Effect of topographic slope on the export of nitrate in humid catchments: a 3D model study

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Key Points

- Young water fractions of Q and ET are correlated to t~~T~~opographic slope negatively and positively, respectively ~~affects in-stream nitrate concentrations in a three-class pattern rather than being exclusively monotonous~~
- ~~Young streamflow fraction and nitrate concentration decrease sharply once flatter landscapes are not able to maintain fast preferential overland flow paths~~Flatter landscapes tend to retain more nitrogen mass in the soil and export less nitrogen mass to the stream
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- ~~High level of~~A large young streamflow fraction~~s~~ is not sufficient for high ~~level of~~ in-stream nitrate concentrations. ~~The seasonal fluctuation of in-stream concentration is caused mainly by the temporal variability of nitrate degradation for catchments in temperate humid climates~~
- ~~Seasonal fluctuations tend to be more pronounced in flatter landscapes.~~

Abstract. Excess export of nitrate to streams affects ecosystem structure and functions and has been an environmental issue attracting world-wide attention. The dynamics of catchment-scale solute export from diffuse ~~nitrate~~ nitrogen sources can be explained by the ~~activation and deactivation~~changes of dominant flow paths, as solute attenuation (including the degradation of nitrate) is linked to the age composition of outflow. Previous data driven studies suggested that catchment topographic slope has strong impacts on the age composition of streamflow and consequently on in-stream solute concentrations. However, the impacts have not been systematically assessed in terms of solute mass fluxes and solute concentration levels~~ and variation~~, particularly in humid catchments with strong seasonality in meteorological forcing. To fill this gap, we modeled the groundwater flow and nitrate transport for ~~a cross-section of~~ a small agricultural catchment in Central Germany. We used the fully coupled surface and subsurface numerical simulator HydroGeoSphere (HGS) to model groundwater and overland flow as well as nitrate transport~~concentrations~~. We computed the water ages using numerical tracer experiments. To represent various topographic slopes, we additionally simulated ten synthetic ~~cross-sections~~catchments generated by modifying the topographic ~~mean~~ slope from the real-world scenario ~~while preserving the land surface micro-topography~~. Results suggest a negative correlation ~~three-class response of~~between the young streamflow fraction and~~in-stream nitrate concentrations to~~ the topographic slope. ~~,~~ This correlation is more pronounced in ~~the~~ flat landscapes with slopes < 1:60.~~from class 1 (slope > 1:60), via class 2 (1:100 < slope < 1:60), to class 3 (slope < 1:100).~~ Flatter landscapes tend to retain more N mass in the soil (including mass degraded in soil) and export less N mass to the stream, due to ~~the~~ reduced leaching~~-~~ and increased~~improved~~ degradation ~~in flatter landscapes~~. The mean in-stream nitrate concen~~r~~tration shows a decreasing trend in respon~~d~~se to a~~the~~ decreasing topographic slope, suggesting that a large~~high level of~~ young streamflow fraction~~s~~ is not sufficient for ~~a~~ high ~~level of~~ in-stream concentrations. ~~Flatter landscapes tend to produce higher in-stream nitrate concentrations within class 1 or class 3, however, not within class 2. Young streamflow fractions and nitrate concentrations decrease sharply when flatter landscapes are not able to maintain fast preferential discharge paths (e.g. seepage). The variation of in-stream concentrations, controlled by degradation variability rather than by nitrate source variability, shows a similar three-class response.~~ Our results improve the understanding of nitrate export in response to topographic slope in a temperate humid climate~~s~~, with important implications for the management of stream water quality.

Keywords: topographic slope, coupled surface-subsurface model, young streamflow, in-stream nitrate, HydroGeoSphere

1 Introduction

Globally nearly 40% of land is used for agricultural activities [*Foley et al.*, 2005], which constitutes the major source of pollution with nutrients such as nitrate (referred as to N-NO_3 in this study). Excess export of nitrate to streams threatens ecosystem structure and functions, as well as human health via drinking water [*Vitousek et al.*, 2009; *Alvarez-Cobelas et al.*, 2008; *Dupas et al.*, 2017]. This has been an environmental issue attracting attention in Germany and world-wide. The dynamics of nitrate export from diffuse nitrogen (N) sources are regulated by the dominant flow paths that determine the speed at which precipitation travels through catchments before it reaches the stream [*Jasechko* et al. 2016]. The process is subject to both hydrological and biogeochemical influences mediated by various factors (e.g. catchment topography, aquifer properties, redox boundaries). From the perspective of sustainable intensification, process understanding and assessment of potential effects of catchment topography on nitrate export are critical for the management of water quality in connection with agricultural activity.

Field observations in central German catchments indicate that in-stream nitrate concentrations (C_Q) ~~are~~show significant differences in ~~the~~ mean concentrations and ~~the~~ seasonal variations ~~generally higher~~ ~~at~~ between downstream areas with gentle topography ~~compared to~~ and more mountainous upstream areas [*Dupas et al.*, 2017; *Nguyen et al.*, 2022]. This provides strong evidence that catchment topographic slope can influence the nitrate export. In terms of water age analyses, *Jasechko* et al. [2016] using oxygen isotope data from 254 watersheds worldwide showed significant negative correlation between the young (age < 3 months) streamflow fraction and the mean topographic gradient. They stated that young streamflow is more prevalent in flatter catchments as these catchments are characterized by shallow lateral flow, while it is less prevalent in steeper mountainous catchments as these catchments promote deep vertical infiltration. This statistically significant trend is consistent with the common finding that fast shallow flow paths produce young discharge and potentially ~~promote~~ influence the ~~high~~ in-stream solute concentrations [*Böhlke* et al. 2007; *Benettin* et al. 2015; *Hrachowitz* et al. 2016; *Blaen et al.* 2017]. However, apart from these data-driven analyses, a more mechanistic examination/explanation with the aid of fully resolved flow paths is still required. Wilusz et al. [2017] used a coupled rainfall-runoff and transit time model to investigate the young streamflow fraction, with a focus on the effect of rainfall variability rather than on topography and solute export. Zarlenga et al. [2022] numerically quantified the relative contributions of hillslopes and the drainage network to age~~s~~ dynamics in streamflow, considering the influences of transmissivity and recharge, ~~but not~~without focusing on topographic slope. The effect of topographic slope on C_Q has ~~not~~ rarely been subject to systematical testing.

Seasonal fluctuation of C_Q is commonplace in catchments under seasonal hydrodynamic forcing. Field observations in mountainous central German catchments indicate that nitrate concentrations, as well as the mass load, in streams vary seasonally, with maxima during the wet winter and minima during the dry summer [*Dupas et al.*, 2017]. Data-driven analyses by *Musolff et al.* [2015] and *Dupas et al.* [2017] suggested the systematic seasonal (de)activation of N ~~nitrate~~ source zones as an explanation for such seasonal variability. Under wetter winter conditions the near-surface N ~~nitrate~~ source zones in agricultural soils are connected to the stream by fast shallow flow paths. Under drier summer conditions those ~~nitrate~~ N source zones are deactivated because their direct hydrologic connectivity to the stream is replaced with deeper flow paths [*Dupas et al.*, 2017]. Based on high-frequency monitoring in the Wood Brook catchment in the UK, *Blaen et al.* [2017] also reported mobilization of nitrate from the uppermost soil layers during high flow conditions via shallow preferential flow paths, which would not occur during base flow in drier periods. This behavior leads to a seasonally-variable nitrate loading due to changing flow paths and the associated variation in transit time that has been observed in many catchments [*Benettin et al.*, 2015; *Hrachowitz et al.*, 2016; *Kaandorp et al.*, 2018; *Rodriguez et al*., 2018; *Yang et al.* 2018]. However, how this fluctuation behaves in response to catchment land surface topography has not been assessed systematically yet. Such an assessment could improve our understanding of nitrate export from catchments of different topographic slopes not only in terms of the mean concentration but also regarding its ~~seasonal~~ temporal variation patterns~~bility~~.

Given that most of the above studies used data driven analysis, numerical modeling is an effective tool for the analysis of water flow, age and solute transport, eliminating the need for large amounts of field data. For example, v~~V~~*an der Velde et al.* [2012] constructed a lumped numerical nitrate transport model for the Hupsel Brook catchment in the Netherlands, without resolving the spatially-explicit details. *Zarlenga and Fiori* [2020] presented a physically~~-~~based framework to model ~~the~~ transient water ages at the hillslope scale, which was later used to investigate the different impacts of hillslopes and the channel network on ~~the~~ water ages in catchments [*Zarlenga et al.*, 2022]~~.~~ Physically-based hydrogeological models (like, e.g., HydroGeoSphere [*Therrien* et al., 2010]) resolve the spatially-explicit details within a catchment including the full variability of 3D flow paths in the subsurface, helping to understand the seasonally changing flow patterns in response to different catchment topographies. Additionally, the widely used fully-coupled surface-subsurface technology simulates the catchment as an integrated system, providing details of surface water-groundwater exchanges fluxes. These details help to identify paths of rapid discharge to the land surface that can considerably improve the interpretation of nitrate-export patterns.

Transit time distributions (TTDs) have been widely used to interpret hydrological and chemical responses in catchment outfluxes – both in discharge (Q) and in evapotranspiration (ET) [*Botter et al*., 2010, 2011; *van der Velde et al*., 2012; *Heidbüchel et al*., 2012; *Rinaldo et al.* 2015; *Harman et al*., 2015; 2019]. They characterize how a catchment stores, mixes and releases water as well as dissolved solutes at large spatial and temporal scales [*Benettin et al.*, 2015; *Harman*, 2015; *van der Velde et al.*, 2010, 2012; *Hrachowitz et al.*, 2015; *Van Meter et al.*, 2017]. Given that the nitrate attenuation is linked to the age composition of outflow, the TTDs are ideal tools for interpreting the concentration dynamics with regard to catchment topographic slope. Estimating water ages in natural catchments is still a challenge due to varying climate conditions, as well as the errors in algorithms (e.g. errors in the flow field during particle tracking) and limited computational capacity. *Yang et al*. [2018] used particle tracking to compute the age distributions in the subsurface of a study catchment (while omitting the 4% of total discharge produced by direct surface runoff and ignoring the frequent exchange fluxes that may be important for solute export due to their short transit times). Zarlenga *et al*., [2022] used a physically-based semi-analytical model to ~~solve~~compute the transient water ages in a catchment, however, without considering ~~the~~ surface run-off and hydrological losses (e.g. ET) ~~being neglected~~. In this study we determined the age compositions of Q and ET using numerical tracer experiments, where advective-dispersive transport of the tracers was solved using the fully-coupled surface-subsurface framework of HydroGeoSphere. The computed age dynamics based on the tracer concentrations were representative as the tracers were able to track all the flow processes such as surface runoff, groundwater flow and surface-subsurface interaction.

In this study, we attempted to systematically assess the effect of catchment topographic slope~~s~~ on the nitrate export dynamics in terms of ~~the~~ mass fluxes, concentration levels and its seasonal variability. We also seek mechanical explanations for the previously found behaviors from data-driven studies (like, e.g., *Jasechko et al*. [2016]) with the help of fully resolved flow paths. First, we ~~chose~~ selected a real-world ~~cross-section from the~~ small agricultural catchment 'Schäfertal' in Central Germany, which is characterized by strong seasonality in hydrodynamic forcing with associated shifts in the dominant flow paths [*Yang et al.*, 2018]. This catchment is typical for many catchments with hilly topography under a temperate humid climate. We created eleven model scenarios by adjusting the mean slope of the real-world ~~cross-section~~catchment while preserving the ~~land surface micro-topography and~~ aquifer heterogeneity. Next, we modeled the water flow and nitrate transport for each ~~cross-section~~catchment. The flow and transport were solved using the fully coupled surface and subsurface numerical simulator HydroGeoSphere, and the water ages were computed using numerical tracer experiments. Finally, the modeled flowpaths, water ages, N mass fluxes and nitrate concentrations under various topographic slopes were analyzed. Through this study, we aimed to (1) examine the relationship between topographic slope and N mass fluxes~~C_Q~~, and to (2) assess ~~the~~ C_Q and its seasonal variation ~~of C_Q and its controls~~ in response to~~regarding~~ different topographic slopes.~~ The results were supposed to~~

~~improve the understanding of the effects of certain catchment characteristics on nitrate export dynamics with potential implications for the management of stream water quality and agricultural activity.~~

2 Data collection

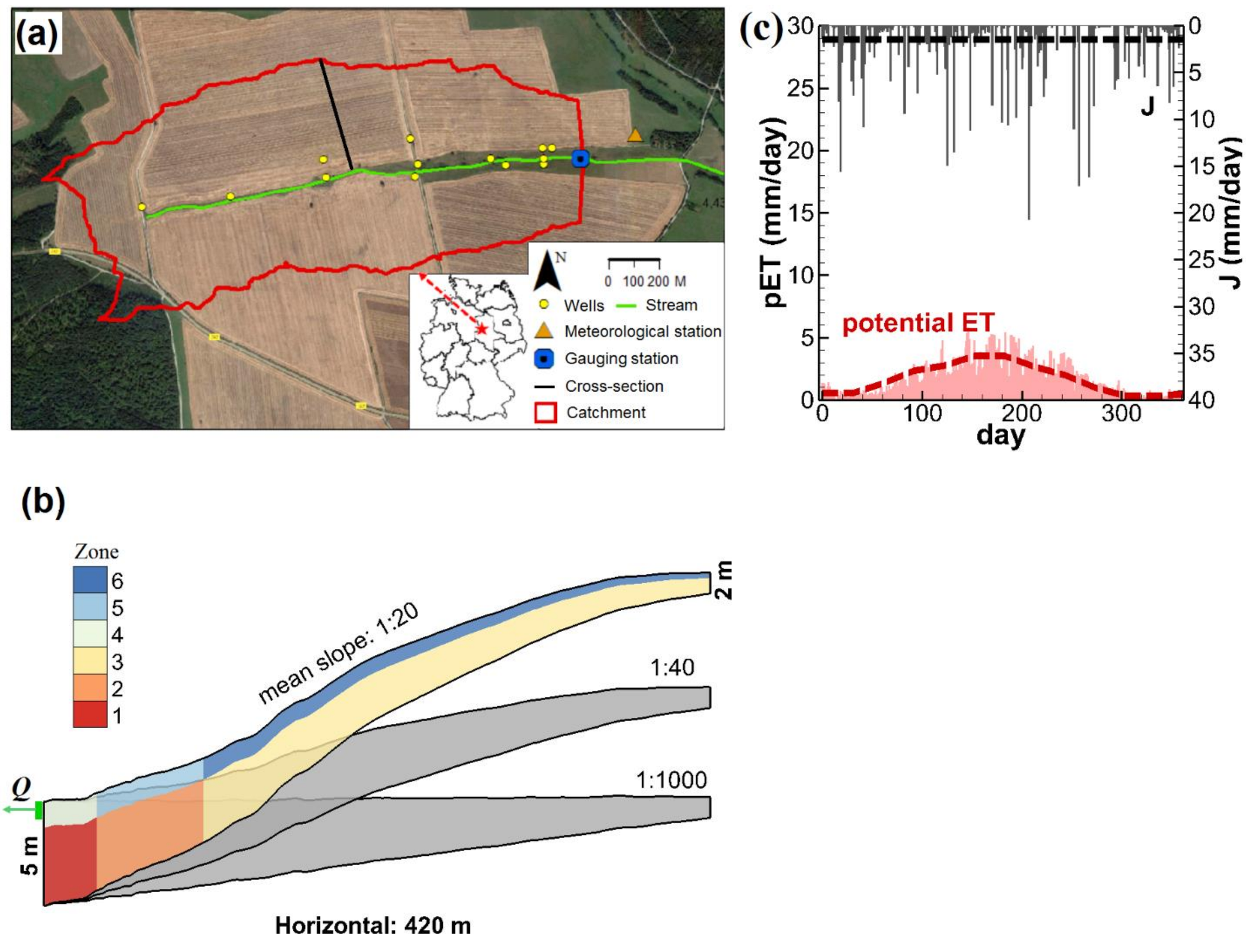
2.1 Real-world and synthetic ~~cross-sections~~catchments

Our study was conducted on ~~a vertical cross-section selected from~~ the catchment 'Schäfertal'~~. This catchment is~~, situated in the lower part of the Harz Mountains, Central Germany (Figure 1~~2~~a). The catchment has an area of 1.44 km^2. The hillslopes are mostly used for intensive agriculture while the valley bottom contains riparian zones with pasture and a small stream draining the water out of the catchment. The gauging station at the outlet of the catchment provides Q records. This gauging station is the only outlet for discharging water from the catchment, because a subsurface wall was erected underneath the gauging station across the valley to block subsurface flow out of the catchment. A meteorological station 200 m from the catchment outlet provides records of precipitation (J), air and soil temperatures, radiation and wind speed. The modeled catchment~~cross-section is perpendicular to the stream with a length of 420 m (Figure 2a, b)~~ ~~and~~ has a mean topographic slope of ~1:20, estimated using a cross-section perpendicular to the stream (Figure 1a). The aquifer thickness varies from ~5 m near the valley bottom to ~2 m at the top of the hillslope. Groundwater storage is low (~500 mm) in such a thin aquifer and mostly limited to the vicinity of the channel with the upper part of the hillslopes generally unsaturated. The stream bed has a depth of 1.5 m below the land surface~~, prescribed on the valley side of the cross-section~~. Aquifer properties (e.g. hydraulic conductivity) change from the hillslope, dominated by Luvisols and Cambisols, to the valley bottom, dominated by Gleysols and Luvisols [*Anis and Rode*, 2015]. Apart from that, the aquifer generally consists of two layers: the top layer of approximately 0.5 m thickness with higher porosity and a developed root zone from crops, and the base layer with smaller porosity due to high loam content [*Yang et al.*, 2018]. Subsequently, ~~six~~ ten property zones were used (Figure 1b), with zonal parameter values following the model in *Yang et al.*, [2018] listed in Table 1.

Based on this real-world~~-~~ catchment~~cross-sectional aquifer~~, ten synthetic ~~cross-sections~~catchments were generated by adjusting elevations (land surface and aquifer bottom), such that the mean topographic slope ranges from 1:20 (steep) to 1:22, 1:25, 1:30, 1:40, 1:60, 1:80, 1:100, 1:200, 1:500 and 1:1000 (flat, Figure 1b).~~,~~ ~~while preserving t~~The~~ land surface micro-topography,~~ aquifer depth and heterogeneity were preserved during the adjustments~~(Figure 1b)~~. In total, eleven ~~cross-sections~~catchments were used for flow and transport simulations. The catchment with the original topography (1:20) is selected as the base scenario.

2.2 Climate~~s~~

The considered climate for the ~~cross-sections~~catchments was derived from the catchment 'Schäfertal' located in a region with temperate humid climate and pronounced seasonality. According to the meteorological data records from 1997 to 2007, the mean annual J and Q (per unit area) are 610 mm and 160 mm, respectively. Actual mean annual ET based on the ten-year water balance ($J = ET + Q$) is 450 mm. Mean annual potential ET is 630 mm [*Yang et al.*, 2018]. The humid climate is representative for wet regions, quantified by an aridity index (J / potential ET [*Li et al.*, 2019]) of 1.0. The ET is the main driver of the hydrologic seasonality as the precipitation is more uniformly distributed across the year (Figure 1c). ~~To acknowledge this fact, we selected the data records of the year 2005, and calculated the annual J and monthly averaged potential ET. Using these averaged values in the study can accelerate the simulations and simplify the analysis while preserving the main characteristics of the meteorological forcing to the system.~~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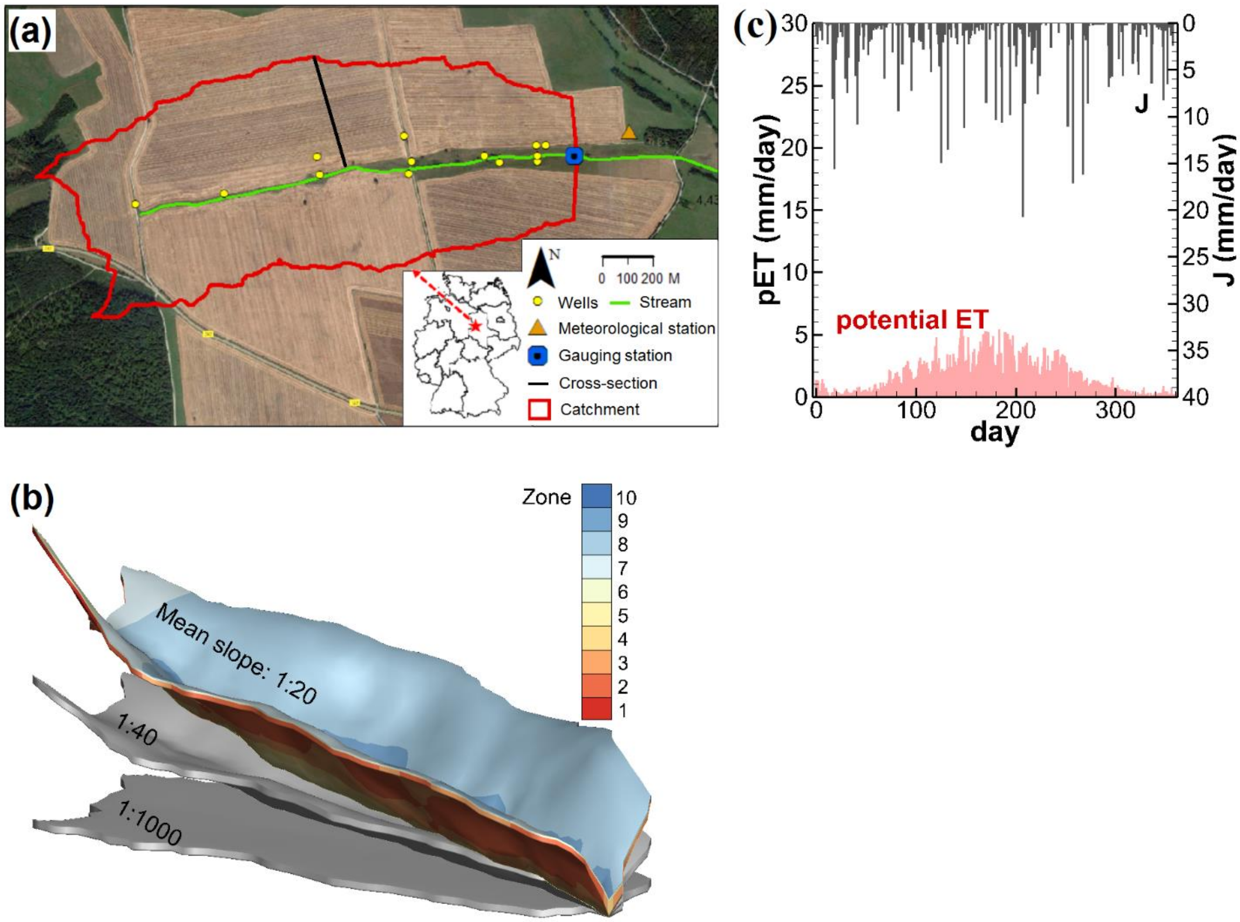

Figure 1. (**a**) The catchment 'Schäfertal', Central Germany (background image from © Google Maps). (**b**) The ~~The cross-sectional~~ catchments~~aquifer marked in (a)~~ with ~~a~~ mean topographic slopes of 1:20, ~~and two synthetic ones with topographic slopes of~~ 1:40 and 1:1000. (**c**) The measured precipitation *J* and the estimated potential evapotranspiration *ET* for the year 2005 under the the humid climate [*Yang et al.*, 2018]. Ten aquifer property zones in (b) were defined in the subsurface of the catchment for zonal parameter values (e.g. ~~the~~ hydraulic conductivity). ~~The dashed lines represent the annual (*J*) and monthly (*ET*) averages.~~

3 Methods

3.1 Flow and nitrate transport

Flow model

It is necessary to solve both groundwater and surface water flow because the spatially-explicit details in the ~~model~~ catchment including the specific flow paths and exchange fluxes are necessary to interpret the effect of varying topographic slope on nitrate transport. We simulated the flow system using the fully coupled surface and subsurface numerical model HydroGeoSphere, which solves for variably saturated groundwater flow with the Richards' equation and for surface flow with the diffusion-wave approximation of the Saint-Venant equations [*Therrien* et al., 2010].

Additionally, the exchange flux between groundwater and surface water can be implicitly simulated. The nitrate transport ~~is~~ is simulated in the groundwater flow, surface flow and exchanges fluxes by solving the advection-dispersion-diffusion equation describing the conservation of nitrate mass. HydroGeoSphere ~~The model~~ has been successfully used to simulate catchment hydrological processes and solute transport in many studies [e.g. *Therrien et al.*, 2010; *Yang et al.*, 2018], therefore governing equations and technical details are not explicitly repeated here.

In our previous work *Yang et al.* [2018], a hydrological flow model has~~was~~ already been established for the catchment 'Schäfertal'. It was calibrated against ~~the~~ measured groundwater levels and ~~the~~ stream discharge Q. The optimized parameter values are listed in Table 1. In this work, we performed our simulations based on that flow model, with the nitrate transport process being added while maintaining~~. However,~~ the model setup~~ is maintained~~. We provide a brief review of that flow model here. Readers may refer to *Yang et al.* [2018] for a full description of the model and its calibration.

The modeled subsurface of the ~~cross-sections~~catchments was discretized into ~~15~~ 9 horizontal ~~element~~ layers~~ of prisms~~~~s~~ between the land surface and the aquifer base, with thinner layers in the upper part (~~∼~~ 0.1~~05~~ m) to better represent the unsaturated zone and compute the ET.~~in more detail and thicker layers in the lower part (∼ 1 m).~~ In total, the subsurface was discretized by a mesh of 13860 prisms, with the horizontal size of the prisms ranging from 30 to 50 m.~~The cross-sections were 420 m long and uniformly discretized into 200 cells. Apart from that, each cross-section had a width (lateral direction perpendicular to the cross-section) of 100 m discretized uniformly into 10 cells. The reason for that was to avoid boundary influences that may have been caused by the lateral flow boundary condition (described later). In total, the discretization led to 30,000 block elements for the surface.~~ The topmost ~~2,000~~1540 triangles ~~rectangles (200×10)~~ were used to discretize the surface domain, where surface flow was simulated. Ten property zones for the subsurface were defined (Figure 1b), being assigned with the zonal hydraulic conductivity and porosity values (Table 1). ET was simulated as a combination of plant transpiration from the root zone (top 0.5 m soil) and evaporation down to the evaporation depth (0.5 m), which are both constrained by soil water saturation. Regarding the flow boundary conditions, spatially uniform and temporally variable J was applied to the land surface. Spatially constant and temporally variable potential ET was applied to the aquifer top to calculate the actual ET. The bottom of the aquifer was considered an~~s~~ impermeable boundary. A critical depth boundary condition was assigned to the catchment outlet to simulate the stream discharge Q, which was compared to~~with~~ the measured Q~~ones~~ during the calibration. The software PEST [Doherty and Hunt, 2010] was used for the transient calibration. After calibration, the time-variable groundwater levels were well replicated by the flow model for most of the wells, with mean coefficients of determination (R^2) of 0.43. The fit between the simulated and measured Q was satisfactory~~ying~~ with a R^2 of 0.61. The calibrated model successfully simulated the flow system from 1997 to 2007.

In this study, we continued to use the above described model setup, including the mesh, the parameters and the flow boundary conditions, for the eleven catchments with~~of~~ different topography. Note that the mesh was adapted to the change of the topography by changing node elevations vertically. However, to simplify the flow simulation and the age computation (described in section 3.2), we selected the year 2005 as a representative year and assumed~~s~~ that all the years have the identical climate (J and potential ET) as the year 2005. Therefore, ~~the~~ J and potential ET of 2005 (Figure 1c) were cycled and applied to the catchments for all the simulated years.

Table 1. The key flow~~aquifer~~ parameters and their values following *Yang et al*., [2018]. ~~Zonal values are ordered from zone 1 to zone 6.~~

Parameter	Process	Type	Value
Hydraulic conductivity	Subsurface	zonal	2.00, 0.13, 1.18, 0.02, 0.02, 2.00 m day^{-1}
Porosity	Subsurface	zonal	0.1, 0.1, 0.1, 0.35, 0.35, 0.35 [-]
Residual saturation	Subsurface	uniform	0.08 [-]
Inverse of air entry pressure α	Subsurface	uniform	3.6 m^{-1}
Pore-size distribution index β	Subsurface	uniform	2 [-]
Manning roughness coefficient	Surface	uniform	$6.34 \cdot 10^{-6}$ day m$^{-1/3}$
Longitudinal dispersivity	Transport	uniform	8 m
Lateral and vertical dispersivity	Transport	uniform	0.8 m
Molecular diffusion coefficient	Transport	uniform	10^{-9} m^2 s^{-1}
Degradation coefficient	Transport	uniform	0.009 day^{-1}
Transpiration fitting parameters:			
C1	ET	uniform	0.17 [-]
C2	ET	uniform	0.00 [-]
C3	ET	uniform	3.00 [-]
Transpiration limiting saturations:			
Wilting point	ET	uniform	0.1 [-]
Field capacity	ET	uniform	0.2 [-]
Oxic limit	ET	uniform	0.9 [-]
Anoxic limit	ET	uniform	1.0 [-]
Evaporation limiting saturations:			
Minimum	ET	uniform	0.1 [-]
Maximum	ET	uniform	0.2 [-]

Parameter	Process	Type	Value
Hydraulic conductivity	Subsurface	zonal	Zonal values (refer to Yang et al., [2018])
Porosity	Subsurface	zonal	Zonal values (refer to Yang et al., [2018])
Residual saturation	Subsurface	uniform	0.08 [-]
Inverse of air entry pressure α	Subsurface	uniform	3.6 m^{-1}
Pore-size distribution index β	Subsurface	uniform	2 [-]
Manning roughness coefficient	Surface	uniform	$6.34 \cdot 10^{-6}$ day $m^{-1/3}$
Longitudinal dispersivity	Transport	uniform	8 m
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C1	ET	uniform	0.17 [-]
C2	ET	uniform	0.00 [-]
C3	ET	uniform	3.00 [-]
Transpiration limiting saturations:			
Wilting point	ET	uniform	0.1 [-]
Field capacity	ET	uniform	0.2 [-]
Oxic limit	ET	uniform	0.9 [-]
Anoxic limit	ET	uniform	1.0 [-]
Evaporation limiting saturations:			
Minimum	ET	uniform	0.1 [-]
Maximum	ET	uniform	0.2 [-]

Transport ~~Parameters and boundary conditions for flow~~

~~The key model parameters for simulating groundwater flow, surface flow and ET are listed in Table 1. Their values were taken from previous work [*Yang et al.*, 2018], where a hydrological flow model was built and calibrated against measured groundwater levels and Q for the entire catchment. For each cross-section, constant J and time-variant potential ET were applied to the aquifer top. HydroGeoSphere calculates actual ET from potential ET taking into account the modeled water content, leaf area index and root depth distributions. A free-drainage boundary condition was assigned to the topmost 1.5 m of the subsurface at the valley side (left side) boundary (Figure 1b), enabling subsurface discharge to the channel. A critical depth boundary [*Therrien et al.*, 2010] was assigned to the left-side edge of the land surface, allowing surface discharge to the channel. In the 3D catchment, surficial flowpaths can connect the surface water ponding in the depressions of the land surface. In our 2D model, it is unrealistic to force these surficial flowpaths to be parallel to the cross-section. Therefore, our model allowed for the lateral exit of surface water via the depressions of the land surface by assigning critical depth boundary conditions there. This lateral exit was also counted as surface discharge to the channel. Finally, the total discharge Q can be calculated by summarizing the subsurface and surface discharge.~~

~~Parameters and~~ boundary conditions ~~for~~ and parameters ~~transport~~

The nitrogen (N) pool is formed in the soil zone of the catchments, representing a nitrate source zone. The N pool ~~The nitrogen pool in the soil~~ is controlled by various complex processes. It is replenished by external inputs from atmospheric deposition, biological fixation, animal manure from the pasture area, and fertilizer from the farmland on the hillslopes. Nitrate ~~N~~ that can be transported with water is formed and leached from this ~~(organic) nitrogen~~ N pool by a microbiological immobile-mobile exchange process [*Musolff* et al., 2017; *Van Meter* et al., 2017]. In our study, we employed the simplified framework by *Yang et al.*, [2021] to track the fate of N in the N pool (Figure 2a). This frame~~-~~work was derived~~modified~~ from the ELEMeNT approach (Exploration of Long-tErM Nutrient Trajectories, Van Meter et al., 2017), which uses a parsimonious modeling framework to estimate the biogeochemical legacy nitrate loading in the N pool and the N fluxes leaching from the N pool to the groundwater. This framework assumes that total N load in the N pool is comprised by inorganic N (SIN) and organic N (SON). Two types of SON are distinguished: active organic N (SON_a) with faster reaction kinetics and protected organic N (SON_p) with slower reaction kinetics. It is assumed that the external N input contributes only to the SON. The SON is mineralized into SIN. The SIN is further consumed by plant~~s~~ uptake and denitrification, and finally leaches to groundwater as dissolved inorganic N (DIN, representing mainly nitrate in the studied catchment [*Yang et al.*, 2018; *Nguyen et al.*, 2021]). The framework is acceptable due to the fact that most of the nitrate fluxes from source zones has undergone biogeochemical transformation in the organic N pool [*Haag and Kaupenjohann*, 2001]. The framework simplifies complexities of different N pools and transformations via mineralization, dissolution, and denitrification within the soil zone [Lindström et al., 2010], while preserving the main pathway for nitrate leachate.

The governing equations to calculate these N fluxes follow~~s~~ the ones in *Yang et al.*, [2021]. A specific portion (*h*) of the external N input contributes to the SON_p pool, and the rest contributes to the SON_a pool. The portion *h* is the land-use dependent protection coefficient [*Van Meter et al.*, 2017]. The mineralization and denitrification are described as first order processes with rate coefficients k_a, k_p, and λ_s respectively, using:

$$MINE_a = k_a \cdot f(temp) \cdot SON_a \qquad (1)$$

$$MINE_p = k_p \cdot f(temp) \cdot SON_p \qquad (2)$$

$$DENI_s = \lambda_s \cdot SIN \qquad (3)$$

where $MINE_a$, $MINE_p$, $DENI_s$ (kg ha^{-1} day^{-1}) are the mineralization rates for SON_a and SON_p, and denitrification rate for SIN. k_a, k_p, and λ_s (day^{-1}) are coefficients for the first order processes. $f(temp)$ is a factor representing a constraint by soil temperature [*Lindström et al.*, 2010]. Note that the mineralization and plant~~s~~ uptake occur in the N pool. Denitrification can occur in both the N pool and later in groundwater. The p~~P~~lant~~s~~ uptake rate UPT follows the equation used in the HYPE model [*Lindström* et al., 2010]:

$$UPT = \min(UPT_P, 0.8 \cdot SIN) \qquad (4)$$

$$UPT_P = p1/p3 \cdot \left(\frac{p1-p2}{p2}\right) \cdot e^{-(DNO-p4)/p3} / \left(1 + \left(\frac{p1-p2}{p2}\right) \cdot e^{-(DNO-p4)/p3}\right)^2 \qquad (5)$$

where UPT and UPT_P (kg day^{-1} ha^{-1}) are the actual and potential uptake rates. The computation of UPT_P considers a logistic plant growth function. *DNO* is the day number. *p1*, *p2*, *p3* are three parameters depending on the crop/plant type, they~~and~~ are in the units of (kg ha^{-1}), (kg ha^{-1}), and (day), respectively. *p4* is the day number of the sowing date.

The l~~L~~eaching process allows for SIN to leach~~es~~ from the soil (N pool) to the groundwater. The leaching rate *LEA* (kg ha^{-1} day^{-1}) is defined~~formed~~ as a first order process as:

$$LEA = f \cdot SIN/\Delta t \qquad (6)$$

$$f = (1 - exp^{-a\frac{wal}{\theta d}}) \qquad (7)$$

$$wal = q \cdot \Delta t \qquad (8)$$

where *f* is a factor, ranging between [0, 1], to determine the portion of SIN that leaches into groundwater during a time step Δt. a is unit-less leaching factor. θ is the soil porosity. d is the soil depth. *wal* [L] is the water available for leaching during Δt. *wal* can be estimated using the Darcy fluxes *q* [LT^{-1}], which are provided by the flow simulations for each cell~~s~~ of the mesh. Physically, *f* is a function of the ratio between *wal* and the volume of soil voids $\theta \cdot d$, representing~~s~~ the ability of water to flush~~wash~~ the SIN. This formulation of *LEA* is modified from the ones used in *Pierce et al.*, [1991], *Shaffer et al.* [1991] and *Wijayantiati et al.* [2017], to comply~~llaborate~~ with the spatially-distributed HydroGeoSphere model.

Table 2. The parameters for the N pool and nitrate transport. The parameters with a range are calibrated. The adjustable ranges are selected to cover the values that the parameters can potentially take on~~reach~~ or the values reported by the referred literature~~s~~.

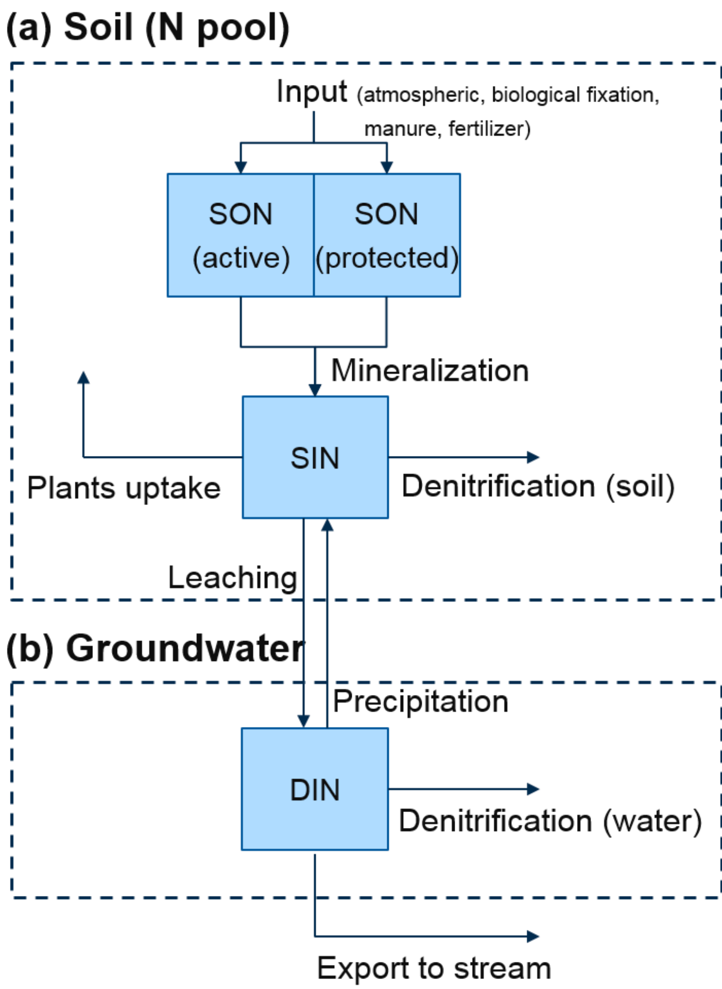
Parameter	**Description**	**Range**	**Reference**	**Best-fit value**
N pool				
d	Soil depth	Fixed	*Yang et al.* [2018]	0.5 m
N Input	N external input	Fixed	*Nguyen et al.* [2021]	180 kg ha^{-1} yr^{-1}
h	protection coefficient	Fixed	*Van Meter et al.* [2017]	0.3 [-]
k_a	Mineralization coef. (DON$_a$)	[0 - 0.7]	*Yang et al.* [2021]	0.011 day^{-1}
k_p	Mineralization coef. (DON$_p$)	[0 - 0.7]	*Yang et al.* [2021]	0.0008 day^{-1}
λ_s	Denitrification coef. (soil)	[0 - 0.7]	*Yang et al.* [2021]	0.0007 day^{-1}
$p1$	Parameter for plants-uptake	[60 - 160]	*Van Meter et al.* [2017]	160 kg ha^{-1}
$p2$	Parameter for plants-uptake	[0 - 10]		9.8 kg ha^{-1}
$p3$	Parameter for plants-uptake	[1 - 60]		25.6 day
$p4$	Parameter for plants-uptake	Fixed		63 day
a	Leaching factor	[0 – 100]		0.154 [-]
Transport				
λ	Denitrification coef. (water)	[0 - 0.7]	*Yang et al.* [2021]	0.0072 day^{-1}
a_L	Longitudinal dispersity	Fixed		8 m
a_T	Transverse dispersivity	Fixed		0.8 m

The N pool is positioned on the top part of the aquifer, used as a boundary condition for the DIN (nitrate) transport. Advective-dispersive transport of DIN in the flow system is simulated using HydroGeoSphere (Figure 2b). ~~it is not necessary to fully implement all the complexities of the different nitrogen pools and transformations into the model,~~

~~because we focus on the in-stream concentration responses with regard to catchment topography, rather than on the full nitrogen cycle of the catchment. Therefore, we assumed that a nitrate source concentration C_j was associated with the precipitation. The C_j, which is time-variant, comprehensively defines the amount of dissolved nitrate that can enter the storage along with precipitation. In this study, the C_j curve followed the time-variant nitrate leaching concentrations calculated by *Nguyen et al.*, [2021] using a mesoscale nitrate export model (Figure 2). Additionally, we also considered cases with constant C_j which is the average of the time-variant values. This constant C_j was used to quantify the source contribution to the variation of instream concentrations (described in section 3.3).~~ Degradation (denitrification in groundwater) during transport is considered as a first order process~~es~~. Degradation is not considered on the land surface (denitrification in surface flow), where ~~the~~ aerobic conditions~~ is more~~ likely ~~to~~ deactivate~~ the~~ denitrification and residence time is short.

To implement the evapoconcentration effect in the transport model, ET is assumed to ~~simplify the transport processes, the~~remove DIN ~~nitrate~~ mass ~~transported with ET (representing plant-uptake) was assumed to not~~without altering the ~~nitrate~~ DIN concentration of the water~~ in storage~~, and to inject that mass back to the SIN pool. This represents a precipitation process from DIN to SIN, which is the~~an~~ inverse process of leaching (Figure 2b). There are two reasons for doing that: (i) the physical process of~~that~~ ET causing~~e~~ the immobilization of DIN can be mathematically considered, and (ii) the N mass balance can be conserved ~~preserved~~as the plants-uptake is already considered in the N pool according to the plant growth function (Equation 4 and 5), being independent from~~on~~ the ET flux.

Regarding the parameters, the soil depth, within which the N pool is implemented, is set to 0.5 m. N external input is 180 kg ha^{-1} yr^{-1} according to Nguyen et al. (2021), where the nitrate balance was simulated for the larger upper Selke catchment~~ (central Germany)~~ that contained~~vered~~ our studied catchment. The external N input is assumed to be spatiotemporally constant due to the limited information on its variation in space and time. The protection coefficient *h* is fixed as 0.3 according to the values reported in *Van Meter et al.* [2017]. The sowing date *p4* is fixed as 63 days according to the fact that sowing activities and plant growth start in early March. Longitudinal and transverse dispersivity values were 8 m and 0.8 m, respectively. Other parameters were set to be adjustable and calibrated (Table 2).



~~neglecting the evapoconcentration effect, because its potential effect to cause source variability was implicitly considered by forcing the source concentration to vary along the Cj curve. The denitrification in the system was described by the first order decay process with a degradation rate coefficient λ of 0.009 day-1 according to Nguyen et al., [2021] studying the area including the catchment Schäfertal. Longitudinal and transverse dispersivity values were 8 m and 0.8 m, respectively.~~

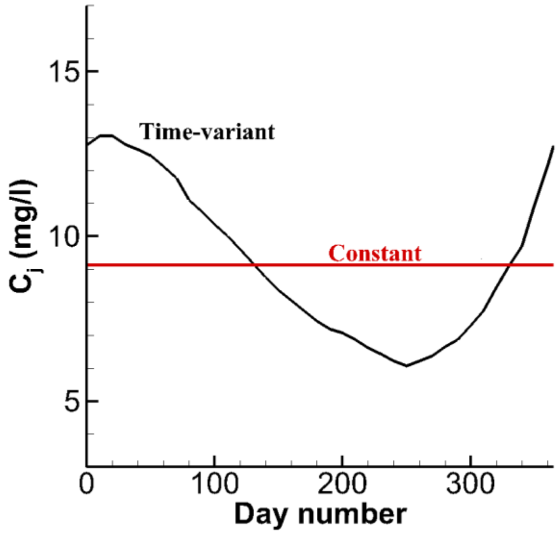


Figure 2. ~~T~~Conceptual framework for nitrogen (N) fluxes (a) in the soil (N pool), and (b) after leaching into the groundwater.~~he variable and the constant nitrate source concentrations. The constant source is the annual average of the variable source.~~

~~In total, we simulated the flow and transport for 22 scenarios (11 topographic slopes × 2 for variable/constant nitrate sources). For each scenario, the simulations were run for 100 years with identical boundary conditions for each year. The first 99 years were used as a spin-up phase to assure a dynamic equilibrium (i.e. to achieve simulated variables, such as heads and concentrations, being identical between years), and the last year was used for actual observation and analysis. The CPU time of each simulation was ~4 hours.~~

Transport calibration

To get reasonable parameter values for the N pool and N transport, a calibration was performed for the transport. The software package PEST [Doherty and Hunt, 2010] was used. In total eight parameters were calibrated (Table 2). Their adjustable ranges were selected according to the literature~~s~~ or to cover the values that the parameters can potentially realistically reach. First, the flow and transport were simulated in the catchment of the base scenario (original topography, section 2.1), for the period from Jul 1999 to Jul 2003. Secondly, PEST was used to obtain a best fit between the simulated results and the data sets by varying the parameter values. We used the measured C_Q and N surplus as the data sets. The N surplus, which is the annual amount of N remaining in the soil after consumption~~ing~~ by plant-uptake~~, form the external input,~~ was estimated as 48.8 kg ha^{-1} yr^{-1} (Yang et al., 2021). Note that the simulation period from Jul 1999 to Jul 2003 was only used for model calibration, rather than for the actual simulations with the eleven catchments of different topographic slope. After calibration, the model with the best-fit parameter values can well replicate the measured C_Q with a Nash-Sutcliffe efficiency (NSE) of 0.75 (see Figure S1 in the supporting information). The simulated N surplus was 50.7 kg ha^{-1} yr^{-1}, ~~being~~ comparable to~~with~~ the measured value.

The best-fit parameter values were also used for the catchments of different topographic slope, assuming that the parameters do not change with the change of topographic slope. In total, we simulated the flow and nitrate transport for eleven scenarios (11 catchments of different topographic slope). For each scenario, the simulations were run for 100 years with identical boundary conditions for each year. The first 99 years were used as a spin-up phase to assure a dynamic equilibrium (i.e. to achieve simulated variables, such as heads and concentrations, that are ~~being~~ identical between years), and the last year was used for actual observation and analysis. The CPU time of each simulation was ~4 hours.

3.2 Water ages

The water stored in a catchment (storage), Q and ET can all be~~is~~ characterized by ~~its~~ age distributions, for they~~as it~~ comprise~~s~~ water parcels of different age from precipitation events that occurred in the past. The age distributions need to be calculated for each aforementioned scenario to assess the responses of water ages on catchment topographic slope. Our model setup (with virtual ~~cross-sections~~catchments and identical climate for each year) allowed us to perform long-term numerical tracer experiments and to extract the age distributions.

We assumed that inert tracers of uniform concentration existed in precipitation. The tracers were applied to the land surface as a third-type (Cauchy) boundary condition and were subjected to transport modeling. Tracer can exit the aquifer via the outfluxes Q and ET. We considered a period of 200 years for the tracer experiments, which was sufficiently long to ensure convergence of the computed water ages. The 200 years period was partitioned into 2400 months (Δt = 1 month). A different tracer was used for each of the periods resulting in a total of 2400 distinct tracers. The injection of tracer *i* started with the precipitation at the beginning of its associated period t_0^i and lasted throughout the period ~~with the precipitation~~. The advective-dispersive multi-solute~~s~~ transport was simulated using HydroGeoSphere. The first 199 years of the simulation period were used as a spin-up phase to ensure a dynamic equilibrium of the calculated ages, minimizing the influence of the initial conditions. The last year was used for the actual observations and the computation of age distributions. Solving the transport of the 2400 tracers ~~is~~ would be computationally expensive. However, because the climate (flow boundary conditions) was identical for each year, the transport simulation was performed only for the first 12 tracers that covered the course of a year. Based on these results, the results for the other 2388 tracers were manually reproduced (e.g., by shifting the concentration breakthrough curves of the 12 tracers in time while maintaining the shapes).

For each tracer, the breakthrough curves of the mass-fluxes of Q and ET, as well as the mass in storage were reported. For a specific time t, the age distributions for Q/ET/storage were computed by calculating the mass fraction of each tracer using:

$$p_{Q/ET/S}(T,t) = \frac{M^i(t)}{\Delta t \sum M^i(t)} \qquad (9)$$

where $p_Q(T,t)$, $p_{ET}(T,t)$ are the age distributions of Q, ET (equivalent to backward transit time distributions - TTDs), and $p_S(T,t)$ is the age distributions of water in storage (equivalent to the residence time distribution - RTD). $M^i(t)$ is the mass-flux of the tracer i in Q or ET, or the mass stored in catchment at time t, $\sum M^i(t)$ is the sum of $M^i(t)$ over all tracers. T is the age ranging within $[t - t_0^i - \Delta t, t - t_0^i]$~~that equals $t -$~~ for tracer i.

For each scenario, the CPU time of the tracer experiment was ~8 hours. Based on the age distributions, we calculated the mean discharge age $T_Q(t)$, which is equivalent to the mean discharge transit time (simply referred to as 'discharge age' in the following sections). We calculated the young water fraction in streamflow $YF_Q(t)$, which is the fraction of streamflow with an age younger than three months (also referred to as 'young streamflow fraction' [*Jasechko et al.* 2016]). Similarly, the ET age $T_{ET}(t)$ and the young water fraction in ET $YF_{ET}(t)$ can be calculated as well (more details are described in Text S1 of the supporting information). Their responses to ~~a~~ changes in topographic slope were analyzed.

~~**3.3 Assessment variables**~~

~~The simulations of flow, nitrate transport and water age provided in-stream nitrate concentrations (t), streamflow ages (t) and young water fractions $YF(t)$ for each scenario. They all fluctuated seasonally over the course of a year. The temporal means and standard deviations σ of these variables can be calculated. The temporal variation in can potentially be split and attributed to (i) the variability in the nitrate source concentration, referred to as source contribution, and (ii) the variability created by degradation associated with variable transit times, referred to as degradation contribution. To understand which of these processes has the dominant effect on C_Q variability, we quantified the source contribution by calculating the relative change of σ for when C_j switches from being time-variant to being constant between separate model scenarios (see section 3.1), as:~~

$$\cancel{Source\ contribution = 1 -}$$

~~The calculated source contribution ranges from 0 (degradation-dominated) to 100 % (source-dominated). Additionally, the *Damköhler* number ($Da = \cdot \lambda$, [*Oldham et al.*, 2013]), which is a dimensionless ratio between the discharge age and the reaction time, can be calculated to indicate the interplay between the rate of degradation and the time-scale of transport. *Da* > 1 indicates a faster degradation time than transport time and vice versa.~~

4 Results and discussion

4.1 Dynamics of water ages and nitrogen fluxes

~~For all the scenario~~Driven by the seasonality of the climate~~ of seasonalitys~~, the simulated Q, ~~in-instream nitrate concentrations C_Q,~~ the young water fractions *YF*, and the water ages all show seasonal fluctuations. Figure 3 shows these fluctuations for the base scenario (original ~~cross-section with~~ topography)~~ic slope of 1:20~~. Q reaches its maximum towards the end of the wet winter in late February and reaches its minimum during the drier late summer in mid-September. Total Q consists of a portion of groundwater discharge (including the flow via vadose zone) and a portion generated via surface-runoff during events of high precipitation (Figure 3a). The calculated~~For~~ YF_{ET} ~~(Figure 3b) show that C_Q, high concentrations are reached during the wet season and low concentrations are reached during~~

~~the dry season (Figure 3b). Figure 3c depicts opposing fluctuation patterns of YF_Q and YF_{ET}.~~ y~~Young water~~ fraction ~~in ET~~ is smallest~~reaches the lowest~~ in April and largest~~the highest~~ in November (Figure 3b), ~~is low during the wet and high during the dry season,~~ while YF_Q ~~young water in Q~~ reaches~~is~~ the~~is smallest~~ ~~low~~est in August and largest~~highest~~ in February~~during the dry and high during the wet season~~. ET generally has larger young water fractions than Q as ET has a higher probability to remove young water from the shallow soil rather than the older water from~~in t~~ the deeper aquifer. Especially during the dry season (summer), most precipitation can be quickly removed by ET. The water ages of Q and ET show generally opposite fluctuation patterns for~~against~~ YF (Figure 3c).~~d shows that~~ The ET age ranges from ~~192~~ 70 to ~~395~~ 115 days, being younger than Q that has the age ranging~~older during the wet and younger during~~

~~the dry season. Simulated discharge age ranges~~ from ~~1259~~ 109 to ~~1490~~ 180 days~~, being younger during the wet and older during the dry season~~.

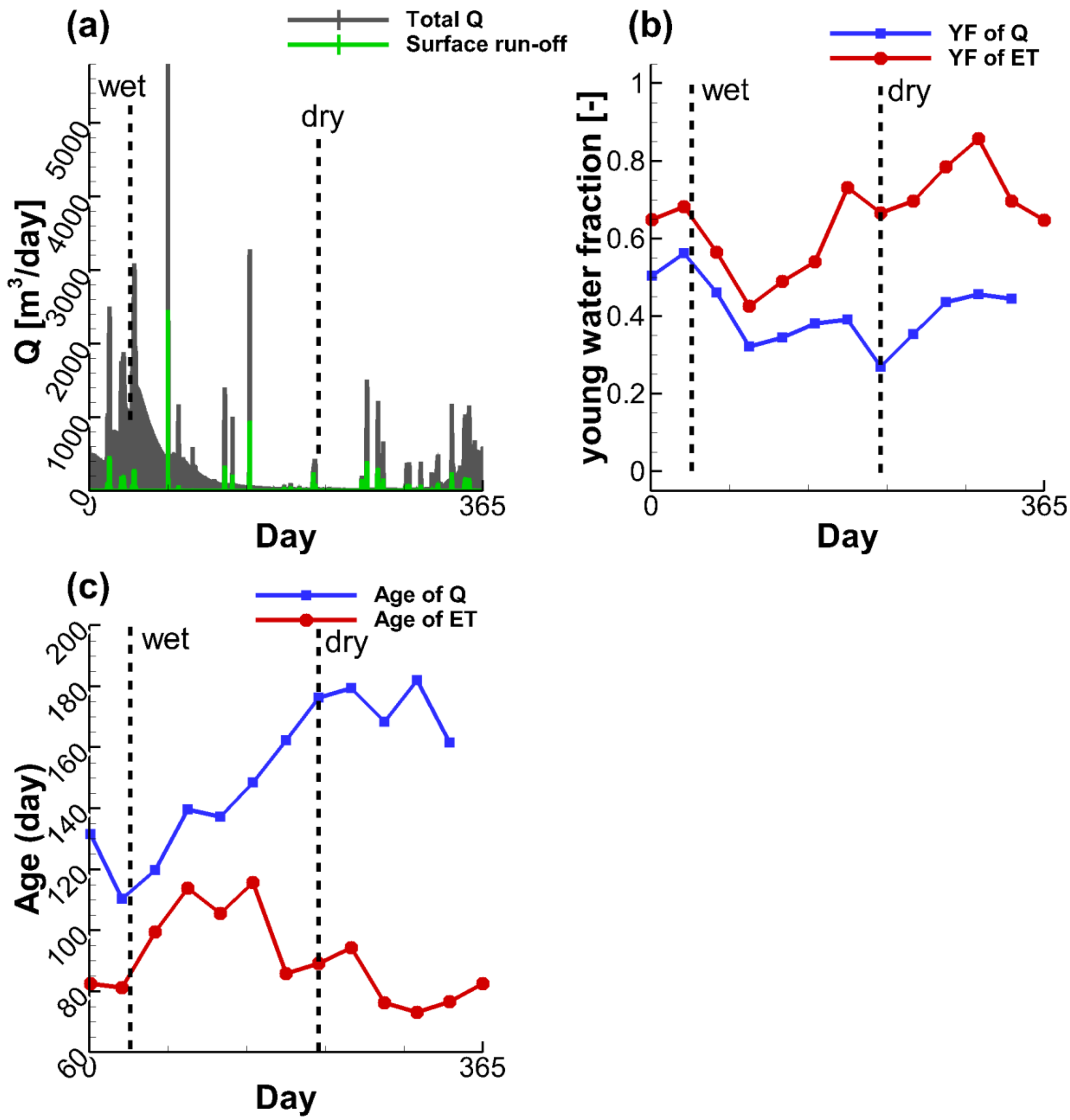


Figure 3. Simulated (**a**) Q, (**b**) young water fractions in streamflow (YF_Q) and evapotranspiration (YF_{ET})~~YF_Q and YF_{ET}~~, and (**c**) water ages for the catchment of the base scenario. The *YF* and water ages are monthly averages~~d~~.

The simulated C_Q shows strong seasonality with~~. The~~ maxima ~~are reached~~ in the wet ~~period~~ and ~~the~~ minima ~~are reached~~ in the dry period, fitting the measured C_Q data well (Figure 4a). Figure 4b lists the calculated annual N mass balance in the catchment of the base scenario. The organic (SONa + SONp) and inorganic (SIN) N load in the soil are 470 kg ha^{-1} and 43 kg ha^{-1}, respectively. The SON accounts for 92% of the total N load, which is consistent with the study of

Stevenson [1995] where the organic N fraction was reported to be greater than 90~~%~~%. The mineralization converts SON into SIN with a rate of 180 kg ha^{-1} yr^{-1}. This rate is equal to the external N input because this way a~~the~~ steady-state of the annual N mass balance was reached in the simulations. About 76~~%~~% of the input N flux is taken up by the vegetation~~plant~~ (136 kg ha^{-1} yr^{-1}). 20~~%~~% is consumed by denitrification (36 kg ha^{-1} yr^{-1}), either in the soil (before leaching) or in~~to~~ the groundwater (after leaching). The remaining~~st~~ 4~~%~~% reaches the stream water and is exported out of the catchment (6 kg ha^{-1} yr^{-1}). The simulated mineralization flux is within the range of [14–187] kg ha^{-1} yr^{-1} reported by *Heumann et al.* [2011] for their study sites in central Germany. The simulated plant uptake and leaching fluxes are comparable to the values suggested in Nguyen et al. [2021] for the same area (120 kg ha^{-1} yr^{-1} for plant uptake and [15–60] kg ha^{-1} yr^{-1} for leaching). The simulated denitrification rate is within the range [8–51] kg ha^{-1} yr^{-1} reported in Hofstra and Bouwman [2005] for 336 agricultural soils located worldwide. Moreover, 80~~%~~% and 20~~%~~% of the leaching N are consumed by denitrification during transport in the groundwater and exported to stream water, respectively. These portions are generally comparable to those~~at~~ reported in Nguyen et al. [2021] (61~~%~~% and 39~~%~~%, respectively). Therefore, the simulated N loads and fluxes for the catchment of the base scenario are considered to be acceptable.

Figure 4c shows the temporal variation of the N load and fluxes. It demonstrates that low levels of SIN are~~is~~ maintained by high plant-uptake before the dry summer arrives (May – June), such that there is little SIN available for leaching. The SIN load reaches its minimum~~a~~ when plant uptake reaches its maximum~~a~~ (marker a in~~,~~ Figure 4c). The cessation of plant-uptake during the dry period leads to the increase of the SIN load as well as the increase of the leaching rate. The mineralization in winter is significantly reduced due to the dropping temperatures, cutting the SIN supply. This results in ~~that~~ the SIN load reaching~~es~~ its high peak in the~~at~~ middle of November (marker b in~~,~~ Figure 4c) and subsequent~~turns into the dropping~~ decrease ~~phase~~ due to increased ~~the~~ leaching and eventually plant~~s~~ uptake. These seasonal fluctuation patterns are generally consistent with the knowledge of N fluxes reported in previous studies [Dupas et al., 2017; Nguyen et al., 2021]. For DIN load in water, it reaches its~~the~~ maximum~~a~~ generally when the leaching ~~becomes~~ weakens in~~at~~ the beginning of March (marker c in~~,~~ Figure 4c), and reaches the minimum~~a~~ just before the leaching process becomes active again in the end of August (marker d in~~,~~ Figure 4c). These low and high peaks of SIN and DIN loads can also be identified by their spatial distributions in the catchment (see Figure S2 in the supporting information).

~~4.2 In-stream nitrate seasonal variations~~

~~Simulated results demonstrate significant seasonal~~Seasonal variations of C_Q ~~for all the scenarios (Figure S2 in the supporting information). Basically, this variation in C_Q~~ can be directly influenced ~~is caused~~ either by the fluctuation of the nitrate ~~source input~~leaching into groundwater, or by fluctuations in the degradation in groundwater~~time~~ associated with ~~the~~ varying transit times (quantified by the young water~~stream~~ fraction in streamflow YF_Q). These two influences represent the effect from the variability in N source and in N transport, respectively. Linear regression analysis shows that C_Q is correlated with leaching flux rate and YF_Q with Spearman rank-correlation coefficients of 0.1 and 0.34, respectively (Figure 5). The seasonal fluctuations of C_Q and l~~L~~eaching flux are temporally out of phase. The maximum leaching occurs~~reaches~~ in December, while the maximum C_Q is reached~~s~~ two months later in February

(Figure 5a). The minimum leaching occurs~~reaches~~ in April, while the minimum C_Q is reached~~s~~ around September. This behavior indicates that C_Q respond~~s~~e later to the changes in N leaching, which is reasonable because the leaching nitrate needs time to travel from the shallow soil to streamflow. The fluctuation of ~~the~~ C_Q and YF_Q are more synchronized, proven~~ed~~ by the fact that both maxima~~ums~~ are reached~~s~~ in February (wet, Figure 5b) and minima~~ums~~ occur~~reaches~~ generally in the dry summer time. Field observations in mountainous central German catchments also indicate that C_Q varies~~y~~ seasonally, with maxima during the wet winter and minima during the dry summer [Dupas et al., 2017]. These seasonal fluctuations of C_Q and YF_Q were frequently explained using the “inverse storage effect” [*Harman*, 2015; *Yang et al.* 2018]: during the wet season Q has a strong preference for young water associated with higher concentrations, which would not occur during dry periods due to the deactivation of the shallow fast flow processes. These patterns generally suggest that ~~The calculated source contribution for our simulated scenarios indicates that only 2 to 33 % of the variation of C_Q can be attributed to the fluctuation of source concentrations (Figure 8a). This means that~~ the C_Q ~~nitrate concentration~~ fluctuation is more attributed to ~~s in all simulated cross-sections are dominated by~~ the variability in the N transport~~degradation time (transit time)~~ rather than to the variability in the N source, echoing ~~with~~ previous observations that 80~~%~~% of the leaching N mass is degraded during transport. However, it is still hard to tell whether the N source or the N transport is dominating the C_Q fluctuation.

~~. In other words, significant seasonal variation of the nitrate concentration in streamflow can be expected under the considered humid climate even when nitrate is applied to the aquifer in a constant manner without any variation. These seasonal fluctuations of transit time and C_Q were frequently explained using the “inverse storage effect” [*Harman*, 2015; *Yang et al.* 2018]: during the wet season Q has a strong preference for young water associated with higher concentrations, which would not occur during dry periods due to the deactivation of the shallow fast flow processes. This effect was revealed in the computed TTDs for Q indicated by the shift between wet and dry seasons (Figure S3 in the supporting information).~~

~~The response of the source contributions to topographic slope is threshold-like (Figure 8a): the source contributions in C1 were significantly higher than the ones in C3. Especially for the landscapes of C3, the fluctuation of C_Q was hardly impacted by source variability. Mechanically, the seasonal source fluctuation is more likely to be damped by relatively longer transit times in C3 landscapes, which are relatively flat.~~

~~Given that the seasonal C_Q variation can be attributed more to the variation in transit times (thus to the variation in the YF_Q), it was expected that the standard deviations of C_Q and YF_Q (Figure 8b, c) had similar responses to the topographic slope. Both of the responses exhibit a threshold-like pattern, similar to the response of the mean C_Q (Figure 4a). This is because C_Q during the dry season is generally low, regardless of whether the landscape is steeper or flatter. The overall response of $\sigma(C_Q)$ to topographic slope is determined by the response of the relatively high C_Q during the wet season, and can be interpreted in the same three-class pattern: $\sigma(C_Q)$ increases with the decrease of slope within C1 (or C3), suggesting that flatter landscapes tend to export nitrate with more seasonal fluctuations in C_Q for C1 (or C3). However, for C2, a significant drop in this fluctuation can be expected when the landscape transforms from C1 to C3. As a result, the maximum seasonal variation was reached at the slope of 1:60. For the mechanistic interpretation please refer to section 4.1.~~

~~Generally, the seasonal fluctuation patterns of C_Q, with both variable source and constant source, are highly correlated with the fluctuation pattern of the YF_Q with Spearman rank-correlation coefficients of 0.81 and 0.93, respectively. The calculated *Da* for streamflow is 13, demonstrating that the degradation time-scale is significantly shorter than the transport time-scale. This means young streamflow is the main contributor of nitrate mass as most of the nitrate in the older water has been degraded before reaching the stream.~~

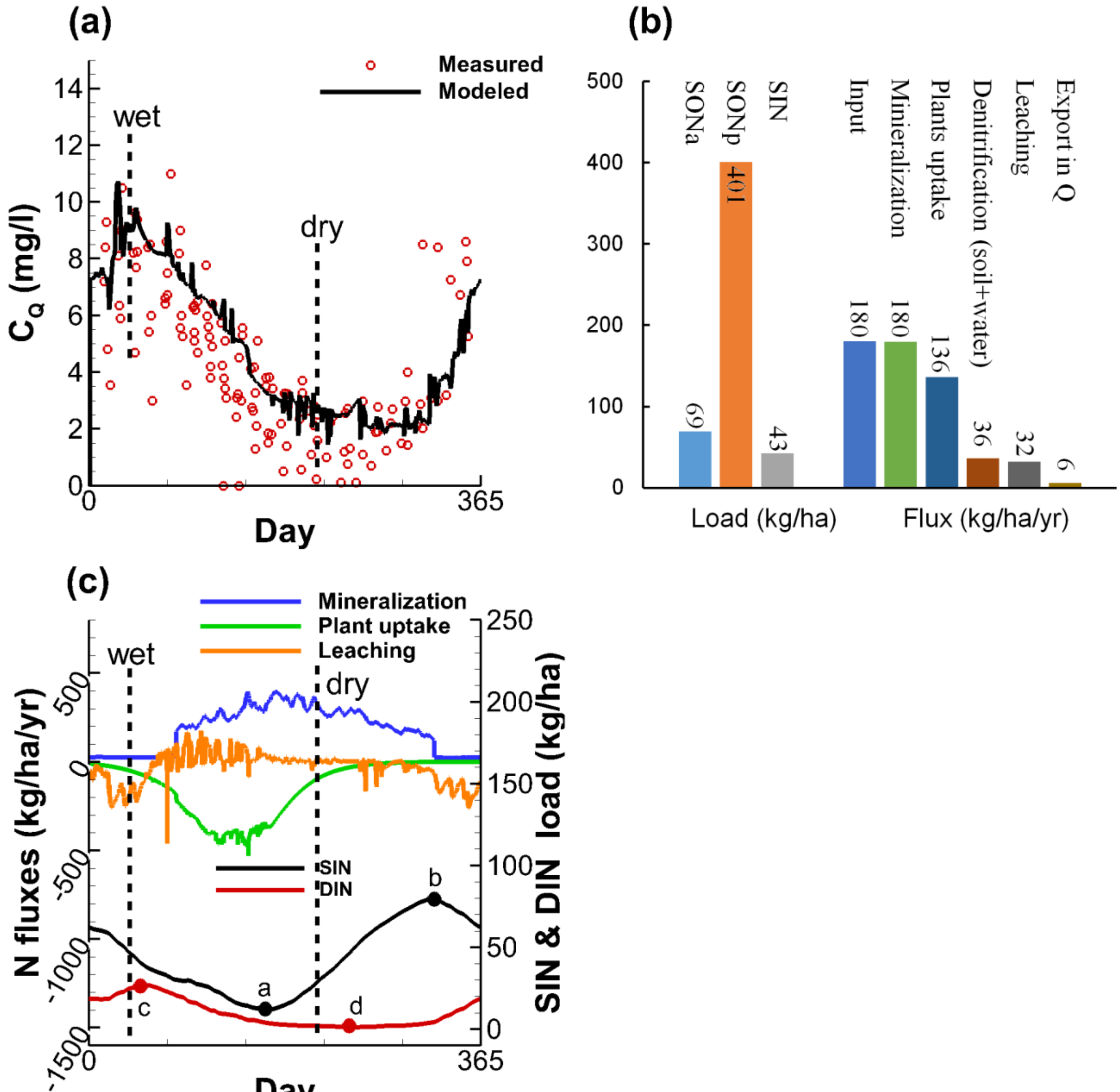


Figure 4. Simulated (a) In-stream nitrate concentration C_Q, (b) N loads and fluxes, and (c) time-variable N fluxes for the catchment of the base scenario. Note that the measured C_Q in (a) includes all the measurements from 2001 to 2010.

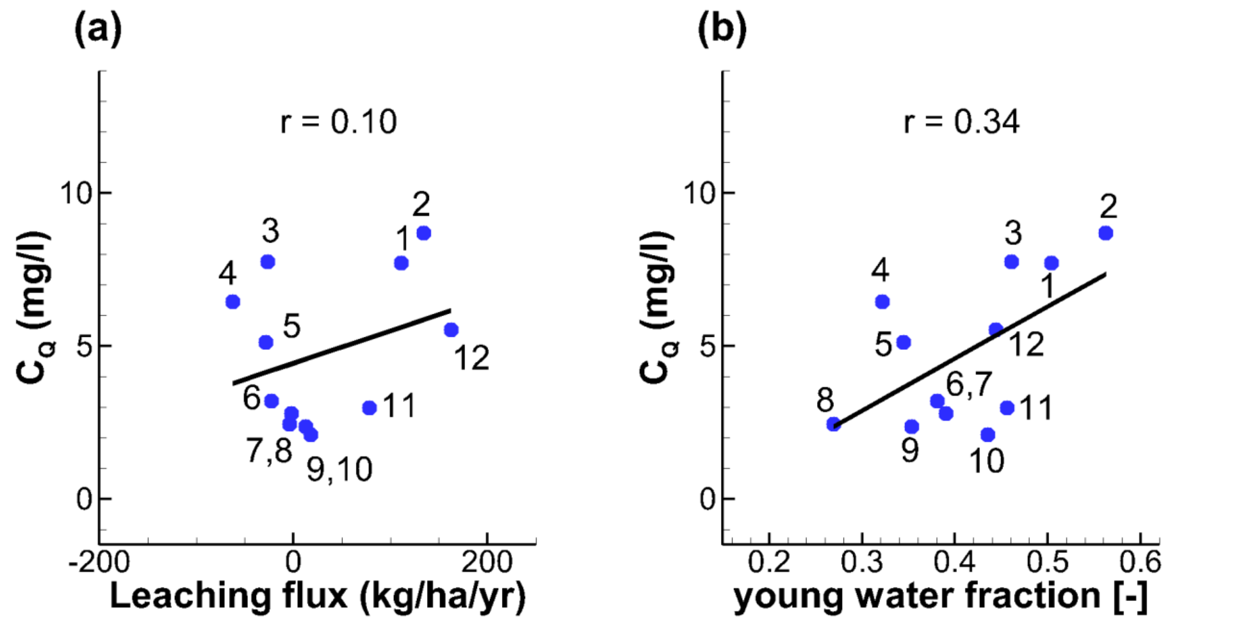
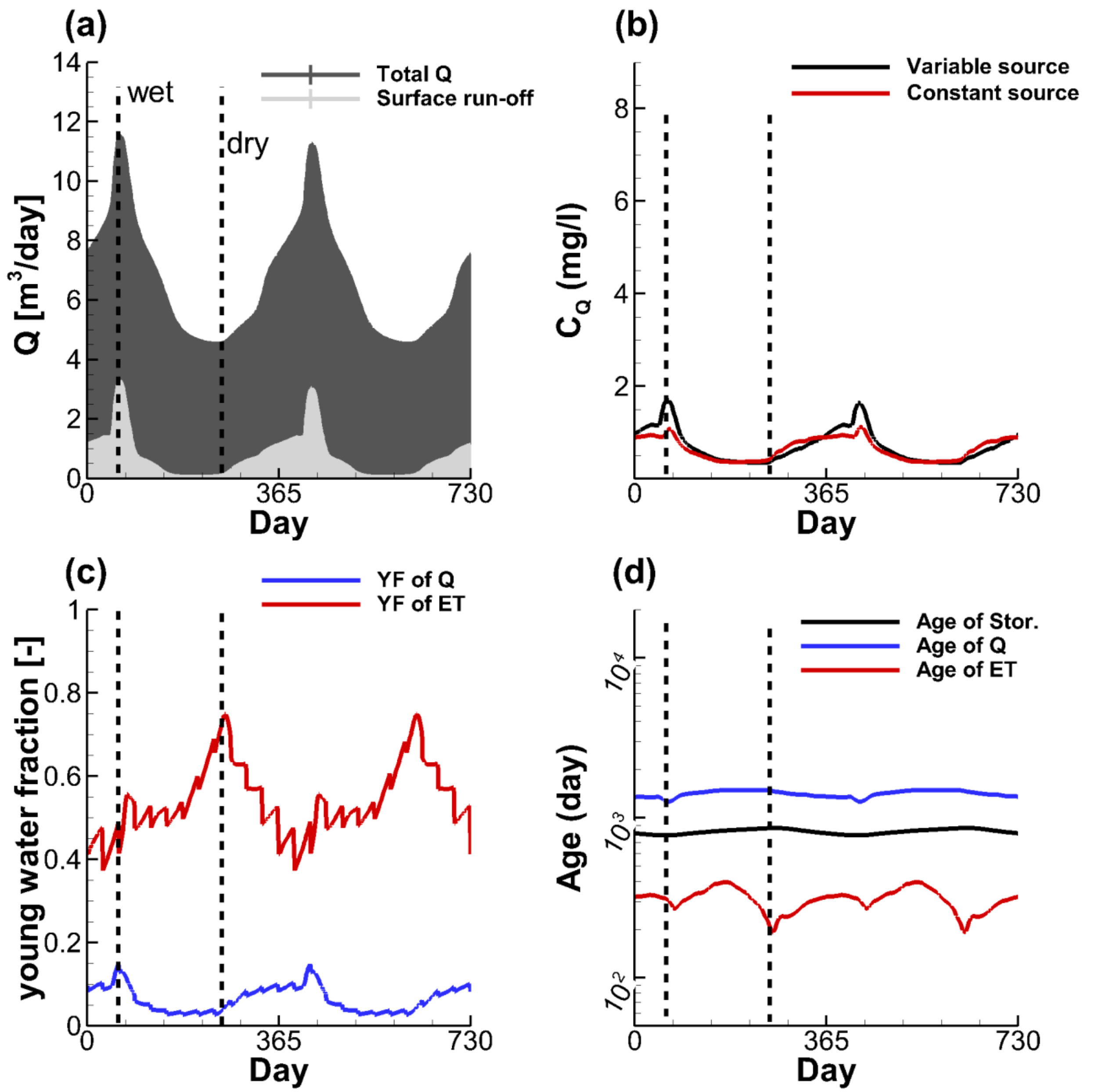


Figure 5. Comparing the monthly averaged C_Q with (**a**) the leaching flux and (**b**) the young water fractions of Q. The black lines are linear fits of the two variables~~ with linear relationship~~, with *r* being the Spearman rank-correlation coefficient. The numbers ~~are ~~refer~~red~~ to the months.



~~**Figure 3.** Simulated (**a**) Q, (**b**) in-stream nitrate concentration C_Q, (**c**) young water fractions YF_Q and YF_{ET}, and (**d**) water ages for the cross-sectional aquifer with topographic slope of 1:20.~~

4.2~~1~~ Effect of topographic slope on flow~~In-stream nitrate level~~

With the help of our simulations, it is possible to systematically explore the influence of topographic slope on the water flow and N fluxes~~concentrations of nitrate exported to the stream~~. Figure 6 shows ~~For each scenario with time-variant nitrate source concentration, we analyzed~~ the responses of temporally-averaged ~~mean~~ Q and ET, the groundwater table depth, and flow weighted mean YF_Q and YF_{ET} to the changes of top~~m~~ographic slope.~~C_Q, as well as the C_Q extracted at a wet time and a dry time (marked with the dashed line in Figure 3b).~~ Under a constant~~unchanged~~ climate, the changes of topographic slope can reshape the water flow via influencing flow partitioning between Q~~discharge~~ and ET. More water is taken up by ET and less water becomes~~by~~ Q in flatter landscapes (Figure 6a). These patterns can be explained by the change of groundwater table depth (Figure 6b), as shallower groundwater tables can be reached by the vegetation in flatter landscapes where ET therefore has a higher chance to remove water from the subsurface. The simulated YF_Q and YF_{ET} show generally increasing and decreasing patterns, respectively, when the topographic slope decreases (Figure 6c), demonstrating that young streamflow is more prevalent in flatter landscape and young ET is more prevalent in steeper landscapes. However, the increasing pattern of YF_Q ~~is~~does not continue~~pronounced~~ in ~~the~~ steep catchments with ~~the~~ slopes > 1:60. Topographic slope ~~has~~ changes~~d the~~ YF_Q not only in terms of its mean value, but also in terms of its~~the~~ temporal variation~~s~~. Figure 6d indicates that the maximum and minimum YF_Q are reached in February and August for the steepest catchment (slope 1:20), respectively, and~~however,~~ in November and April for the flattest catchment (slope 1:1000).

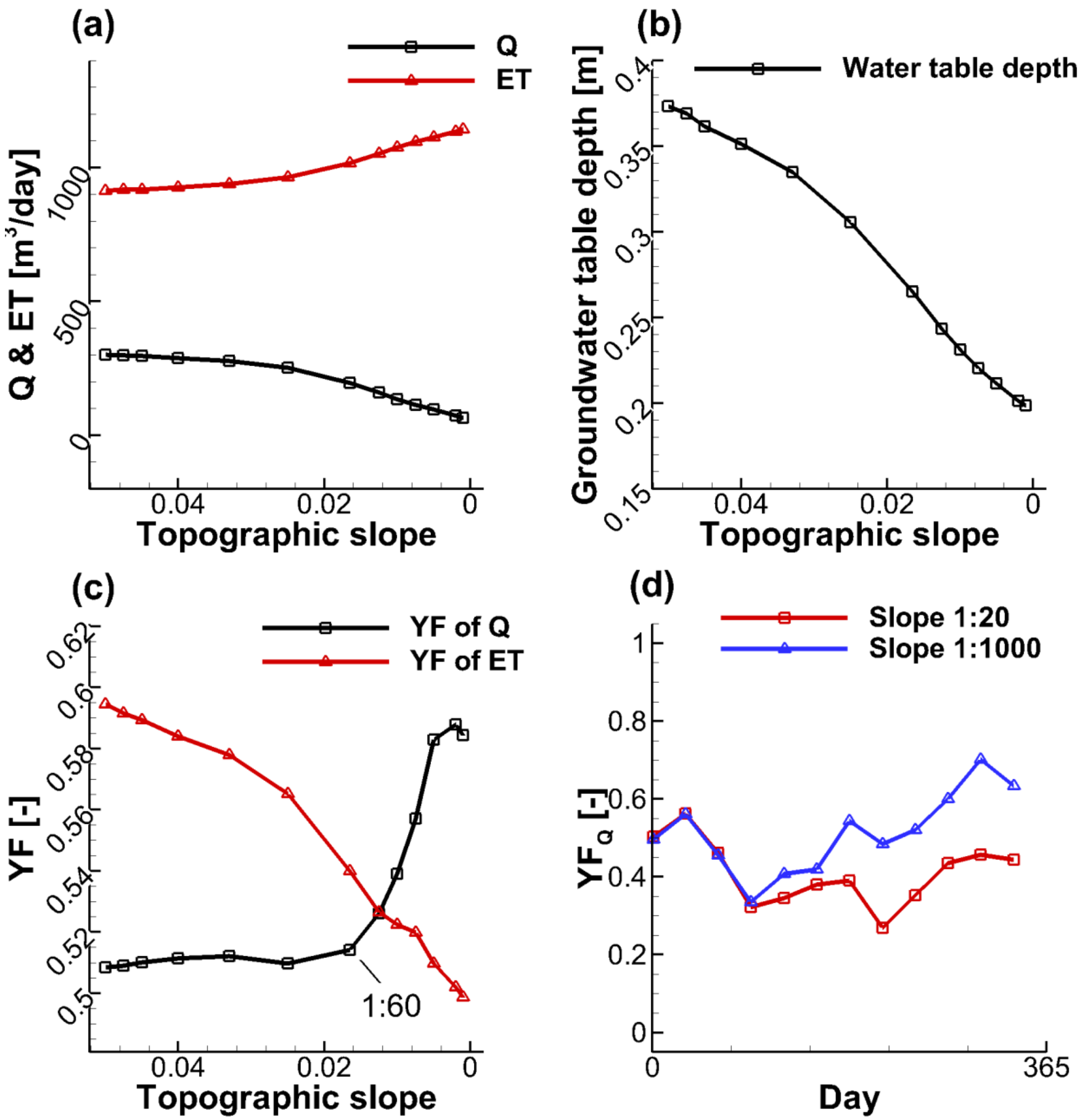


Figure 6. The simulated (**a**) Q and ET, (**b**) spatially-averaged depth of the groundwater table from the land surface, (**c**) young water fraction in streamflow YF_Q and evapotranspiration~~ET~~ YF_{ET}, in relation to the topographic slope for the simulated catchments. (**d**) ~~compares the~~ temporal variations of~~time variable~~ YF_Q ~~between~~for a steep landscape (slope 1:20) and a flat land scape (slope 1:1000).

I~~Mechanistically i~~nterpreting the ~~three-class~~ response of the YF_Q to topographic slope mechanistically requires a closer look at the flow processes using~~with~~ a~~in the~~ cross-sectional views~~s~~. We plotted the subsurface flow fields for the~~at~~~~for the~~ wet season at~~for the~~ a cross-section~~s~~ of the catchments with slopes 1:20 ~~, 1:60, 1:100,~~ and 1:1000 (Figure 7~~5~~).

~~(1) For C1 (slope 1:20 – 1:60),~~ Figure 7~~5~~a reveals that the hillslope part of the ~~aquifer~~ catchment with a slope of 1:20 is largely unsaturated so that the flow paths in this area are characterized by vertical infiltration ~~(Figure 5a)~~. In contrast, the valley bottom is fully saturated. Overall, 34% of the subsurface domain ~~(in volume)~~ is characterized by vertical flow (flow in 34% of the total aquifer volume is more vertical than horizontal). For this scenario two main discharge routes to the stream can be identified: (i) A fraction of the groundwater flows through the fully saturated zone and exits the aquifer to the stream, and (ii) another fraction exits the aquifer via seepage near to where the groundwater table intersects the land surface, indicated by a large exchange flux (from subsurface to surface, positive). The seepage represents a preferential flow path allowing for ~~rapid~~ discharge via overland flow instead of ~~slower~~ discharge via the sub-surface with longer transit times. Note that both of the discharge routes provide the pathways for the rainfall falling on the top hillslope to reach the stream.

When the slope is reduced to 1:1000, the flow pattern experiences significant changes (Figure 7b) compared~~ing~~ to ~~with~~ the catchment with a~~of~~ slope of 1:20.

~~(2) For C2 (slope 1:60 – 1:100), even though the groundwater table depth is still decreasing with decreasing slope, the flow pattern experiences a rapid change. The seepage flow vanishes because the groundwater table (fully or partially) disconnects from the land surface (Figure 5c). The water that would have flown to the stream via seepage has to take slower flow paths in the subsurface to the valley bottom. The surface run-off dropped significantly from 7.1 m³/day to 0.5 m³/day (Figure 5c, d). Basically, decreasing the topographic slope reduces the horizontal component of the hydraulic head gradients, which is obvious as part of the precipitation falls at lower elevations instead of farther up the hillslope. The reduced head gradient generally slows down the groundwater flow velocity.~~

Several hydrologic studies have described two different flow systems in aquifers: (i) a recharge-limited system where the thickness of the unsaturated zone is sufficient to accommodate any water-table rise and thus the elevation of the groundwater table is limited by the recharge, and (ii) a topography-limited system where the groundwater table is close or connected to the land surface such that any fluctuation in groundwater table can result in considerable change in surface runoff [*Werner and Simmons*, 2009; *Michael et al.*, 2013]. In the selected cross sections~~our study~~, the steeper one (slope 1:20) ~~aquifer of C1~~ is a partially topography-limited system (~~e.g.~~ Figure 7~~5~~a~~, b~~) (the hillslope is recharge-limited while the valley bottom is topography-limited). ~~In C2~~The flat one (slope 1:1000) ~~the aquifer~~ is transformed into a fully recharge-limited system (from Figure 7~~5~~b~~ to 5c~~) due to the reduced hydraulic head gradients. This transformation leads to three main effects: (i) The seepage flow vanishes because the groundwater table disconnects from the land surface. The seepage route that would discharge water from the top of hillslope to the stream is cut off, ~~This transformation switches off the preferential flow paths via seepage to the land surface and significantly reduces the YF_Q.~~

~~Reducing the topographic slope to 1:60 does not significantly change the flow pattern (Figure 5b). However, the spatially averaged depth of the groundwater table is reduced from 1.5 m to 0.8 m (Figure 4d). This change leads to two main effects:~~ (ii~~i~~) the infiltration processes is weakened, indicated by the fact that the portion of subsurface domain characterized by vertical flow is reduced from 34% to 18~~22~~%, and (iii~~(ii~~) ~~the shallow subsurface flow processes, such as seepage, are promoted, increasing the amount of water taking the short shallow flow paths in the system. This is proved by that the portion of streamflow generated by surface run-off increased from 3.2 m^3/day to 7.1 m^3/day (Figure 5a, b).~~

~~Subsequently, the contribution of young water to streamflow significantly increases when the slope decreases from 1:20 to 1:60, also supported by the computed TTDs (Figure 6a). Given that the groundwater storage significantly increases with decreasing slope, this effect is similar to the "inverse storage effect" that has been described in *Harman*, [2015] as the relative contribution of young water to stream flow increasing with increasing storage. *Kim et al.*, [2016] also reported based on their lysimeter experiments that younger water was discharged in greater proportion under wetter conditions compared to drier conditions. However, the observed changes in groundwater table depth (thus storage) in our study were caused by topography rather than by climate.~~

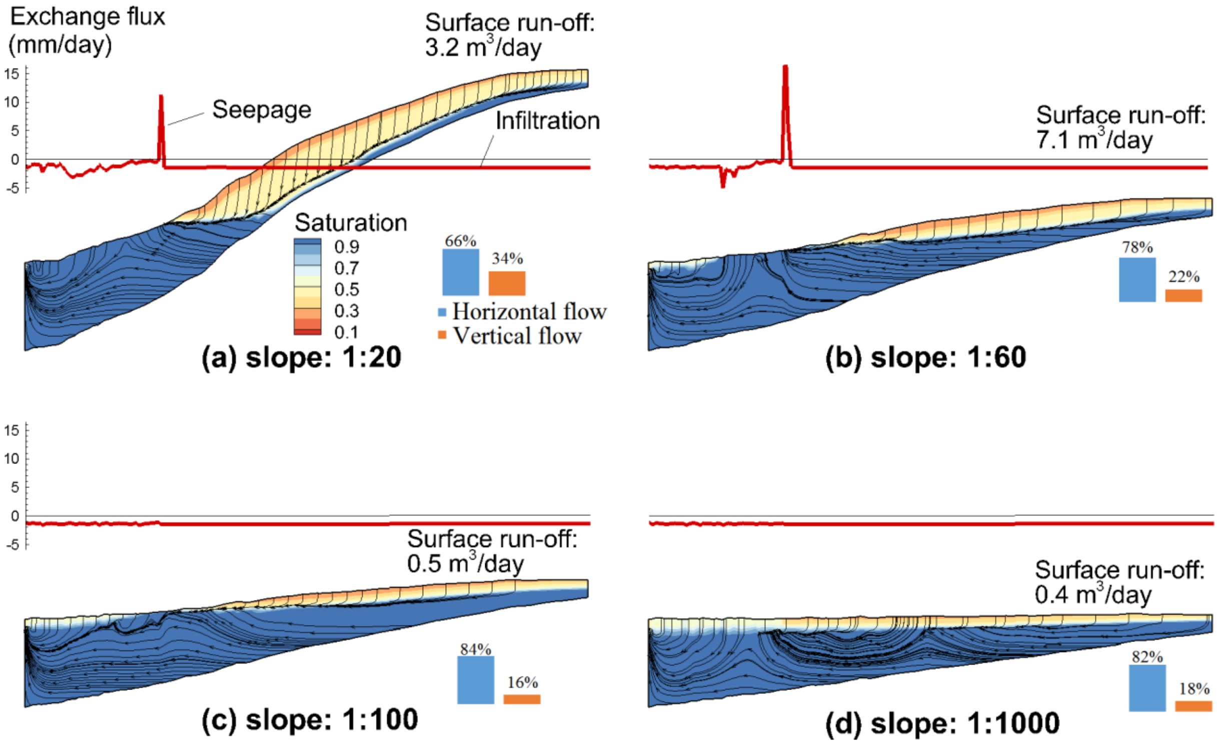
~~-~~**~~(3) For C3~~** ~~(slope 1:100 – 1:1000), the aquifer is fully recharge-limited without any preferential flow via land surface. Further reducing the topographic slope to 1:1000 mainly changes the spatial distribution of the unsaturated zone (comparing Figure 5d with 5c). Because the groundwater table depth (thus the storage) more or less remains unchanged (Figure 4d), interestingly, here the "inverse storage effect" does not apply anymore and cannot explain the increase of the~~ ~~YF_Q~~ ~~when the topography becomes flatter.~~

~~However, on flatter landscapes,~~ local flow cells are more likely to form, where water infiltrates to the aquifer and eventually exits the aquifer via ET rather than via flow to the stream (Figure 7~~5~~b~~d~~, the local flow cells are more pronounced in the dry season, see Figure S3~~1-~~b~~d~~ in the supporting information).

Because of the three aforementioned~~ three~~ effects~~Simply put~~, the connectivity between the stream and the more distant hillslopes is significantly reduced. P~~p~~recipitation falling farther from the stream has a lower chance to reach the stream and a higher change to be intercepted by ET on its way to the stream~~, because~~ ~~.the~~ The hillslope that used to generate old streamflow does not contribute to streamflow anymore. ~~flow velocity is much lower due to the smaller horizontal component of hydraulic head gradient.~~ While precipitation water close to the stream has a higher chance to contribute to streamflow. We ~~hypothesize~~ concluded that the increase of the YF_Q~~,~~ in flat landscapes ~~as indicated by the computed TTDs (Figure 6b),~~ is due to this reduction of the longer flow paths and the persistence of shorter flow paths, as indicated by the computed TTDs (Figure 7c).~~.~~

~~To further verify our hypothesis, we mapped the land area contributing to the streamflow (streamflow generation zone) using a particle tracking algorithm in HydroGeoSphere [*Yang et al.*, 2018]. Figure 7 demonstrates the streamflow generation zone in February for the slope 1:100 and 1:1000, respectively. For the aquifer with a slope of 1:100, the zone extends further into the hillslope, with relatively younger streamflow generated close to the stream and old~~

~~streamflow (i.e. age > 5 years) generated further up the hillslope. When the slope is reduced to 1:1000, the streamflow generation zone is much closer to the stream. The hillslope that used to generate old streamflow does not contribute to streamflow anymore. This means that in flatter landscapes, the evolution of local flow cells reduces the connectivity between the stream and the more distant hillslopes by intercepting the longer flow paths at the land surface before they can reach the stream (Figure 7b), leading to an increase in the YF_Q. We refer to this as the "local flow cells effect".~~


Exchange flux
(mm/day)
Surface run-off:
3.2 m³/day
Seepage
Infiltration
Saturation
0.9
0.7
0.5
0.3
0.1
66%
34%
Horizontal flow
Vertical flow
(a) slope: 1:20
Surface run-off:
7.1 m³/day
78%
22%
(b) slope: 1:60
Surface run-off:
0.5 m³/day
84%
16%
(c) slope: 1:100
Surface run-off:
0.4 m³/day
82%
18%
(d) slope: 1:1000

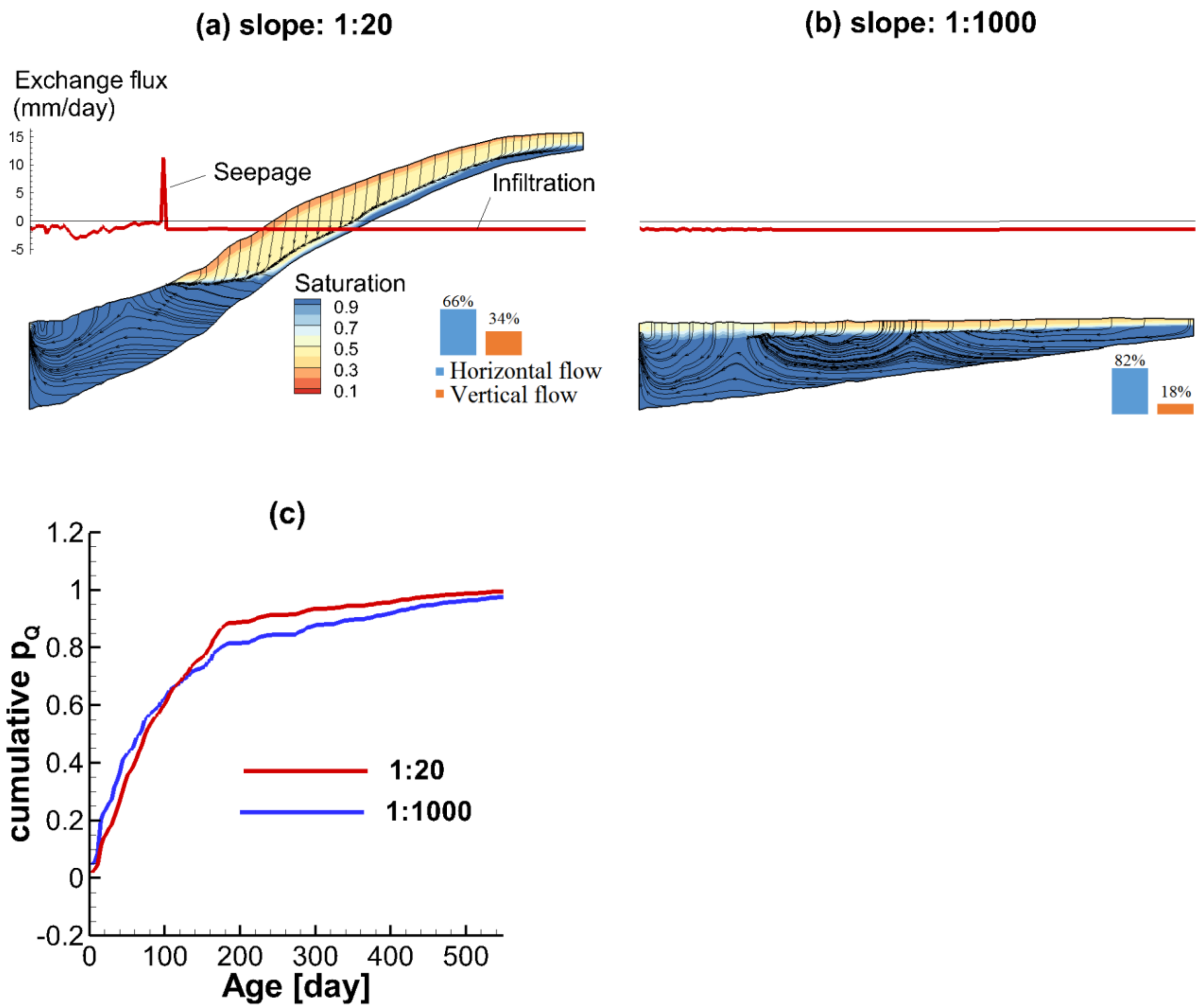
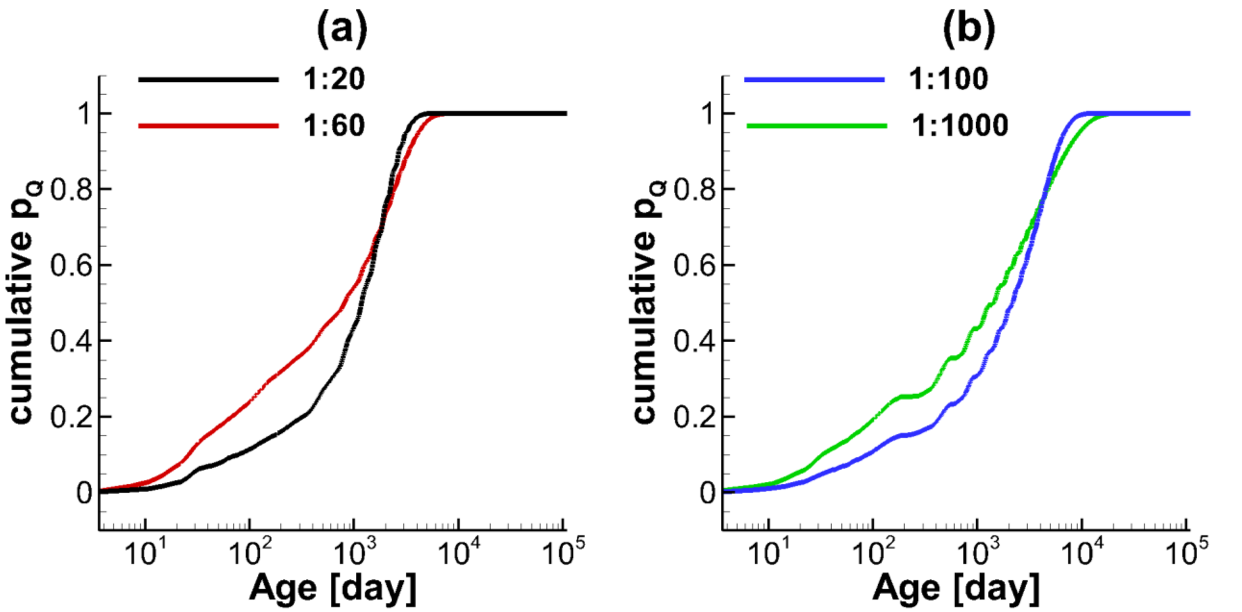
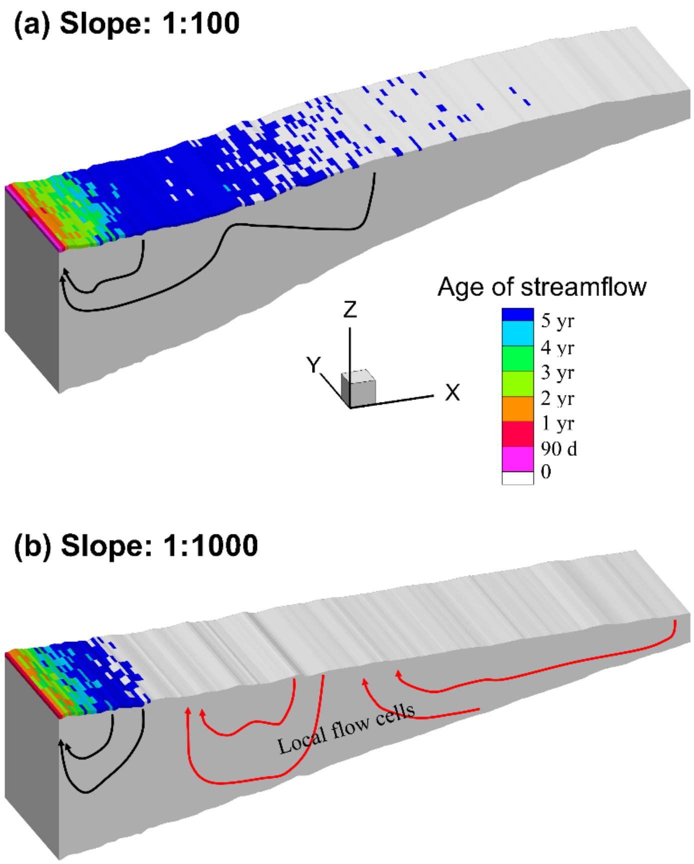


Figure 7~~5~~. ~~The c~~Cross-sectional view of~~for the distributions of~~ saturation, flow paths, and exchange fluxes between the surface and the subsurface in the wet season (February) for ~~for the~~ catchments~~aquifer~~ with topographic slope (**a**) 1:20, and ~~-~~(**b**) ~~1:60, (c) 1:100, and (d)~~ 1:1000. The cross-section is marked in Figure 1a. ~~-~~The black lines represent the flow paths. The red curves show exchange fluxes (along the cross-sectional profiles), positive values indicate seepage to the land surface and negative values indicate infiltration to the subsurface. (**c**) The computed cumulative TTDs for Q during the wet season (February), for the catchment with topographic slope of 1:20 and 1:1000.



~~**Figure 6.** The computed cumulative TTDs for Q during the wet season (February), for the cross-sections with topographic slope of (**a**) 1:20 and 1:60, and (**b**) 1:100 and 1:1000.~~



~~**Figure 7.** Maps showing the land areas that contribute to streamflow via subsurface flow through the aquifer with topographic slopes of **(a)** 1:100 and **(b)** 1:1000. The color indicates the age of the streamflow. Black lines indicate the flow paths to the stream, and red lines indicate the local flow cells that are not connected to stream.~~

In summary, we identified a generally increasing pattern of YF_Q~~the young stream flow fraction~~ in response to the decreasing topographic slope. ~~three classes for the response of in-stream concentrations to topographic slope under a humid climate.~~ When the landscape becomes flatter, the hydraulic head gradient as the main driving force~~,~~ changes the aquifer from a partially topography-limited system ~~with preferential overland flow (C1)~~ to a recharge-limited system that is more likely to form local flow cells~~(C3)~~. ~~For the aquifer of C2, which is a transitional class between C1 and C3, YF_Q and nitrate concentrations experience a sharp drop once the preferential overland flow paths cannot be maintained. For the aquifer of C1 (or C3), decreasing slopes tend to generate a higher fraction of young streamflow and export nitrate at higher concentrations. However, the former is dominated by the "inverse storage effect" while the latter is dominated by the "local flow cells effect". In this sense, the response of in-stream concentrations to topographic slope is threshold-like rather than monotonous.~~

4.3 Effect of topographic slope on N export

Simulated results show that the topographic slope can influence~~s~~ the N loads and fluxes in ~~the~~ catchments. Figure 8a demonstrates that ~~the~~ SIN tends to be higher in flatter ~~landscape~~ and lower in steeper landscapes. This generally indicates that a~~the~~ flat landscape has a higher potential to retain ~~the~~ N in the soil. However, the DIN is not significantly influenced by the topographic slope. N fluxes of leaching and export to the stream exhibit the opposite pattern. For the N fluxes, the leaching into groundwater decreases with the decrease of topographic slope (Figure 8b). This is mainly because the flow velocity (influencing the~~e~~ leaching rate according to equation 6) in flatter landscape is lower due to the reduced hydraulic head gradient. Comparing the time-variable leaching between the steepest and flattest catchments (slope 1:20 and 1:1000, Figure 8c), it can be observed that the leaching reduction in the flatter landscape mainly occurs in the wetting period (Nov to Dec). This may be because ~~that~~ the responses of flow velocity in the flatter catchment is not as large as that in the steeper catchment when the system transitions from dry to wet conditions. A l~~L~~arge portion of the leached~~ing~~ N mass has been degraded during transport in the groundwater, with the fraction~~partition~~ rising from 80% in~~at~~ the steepest landscape to 95% in~~at~~ the flattest landscape (Figure 8b). Mechanically, the reduced connectivity between the stream and more distant hillslopes in flatter landscapes inhi~~a~~bits the N export to the stream ~~and~~ promoting the degradation by increasing the N residence time in the catchment. Subsequently, the N export shows a decreasing pattern with the decrease of topographic slope (Figure 8b).

~~Figure 4a~~ The calculated flow-weighted ~~shows that the~~ mean C_Q shows a decreasing trend in respon~~d~~se to the decreasing~~changes in~~ topographic slope (Figure 8d)~~: (1) the mean C_Q increases when the topographic slope decreases from 1:20 to 1:60, (2) the mean C_Q drops sharply when the topographic slope further decreases to 1:100, and (3) the mean C_Q increases again when the topographic slope decreases from 1:100 to 1:1000.~~, from 7.3 mg l^{-1} in~~at~~ the steepest catchment ~~and~~ to 4.2 mg l^{-1} in~~at~~ the flattest catchment. Even though both ~~of~~ Q and N export show decreasing patterns with the decrease of topographic slope, the N export decreases to a higher~~more in~~ degree than Q, indicated by the~~ir~~ normalized values (Figure 8e). Comparing the time-variable C_Q between the steepest and flattest catchments (slope 1:20 and 1:1000, Figure 8f), it can be observed that the topographic slope influences~~has reshaped~~ the C_Q in two~~fold~~ ways: (i) The C_Q is generally lower (but not always) in the flatter landscape over most of the time in a year, and (ii) the high peaks of C_Q in flatter landscapes are~~is~~ delayed in time. However, ~~both of~~ the high concentrations always occur in the wet periods (Jan – Apr) and low concentrations always occur in the dry periods (Jul – Oct). ~~The maximum and minimum values are reached at topographic slopes of 1:60 and 1:100, respectively, rather than in the flattest or steepest landscapes. According to the distinct responses within different ranges of topographic slopes, we sorted the virtual catchments into three classes in terms of the mean topographic slopes of the aquifer (or the landscape) as follows (Figure 4a):~~

~~**C1**, with topographic slope in the range [1:20 – 1:60]~~

~~**C2**, with topographic slope in the range [1:60 – 1: 100]~~

~~**C3**, with topographic slope in the range [1: 100 – 1: 1000]~~

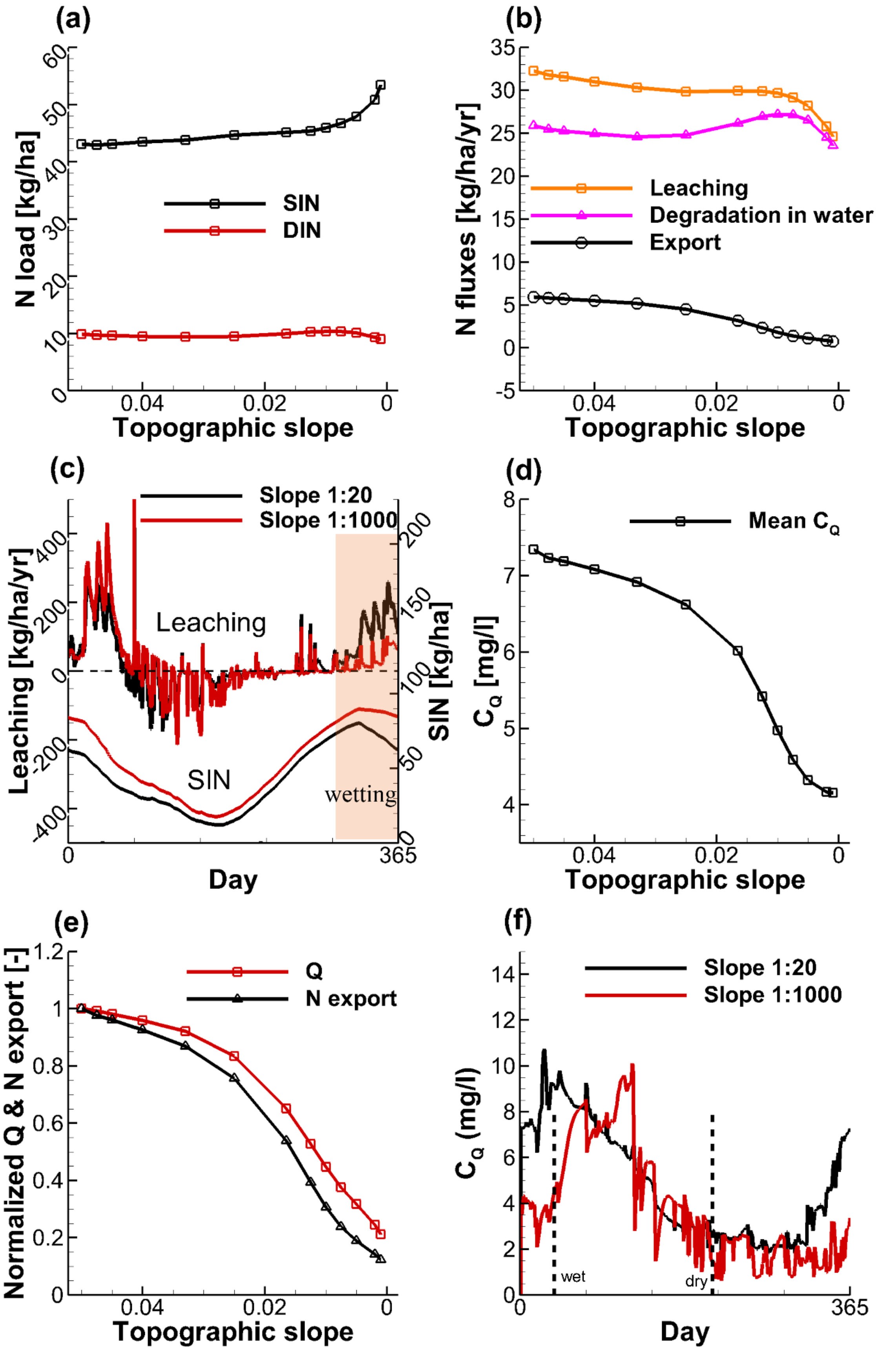
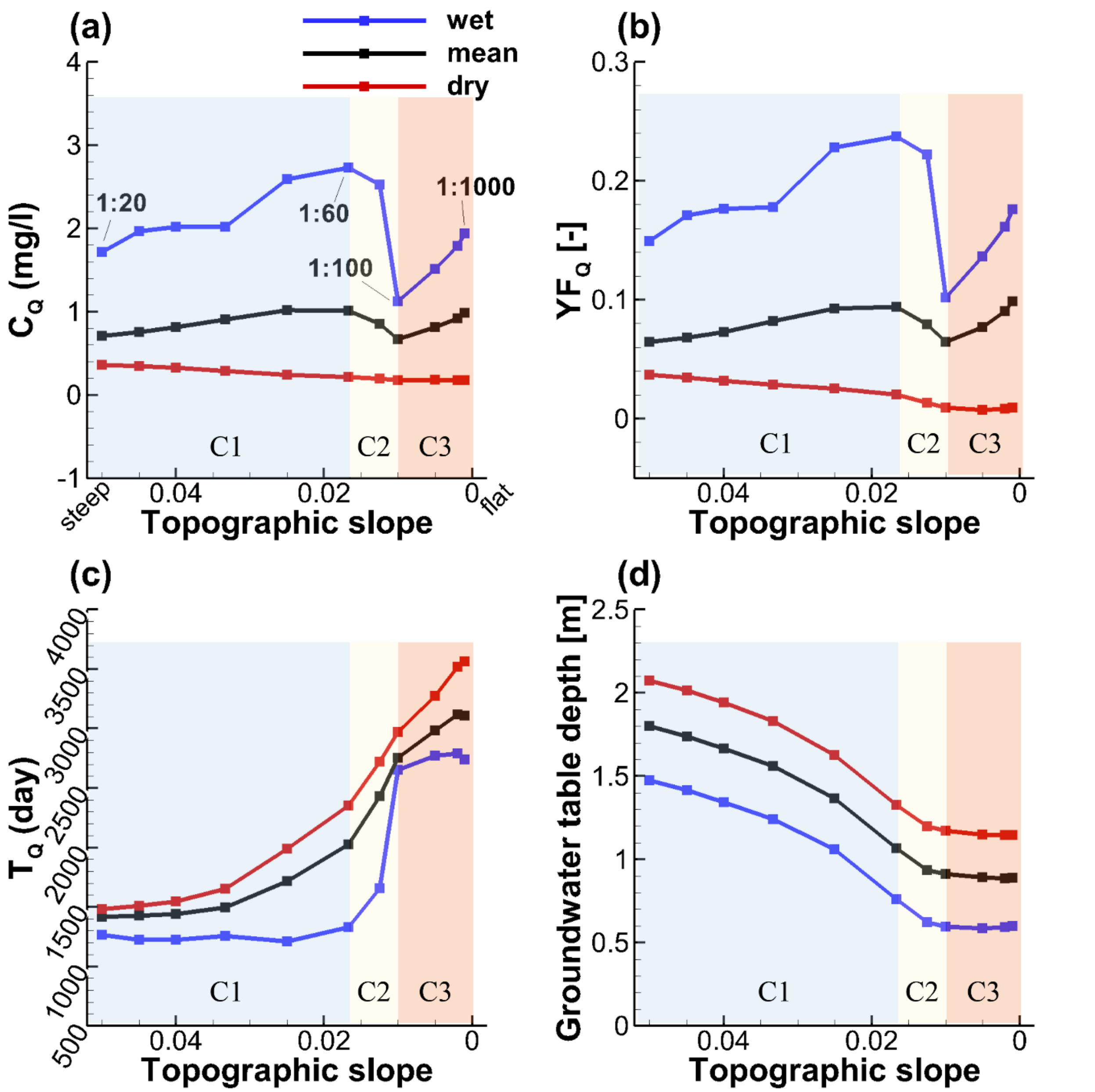

(a)
N load [kg/ha]
SIN
DIN
Topographic slope
(b)
N fluxes [kg/ha/yr]
Leaching
Degradation in water
Export
Topographic slope
(c)
Slope 1:20
Slope 1:1000
Leaching [kg/ha/yr]
SIN [kg/ha]
Leaching
SIN
wetting
Day
(d)
Mean C_Q
C_Q [mg/l]
Topographic slope
(e)
Normalized Q & N export [-]
Q
N export
Topographic slope
(f)
Slope 1:20
Slope 1:1000
C_Q (mg/l)
wet
dry
Day

Figure 8. The simulated (**a**) N loads, (b) N fluxes in relation to the topographic slope for the simulated catchments. (**c**) C~~c~~omparison of~~es~~ the time variable N loads and fluxes between a steep ~~landscape~~ (slope 1:20) and a flat land scape (slope 1:1000). The simulated (d) flow-weighted mean C_Q, and (e) the normalized Q and N export (normalized to their values of the base scenario) in relation to the topographic slope. (**f**) C~~c~~omparison of~~e~~ the time variable C_Q between a steep ~~landscape~~ (slope 1:20) and a flat land scape (slope 1:1000). Note that for the leaching fluxes in **(c)**, positive values are referred to as the N leaching from the soil to the groundwater, negative values are referred to as the precipitation of N from g~~mou~~roundwater to the soil by the evapoconcentration effect. The vertical dashed lines indicate the time when the catchment reaches the wettest (left) and the driest (right) conditions.

~~A similar three-class response can be observed for the wet-time C_Q (blue line in Figure 4a), it is even more pronounced than the one for the mean C_Q. The dry-time C_Q decreases linearly from steeper to flatter landscapes, not exhibiting specific classes. The effect of topographic slope on C_Q is hence dominated by the wet season response as most of the discharge was produced during the wet season. The response pattern of the YF_Q is highly identical to the C_Q response patterns, also showing a three-class response (Figure 4b). This indicates that the topographic slope influences the C_Q levels via changing the young water fraction. Figure 4c demonstrates that the discharge age T_Q tends to be younger in steeper and older in flatter landscapes, especially during the dry season. This pattern did not show any correlation to the response of C_Q, thus suggesting that discharge age T_Q is not the most valuable predictor of C_Q.~~

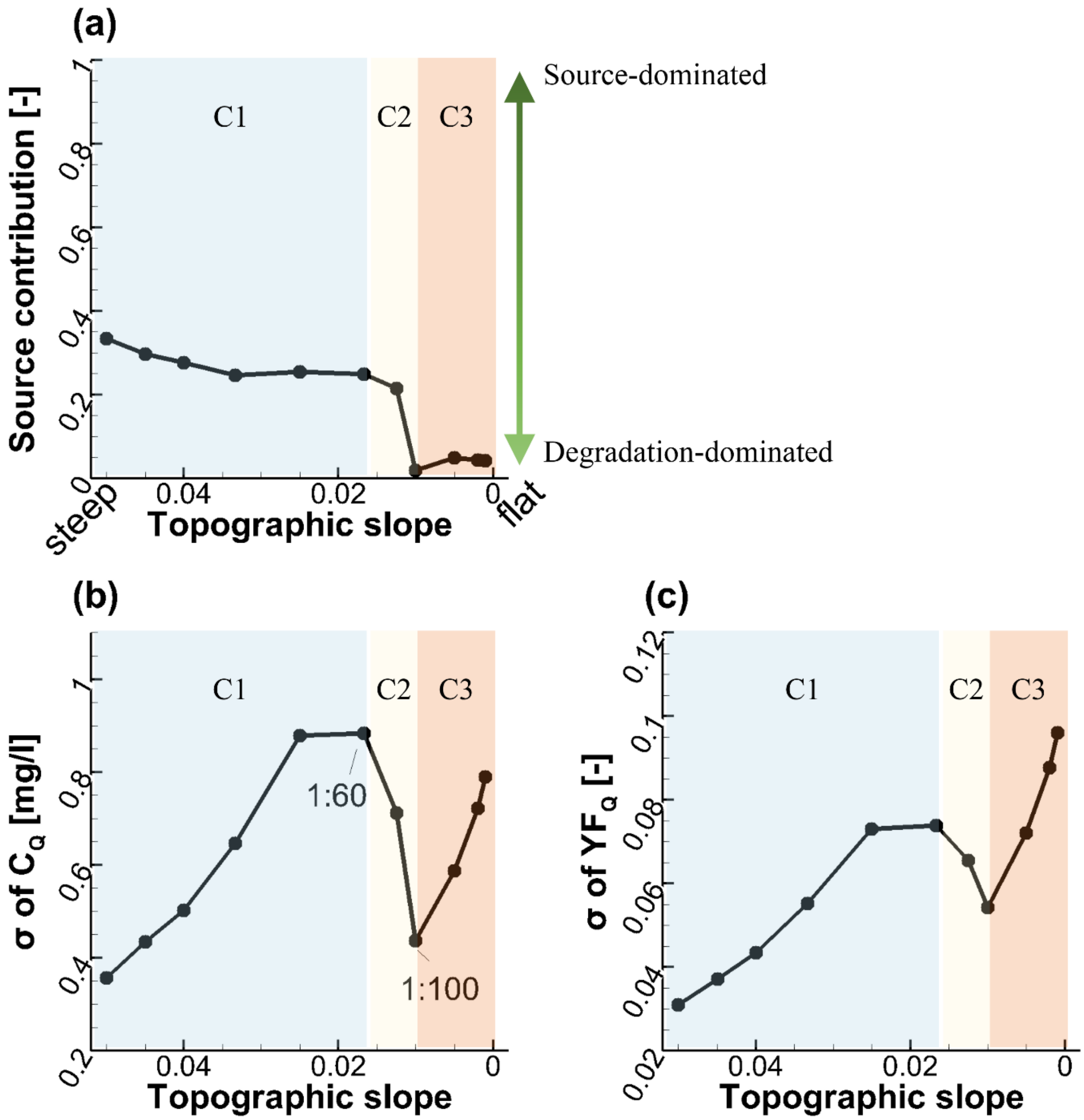
~~Subsequently, the contribution of young water to streamflow significantly increases when the slope decreases from 1:20 to 1:60, also supported by the computed TTDs (Figure 6a). Given that the groundwater storage significantly increases with decreasing slope, this effect is similar to the "inverse storage effect" that has been described in *Harman*, [2015] as the relative contribution of young water to stream flow increasing with increasing storage. *Kim et al.*, [2016] also reported based on their lysimeter experiments that younger water was discharged in greater proportion under wetter conditions compared to drier conditions. However, the observed changes in groundwater table depth (thus storage) in our study were caused by topography rather than by climate.~~



~~**Figure 4.** The simulated (**a**) in-stream concentration C_Q, (**b**) young water fraction in streamflow YF_Q, (**c**) discharge age T_Q, and (**d**) spatially-averaged depth of the groundwater table from the land surface, in relation to the topographic slope for the simulated cross-sections. The temporal mean, the dry time value and the wet time value of these variables were plotted. C1, C2 and C3 represent the landscape classes 1, 2, and 3, respectively.~~

~~The response of the source contributions to topographic slope is threshold-like (Figure 8a): the source contributions in C1 were significantly higher than the ones in C3. Especially for the landscapes of C3, the fluctuation of C_Q was hardly impacted by source variability. Mechanically, the seasonal source fluctuation is more likely to be damped by relatively longer transit times in C3 landscapes, which are relatively flat.~~

~~Given that the seasonal C_Q variation can be attributed more to the variation in transit times (thus to the variation in the YF_Q), it was expected that the standard deviations of C_Q and YF_Q (Figure 8b, c) had similar responses to the topographic slope. Both of the responses exhibit a threshold-like pattern, similar to the response of the mean C_Q (Figure 4a). This is because C_Q during the dry season is generally low, regardless of whether the landscape is steeper or flatter. The overall response of $\sigma(C_Q)$ to topographic slope is determined by the response of the relatively high C_Q during the wet season, and can be interpreted in the same three-class pattern: $\sigma(C_Q)$ increases with the decrease of slope within C1 (or C3), suggesting that flatter landscapes tend to export nitrate with more seasonal fluctuations in C_Q for C1 (or C3). However, for C2, a significant drop in this fluctuation can be expected when the landscape transforms from C1 to C3. As a result, the maximum seasonal variation was reached at the slope of 1:60. For the mechanistic interpretation please refer to section 4.1.~~



~~Figure 8.~~ ~~The calculated~~ **~~(a)~~** ~~source contribution to the variation of in-stream concentration C_Q,~~ **~~(b)~~** ~~σ of C_Q,~~ **~~(c)~~** ~~σ of YF_Q. C1, C2 and C3 represent for the landscape classes 1, 2, and 3, respectively.~~

4.4~~3~~ Discussion

Jasechko et al., [2016] reported that (the logarithm of) catchment topographic slope was significantly negatively correlated with young streamflow fractions with a spearman rank correlation of -0.36. This conclusion was made statistically based on their observed 254 sites. Our numerical study based on the eleven ~~cross-sectional aquifers~~catchments with different slopes but identical climate conditions resulted in more physically-based information that goes beyond such statistical correlations. Our results confirm~~show~~ that young streamflow fraction and slope generally exhibit~~possess~~ a -negative correlation~~threshold-like three-class relation instead of a monotonous relation~~. Additionally, our results show that the young water fraction in ET is positively correlated with the slope. ~~The negative correlation between slope and young streamflow fraction can be found in slope classes C1 and C3, but not in the slope class C2.~~

~~For~~ From the steepest landscape to the flattest landscape, ~~the landscapes of the C1 class,~~ catchments are likely to transition from a ~~form a~~ partially topography-limited flow system to a recharged limited system,~~with preferential flow paths~~ due to ~~the~~ the reduction of ~~relatively high~~ hydraulic gradient. The g~~G~~roundwater table ~~level~~ ~~storage~~ is ~~more~~ closer to the land surface~~larger~~ when the landscape becomes flatter. The larger~~higher~~ young streamflow fraction in flatter landscapes ~~The "inverse storage effect" explains the increases of young streamflow in flatter landscapes during the wet season. This~~ is consistent with the statement made by *Jasechko et al*.~~,~~ [2016] that~~as~~ the young streamflow fraction is more prevalent in flatter catchments which are characterized by more shallow lateral flow and less vertical infiltration. This phenomenon is also consistent with a negative correlation between groundwater table depth and young streamflow fraction, which has been frequently reported [*Bishop et al., 2004; Seibert et al., 2009; Frei et al., 2010; Jasechko et al., 2016*]. Using the insight into the flow processes of the catchment, we found that the connectivity between the stream and the more distant hillslopes is reduced in flatter ~~For~~ landscape, due to the reduced~~vanished~~ seepage flow, the weakened infiltration and the formation of local flow cells~~s~~ that do not deliver flow~~reach~~ to the stream.~~of the C3 class, the negative correlation between young streamflow fraction and slope was also confirmed. However, here, the "inverse storage effect" fails to explain this correlation because neither the groundwater storage nor the groundwater table depth undergo any significant change.~~ Our study points ~~at~~ out that the ~~the~~ reduction of this connectivity, which results in the reduction of the longer flow paths and the persistence of shorter flow paths, ~~formation of local flow cells that do not reach the stream~~ causes~~ing~~ the increase of the young streamflow fraction.

~~This phenomenon has not yet been reported to the best of our knowledge. However, for landscapes of the C2 class, our results suggest that young streamflow can be more prevalent in steeper landscapes with active preferential overland flow paths than in flatter landscapes with the fast preferential flow paths deactivated. This trend violates the otherwise negative correlation between topographic slope and young streamflow fraction. In this sense, the negative correlation between catchment topographic slope and young streamflow fraction is not conclusive.~~

Basically, the position of the groundwater table, flow path lengths and flow velocities, which are all different for different topographic slopes, jointly affect the young streamflow fractions~~ and nitrate export concentrations~~. Besides that, temporal variability of these three factors drives the distinct responses of the young streamflow fraction to topographic slope between seasons. In our simulated catchments, the negative correlation between young streamflow fraction and topographic slope is ~~For example, the three-class response is~~ more pronounced in the flat landscapes with slopes < 1:60~~ wet winter than in the dry summer~~. This demonstrates that the system is complex and apparently contains various threshold effects disturbing a straightforward monotonous relationship between ~~any~~ catchment characteristics (e.g. slope) and young water fraction (or streamflow concentration). In this sense, systematically investigating the reaction of the flow dynamics to catchment characteristic is necessary, rather than assuming a straightforward cause-effect relationship that can be misleading.

Our results demonstrate that stream water quality is potentially ~~more~~ less vulnerable in flatter landscapes ~~when the compared catchments have consistent flow patterns (e.g., both are C1 or C3 aquifers)~~. The flatter landscapes tend to retain~~preserve~~ more N mass in the soil and export less N mass ~~in~~to the stream. This~~ese~~ behavior~~s~~ can be~~are~~ attributed to (i) the reduced leaching in flat landscapes since~~as~~ the decreased flow velocity physically reduces the potential of water to solve and transport~~wash~~ the solute, and (ii) the increased potential of degradation because~~as~~ the connectivity between the stream and hillslope is blocked (i.e. there is more time for decay). ~~The~~ Our results also show that higher C_Q is more prevalent in steeper landscapes. Note that this is concluded for~~in the perspective of~~ average concentrations. Observations from the Selke catchment, central Germany show~~s~~ that the C_Q is not always lower in ~~the~~ flatter ~~lower~~ regions [*Dupas et al.*, 2017; Nguyen *et al.*, 2022]. In the future m~~M~~ore attention should be paid to the temporal variation and the time-scale concerning the effect of topographic slope on C_Q. Additionally, our results show that we can expect lower C_Q and higher young streamflow fractions in flatter landscapes ~~is where lower C_Q and higher young streamflow fraction are expected~~. This ~~highlight~~ suggests ~~th~~that, ~~concerting~~ with regard to the N transport in catchments, a large~~high level of~~ young streamflow fraction~~s~~ is not sufficient for high levels of C_Q. This phenomenon has not yet been reported to the best of our knowledge.~~e importance of fast preferential flow on exporting the young water and nitrate. In mountainous central German catchments, these groundwater seepages to the land surface can be frequently observed. They can be identified as "hot spots" allowing for the export of nutrients with higher concentrations. This suggests that more attention should be paid to catchments with "hot spots" concerning the management of stream water quality and agricultural activity.~~

Concerning the seasonal variations of ~~nitrate export~~ C_Q, our results showed that significant seasonal variation can be expected under ~~such~~ temperate humid climates regardless of topographic slope. T~~t~~he high peak concentrations occurred in the wet and the low in the dry seasons, being consistent with the findings of previous studies [*Benettin et al.* 2015; *Harman*, 2015; *Kim et al.*, 2016; *Yang et al.*, 2018]. However, the topographic slope can slightly shift the high peak concentrations in time.

~~The lowest concentrations were hardly affected by topographic slope, therefore the magnitude of seasonal variations depended on how high the C_Q rises during the wet seasons. This indicates that, for similar catchments in temperate humid climates, a high mean in-stream concentration level also means a high seasonal variation. The source contribution to seasonal variations is higher for C1 landscapes (> 0.2) than for C3 landscapes (almost zero). This implies that changes in the nitrate source input due to, e.g., changing crop type, land use or fertilizer application amount, are more likely to cause a detectable short-term (e.g. seasonal) response of the in-stream concentration for mountainous catchments. For flat landscapes, this response would be weaker.~~

4.5~~4~~ Limitations and outlook

The cross-comparison between ~~cross-sectional aquifers~~catchments with differing topographic slopes provides physically-based insights into the effects of topographic slope on nitrate export responses in terms of N fluxes and mean concentrations ~~level and seasonal variations~~. However, this study is limited in scope in that it neglects other factors that may also have important impacts on the young streamflow and nitrate export processes:

First, ~~the~~ our study only considered the ~~modeled cross-sectional~~ aquifers that is~~were~~ unconfined with an impermeable base and prescribed heterogeneity~~. Our model conclusions may be limited to the regional scale~~. Other catchment characteristics such as landscape aspect, catchment area, aquifer permeability or drainage ability, aquifer depth, stream bed elevation, ~~and~~ fractured bedrock permeability, bedrock slope and shape of basin can potentially change the flow patterns and age composition in streamflow [*McGlynn et al.*, 2003*; Broxton et al.*, 2009; *Sayama and McDonnell*, 2009; *Stewart et al*., 2010; *Jasechko et al*., 2016; *Heidbüchel et al*., 2013, 2020; *Zarlenga and Fiori*, 2020]. For example, aquifers with high permeability or highly fractured bed rock are more likely to use deep rather than shallow flow paths and preferential discharge routes that lead to rapid drainage. Apart from that, it was reported that hydrological features such as precipitation variability, ET, antecedent soil moisture are also significantly linked to transit times [*Sprenger* et al., 2016; *Wilusz et al*. 2017; *Evaristo et al*., 2019; *Heidbüchel et al*., 2013, 2020]. For example, compared to uniform precipitation, event-scale precipitation is more likely to trigger rapid surface runoff and intermediate flow, such that the contribution of young water from storage to streamflow can be increased. Therefore, further research should consider a more complex model structure involving various heterogeneity and climate types.

Second, several main simplifications were used in the formulation of the nitrate transport processes. (i) Transport modelling employed a constant degradation rate coefficient assuming that transit time was the only factor to determine degradation. This assumption neglected other factors that can spatially and temporally affect denitrification rates, such as temperature, redox boundaries (e.g., high oxygen concentration in shallow flow paths), the amount of other nutrients (e.g. carbon), which also contribute to the seasonality in nitrate concentrations [*Böhlke et al.*, 2007]. Apart from that, we did not account for the long-term (decades [*Van Meter et al.*, 2017]) nitrate legacy effect as the dissolved nitrate in groundwater reservoirs degraded continuously in our model, which would not occur in older reservoirs where the denitrification is very slow or deactivated (e.g. due to the lack of a carbon source). (ii) ~~In our simulations, the complexities of the nitrogen pool were simplified by integrally defining a source concentration curve. The variability of the source input was implicitly considered by forcing the source concentration to vary along that curve over the course of a year. The accurate simulation of C_Q would depend on a realistic estimation of the input source curve. However, it is not that important in our study as we were focused on understanding how the response changes with regard to topographic slope rather than on accurately reproducing C_Q. (iii)~~ The ~~nitr~~N external input~~ate~~ source was uniformly applied across the land surface in our modelling. However, strong source heterogeneity may exist in catchments. For example, the N external input ~~source concentrations~~ varies~~y~~ between land uses or along the soil profile [*Zhi et al.*, 2019]. This spatial source heterogeneity could affect the seasonal variations of C_Q [*Musolff et al.*, 2017; *Zhi et al*., 2019] and should be considered in further research.

Despite these limitations, the numerical experiments in this study could clearly identify ~~a three-class~~the response of young streamflow and nitrate export to topographic slope under a humid seasonal climate, and show that hydraulic gradient is an important factor causing ~~the~~ flow field differences between the ~~classes~~catchments. This was achieved by using the advantages of a physically-based flow simulation that allows for a more mechanistic evaluation of flow processes, which would be impossible with a purely data driven analysis based on, e.g., isotopic tracers only.

5 Conclusions

Previous data driven studies suggested that catchment topographic slope impacts the age composition of streamflow and consequently the in-stream concentrations of certain solutes [*Jasechko et al*., 2016]. We attempted to find more mechanistic explanations for these effects. We chose ~~a cross-section from~~ the small agricultural catchment 'Schäfertal' in Central Germany and, based on it, generated eleven synthetic ~~cross-sections~~catchments of varying topographic slope. The groundwater and overland flow, and the ~~nitrate~~ N transport in these ~~cross-sections~~catchments were simulated using a coupled surface-subsurface model. Water age compositions for Q and ET were determined using numerical tracer experiments. Based on the calculated flow patterns, ~~in-stream nitrate concentration C_Q and~~ young water fractions in streamflow YF_Q, N mass fluxes and in-stream nitrate concentration C_Q, we systematically assessed the effects of varying catchment topographic slopes on the nitrate export dynamics in terms of the mass fluxes and annual mean concentration level~~s (annual mean) and its seasonal variability~~. The main conclusions of this study are:

- Under the considered humid climate, YF_Q ~~C_Q~~ is generally negatively correlated ~~related~~ to topographic slope ~~by a three-class response~~. When the landscape becomes flatter, the hydraulic head gradient is the main driving force to~~,~~ change~~changing~~ the aquifer from a partially topography-limited system ~~with preferential overland flow (C1)~~ to a recharge-limited system, reducing the connectivity between the stream and the more distant hillslopes ~~that is more likely to form local flow cells (C3)~~. This change results in the reduction of longer flow paths and the persistence of shorter flow paths, subsequently causing the ~~For landscapes falling into the classes C1 or C3, f~~flatter landscapes ~~tend~~ to generate ~~more~~ younger streamflow ~~and export nitrate of higher C_Q~~. ~~However, for the former this is due to the "inverse storage effect" and for the latter this is due to the "local flow cells effect". For the transitional class C2, YF_Q and nitrate concentration decrease sharply once the flatter landscapes are no longer able to maintain the fast preferential overland flow paths.~~

- The flatter landscapes tend to retain~~preserve~~ more N mass in soil and export less N mass to the stream. These patterns are attributed to (i) the reduced leaching in flat landscape as the decreased flow velocity physically reduces the potential of water to transport~~wash~~ the solute towards the stream, and (ii) the increased potential of degradation as the connectivity between the stream and hillslope is blocked and the solute stays inside the aquifer longer.~~For catchments in temperate humid climates with considerable seasonality in wetness conditions, the seasonal variation of C_Q is dominated by the variability in transit times and in turn degradation, rather than by the variability in the nitrate source. Especially for the aquifer of the C3 class, significant seasonal variation of C_Q can be generated even without any variability in the nitrate source.~~

- For the considered catchment, the annual mean C_Q shows a decreasing trend in response~~ds~~ to the decreasing topographic slope, because the N export decreases to a higher~~more in~~ degree than Q. Flatter landscapes tend to generate larger~~higher~~ young streamflow fractions (but lower C_Q), suggesting that a large~~high level of~~ young streamflow fraction~~s~~ is not sufficient for a high level of C_Q.

- ~~The response of the seasonal variation of C_Q to topographic slope is similar to the one of the mean C_Q. For the landscapes of the C1 or C3 classes, seasonal variation tends to be more pronounced for flatter landscapes. However, for the C2 class, a significant decrease in this variation can be expected when fast preferential overland flow paths are switched off on flatter landscapes.~~

Overall, this study provided~~s~~ a mechanistic perspective on how catchment topographic slope affects young streamflow fraction and nitrate export patterns. The use of a fully-coupled flow and transport model extended~~s~~ the approach to investigate the effects of catchment characteristics beyond the frequently used tracer data-driven analysis. It can be used for similar studies of other catchment characteristics and for other solutes. The results of this study improved the understanding of the effects of certain catchment characteristics on nitrate export dynamics with ~~reveal~~ potential implications for the management of stream water quality and agricultural activity, in particular for catchments in temperate humid climate~~s~~ with pronounced seasonality. Given the limitations of this study, future work should be devoted to improve the degradation formulation, to investigate further catchment characteristics, as well as to consider various climate types.

Notation

t	[T] time
T	[T] age / transit time / residence time
J	[LT^{-1}] precipitation
ET	[LT^{-1}] evapotranspiration
Q	[LT^{-1}] discharge / streamflow
p_S	[-] age distribution of storage
$p_{ET/Q}$	[-] age distribution for evapotranspiration / discharge, equivalent to TTD
C	[ML^{-3}] concentration
~~C_j~~	~~[ML^{-3}] source concentration~~
C_Q	[ML^{-3}] in-stream solute (nitrate) concentration
T_Q	[ML^{-3}] age (transit time) of discharge
~~***Da***~~	~~[-] Damköhler number~~
YF_Q	[-] young water fraction in streamflow, or young streamflow fraction
YF_{ET}	[-] young water fraction in ET
SON	[$M\ L^{-2}$] soil organic nitrogen
SIN	[$M\ L^{-2}$] soil inorganic nitrogen
DIN	[$M\ L^{-2}$] dissolved inorganic nitrogen in water

Code/Data availability

All data used in this study are listed in the supporting information and uploaded separately to HydroShare [Yang, 2022~~0~~].

Author contributions

JY: conceptualization, methodology, software, formal analysis, visualization, writing - review & editing; QW: modelling, analysis, writing; IH: writing - review & editing; CL: conceptualization, methodology, review & editing; YX: methodology; AM: conceptualization; JF: conceptualization, review & editing.

Competing interests

The authors declare that they have no conflict of interest.

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