically speaking, according to Eq. (4), the sensitivity index of a model parameter for a single model under a single scenario is the ratio between the variance related to the parameter (e.g., the numerator of Eq. (4)) and the variance related to all model parameters (e.g., the denominator of Eq. (4)). Since the two variances vary between models under different scenarios, the sensitivity index changes for different models and scenarios. For example, since the numerator-variance for parameter K_{den} and the denominator-variance are 0.435 and 0.491, respectively, for model T2M2 under scenario S15P, the corresponding sensitivity index

is 88.52%. For model T1M1 under scenario S5P, the numerator-variance and the denominator-variance become 1.268 and 2.026, which leads to the sensitivity index of 62.59%. Therefore, the sensitivity indices of individual models under individual scenarios are not comparable, and cannot be used to select the important parameters.

To confirm the identified important parameters for the individual models and scenarios, we compare the variance of simulated nitrate concentration for two cases by varying all parameters in the parameter ranges given in Section 3.3 and by reducing the parameter range by 40% (e.g., the 20%–80% of the original range) for one parameter value at a time. The basic idea is that, if a parameter is more important than other parameters, reducing its parameter range will lead to a larger reduction of the variance of simulated nitrate concentration. Fig. 3 plots the marginal distributions of simulated nitrate concentration for the two cases, and the corresponding variance for the two cases are also shown in the figure. In Fig. 3(a) for model T1M1 and scenario S15P, fixing the most important parameter (K_{den}) leads to a variance reduced from 3.868 to 2.134, the largest reduction for all the parameters. The amount of variance reduction is consistent with the ranking of model importance given by the sensitivity index listed in Table 2. In other words, fixing the value of a more important parameter leads to large variance reduction. This indicates that the Sobols' sensitivity index can be used to identify important model parameters. Comparing Fig. 3(a) with Fig. 3(b) (for model T1M1 and scenario S5P) and Fig. 3(c) (for model T2M1 and scenario S5P) indicates that the values of variance and the amounts of variance reduction change for different models and/or different scenarios. Therefore, without considering model uncertainty and scenario uncertainty, an inaccurate selection of important parameters may occur.

5.2. Reasons for conflicting results reported in literature

The variability of the sensitivity index may be used to explain different conclusions reported in literature about the importance of the parameters related to nitrification and denitrification processes. In Table 4, we reviewed some conflicting conclusions which were obtained by various methods. The conclusion of Wang et al. (2005) is supported by the summation of the sensitivity index of Q_{10} and T_r , because the index ranges between 24.87% (for model T1M2 and scenario S15P) and 39.39% (for model T1M2 and scenario S25P), suggesting that temperature is important to nitrogen transformation. However, our results demonstrate that the optimal denitrification rate, K_{den} , is more important. The conclusion of Heinen (2006) is supported by the sensitivity index of model T1M2, for which the sensitivity index of K_{den} increases when precipitation increases in the wet scenario. For example, the sensitivity index increases from 26.05% under scenario S5P to 55.13% under scenario S5W. It should be noted that nitrogen reaction is sensitive to moisture function doesn't mean it is sensitive to the parameter in moisture function, since the parameter here, m , is always unimportant under all conditions in this study. A detailed discussion about this phenomenon is further presented in Section 5.4.

The results in Table 2 also qualitatively support the observation that the nitrification and denitrification processes alternately dominate nitrogen transformation. Bateman and Baggs (2005) concluded that nitrification is the dominant process in nitrogen reactive at low moisture. Our study on model T1M2 is consistent with their conclusion, where the optimal nitrification rate is the most important parameter under Scenario S5P (lower moisture) comparing with Scenario S5W (higher moisture). However, the optimal denitrification rate is most important under other conditions, which suggests denitrification is a more important process that affects nitrate concentration than nitrification. Stevens et al. (1997) also found the similar conclusion that denitrification and nitrification are alternately dominant. However, such alternation also depends on the selected models. The change of parameter importance for different models and under different scenarios suggests again the need of considering model and scenario uncertainties

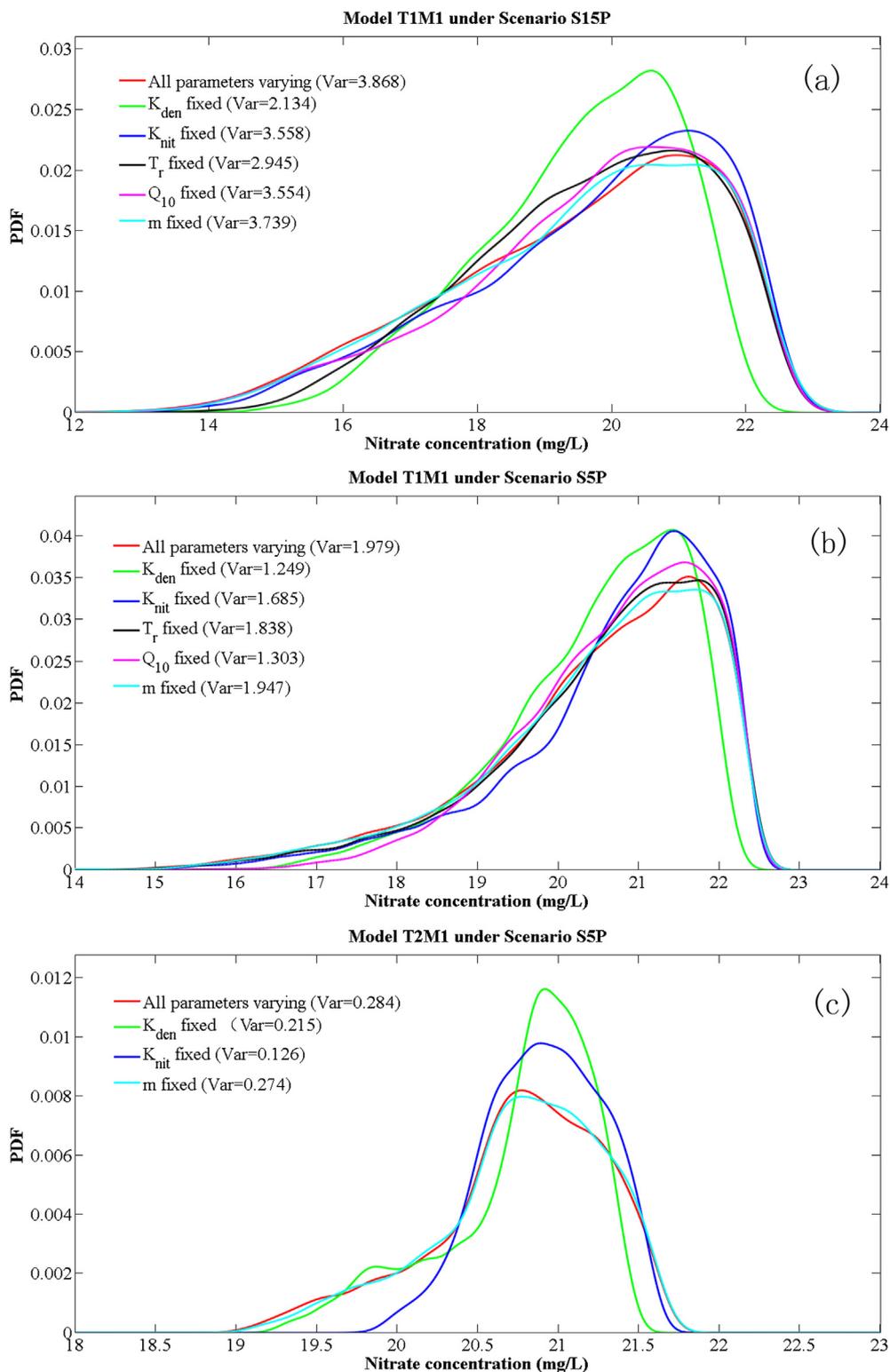


Fig. 3. Probability density function (PDF) of simulated nitrate concentration by using (a) model T1M1 and scenario S15P, (b) model T1M1 and scenario S5P, and (c) model T2M1 and scenario S5P. In each combination of model and scenario, different cases of model simulations are made by varying all parameters or fixing one parameter. The variance of simulated nitrate concentration for each case is shown in the brackets.

when selecting important parameters for nitrification and denitrification processes.

5.3. Identification of important parameters with model and scenario averaging method

Using the multi-model sensitivity index makes it unnecessary to compare the sensitivity indices of different models, which are actually incomparable because of the different variance values of different

Table 4
Conclusion comparison between existing literature and present study.

Literature source	Method	Reported Conclusion	This present study
Heinen (2006)	Normalized sensitivity (elasticity) analysis	Denitrification is most sensitive to moisture function	Nitrogen process (including denitrification and nitrification) is sensitive to moisture condition instead of to the parameter of moisture function (see Section 5.4).
Wang et al. (2005)	Two-step global sensitivity analysis	Nitrogen simulation is sensitivity to denitrification parameters on temperature	Parameters on temperature function are important. However, the optimal denitrification rate is more important (see Table 2 and 6)
Bateman and Baggs (2005)	Laboratory experiment	Nitrification is the main process in nitrogen reactive at low moisture	The importance of nitrification activity increases with low soil moisture. Nitrification also becomes more important at low temperature (see Table 2 and 6). Furthermore, the increasing importance of nitrification activity with decreased temperature depends on the selected model (see Table 2 and 6).
Stevens et al. (1997)	Laboratory experiment	Denitrification and nitrification are alternately dominant.	Our study is consistent with their conclusion. However, such alternation also depends on the selected models (see Table 2 and 6).
McIntyre et al. (2005)	Regionalized sensitivity analysis	The most sensitive parameters were spatially inconsistent	The importance of parameter not only varies with space, but also varies substantially among models and scenarios (see Table 6).

models (i.e., the denominator of Eqs. (3) and (4)). More importantly, using the multi-model sensitivity index avoids the problem of inaccurate selection of important parameters. Taking parameter K_{nit} under scenario S5P as an example, the index values in Table 2 indicate that this parameter is the third important parameter in model T1M1 (with the index value of 10.92%) but the most important parameter in model T2M2 (with the index value of 95.51%). The multi-model sensitivity index listed in Table 3 suggests that this parameter is the second most important parameter, with the index value of 28.00%. These results show that a parameter important in one model may not be important in another model, and the multi-model sensitivity index is a more reasonable indicator for evaluating the relative importance of model parameters.

The change of the sensitivity index values after model averaging can be qualitatively understood by examining the PDFs shown in Fig. 3. The figure shows that, for scenario S5P, the variance of model T1M1 is significantly larger than that of model T2M2. Quantitatively speaking, the sensitivity index of 95.51% for model T2M2 corresponds to a small total variance of 0.204, whereas the sensitivity index of 10.92% for model T1M1 corresponds to a larger total variance of 2.026. The variance of model-averaging is the average of the variance of each model, which equals 0.720. Similarly, the variance caused by K_{nit} under model averaging is 0.202. These results explain why the multi-model sensitivity index value of K_{nit} listed in Table 3 is smaller than the sensitivity index of the three models (T2M1, T1M2, and T2M2) listed in Table 2.

Table 5 lists the data that helps gain a quantitative understanding why the multi-model index is better than the individual-model index. The second row of the table lists the variance of simulated nitrate concentration given by the four models and model averaging under scenario S5P. The variance of model T2M2 is the smallest of the four models, less than 10% of that of model T1M1. The other five rows of Table 4 list the variance of simulated nitrate concentration obtained by fixing one parameter at a time. Similar to the discussion in Section 5.2, the reduction of variance between the two cases (all parameter varying and one parameter fixed) is used to understand why the multi-model index is better than the individual-model index for identifying

Table 5
Variance of simulated nitrate concentration for individual models (columns 2–5) and model-averaging (the last column) under scenario S5P with all parameters varying and one parameter fixed at a time.

	T1M1	T1M2	T2M1	T2M2	Model Averaging
All parameters	1.979	0.280	0.284	0.172	0.679
K_{den} fixed	1.249	0.271	0.215	0.166	0.475
K_{nit} fixed	1.685	0.072	0.126	0.025	0.477
T_r fixed	1.829	0.278	0.284	0.172	0.641
Q_{10} fixed	1.322	0.272	0.284	0.172	0.512
m fixed	1.947	0.280	0.274	0.172	0.668

important model parameters. Taking parameter K_{nit} as an example, although fixing this parameter reduces the variance substantially (from 0.172 to 0.025) for model T2M2, the reduction is smaller than the corresponding reduction of the other three models, because the total variance (when all parameter varies) of model T2M2 is significantly smaller than the corresponding total variance of the other three models. More importantly, the variance reduction of 0.147 achieved by fixing parameter K_{nit} in model T2M2 is significantly smaller than the variance reduction of 0.73 achieved by fixing parameter K_{den} in model T1M1. In line with this, the reduction of model-averaging variance by fixing one parameter a time is the largest for parameter K_{den} and the second largest for parameter K_{nit} . This example illustrates that, the multi-model sensitivity index considers the variance reduction of not a single model but of all the models, and thus identify the parameters that are important not to a single model but to all the models. This is necessary in the situation when model uncertainty exists. The same conclusion can be drawn for the multi-scenario and individual-scenario sensitivity indices, although results are not shown.

5.4. Comparison between one-layer case and two-layer case

Table 6 lists the sensitivity analysis index of each parameter for the two-layer case. The results show that after considering biochemical heterogeneity the importance of parameters for model output shares some similarities with the single-layer case. For example, parameter K_{den} ($K_{den,up}$ and $K_{den,bot}$) often plays a dominant role. The results also show that the importance of one parameter varies between layers. Parameter in bottom layer always has larger sensitivity index than in top layer under each model and scenario. Since denitrification process is the controlling process of affecting nitrate concentration in this study and denitrification activity in the bottom layer (caused by larger moisture content in this layer) is significantly stronger than the top layer, it is reasonable that the model output (nitrate concentration) more depends on the parameters in the bottom layer.

Nitrogen reaction activity gains with the increase of soil moisture and temperature. Since output nitrate concentration uncertainty increases with higher reactive rate, the importance of parameters becomes larger in the area with higher moisture content and temperature than in the area with lower soil moisture and temperature. It is observed that in this two-layer case, moisture content is higher in the bottom layer, while the temperature is opposite. The larger importance of bottom parameters indicates that soil moisture contributes more uncertainty than temperature. The results suggest that spatial distribution of soil moisture needs more delicate attention than the temperature in order to better characterize the nitrogen reactive transport. However, it is not necessary to conclude that parameter related to soil moisture response function is more important than parameters associated with temperature response function. From Table 6, m is always less important than T_r and Q_{10} . This phenomenon indicates that the

Table 6
Average total sensitivity index (%) of the nitrate concentration at simulation time of 100 days evaluated for individual models and scenarios in the two-layer domain.

	Scenario 1 (S15P)				Scenario 2 (S5P)				Scenario 3 (S25P)			
	T1M1	T2M1	T1M2	T2M2	T1M1	T2M1	T1M2	T2M2	T1M1	T2M1	T1M2	T2M2
$K_{den,up}$	10.46	13.74	0.01	0.01	7.70	0.05	0.01	0.00	11.70	18.39	0.01	0.02
$K_{den,bot}$	60.37	80.30	31.30	72.26	45.43	20.97	12.07	1.81	63.05	79.33	57.74	95.44
$K_{nit,up}$	3.79	1.20	16.53	7.28	10.07	1.33	22.18	1.71	1.09	0.26	6.76	1.44
$K_{nit,bot}$	9.47	2.42	46.25	19.12	22.65	77.11	58.66	97.68	2.43	0.41	17.33	3.96
T_r,up	2.57	0.00	1.71	0.00	1.35	0.00	3.48	0.00	4.51	0.00	0.54	0.00
T_r,bot	14.93	0.00	9.75	0.00	6.44	0.00	6.12	0.00	19.81	0.00	23.59	0.00
$Q_{10,up}$	1.37	0.00	1.19	0.00	3.87	0.00	5.55	0.00	1.07	0.00	0.12	0.00
$Q_{10,bot}$	5.31	0.00	3.95	0.00	17.64	0.00	10.57	0.00	6.34	0.00	7.55	0.00
m_{up}	0.01	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m_{bot}	0.01	0.00	0.00	0.00	0.05	0.12	0.00	0.00	0.00	0.00	0.00	0.00
	Scenario 4 (S15W)				Scenario 5 (S5W)				Scenario 6 (S25W)			
	T1M1	T2M1	T1M2	T2M2	T1M1	T2M1	T1M2	T2M2	T1M1	T2M1	T1M2	T2M2
$K_{den,up}$	8.92	11.90	0.11	0.14	7.18	0.04	0.08	0.00	10.22	16.36	0.12	0.17
$K_{den,bot}$	62.78	85.63	61.62	93.90	50.33	24.80	40.61	6.28	65.57	82.09	72.67	99.42
$K_{nit,up}$	2.64	0.67	5.44	1.50	6.59	1.18	12.20	1.74	0.63	0.16	1.34	0.23
$K_{nit,bot}$	8.54	1.95	19.47	5.76	20.01	74.39	41.95	93.97	2.14	0.38	5.15	0.98
T_r,up	2.16	0.00	0.51	0.00	1.07	0.00	1.63	0.00	3.77	0.00	0.13	0.00
T_r,bot	17.71	0.00	16.18	0.00	6.81	0.00	6.03	0.00	19.85	0.00	25.26	0.00
$Q_{10,up}$	1.06	0.00	0.31	0.00	3.44	0.00	2.76	0.00	0.88	0.00	0.03	0.00
$Q_{10,bot}$	5.43	0.00	6.01	0.00	19.51	0.00	15.80	0.00	6.10	0.00	7.69	0.00
m_{up}	0.01	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m_{bot}	0.01	0.00	0.00	0.00	0.02	0.08	0.00	0.00	0.00	0.00	0.00	0.00

response of nitrate reaction to an environmental factor (i.e., moisture content) sometimes is more controlled by that factor itself but not parameter. The above sensitivity analysis can help modeler to contemplate the focus of establishing a nitrogen reactive transport model.

It is worthy to note that the sensitivity index of one parameter in the single-layer case may have a considerable difference with the sum of indices of the same parameter in the top and bottom layers. For example, sensitivity index of K_{nit} is 57.93% under Model T2M1 and Scenario S5P in the single-layer case, which is significantly different with 78.44%, the value of the sensitivity index of $K_{nit,sum}$ (summing indices of $K_{nit,up}$ and $K_{nit,bot}$) in the two-layer case. This is understandable since model output (nitrate concentration here) responds to different number of parameters in different ways by including stratification or not. From another perspective, the stratification strategy of biochemical reaction parameters can be regarded as another source of model uncertainty. Recalling the findings when considering various response functions of soil moisture and temperature, the new results reconfirm that sensitivity analysis outcomes unavoidably vary between different models, no matter where the model uncertainty originates. Attention must be paid to the model uncertainty when a reasonable sensitivity analysis is required.

Table 7 lists sensitivity indices under model averaging and/or scenario averaging. By comparing the column 7 in Tables 3 and 7, it is interesting to find that parameter K_{den} is still the most important one to model output under model and scenario averaging, T_r is still more

Table 7
Approximatively summing sensitivity index of same parameter in two layers for multiples models but individual scenarios (columns 2–7) and for multiple models and multiple scenarios (the last column).

	S15P	S5P	S25P	S15W	S5W	S25W	S
$K_{den,sum}$	81.14	30.75	88.12	86.47	40.90	89.85	81.86
$K_{nit,sum}$	12.15	61.70	3.09	8.02	51.00	1.94	10.48
T_r,sum	6.17	5.22	9.11	6.87	5.33	9.07	7.93
$Q_{10,sum}$	2.40	12.56	2.79	2.34	14.68	2.71	3.85
m_{sum}	0.01	0.06	0.00	0.01	0.04	0.00	0.01

important than Q_{10} , and parameter m remains least important. The only exception is that K_{nit} is more important than T_r . The results from this case, together with the results from single-layer case, indicate that introduced global sensitivity analysis method could largely avoid the inaccurate selection of important parameters under model and scenario uncertainties in a broad sense. Although the inclusion of stratification produces rather complicated parameter importance rank under each mode and scenario (Table 6), the results in Table 7 positively imply that regardless of the possibly biochemical heterogeneity in nitrogen reactive transport model, the global sensitivity analysis by considering model and scenario uncertainties produce fairly consistent parameter importance rank.

5.5. Limitations of this study

There are some limitations to this study: (1). The parameter, model, and scenario uncertainty are considered within a hierarchical framework. The interactions between different uncertainty sources are not expressed explicitly during the variance decomposition (Eq. (1)) and sensitivity analysis (Eqs. (3), (4), (8), (9), (10), and (11)). Thus, the interactions and their impact on output are not quantified in this study. (2). Since models are conditioned on scenarios and parameters are conditioned on models and scenarios under the given hierarchical framework, it is not able to quantify the marginal effect of model and scenario on the outputs by changing models (scenarios) while keeping parameters (and models) fixed in this study.

6. Conclusions and future research recommendations

This study conducts a global sensitivity analysis to identify important parameters to the nitrification and denitrification processes in nitrogen reactive transport modeling. The reduction functions of soil temperature and moisture content are developed for the scenarios of yearly-average temperature and precipitation, and the reduction functions have their own parameters that are treated as random variables. The five parameters considered in this study are the optimal nitrification and denitrification rates (K_{den} and K_{nit}), the two parameters (T_r and

Q_{10}) related to the reduction function of temperature, and the parameter (m) related to the reduction function of moisture content. To our knowledge, this is the first attempt of global sensitivity analysis for nitrification and denitrification processes with simultaneous consideration of parametric uncertainty, model uncertainty, and scenario uncertainty. While the results are specific to the numerical models in this study, the results may be useful for understanding variably saturated flow and nitrogen reactive transport. This study leads to the following major conclusions:

- (1) The results highlight the complexity of identifying important parameters for nitrogen reactive transport when faced with multiple choices of describing nitrogen reaction and diversely possible temperature and soil moisture variations. It is not appropriate to compare the global sensitivity index values under different scenarios and models due to the difference of total variance of prediction. The rank of important nitrogen parameters also shows notable disparities. The impact of soil temperature and soil moisture content on nitrification and denitrification process can only be properly evaluated by further considering model and scenario uncertainty. By introducing the new global sensitivity index, the comparison between sensitivity analysis results under different models and scenarios becomes unnecessary.
- (2) A multi-model and scenario study reveals that nitrification process becomes more important at either low moisture content or low temperature. Moreover, the increasing importance of nitrification activity with decreased temperature strongly depends on the selected model. Under given environment, model averaging is suggested to make an objective assessment to nitrification (or denitrification) activity contribution to avoid artificial model error.
- (3) For the five parameters used for simulating the nitrification and denitrification processes in a single-layer and two-layer case, the multi-model and multi-scenario sensitivity analysis in this study presents a few common features: optimal denitrification rate (K_{den}) is the most important parameter; reference temperature (T_r) is more important than temperature coefficient (Q_{10}); m is the least important one.
- (4) Both environmental factors (soil moisture content and temperature) themselves and the parameters of response functions impose effect on output nitrate concentration. However, the response of nitrate reaction to soil moisture depends more on moisture content itself but not moisture function parameter m , and the spatial distribution of soil moisture play a more decisive role controlling nitrogen reaction than temperature.

Several future directions are recommended. First, the equal probability for the four models and six scenarios are assumed in this current study. The evaluation of model probability based on observations can be done in various ways (e.g., Ye et al., 2008; Lu et al., 2013; 2015; Liu et al., 2016), and scenario probability can be estimated based on expert judgment (Meyer et al., 2007). Another future work is to evaluate model probability and scenario probability conditioned on observations of state variables (e.g., moisture content and nitrogen concentration). It is expected that by infusing these data into the modeling system, uncertainties brought by parameter and model can be restrained. However, the reduction of scenario uncertainty relies on the improvement on the reliability of future forcing data (e.g., precipitation, temperature, evapotranspiration). The total uncertainty of model output consists of three parts: parametric, model and scenario uncertainty, while the interactions between them are ignored in this study. The evaluation of marginal effects from models, scenarios, and their interactions with parameters require further investigation.

Acknowledgments

This study was supported by the National Natural Science

Foundation of China Grants 51629901, 51522904, and 51328902. The second author was partially supported by “111 Project” (B18037). The third author was supported in part by DOE Grant DE-SC0008272 and NSF-EAR Grant 1552329. The example and data are available from the corresponding author upon request.

References

- European Environment Agency (EEA), 2000. Groundwater Quality and Quantity in Europe. Environmental Assessment European Environment Agency, Copenhagen and Quantity in Europe. European Environment Agency, Copenhagen Report No. 3.
- Bateman, E.J., Baggs, E.M., 2005. Contributions of nitrification and denitrification to N₂O emissions from soils at different water-filled pore space. *Biol. Fertil. Soils* 41 (6), 379–388. <http://dx.doi.org/10.1007/s00374-005-0858-3>.
- Bengtsson, G., Bengtson, P., Månsson, K.F., 2003. Gross nitrogen mineralization-, immobilization-, and nitrification rates as a function of soil C/N ratio and microbial activity. *Soil Biol. Biochem.* 35 (1), 143–154. [http://dx.doi.org/10.1016/S0038-0717\(02\)00248-1](http://dx.doi.org/10.1016/S0038-0717(02)00248-1).
- Dai, H., Ye, M., 2015. Variance-based global sensitivity analysis for multiple scenarios and models with implementation using sparse grid collocation. *J. Hydrol.* 528, 286–300. <http://dx.doi.org/10.1016/j.jhydrol.2015.06.034>.
- de Neergaard, A., Hauggaard-Nielsen, H., Jensen, L.S., Magid, J., 2002. Decomposition of white clover (*Trifolium repens*) and ryegrass (*Lolium perenne*) components: C and N dynamics simulated with the DAISY soil organic matter submodel. *Eur. J. Agron.* 16 (1), 43–55. [http://dx.doi.org/10.1016/S1161-0301\(01\)00118-6](http://dx.doi.org/10.1016/S1161-0301(01)00118-6).
- Eckersten, H., Torssell, B., Kornher, A., Boström, U., 2007. Modelling biomass, water and nitrogen in grass ley: estimation of N uptake parameters. *Eur. J. Agron.* 27 (1), 89–101. <http://dx.doi.org/10.1016/j.eja.2007.02.003>.
- Frolking, S.E., Mosier, A.R., Ojima, D.S., Li, C., Parton, W.J., Potter, C.S., Priesack, E., Stenger, R., Haberbosch, C., Dörsch, P., 1998. Comparison of N₂O emissions from soils at three temperate agricultural sites: simulations of year-round measurements by four models. *Nutr. Cycl. Agroecosyst.* 52 (2–3), 77–105. <http://dx.doi.org/10.1023/A:1009780109748>.
- Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R., Vöösmary, C.J., 2004. Nitrogen cycles: past present, and future. *Biogeochemistry* 70 (2), 153–226. <http://dx.doi.org/10.1007/s10533-004-0370-0>.
- Griensven, A.V., Meixner, T., Grunwald, S., Bishop, T., Diluzio, M., Srinivasan, R., 2006. A global sensitivity analysis tool for the parameters of multi-variable catchment models. *J. Hydrol.* 324 (1), 10–23. <http://dx.doi.org/10.1016/j.jhydrol.2005.09.008>.
- Hansen, S., Jensen, H.E., Nielsen, N.E., Svendsen, H., 1993. User's Guide to the DAISY Simulation Model. The Royal Veterinary and Agricultural University, Copenhagen, Denmark.
- Hansen, S., Shaffer, M.J., Jensen, H.E., 1995. Developments in modeling nitrogen transformations in soil. *Nitrogen Fertil. Environ.* 83–107.
- Heinen, M., 2006. Simplified denitrification models: overview and properties. *Geoderma* 133 (3–4), 444–463. <http://dx.doi.org/10.1016/j.geoderma.2005.06.010>.
- Johnsson, H., Bergstrom, L., Jansson, P., Paustian, K., 1987. Simulated nitrogen dynamics and losses in a layered agricultural soil. *Agric. Ecosyst. Environ.* 18 (4), 333–356. [http://dx.doi.org/10.1016/0167-8809\(87\)90099-5](http://dx.doi.org/10.1016/0167-8809(87)90099-5).
- Korom, S.F., 1992. Natural denitrification in the saturated zone: a review. *Water Resour. Res.* 28 (6), 1657–1668. <http://dx.doi.org/10.1029/92WR00252>.
- Liang, H., Hu, K., Li, B., Liu, H., 2014. Coupled simulation of soil water-heat-carbon-nitrogen process and crop growth at soil-plant-atmosphere continuum system. *Trans. Chin. Soc. Agric. Eng.* 30 (24), 54–66.
- Liu, P., Elshall, A.S., Ye, M., Beerli, P., Zeng, X., Lu, D., Tao, Y., 2016. Evaluating marginal likelihood with thermodynamic integration method and comparison with several other numerical methods. *Water Resour. Res.* <http://dx.doi.org/10.1002/2014WR016718>.
- Lu, D., Ye, M., Meyer, P.D., Curtis, G.P., Shi, X., Niu, X.F., Yabusaki, S.B., 2013. Effects of error covariance structure on estimation of model averaging weights and predictive performance. *Water Resour. Res.* 49 (9), 6029–6047. <http://dx.doi.org/10.1002/wrcr.20441>.
- Lu, D., Ye, M., Curtis, G.P., 2015. Maximum likelihood Bayesian model averaging and its predictive analysis for groundwater reactive transport models. *J. Hydrol.* 529 (3), 1859–1873. <http://dx.doi.org/10.1016/j.jhydrol.2015.07.029>.
- McIntyre, N., Jackson, B., Wade, A.J., Butterfield, D., Wheatler, H.S., 2005. Sensitivity analysis of a catchment-scale nitrogen model. *J. Hydrol.* 315 (1–4), 71–92. <http://dx.doi.org/10.1016/j.jhydrol.2005.04.010>.
- Mendoza, C.A., Therrien, R., Sudicky, E.A., 1991. ORTHOFEM User's Guide. Version 1.02. Waterloo Centre for Groundwater Research, Univ. of Waterloo, Waterloo, ON.
- Meyer, P.D., Ye, M., Rockhold, M.L., Neuman, S.P., Cantrell, K.J., 2007. NUREG/CR-6940 (PNNL-16396) In: Combined Estimation of Hydrogeologic Conceptual Model, Parameter, and Scenario Uncertainty with Application to Uranium Transport at the Hanford Site 300 area. U.S. Nuclear Regulatory Commission, Washington, DC. <http://dx.doi.org/10.2172/921264>.
- Meyer, P.D., Ye, M., Nicholson, T., Neuman, S.P., Rockhold, M., 2014. Incorporating scenario uncertainty within a hydrogeologic uncertainty assessment methodology. In: Mosleh, Ali, Jeffery, Wood (Eds.), Proceedings of the International Workshop on Model Uncertainty: Conceptual and Practical Issues in the Context of Risk-Informed Decision Making. International Workshop Series on Advanced Topics in Reliability and Risk Analysis, Center for Risk and Reliability, University of Maryland, College

- Park, MD, USA, 2014, pp. 99–119 (ISSN: 1084-5658).
- Mishra, S., Deeds, N., Ruskauuff, G., 2009. Global sensitivity analysis techniques for probabilistic ground water modeling. *Ground Water* 47 (5), 727–744. <http://dx.doi.org/10.1111/j.1745-6584.2009.00604.x>.
- Pohlert, T., Huisman, J.A., Breuer, L., Frede, H.G., 2007. Integration of a detailed biogeochemical model into SWAT for improved nitrogen predictions—model development, sensitivity, and GLUE analysis. *Ecol. Model.* 203 (3–4), 215–228. <http://dx.doi.org/10.1016/j.ecolmodel.2006.11.019>.
- Rakovec, O., Hill, M.C., Clark, M.P., Weerts, A.H., Teuling, A.J., Uijlenhoet, R., 2014. distributed evaluation of local sensitivity analysis (DELSA), with application to hydrologic models. *Water Resour. Res.* 50 (1), 409–426. <http://dx.doi.org/10.1002/2013WR014063>.
- Razavi, S., Gupta, H.V., 2015. What do we mean by sensitivity analysis? the need for comprehensive characterization of “global” sensitivity in earth and environmental systems models. *Water Resour. Res.* 51 (5), 3070–3092. <http://dx.doi.org/10.1002/2014WR016527>.
- Razavi, S., Gupta, H.V., 2016a. A new framework for comprehensive, robust, and efficient global sensitivity analysis: 1 theory. *Water Resour. Res.* 52, 423–439. <http://dx.doi.org/10.1002/2015WR017558>.
- Razavi, S., Gupta, H.V., 2016b. A new framework for comprehensive, robust, and efficient global sensitivity analysis: 2 application. *Water Resour. Res.* 52, 440–455. <http://dx.doi.org/10.1002/2015WR017559>.
- Rijtema, P.E., Kroes, J.G., 1991. Some results of nitrogen simulations with the model ANIMO. *Nutr. Cycl. Agroecosyst.* 27 (2), 189–198. http://dx.doi.org/10.1007/978-94-011-3434-7_6.
- Rivett, M.O., Smith, J., Buss, S.R., Morgan, P., 2007. Nitrate occurrence and attenuation in the major aquifers of England and Wales. *Q. J. Eng. Geol. Hydrogeol.* 40 (4), 335–352. <http://dx.doi.org/10.1144/1470-9236/07-032>.
- Rodrigo, A., Recous, S., Neel, C., Mary, B., 1997. Modelling temperature and moisture effects on C-N transformations in soils: comparison of nine models. *Ecol. Model.* 102 (2–3), 325–339. [http://dx.doi.org/10.1016/S0304-3800\(97\)00067-7](http://dx.doi.org/10.1016/S0304-3800(97)00067-7).
- Rysgaard, S., Glud, R.N., Risgaard, N., Dalsgaard, T., 2004. Denitrification and anammox activity in Arctic marine sediments. *Limnol. Oceanogr.* 49 (5), 1493–1502. <http://dx.doi.org/10.4319/lo.2004.49.5.1493>.
- Saad, O.A.L.O., Conrad, R., 1993. Temperature dependence of nitrification, denitrification, and turnover of nitric oxide in different soils. *Biol. Fertil. Soils* 15 (1), 21–27. <http://dx.doi.org/10.1007/BF00336283>.
- Saltelli, A., Annoni, P., Azzini, I., Campolongo, F., Ratto, M., Tarantola, S., 2010. Variance based sensitivity analysis of model output Design and estimator for the total sensitivity index. *Comput. Phys. Commun.* 181 (2), 259–270. <http://dx.doi.org/10.1016/j.cpc.2009.09.018>.
- Simunek, Jirka, Van Genuchten, M.Th., Sejna, M., 2005. The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. *Univ. California Riverside Res. Rep.* 3, 1–240.
- Song, X., Zhang, J., Zhan, C., Xuan, Y., Ye, M., Xu, C., 2015. Global sensitivity analysis in hydrological modeling: review of concepts, methods, theoretical framework, and applications. *J. Hydrol.* 523, 739–757. <http://dx.doi.org/10.1016/j.jhydrol.2015.02.013>.
- Stevens, R.J., Laughlin, R.J., Burns, L.C., Arah, J.R.M., Hood, R.C., 1997. Measuring the contributions of nitrification and denitrification to the flux of nitrous oxide from soil. *Soil Biol. Biochem.* 29 (2), 139–151. [http://dx.doi.org/10.1016/S0038-0717\(96\)00303-3](http://dx.doi.org/10.1016/S0038-0717(96)00303-3).
- van Genuchten, M.T., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 44 (5), 892–898. <http://dx.doi.org/10.2136/sssaj1980.03615995004400050002x>.
- Wainwright, H.M., Finsterle, S., Jung, Y., Zhou, Q., Birkholzer, J.T., 2014. Making sense of global sensitivity analyses. *Comput. Geosci. U.K.* 65, 84–94. <http://dx.doi.org/10.1016/j.cageo.2013.06.006>.
- Wang, L., Ye, M., Lee, P.Z., Hicks, R.W., 2013. Support of sustainable management of nitrogen contamination due to septic systems using numerical modeling methods. *Environ. Syst. Decis.* 33 (2), 237–250. <http://dx.doi.org/10.1007/s10669-013-9445-6>.
- Wang, X., Youssef, M.A., Skaggs, R.W., Atwood, J.D., Frankenberger, J.R., 2005. Sensitivity analyses of the nitrogen simulation model DRAINMOD-N II. *Trans. ASAE* 48 (6), 2205–2212. <http://dx.doi.org/10.13031/2013.20106>.
- Wu, L., McGechan, M.B., 1998. A review of carbon and nitrogen processes in four soil nitrogen dynamics models. *J. Agric. Eng. Res.* 69 (4), 279–305. <http://dx.doi.org/10.1006/jaer.1997.0250>.
- Yang, J., Wang, L., Lu, C., Jayawardane, N., 2008. Experiment and numerical simulation of nitrogen transport in soils irrigated with treated sewage. *Irrig. Drain* 57 (2), 203–217. <http://dx.doi.org/10.1002/ird.354>.
- Ye, M., Philip, D.M., Shlomo, P.N., 2008. On model selection criteria in multimodel analysis. *Water Resour. Res.* 44 (3). <http://dx.doi.org/10.1029/2008WR006803>.
- Zhang, C.J., Chu, Fu, G., 2013. Sobol’s sensitivity analysis for a distributed hydrological model of Yichun River Basin, China. *J. Hydrol.* 480, 58–68.