Sensitivity Analysis of Fully Distributed Parameterization Reveals Insights Into Heterogeneous Catchment Responses for Water Quality Modeling

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Abstract  Spatially distributed parameterization is preferable in capturing the heterogeneity of catchment properties and in allowing a better model representation of catchment responses. In hydrological modeling, sensitivity analysis is recommended to address the high-dimensional parametric problems. However, less has been focused on water quality modeling, presumably due to the lack of suitable fully distributed models. Based on the newly developed mesoscale hydrological-nitrate model, we investigated for the first time the spatially distributed sensitivity of nitrate model parameters and correlated the sensitivity indices with multiple catchment characteristics. The study was conducted in the highly heterogeneous Selke catchment, central Germany. Three nested catchments were defined based on the heterogeneous catchment responses (gauged by three nested stations). Results showed that parameters of soil denitrification, in-stream denitrification, and in-stream assimilatory uptake were the most sensitive parameters throughout the catchment. They all showed high spatial variability, which also varied when different gauging stations were considered. Spearman rank correlation indicated that the sensitivity of soil denitrification was controlled mainly by the relative limitations between the terrestrial hydrological transport capacity and the soil nitrate availability; the sensitivity of in-stream processes was predominated by the spatial variability within the river network (e.g., the proximity to the gauging station), rather than the local biogeochemical factors. Based on the insights gained from the spatial sensitivity and correlation analyses, we suggested that an appropriate monitoring scheme is important in reflecting actual catchment responses, and a cautious statistical correlation is informative in benefiting future parameter regionalization of water quality models.

1. Introduction

Nonpoint source pollution due to intensive agricultural activities has become one of the major causes of water quality deterioration (EEA, 2005). Catchment water quality models have been widely accepted in formulating the current understanding of catchment functioning and further guiding mitigation measures to protect and improve our living environment (Rode et al., 2010; Wellen et al., 2015). In the context of specific process descriptions, the model applicability depends mainly on the spatial discretization of forcing data and the appropriateness of parameterization (Beven, 1993; Clark et al., 2015; Wagener et al., 2001). By allowing the forcing data to vary spatially, fully distributed models are particularly preferable in pursuing a better spatial representation of catchment properties. Meanwhile, such model structure offers high potential for spatially differentiated parameterization to better capture heterogeneous catchment responses. However, the cost of increased complexity has also been well documented (Razavi & Gupta, 2016; Sheikholeslami et al., 2019), for example, the complexity of high-dimensional, nonlinear parameter spaces. Such high model complexity inhibits the identification of appropriate parameter values and diagnostic of model behaviors (Gupta et al., 2008; Pianosi et al., 2016). Efforts have been made to address the parametric difficulties in hydrological modeling through, for example, parameter regionalization (Oudin et al., 2008; Samaniego et al., 2010) and spatially explicit configurations (Herman et al., 2013a, 2013b; Tang et al., 2007). However, few studies have focused on the water quality modeling.

Excessive nitrate export is one of the main reasons for water pollution and eutrophication (Yu et al., 2019). Nitrate terrestrial leaching and in-stream transport are mostly driven by hydrological processes. In the process of adding on significant anthropogenic impacts, catchment nitrate behaviors show a higher degree of spatial heterogeneity than the hydrological basics (e.g., Yang et al., 2018). Aiming to balance the process

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representation and the model complexity in process-based modeling (Rode et al., 2010), the conceptualization and parameterization of nitrate processes are normally formulated in two parts: (1) The impacts of known factors are quantified through empirical equations, for example, the temperature impacts on denitrification (Stanford et al., 1975); and (2) the impacts of biogeochemical reactions are reflected by model parameters (referred as reaction “rate”). These rates are usually assigned as land cover/soil type dependent in catchment model developments, partially intending to be compatible with the hierarchical structure of semi-distributed models (i.e., catchment, subcatchments, and basic calculating units) (Huang et al., 2009; Lindström et al., 2010; Wade et al., 2002). However, such a parameterization scheme restricts the parameter only to land cover or soil information, which likely underestimates the spatial heterogeneity and its relevance in nature (Clark et al., 2017). Alternatively, fully distributed parameterization provides the opportunity to spatially link the reaction rates with multiple catchment characteristics, including meteorological forcing, catchment properties, and modeled state variables and fluxes. However, the number of available models and their applications are still limited (see the review by Wellen et al., 2015), especially in larger catchments (e.g., >200 km²). Recently, Yang et al. (2018) developed a fully distributed catchment nitrate model (i.e., the mHM-Nitrate model) based on the gridded implementation of the mesoscale Hydrological Model (mHM) (Kumar et al., 2013; Samaniego et al., 2010). The model balances the spatial representation and the model complexity using the multi-resolution structure and the multi-scale parameter regionalization technique (Samaniego et al., 2010). The model has been evaluated in terms of reproducing heterogeneous flow and nitrate concentrations and providing detailed spatial information of flow and nitrate fluxes (Yang et al., 2018). In addition, the in-stream assimilatory uptake has been regionalized and improved based on the high-frequency sensor data (Yang et al., 2019). The model is, therefore, a promising tool to further investigate the spatially distributed parameterization of the biogeochemical reactions and their links with multiple catchment information.

Sensitivity analysis has long been taken as a foundational diagnostic approach in revealing insights into the model responses regarding variations in input factors, including model parameters (Pianosi et al., 2016; Razavi & Gupta, 2015). It is still challenging to accurately estimate the sensitivity indices (Gupta & Razavi, 2018), especially for the spatially distributed configuration. Therefore, parameter ranking and screening are more interesting for the earth and environmental system modeling community (Sheikholeslami et al., 2019). They are commonly recommended to reduce the dimensionality by determining the (non)informative parameters (e.g., Cuntz et al., 2015) and to identify spatially differentiated model controls under varying conditions (e.g., the impacts of spatial distributions of event-scale precipitation; Tang et al., 2007; van Werkhoven et al., 2008a). Meanwhile, consistent model performance could be achieved under parameter-/cell-based screening strategies (Cuntz et al., 2015; Tang et al., 2007). The spatio-temporal distributions of parameter sensitivity by Herman et al. (2013a) explicitly revealed that different processes dominated in different periods and at different locations of the catchment. However, most of the grid-based studies only qualitatively attribute the spatial variations of parameter sensitivity to the variations of catchment characteristics while ignoring the information that can be derived from quantitative correlation investigations. For instance, van Werkhoven et al. (2008b) demonstrated significant correlations between parameter sensitivity and catchment characteristics in 12 catchments, which further extended the number of identifiable parameters more than usually assumed.

In this study, we revise the parameterization scheme for the nitrate processes of the mHM-Nitrate model in a fully spatially distributed manner, i.e., each nitrate submodel parameter varies independently in each grid cell (for terrestrial parameters) or each stream reach (for in-stream parameters). By conducting the global parameter sensitivity analysis, spatial distributions of parameter sensitivity indices are obtained, revealing the relative importance of each nitrate process and its spatial variability. Further, the spatial sensitivity information is correlated with a wide range of catchment characteristics in each grid cell/stream reach, including meteorological forcing, catchment properties, and modeled state variables and fluxes of flow and nitrate. We conduct our analysis in the highly heterogeneous Selke catchment (in terms of meteorological and landscape conditions), where three nested gauging stations are deployed to capture the heterogeneous catchment responses (Yang et al., 2018). The objectives of this study are (1) to analyze the full-spatial variability of parameter sensitivity in the domain of process-based catchment nitrate modeling, (2) to determine the most influential catchment characteristics for the sensitive nitrate processes and the spatial variations of such correlations, and (3) to reveal insights into the catchment nitrate responses under heterogeneous meteor-
hydrological and anthropogenic conditions. The anticipant insights can provide implications on future parameter regionalization of catchment water quality modeling.

2. Methodology

2.1. Morris Method

The method of Morris (1991), also called the elementary effect (EE) test, is a multistarts perturbation sensitivity analysis method (Pianosi et al., 2016). Based on the one-at-a-time method, an individual trajectory is created by perturbing each parameter \( p_i \) by a variation \( \Delta_i \). The number of perturbations of each trajectory is equal to the number of parameters \( (n, i = 1, 2, \cdots, n) \). The EE of the \( i \)th parameter \( (EE_i) \) is, therefore, estimated as follows:

\[
EE_i = \frac{f(X_{p_i+\Delta_i}) - f(X_{p_i})}{\Delta_i},
\]

where \( f(X) \) denotes the evaluation metrics used for sensitivity analysis. Here we used two metrics: the root mean squared error (RMSE) and the Kling-Gupta Efficiency (KGE) (Gupta et al., 2009). Starting from multiple points within the feasible parameter space, multiple trajectories \( (r) \) are generated to compute the sensitivity indices, i.e., the mean of EEs \( (\mu'_i) \) denoting the global sensitivity of each parameter and the standard deviation of EEs \( (\sigma_i) \) denoting the interaction with other parameters. Equation (2) gives the calculations of these indices suggested by Campolongo et al. (2007):

\[
\mu'_i = \frac{1}{r} \sum_{j=1}^{r} \left| EE_j \right|, \quad \sigma_i = \sqrt{\frac{1}{r-1} \sum_{j=1}^{r} \left( EE_j - \mu'_i \right)^2},
\]

where \( EE_j \) denotes the \( EE_i \) of the \( j \)th trajectory.

Sampling strategies differ mainly in the starting-point sampling and the trajectory generation. A proper sampling strategy can efficiently improve the accuracy of the sensitivity estimates (Pianosi et al., 2016). Aiming to balance the sampling efficiency and coverage within the feasible space, we used the Latin-Hypercube sampling method (van Griensven et al., 2006) to generate the starting points and \( \Delta_i \). Instead of sequential trajectory, we used the radial-based one-at-a-time design (Campolongo et al., 2011) to generate the trajectories. This approach takes \( \Delta_i \) for each \( p_i \) all from the starting point of each trajectory, which has been proofed to be more efficient (Campolongo et al., 2011). The sensitivity analysis was performed using the SAFE (Sensitivity Analysis For Everybody) tool by Pianosi et al. (2015).

The Morris method requires \( n+1 \) model runs for each trajectory and, therefore, \( r \times (n+1) \) runs for computing the global sensitivity indices. The computation requirement of the Morris method is far lower than the majority of other all-at-a-time based methods (Pianosi et al., 2016). This advantages its utility for the sensitivity analysis of the spatially distributed parameterization, which is characterized as a high-dimensional, time-consuming problem. The method is also particularly suitable and efficient for ranking and screening purposes (Herman et al., 2013b; Pianosi et al., 2016).

2.2. Spearman Rank Correlation

Based on the sensitivity results, we further correlated the parameter indices with multiple catchment characteristics using the Spearman rank correlation.

The Spearman rank correlation measures the strength and direction of the monotonic relationship between rankings of two variables, which are assumed to be independent. The monotonic relationship is not strictly an assumption but a measure to determine if there is a monotonic component associated between the two variables. It can be taken as a nonparametric version of the Pearson correlation and is normally performed when the assumptions of the Pearson correlation (i.e., normality and linearity) cannot be fulfilled. The Spearman coefficient \( (\rho) \) is calculated to assess the correlation strength and direction:
### Brief Parameter Descriptions of the Nitrate Submodel in the mHM-Nitrate Model

| Parameter | Description | Biogeochemical transformation |
|-----------|-------------|-------------------------------|
| denis     | Rate of soil denitrification (day\(^{-1}\)) | Permanent removal of nitrate in soil phase by denitrification process |
| minlr     | Rate of soil N mineralization (day\(^{-1}\)) | From the dissolved and the active part of solid organic nitrogen pools to the nitrate pool in soil moisture by mineralization process |
| degdr     | Rate of soil N degradation (day\(^{-1}\)) | From the inactive part of solid organic nitrogen pool to the active part of soil organic nitrogen pool by degradation process |
| dislr     | Rate of soil N dissolution (day\(^{-1}\)) | From the active part of solid organic nitrogen pool to the dissolved organic pool in soil moisture by dissolution process |
| deniw     | Rate of in-stream denitrification (kg m\(^{-2}\) day\(^{-1}\)) | Permanent removal of nitrate in stream water by denitrification process |
| npprt     | Rate of in-stream assimilatory N uptake (kg m\(^{-2}\) day\(^{-1}\)) | In-stream assimilatory uptake of nitrate in the stream water due to autotrophic uptake and remineralization processes |

\[
\rho = 1 - \frac{6 \sum d}{N(N^2-1)},
\]  

where \(N\) denotes the number of activated grid cells in this study and \(d\) denotes the ranking distance. The positive value of \(\rho\) denotes positive correlation and vice versa.

### 2.3. The Catchment Hydrological Nitrate Model—mHM-Nitrate

The mHM-Nitrate model is a fully distributed, process-based catchment nitrate model (Yang et al., 2018). The model is developed based on the grid-based mHM platform (Kumar et al., 2013; Samaniego et al., 2010). Nitrate process descriptions are mainly introduced from the Hydrological Predictions of the Environment model (Lindström et al., 2010). The mHM-Nitrate model simulates state variables and fluxes of flow and nitrate in both terrestrial and in-stream phases at a daily step. In the terrestrial phase, along with hydrological processes, the nitrate submodule considers atmospheric deposition, fertilizer and manure application, plant/crop uptake, denitrification, infiltrations through multiple soil layers, percolation to the deep groundwater, and export to the surface water. The physical and biochemical transformations (Table 1) within four nitrogen forms (i.e., dissolved inorganic nitrogen, dissolved organic nitrogen, and active and inactive solid organic nitrogen) are considered for each soil layer, and the pool size of each form is updated at each time step. The number of soil layers and the depth of each layer can be specified by users, and the total soil depth depends on the available soil property information (as one of the model input data, including soil texture and bulk density information for the soils). Groundwater beneath the soil layers is referred to as deep groundwater, which is further separated into relatively small hydrologically active storage and relatively large retention storage for flow and nitrate dynamics, respectively. The biogeochemical retention in the deep groundwater is largely simplified in the current version of the model (see detailed discussion in Yang et al., 2018). For each grid cell, total terrestrial exports of nitrate-N (\(N−NO_3^−\)) are calculated from the four runoff components (i.e., direct runoff from the impervious area, fast interflow, slow interflow, and baseflow) and the corresponding \(N−NO_3^−\) concentrations therein. Each grid cell is connected to neighboring cells according to the main flow direction and eventually formulates the modeled river network. A complete set of in-stream flow routing and nitrogen transformations (i.e., denitrification, assimilatory uptake, and remineralization) is computed for each stream reach. Detailed model descriptions of mHM and mHM-Nitrate are given by Samaniego et al. (2010) and Yang et al. (2018), respectively.

Nitrate submodule parameters are parsimoniously introduced, representing individual or combined biogeochemical transformation(s) (Table 1). The model descriptions of soil denitrification, soil N mineralization, soil N degradation, soil N dissolution, and in-stream denitrification processes remain the same as the original mHM-Nitrate model (Yang et al., 2018). These transformations are conceptualized considering the impacts of the well-known physical factors, the availability of source nitrogen forms, and the biogeochemical reaction rates. The pool sizes of nitrogen forms are updated for each simulation time step considering both physical flux exchanges and biogeochemical transformations. The impacts of well-known factors (e.g., soil or water temperature) are estimated using widely accepted empirical equations (supporting...
The in-stream assimilatory uptake process has recently been refined based on a new regionalization approach proposed by Yang et al. (2019). They demonstrated that the assimilatory nitrate uptake is mainly driven by the stream surface light availability, which is further regionalized using global radiation (representing the light availability above stream canopy) and leaf area index (representing the shading effect of riparian vegetation) data. Both types of data are normalized, respectively, to generate the time series of the above-canopy light availability ($f_{GR}$) and the riparian shading ($f_{LAI}$). The overall near-surface light availability ($f_{SL} = f_{GR} \cdot (1 - f_{LAI})$, $\in [0,1]$) can be obtained. The rational and transferability of the approach have been validated in the agricultural and forested streams of the study catchment (the Selke catchment), where continuous daily autotrophic uptake data are available based on the high-frequency sensor data. Notably, part of the autotrophically assimilated nitrate can be remineralized and returned back to stream waters, and the in-stream remineralization is assigned as a proportion of the autotrophic uptake. The parameter $nppt$ is introduced to represent the overall assimilatory uptake rate (Table 1). The approach has been integrated into the mHM-Nitrate model for the networked uptake estimation, assuming the stream riparian vegetation is similar to the surrounding land use (Yang et al., 2019). We adopted the new approach in this study. Detailed descriptions of the transformations and parameterizations were provided in Text S1 and references therein.

The mHM-Nitrate model has a flexible structure, which balances the spatial representation and the model complexity. The mHM platform integrates a MPR technique (Samaniego et al., 2010): Hydrological parameters are firstly related to geographic characteristics using a set of transfer functions at the basic geographic data level; then, the regionalized hydrological parameters, together with catchment characteristics and meteorological forcing, are scaled to the modeling level. Hydrological parameters introduced in those transfer functions are taken as transferable and quasi scale-invariant (Kumar et al., 2013), and their sensitivities are well documented in Cuntz et al. (2015). Therefore, we exclusively focused on the nitrate submodel parameters.

2.4. Study Site and Model Setup

The study was conducted in the Selke catchment (456 km²; Figure 1a), a subcatchment of the Bode catchment in central Germany (The TERENO Harz/Central German lowland observatory; Wollschläger et al., 2016). The catchment has strong physiographic gradients from upper mountainous areas to lowland areas. Annual precipitation decreases from 790 to 450 mm, with the overall mean of 660 mm. Arable lands dominate the lowland areas, whereas forests are predominant land use type in the upper mountains, with considerable arable lands and pastures in the upper plateau (Figure 1b). Cambisols and chernozems are the main soil types in the upper and lower parts of the catchment, respectively; shallow schist/claystone and deep tertiary sediments formulate the geological conditions (see details in Yang et al., 2018). The shallow impermeable schist leads a preference of flashier flow path in the upper areas, whereas flow path in the lowland areas is slower and deeper due to the permeable sedimentary materials (Dupas et al., 2017; Jiang et al., 2014).

Due to such a high heterogeneity, three nested gauging stations (i.e., Silberhütte [SILB], Meisdorf [MEIS], and Hausneindorf [HAUS]) are located along the main stem of the Selke River (Figure 1a). Areas above Station SILB (SILB catchment, 99 km²) are predominated by forest (60%), with considerable arable lands (25%). Station MEIS is located at the exit of the forested areas. For the whole drainage area upstream of Station MEIS (MEIS catchment, 184 km²), the share of the forest increased up to 72%. The area between Station MEIS and the Outlet HAUS is occupied mainly by arable lands (almost 80%) and urban areas. During the high-flow conditions (e.g., $Q > 2$ m³s⁻¹, the third quartile at HAUS), flow is generated mostly from the upper mountains ($Q$ at Station MEIS accounts for 80 ± 15% of that at Station HAUS). During low-flow periods ($Q < 0.65$ m³s⁻¹, the first quartile at HAUS), upper and lower subareas contribute equivalently to the outlet discharge ($Q$ at Station MEIS accounts for 62 ± 20% of that at HAUS). The region has long been intensively cultivated. The rotation sequence of four main crops (winter wheat, sugar beet, winter
barley, and rapeseed) was considered for all arable lands. Mineral fertilizer and manure were applied in the middle-late spring, and the total amount ranged from 130 to 190 kg N ha\(^{-1}\)yr\(^{-1}\) depending on specific crop type. Due to the long-term agricultural activities, \(N-NO_3\) concentration in the lowland soil water can reach up to higher than 25 mg N l\(^{-1}\). Although a similar amount of fertilizer was applied in the upper arable lands, the flashier flow path prevents nutrients from accumulating in the soil water and percolating to the deep groundwater (Dupas et al., 2017). Therefore, the ranges and seasonal patterns of \(N-NO_3\) concentration are similar at the Upper Stations SILB and MEIS (mean ± SD = 1.37 ± 1.08 and 1.60 ± 1.00 mg N l\(^{-1}\), respectively) but different from the Outlet Station HAUS (3.61 ± 1.09 mg N l\(^{-1}\)).

Daily simulation of the mHM-Nitrate model was set up in the Selke catchment using a 1 km\(^2\) cell size for both terrestrial and in-stream phases. Figure 1c showed the model discretization of the Selke catchment (533 grid cells in total) and the grid cell connections (i.e., model river network and 532 stream reaches). Note that the area of the border grid cells can be <1 km\(^2\), depending on the actual area that belongs to the catchment. Basic geographic data (i.e., elevation, land use, soil type, and geological unit) were all resampled to 100 m resolution, and meteorological data from DWD (German Weather Service) were interpolated to 1 km\(^2\) resolution. For details on data sources and model boundary conditions, please refer to Yang et al. (2018). Continuous daily discharge and \(N-NO_3\) concentration in the period of 2011–2015 were collected from LHW (the State Agency for Flood Protection and Water Management of Saxony-Anhalt, Germany) and the TERENO Project (coordinated by Helmholtz Centre for Environmental
Research-UFZ), respectively. The data at the three gauging stations were used to validate the mHM-Nitrate model performance and to calculate the evaluation metrics RMSE and KGE.

3. Computational Design

Following the multiobjective calibration strategy by Yang et al. (2018), we first recalibrated the mHM-Nitrate model against the daily observations of both discharge and nitrate concentration (2011–2015) at the three gauging stations. At this stage, nitrate submodel parameters remained as traditionally land use dependent. The purpose of this step was to obtain hydrological and $N-NO_3^-$ simulations, in terms of (1) discharge and $N-NO_3^-$ concentrations at each stream reach and (2) state variables and fluxes of both flow and $N-NO_3^-$ in each grid cell. Second, we revised the six nitrate submodel parameters (Table 1) to grid cell/stream reach dependent, which results in a total number of 3,196 parameters ($533 \times 4 = 2,132$ and $532 \times 2 = 1,064$ parameters for the four terrestrial parameters and the two in-stream parameters, respectively). Then, the grid-based modeled information, together with meteorological forcing and catchment properties, was used for the Spearman rank correlation analysis.

Given the large number of parameters, the computational load would increase sharply depending on the number of trajectories ($r$) of the Morris method. Pianosi et al. (2016) suggested that 10–100 trajectories would be sufficient. Herman et al. (2013b) compared the Morris performances in hydrological modeling using different values of $r$ and further referred them to a baseline performance of the Sobol’ (2001) method. They demonstrated that the performance of the low-sample Morris experiment is comparable with the baseline performance. In this study, we used a relatively large number of trajectories ($r = 80$, resulting in the total number of model runs as 255,760) to ensure the robustness of the sensitivity results (see the convergence plot in Figure S3).

The sensitivity indices were calculated based on RMSE and KGE, respectively, over the whole period (2011–2015). We calculated parameter sensitivity indices for each of the three nested catchments (i.e., the SILB catchment, the MEIS catchment, and the HAUS catchment; Figure 1c) based on the $N-NO_3^-$ concentration observations at Stations SILB, MEIS, and HAUS, respectively. The term “HAUS catchment,” covering the entire area of the Selke catchment, was used to emphasize that all the calculations only used observations at the Outlet Station HAUS. The Spearman rank correlations between sensitivity indices and catchment characteristics were performed for the three nested catchments. Additionally, the correlations were calculated exclusively for the lowland arable areas (i.e., the areal proportion of arable land $>0.70$; Figure 1c) in the domain of the HAUS catchment.

4. Results

The mHM-Nitrate model performed well in terms of simulating both discharge and $N-NO_3^-$ concentration (Figure S1 and Table S1). Nash-Sutcliffe efficiency coefficients were ~0.80 and above 0.43 for discharge and $N-NO_3^-$ concentration simulations, respectively, at the three stations. Due to similar model setup and boundary conditions, results were in line with those provided by Yang et al. (2018), where a detailed discussion of the model performance and rationality are provided. Catchment characteristics for each grid cell and each stream reach were, therefore, calculated and provided in the repository (https://git.ufz.de/yangx/sensitivity-analysis), with selected characteristics provided in Figure 2.

4.1. Overall Sensitivity Ranking

Given the potential influence from the selection of evaluation metrics (Wagener et al., 2009), we calculated the sensitivity indices based on both RMSE and KGE, which mathematically biases more weight during high-value periods and balances different components of time series, respectively. Results showed that parameter sensitivity rankings were consistent with each other (Pearson $R^2 > 0.97, p < 0.01$; Figure S2). Therefore, from here on, our analysis focused exclusively on the RMSE-based indices. The convergence of the sensitivity index $\mu^*$ was further examined using an increasing sample size. All parameters showed convergent trends as the sample size increases; the top 50 sensitive parameters converged mostly within the range of $[0, 1.00e-2]$ after 150,000 model runs (Figure S3).

For each catchment, parameter sensitivity ranking was demonstrated by plotting $\mu^*$ versus $\sigma_1$ (Figure 3). The more to the right-up section the point, the more sensitive and interactive, respectively, the parameter
becomes. In general, the sensitive zone (i.e., the right-up section of the plot) was occupied by parameters denis, deniw, and npprt, indicating that soil denitrification, in-stream denitrification, and in-stream assimilatory uptake processes, respectively, were the most influential processes for nitrate dynamics throughout the three nested catchments. Parameter minlr (rate of soil N mineralization) was located in the middle section, indicating relatively moderate sensitivity of soil mineralization process. Parameters degdr (rate of soil N degradation) and dislr (rate of soil N dissolution) were consistently located in the

Figure 2. Spatial distributions of selected catchment characteristics, that are strongly supportive for the discussion, including (a) areal proportion of arable land, areal proportions of (b) sand and (c) clay soils, (d) annual precipitation, (e) soil moisture content, (f) annual total runoff, mean concentrations in (g) soil water and (h) total runoff, (i) annual terrestrial export, (j) mean stream benthic area, (k) mean stream discharge, and (l) mean stream concentration. https://git.ufz.de/yangx/sensitivity-analysisThe title of each subplot provides the brief meaning, abbreviation, and unit of the presenting factor. Detailed descriptions were given in Table 1A. For values of the complete set of catchment characteristics, please visit the repository (https://git.ufz.de/yangx/sensitivity-analysis).
left-low section of each subplot, indicating transformations within soil organic nitrogen forms were not important for nitrate dynamics. In-stream parameters were mostly located lower than terrestrial parameters, reflecting that in-stream processes were less interactive than terrestrial processes. Parameter deniw was mostly located more right and higher than parameter npprt, indicating that in-stream denitrification was relatively more sensitive and less independent, respectively, than in-stream assimilatory uptake.

The $\mu^*$ values showed large variations within and between the six groups of parameters (note the log scales in Figure 3 and statistic values shown in Table 2). The $\mu^*$ means of the most sensitive parameters (e.g., denitrification-related parameters denis and deniw) were 3 to 4 orders of magnitude higher than those of insensitive parameters (e.g., organic N transformation parameters degdr and dislr). The $\mu^*$ values of parameter denis were intensively crowded in the sensitive zones for the three nested catchments, and the coefficients of variation (CVs) were relatively low compared to those of other parameters. In-stream parameters deniw and npprt spanned from the upper-right sections to the lower-left sections, with the highest CV values, indicating a generally high degree of heterogeneity of in-stream processes throughout the river network. In the HAUS catchment, the most sensitive parameters belonged to the parameter group of in-stream denitrification rate (deniw), and the mean $\mu^*$ value of parameter deniw was similarly high as that of parameter denis. This indicated that the relative importance of the in-stream process increased with increasing catchment size. Moreover, CVs of all parameters increased when moving from the uppermost SILB catchment to the HAUS catchment (Table 2), indicating increasing spatial variability.

**Figure 3.** Morris sensitivity ranking of the nitrate submodel parameters for the (a) SILB, (b) MEIS, and (c) HAUS catchments. The parameters are colored and divided into six groups, representing different biogeochemical transformations. Terrestrial parameters denis, minlr, degdr, and dislr are the rates of soil denitrification, soil N mineralization, soil N degradation, and soil N dissolution, respectively; in-stream parameters deniw and npprt are the rates of in-stream denitrification and in-stream assimilatory N uptake, respectively (please refer to Table 1 and Text S1 for details). The points of each group represent the reaction rates in the activated grid cells/stream reaches. Note that we omitted the grid cells/stream reaches that have extremely low $\mu^*_i$ values (i.e., $\leq 10^{-10}$).
4.2. Spatial Distributions of the Parameter Sensitivity

Among the three nested catchments, the grouping of sensitive and insensitive parameters was consistent, while the most sensitive parameters showed high spatial variability. Therefore, detailed spatial distributions of the four most sensitive parameter groups (i.e., \( \text{denis} \), \( \text{deniw} \), \( \text{npprt} \), and \( \text{minlr} \)) were further analyzed and compared.

In the uppermost SILB catchment, the \( \mu^* \) values of parameter \( \text{denis} \) were relatively high compared to those of other parameters (Figure 4a). The highest values were derived in the grid cells that are coincidently characterized as the arable-dominant area (defined as areal proportion of arable land, \( P_{\text{arable}} \); >0.70; Figure 2a) and the wet area (defined as annual precipitation, \( \text{precipi} \); >660 mm; Figure 2d). Moreover, the sensitivity of the forest/pasture cells within the wet area (i.e., the mountainous boundary areas) was equivalent to that of the arable-dominant cells outside of the wet area (i.e., the central arable areas; Figure 4a). The \( \mu^* \) values of parameter \( \text{minlr} \) were homogeneously low (Figure 4b). Therefore, the soil mineralization process was taken as homogeneously insensitive for \( N-\text{NO}_3^- \) concentration. The sensitivities of in-stream parameters \( \text{deniw} \) and \( \text{npprt} \) showed large spatial variability (Figures 4c and 4d). Parameters of higher-order reaches were generally more sensitive than those of headwater reaches (i.e., first and second orders). Unlike the smooth increase of the sensitivity of parameter \( \text{npprt} \), parameter \( \text{deniw} \) of few individual downstream reaches showed extraordinarily higher sensitivity (Figure 4c). These reaches were receiving water and nitrate fluxes from arable-dominant grid cells with high terrestrial \( N-\text{NO}_3^- \) exports (\( \text{Ter}_{\text{Nxprt}} = 8.28 \pm 1.64 \) (mean \( \pm \) SD), kg N ha\(^{-1}\) yr\(^{-1}\); Figure 2i).

The in-between area of Stations SILB and MEIS was occupied mainly by natural forests (~87% of the area), where \( \text{Ter}_{\text{Nxprt}} \) was very low (1.29 \( \pm \) 0.73 kg N ha\(^{-1}\) yr\(^{-1}\)). Consequently, the \( N-\text{NO}_3^- \) load at Station MEIS was mostly contributed from the upper area that also belongs to the SILB catchment. Therefore, the spatial sensitivity distribution of parameter \( \text{denis} \) was generally maintained from the upper SILB catchment to the MEIS catchment (Figure S4a). The sensitivity of in-stream parameters \( \text{deniw} \) and \( \text{npprt} \) generally followed the same spatial pattern as in the SILB catchment, resulting in higher \( \mu^* \) values in the downstream higher-order reaches (Figures S4c and S4d).

For the HAUS catchment, however, the spatial sensitivity pattern and the relative importance of each parameter varied largely (Figure 5). The \( \mu^* \) values of parameter \( \text{denis} \) scattered throughout the catchment (Figure 5a): The spatial pattern of the upper grid cells was similar to that observed in the upper catchments, but the relative importance reduced; the values of the lowland grid cells spanned at a larger range, including the highest ones for the whole catchment. Parameter \( \text{minlr} \) showed low sensitivity and spatial homogeneity (Figure 5b). Therefore, the soil mineralization process was excluded in further analysis in this study. The \( \mu^* \) values of both in-stream parameters \( \text{deniw} \) and \( \text{npprt} \) were significantly higher in the lowland reaches than in the reaches upstream of Station MEIS (ANOVA test, \( p < 0.01 \)) (Figures 5c and 5d). In-stream parameters of higher-order reaches were generally more sensitive than those of headwater reaches, respectively, within the upland and lowland areas. Among all parameters, the highest \( \mu^* \) values were derived from parameter \( \text{deniw} \) of the downstream reaches that are close to the Outlet Station HAUS (Figure 5c).

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**Table 2**

Statistics of the Mean Elementary Effects (\( \mu^* \)) of Each Parameter in the Three Nested Catchments

| Parameter | SILB   | MEIS   | HAUS   |
|-----------|--------|--------|--------|
|           | Mean   | SD     | CV     | Mean   | SD     | CV     | Mean   | SD     | CV     |
| \( \text{denis} \) | 2.50e-3 | 2.00e-3 | 8.02e-1 | 9.17e-4 | 8.25e-4 | 9.01e-1 | 1.80e-4 | 2.61e-4 | 1.45e+0 |
| \( \text{deniw} \) | 5.46e-4 | 8.55e-4 | 1.57e+0 | 2.26e-4 | 4.23e-4 | 1.87e+0 | 1.54e-4 | 4.71e-4 | 3.06e+0 |
| \( \text{npprt} \) | 1.72e-4 | 3.53e-4 | 2.05e+0 | 9.00e-5 | 2.08e-4 | 2.32e+0 | 6.43e-5 | 2.17e-4 | 3.39e+0 |
| \( \text{minlr} \) | 6.68e-5 | 5.70e-5 | 8.53e-1 | 2.31e-5 | 2.63e-5 | 1.14e+0 | 4.31e-6 | 5.21e-6 | 1.21e+0 |
| \( \text{dislr} \) | 6.77e-7 | 4.78e-7 | 7.05e-1 | 2.49e-7 | 2.41e-7 | 9.66e-1 | 5.73e-8 | 5.11e-8 | 8.92e-1 |

*Note. SD denotes standard deviation, and CV denotes coefficient of variation.*
4.3. Correlations Between Parameter Sensitivity and Catchment Characteristics

The correlations were conducted using the Spearman rank correlation for the three nested catchments and exclusively for the lowland arable areas (Table 3). In the SILB catchment, Spearman coefficients showed that the sensitivity of parameter \( \text{denis} \) was highly correlated with terrestrial \( N-\text{NO}_3 \) state variables and fluxes (\( \rho \geq 0.77 \)) but nonsignificantly correlated with terrestrial flow state variables and fluxes (\( p > 0.01 \)). It was also significantly correlated with areal proportion of arable land (\( P_{\text{arable}}, \rho = 0.65 \)) and annual precipitation (\( \text{precipi}, \rho = 0.39 \)). The sensitivities of in-stream parameters \( \text{deniw} \) and \( \text{npprt} \) were both highly correlated with stream discharge (\( SW_q \)) and stream benthic area (\( SW_{\text{area}} \)), e.g., \( \rho \geq 0.75 \) and 0.88, respectively, but were nonsignificantly correlated with stream \( N-\text{NO}_3 \) concentration (\( SW_{\text{Nconc}}, p > 0.01 \)). The sensitivities of both in-stream parameters also showed slight negative correlations with terrestrial flow state variables and fluxes and nonsignificant correlations with terrestrial \( N-\text{NO}_3 \) state variables and fluxes.

Compared to the results in the SILB catchment, the correlations between the sensitivity of parameter \( \text{denis} \) and terrestrial \( N-\text{NO}_3 \) state variables and fluxes remained relatively high in the MEIS catchment (\( \rho \geq 0.56 \)), while the correlation with \( \text{precipi} \) strengthened (\( \rho = 0.63 \)) and the correlations with flow state variables and fluxes became significant (\( \rho = 0.37-0.51, p < 0.01; \) Table 3). The sensitivities of in-stream parameters \( \text{deniw} \) and \( \text{npprt} \) were still highly correlated with \( SW_q \) and \( SW_{\text{area}} \) (\( \rho \geq 0.73 \) and 0.82, respectively), while the correlation between parameter \( \text{deniw} \) with \( SW_{\text{Nconc}} \) became significant (\( \rho = 0.46, p < 0.01 \)). The sensitivity of parameter \( \text{deniw} \) was slightly correlated with terrestrial \( N-\text{NO}_3 \) state variables (\( \rho = -0.24 \)), and the sensitivity of parameter \( \text{npprt} \) was negatively correlated with terrestrial flow state variables and fluxes (\( \rho \) mostly equals to \(-0.50 \)).

Figure 4. Spatial distributions of parameter sensitivities in the uppermost SILB catchment (grid size 1 km\(^2\)). The \( \mu^* \) (absolute mean of EEs) values are scaled into the range of [0, 1] for the four most sensitive parameters: (a) \( \text{denis} \) = rate of soil denitrification; (b) \( \text{minlr} \) = rate of soil N mineralization; (c) \( \text{deniw} \) = rate of in-stream denitrification; and (d) \( \text{npprt} \) = rate of in-stream assimilatory N uptake. The inserted histogram plot represents the distribution of the scaled \( \mu^* \) values for each parameter. The y axis denotes the frequency of grid cells/stream reaches and has been log-transformed. Deactivated grid cells and stream reaches were excluded and shown in gray lines, respectively.
For the HAUS catchment, the sensitivity of parameter \textit{denis} was highly correlated with annual precipitation (\textit{precipi}, $\rho = 0.64$) and significantly correlated with most flow state variables and fluxes in a weaker manner ($\rho = 0.43$–0.60; Table 3). The correlation with terrestrial $N-\text{NO}_3$ export (\textit{Ter_Nxprt}) was still positive, but the strength reduced compared to that in the upper catchments ($\rho = 0.41$ versus $\approx 0.80$, respectively). Moreover, the high correlation with \textit{P_arable} was eliminated ($\rho = 0.15$). The correlations of in-stream parameters \textit{deniw} and \textit{npprt} differed largely compared to the upper catchments (Table 3). Results showed that their sensitivities correlated in a higher degree with \textit{SW_Nconc} ($\rho \approx 0.50$) than with \textit{SW_q} and \textit{SW_area} ($\rho \approx 0.35$ and $\approx 0.47$, respectively). Their sensitivities also correlated with terrestrial $N-\text{NO}_3$ state variables ($\rho > 0.55$) and negatively with terrestrial flow statues and fluxes ($|\rho| > 0.65$).

Interestingly, correlations exclusively within the lowland arable areas differed compared to the whole HAUS catchment (Table 3). The correlation coefficient of parameters \textit{denis} with \textit{precipi} decreased ($\rho = 0.40$), but the correlations with flow state variables and fluxes remained similarly high ($\rho > 0.54$). The correlation with \textit{P_arable} remained weak ($\rho = 0.26$), while the correlations with areal proportions of clay and sandy soils became relevant ($\rho = 0.40$ and $-0.46$ for \textit{P_clay} and \textit{P_sand}, respectively). The sensitivities of both in-stream parameters were highly positively correlated with \textit{SW_q} and \textit{SW_area} ($\rho \geq 0.69$ and 0.79, respectively) and negatively correlated with \textit{SW_Nconc} ($\rho = -0.40$).

5. Discussion

The Selke catchment is characterized by high spatiotemporal variability of meteor-hydrological and nitrate dynamics, resulting from the highly heterogeneous catchment conditions. These variations are well gauged...
Table 3
The Spearman Rank Correlation Coefficients (ρ) Between Sensitivities of Nitrate Submodel Parameters and Catchment Characteristics in Three Nested Catchments and the Lowland Arable Areas

| Characteristic          | SILB  | MEIS  | HAUS  | Lowland arable areas |
|-------------------------|-------|-------|-------|----------------------|
|                         | denis | deniw | npprt | denis | deniw | npprt | denis | deniw | npprt | denis | deniw | npprt |
| P_\text{arable}        | 0.65  | 0.09  | −0.01 | 0.62  | 0.12  | −0.12 | 0.15  | 0.59  | 0.52  | 0.26  | −0.03 | −0.12 |
| P_\text{clay}          | −0.06 | −0.04 | −0.12 | 0.27  | 0.07  | −0.15 | 0.38  | −0.46 | −0.49 | 0.40  | −0.21 | −0.25 |
| P_\text{sand}          | 0.08  | −0.02 | 0.06  | −0.17 | 0.02  | 0.15  | −0.22 | −0.18 | −0.16 | −0.46 | 0.35  | 0.40  |
| T                       | 0.04  | 0.33  | 0.51  | −0.46 | 0.17  | 0.51  | −0.46 | 0.72  | 0.75  | −0.40 | 0.43  | 0.43  |
| ET                      | −0.42 | −0.10 | −0.03 | −0.43 | −0.07 | 0.13  | 0.07  | −0.14 | −0.10 | 0.06  | 0.01  | −0.04 |
| precipi                 | 0.39  | −0.17 | −0.41 | 0.63  | −0.14 | −0.50 | 0.64  | −0.48 | −0.58 | 0.40  | −0.29 | −0.29 |
| SM                      | 0.13  | −0.26 | −0.47 | 0.51  | −0.21 | −0.53 | 0.60  | −0.67 | −0.72 | 0.57  | −0.31 | −0.36 |
| R_total                 | 0.04  | −0.30 | −0.52 | 0.49  | −0.18 | −0.51 | 0.43  | −0.69 | −0.73 | 0.54  | −0.30 | −0.34 |
| R_\text{slow}          | −0.12 | −0.33 | −0.50 | 0.38  | −0.23 | −0.51 | 0.57  | −0.67 | −0.71 | 0.59  | −0.28 | −0.33 |
| R_\text{base}          | 0.22  | −0.24 | −0.35 | 0.37  | −0.11 | −0.34 | 0.54  | −0.65 | −0.68 | 0.58  | −0.17 | −0.21 |
| SMC                     | 0.78  | 0.14  | 0.06  | 0.70  | 0.23  | −0.04 | 0.06  | 0.63  | 0.56  | −0.08 | 0.28  | 0.25  |
| RC_\text{total}        | 0.81  | 0.11  | −0.01 | 0.73  | 0.24  | −0.05 | −0.01 | 0.69  | 0.63  | −0.25 | 0.29  | 0.27  |
| RC_\text{slow}         | 0.78  | 0.14  | 0.06  | 0.69  | 0.24  | −0.04 | 0.06  | 0.63  | 0.55  | −0.08 | 0.27  | 0.25  |
| RC_\text{base}         | 0.77  | 0.15  | 0.06  | 0.56  | 0.27  | 0.11  | −0.02 | 0.66  | 0.62  | 0.30  | 0.04  | 0.04  |
| Ter_\text{ Nxprt}      | 0.78  | −0.02 | −0.17 | 0.79  | 0.04  | −0.33 | 0.41  | 0.34  | 0.25  | 0.58  | −0.20 | −0.25 |
| SW_q                    | —     | 0.84  | 0.75  | —     | 0.85  | 0.73  | —     | 0.37  | 0.35  | —     | 0.73  | 0.69  |
| SW_\text{Nconc}        | —     | 0.18  | 0.11  | —     | 0.46  | 0.19  | —     | 0.54  | 0.50  | —     | −0.40 | −0.40 |
| SW_\text{area}         | —     | 0.89  | 0.88  | —     | 0.88  | 0.82  | —     | 0.47  | 0.48  | —     | 0.79  | 0.85  |

Note: The bold and italic values denote highly significant (i.e., |p| ≥ 0.60) and nonsignificant (i.e., p value > 0.01) correlations, respectively. The characteristics were grouped orderly into catchment properties, meteorological forcing, flow state variables and fluxes, N−NO₃⁻ state variables and fluxes, and in-stream state variables and fluxes (please refer to Table A1 for detailed instructions).

5.1. Soil Denitrification

For all nested catchments, soil denitrification rate was identified as one of the most sensitive parameters with high spatial variability. The sensitivity indices were most correlated with terrestrial N−NO₃⁻ exports (i.e., Ter_\text{ Nxprt}, kg N ha⁻¹ yr⁻¹; Table 3), which integrate the overall transports of flow and N−NO₃⁻ from the terrestrial phase. However, the mechanisms were likely different in the upper and lower sub-areas of the Selke catchment due to the different meteor-hydrological conditions and anthropogenic impacts. In the uppermost SILB catchment, the spatial sensitivity pattern generally followed the distribution of the arable land (Figures 4a and 2a, respectively); the sensitivity indices were highly positively correlated with terrestrial N−NO₃⁻ state variables and fluxes (Table 3). The soil moisture content and runoff generation were homogeneously high within the SILB catchment (Figures 2e and 2f, respectively), while much higher N−NO₃⁻ supplies were observed in the arable lands (25% of the total area) compared to the rest pristine forest and pasture areas. This resulted in an overall soil N−NO₃⁻ limitation in the upper part of the Selke catchment. In contrast, within the lowland arable areas, the sensitivity distribution followed the distributions of soil moisture content and runoff generation (Figures 4a and 2e, respectively); flow state variables and fluxes became highly correlated (Table 3). Due to long-term agricultural activities, soil N−NO₃⁻ was homogenously sufficient in lowland arable lands (Figure 2g), while the soil moisture content and the subsequent runoff generation (Figures 2e and 2f, respectively) varied largely due to the heterogeneous soil properties (areal proportions of sand and clay soils shown in Figures 2b and 2c, respectively). Therefore, hydrological transport limitation is likely pronounced in the lowland part of the catchment. Overall, the sensitivity of soil...
5.2. **In-stream Denitrification and Assimilatory Uptake**

Compared to the terrestrial processes, in-stream processes showed a higher degree of spatial heterogeneity, and their general importance likely increased with increasing catchment size. Both in-stream denitrification and assimilatory uptake showed generally higher sensitivities in downstream, higher-order reaches. This effect of proximity to evaluation location was confirmed by high correlations between the parameter sensitivities and stream discharge and stream benthic area (Table 3). First, processes happened in downstream reaches close to the evaluation station would have a stronger influence due to the short transport time (Tang et al., 2007; Wagener et al., 2009). Second, stream benthic area would increase as flow accumulating to higher-order reaches (Figure 2f), which likely increases the opportunity for nitrate to be denitrified and/or to be assimilated by periphyton. The in-stream processes were positively and negatively correlated with stream $N-\text{NO}_3^-$ concentration in the forested MEIS catchment and the lowland arable areas, respectively (Table 3). However, the observed correlations with stream $N-\text{NO}_3^-$ concentrations are likely caused by the large concentration gradients between the main stem of the Selke River and the tributaries (Figure 2f). Moreover, the correlations were nonsignificant in the SILB catchment, although the concentrations varied largely due to the more scattered mixture of forests and arable lands. Overall, in-stream processes at river network scale are predominated by the proximity to evaluation location and unlikely influenced by the stream $N-\text{NO}_3^-$ concentration. The high degree of spatial variability plausibly surpasses the local biogeochemical factors in controlling the fate of nitrogen at catchment scale (Gomez-Velez et al., 2015).

In water quality modeling, it is difficult to distinguish in-stream $N-\text{NO}_3^-$ removals between the highly confounded denitrification and assimilatory uptake processes (Wollschläger et al., 2016). In this study, the sensitivity indices of both process parameters did highly correlate with each other (Pearson’s $r^2 > 0.90$), indicating potential “equifinality” effects. Nevertheless, from the process understanding perspective, increased $N-\text{NO}_3^-$ concentration can likely stimulate in-stream denitrification (Beaulieu et al., 2011).
While for in-stream assimilatory uptake, light availability is the predominant factor as nutrients are usually not limiting in most anthropogenically impacted rivers (Yang et al., 2019). In this study, we adopted these state-of-the-art process understandings (Text S1), and such different process descriptions were somehow reflected in the sensitivity distributions. For instance, the sensitivity of parameter $\text{npprt}$ increased in a more gentle way than that of parameter $\text{deniv}$ moving to the downstream, higher-order reaches. This implicated that research efforts in process understanding would help in addressing the complexity of model parameterization and, therefore, should be embedded in model development activities.

### 5.3. Implications and Future Work

Catchment functioning of hydrology and nutrient dynamics varies under different catchment and anthropogenic conditions. Parameters are introduced in the model development to tolerate such variations while maintaining the main describing equations (Beven, 1995). Parameter sensitivity analysis in specific catchment indicates relative importance of different processes on catchment response; while the catchment response relies on the information provided by the gauging network. Therefore, an appropriate monitoring scheme that can truly reflect heterogeneous catchment responses is critical for parameter sensitivity analysis in the first place. Insights into the catchment functioning through sensitivity analysis is only possible if it is conducted based on adequate information (e.g., referred as the choice of model response by Gupta & Razavi, 2018). In the Selke catchment, the distinct stream $\text{N}−\text{NO}_3^−$ concentration dynamics in the upper and lower parts are well captured by the three nested stations. Parameter sensitivity derived from the corresponding nested catchments showed large differences in terms of spatial distributions (Figures 4 and 5). The “hot spots” of soil denitrification in the upper part of the catchment could not be sufficiently reflected when only using the $\text{N}−\text{NO}_3^−$ dynamic information at the outlet. Likewise, the relative importance and spatial variability of in-stream processes in the upper stream reaches attenuated largely when only using the data at the outlet. Therefore, we suggest that multisite sensitivity evaluation is needed to make the most of the information provided by the monitoring scheme and to obtain the actual spatial distribution of parameter sensitivity, as shown in Figure 6 (the sensitivity indices were calculated based on data at all three stations).

In addition to advancing process understanding, correlating parameter sensitivity with catchment characteristics also provides insights into the heterogeneous nitrate behaviors at catchment scale. In this study, the sensitivity of soil denitrification process was limited by soil $\text{N}−\text{NO}_3^−$ availability (indicated by, e.g., areal proportion of arable lands) and hydrological transport capacity (indicated by, e.g., soil moisture content) in upper forests and lower arable lands, respectively. Moreover, higher hydrological transport capacity could likely compensate the deficit in soil $\text{N}−\text{NO}_3^−$ availability based on the physical and microbial mechanisms. In-stream denitrification and assimilatory uptake processes at network scale were mainly controlled by the spatial variability (indicated by, e.g., the proximity to evaluation stations), rather than the local biogeochemical factors (e.g., the stream $\text{N}−\text{NO}_3^−$ concentration). Cautiously, one should also be aware that the statistical correlations might be misleading. For instance, soil denitrification appeared to be exclusively correlated with meteor-hydrological properties for the HAUS catchment (Table 3). This is mainly due to the high meteor-hydrological gradients moving from the upper to the lowland areas, for example, annual total runoff ($R_{\text{total}}$) decreased from 206.9 ± 46.8 to 44.5 ± 21.9 mm (Figure 2f). Such high gradients plausibly override the actual influential factors identified when investigating separately in the SILB catchment and the lowland arable areas.

The insights can offer new prospects for future model parameterization. Current parameterization schemes of water quality models are mostly based on broadly defined landscape information (e.g., land use/soil types), which likely underestimates the actual heterogeneity in nature (Clark et al., 2017). Based on the parameter sensitivity analysis in the context of fully distributed parameterization, the identified controlling factors could lead to a better modeling representation of processes in terms of spatial heterogeneity and relevance. For instance, soil denitrification rate is not only influenced by land use but also the hydrological connectivity. The latter factor is likely more influential than the former, but this has been overlooked by most current models. The Spearman rank correlation is, however, theoretically weak in directly guiding quantitative relationship for new regionalization approaches. Similar analysis needs to be conducted in more catchments across different regions. Then, sound spatial relationships between parameters and controlling factors could be obtained; with this, advanced process conceptualization and quantitative parameter regionalization schemes can potentially be developed and validated.
To the authors’ knowledge, for the first time, this study explicitly investigated the parameter sensitivity of fully distributed parameterization for a water quality model. Several issues are worth to be further investigated. First, temporal variability of parameter sensitivity in catchment nitrogen models can be highly pronounced due to the high seasonality of nitrate biogeochemical processes but has rarely been investigated (but see Haas et al., 2015). Moreover, the combined spatiotemporal sensitivity analysis, like in Herman et al. (2013a) for hydrological modeling, is still missing in water quality modeling. Second, in obtaining sound relationships for parameter regionalization, the correlations between parameter sensitivity and catchment properties should be analyzed in a wide range of meteor-hydrological conditions and anthropogenic impacts. In addition, we are also aware of the methodological limitations of this study that should be further addressed, including preliminary mapping for better parameter ranges (Bai et al., 2009), the selection of model response (Gupta & Razavi, 2018; Wagener et al., 2009), and a more comprehensive analysis of the robustness of the computational design (Sarrazin et al., 2016; Sheikholeslami et al., 2019).

6. Conclusions

Based on the fully distributed mHM-Nitrate model, we explicitly investigated the spatially distributed sensitivity of the nitrate submodel parameters. Parameters of soil denitrification, in-stream denitrification, and in-stream assimilatory uptake were identified as the most sensitive parameters throughout the nested Selke catchment, while they all showed high spatial variabilities. Moreover, the sensitivity rankings and
spatial distributions varied among the three nested catchments (gauged by the nested SILB, MEIS, and HAUS stations). Spearman rank correlations confirmed that the parameter sensitivity was predominated by variable catchment characteristics at different locations, presumably due to the high heterogeneity of geographical, meteor-hydrological, and anthropogenic conditions within the Selke catchment. Insights into catchment nitrate behaviors were derived from the spatial sensitivity and correlation analyses. The importance of soil denitrification process depended on the relative limitations between soil nitrate availability and hydrological transport capacity. The latter could likely compensate for the former but not vice versa. Compared to the terrestrial processes, the relative importance of the in-stream processes increased with increasing catchment size; meanwhile, their spatial distributions throughout the river network were predominated by spatial variability (e.g., the proximity to evaluation station), rather than local biogeochemical factors (e.g., the stream $N-NO_3^-$ concentration).

These insights are informative in advancing our understanding of the heterogeneous catchment nitrate behaviors. However, sensitivity results rely largely on the information provided by gauging networks. Therefore, we recommend that (1) an appropriate monitoring scheme, which can truly reflect heterogeneous catchment responses, is important in the first place; and (2) sensitivity evaluation should make most use of the gauging information to achieve a better representation of the spatial heterogeneity of processes. As a step further, the correlations between parameter sensitivity and catchment characteristics can reveal varying controlling factors of important processes within the catchment/river network. Therefore, the statistical correlation, with cautious selection of catchment factors, can guide future model parameterization to achieve a better spatial representation of process heterogeneity and relevance.

**Appendix**

**A. Description of Catchment Characteristics**

Based on the multiresolution structure, the mHM-Nitrate model explicitly provides multiple catchment information of each grid cell and stream reach. Table A1 presented 18 representative characteristics covering meteorological forcing, catchment landscape properties, and modeled state variables and fluxes of flow and

| Category | Characteristic | Description | Note |
|----------|----------------|-------------|------|
| Catchment properties | $P_{\text{arable}}$ | Areal proportion of arable land ($\in [0,1]$) | Land use input |
| | $P_{\text{clay}}$ | Areal proportion of clay soil ($\in [0,1]$) | Soil type and soil property inputs |
| | $P_{\text{sand}}$ | Areal proportion of sand soil ($\in [0,1]$) | Soil type and soil property inputs |
| Meteorological forcing | $T$ | Annual mean of mean daily air temperature ($^\circ$C) | Meteorological input |
| | $ET$ | Annual evapotranspiration (mm) | Meteorological input |
| | precipi | Annual precipitation (mm) | Meteorological input |
| Flow state variables and fluxes | $SM$ | Annual mean soil moisture content ($\in [0,1]$) in the third soil layer (50–200 cm) | mHM state variable: "L1\_soilMoist" |
| | $R_{\text{total}}$ | Annual total runoff (mm) | mHM flux: "L1\_total\_runoff" |
| | $R_{\text{slow}}$ | Annual runoff component of slow interflow (mm) | mHM flux: "L1\_slowRunoff" |
| | $R_{\text{base}}$ | Annual runoff component of baseflow (mm) | mHM flux: "L1\_baseflow" |
| $N-NO_3^-$ state variables and fluxes | $SMC$ | Mean $N-NO_3^-$ concentration in soil water of the third soil layer (mg N l$^{-1}$) | mHM-Nitrate state variable: "L1\_soilMoist" |
| | $RC_{\text{total}}$ | Mean $N-NO_3^-$ concentration in total runoff (mg N l$^{-1}$) | mHM-Nitrate state variable: "L1\_total\_runoff" |
| | $RC_{\text{slow}}$ | Mean $N-NO_3^-$ concentration in slow interflow (mg N l$^{-1}$) | mHM-Nitrate state variable: "L1\_slowRunoff" |
| | $RC_{\text{base}}$ | Mean $N-NO_3^-$ concentration in baseflow (mg N l$^{-1}$) | mHM-Nitrate state variable: "L1\_baseflow" |
| | $Ter_{\text{Nxprt}}$ | Mean annual terrestrial $N-NO_3^-$ export load (kg N ha$^{-1}$ yr$^{-1}$) | mHM-Nitrate flux: "L1\_total\_runoff" $\times$ L1\_total\_runoff $\times$ 0.01 |
| In-stream state and fluxes | $SW_{\text{q}}$ | Annual mean stream discharge (m$^3$ s$^{-1}$) | mHM output: "L1\_qMod" |
| | $SW_{\text{Nconc}}$ | Annual mean stream $N-NO_3^-$ concentration (mg N l$^{-1}$) | mHM-Nitrate output: "L1\_concMod" |
| | $SW_{\text{area}}$ | The mean stream benthic area (m$^2$) | mHM-Nitrate state variable: "L1\_length" $\times$ mean width$^*$ |

*Note. The last column notes the original information from the model implementation perspective. Note that *mean width* is calculated based on the mean discharge and the empirical equation by Rode et al. (2016) (see also Text S1).
nitrates. They were calculated either from model inputs/outputs or from model state variables. All information can be easily written-out and obtained. Please refer to the implementations of mHM (https://git.ufz.de/mhm/mhm) and mHM-Nitrate (https://git.ufz.de/yangx/mHM-Nitrate) for details.

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Acknowledgments

Xiaoqiang Yang is funded by the Chinese Scholarship Council (CSC). We would like to thank the Editor Martyn Clark, the Associate Editor Juliane Mai, and three anonymous Reviewers for their constructive comments, which helped to improve the manuscript significantly. We thank the German Weather Service (DWD), Federal Institute for Geosciences and Natural Resources (BGR), and State Agency for Flood Protection and Water Management of Saxony-Anhalt (LHW) for providing the data used for setting up the model. The daily nitrate observations are obtained from the TERENO (Terrestrial Environment Observatories) project coordinated by Helmholtz Centre for Environmental Research-UFZ. The data used are presented in the tables, figures and supplements, and the open-access UFZ-GitLab repository (https://git.ufz.de/yangx/sensitivity-analysis).
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