



1 **The effect of rainfall variability on Nitrogen**
2 **dynamics in a small agricultural catchment**

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Abstract. Throughout history, extreme storms and droughts have had serious impacts on society and ecosystems globally. Rainfall variability in particular has been identified as a primary performance of climate change. However, so far little has been done to explore the effect of rainfall variability on water quality. This study is aimed at investigating the effect of rainfall variability on nitrogen (N) dynamics and its potentially negative influence on water quality. The transport of water and nitrate was simulated for a small agricultural catchment in Central Germany using the fully coupled surface-subsurface model HydroGeoSphere. Rainfall time series with specific climatic characteristics were generated using a stochastic rainfall generator. N transformation and transport were compared for four scenarios (with high, normal, low annual precipitation amounts, and low annual precipitation amounts coupled with reduced plant uptake, respectively) in order to identify the impact of inter-annual rainfall variability on N dynamics. The results suggest that higher annual precipitation amounts can enhance the transformation and transport of nitrogen. Lower annual precipitation amounts are conducive to nitrogen retention. Nonetheless, when vegetation suffers from drought stress, the retention capacity will decline markedly, suggesting that vegetation plays a vital role in N dynamics under extreme droughts. The linear regressions between selected parameters of the rainfall generator and N loads / fluxes were analyzed to elucidate the impact of intra-annual rainfall variability on N dynamics. The results indicate that wet / dry conditions and different dry-wet patterns caused by the distribution of storm durations and inter-storm periods over the course of a year can significantly affect N loads and in-stream nitrate concentration, respectively. In the warm season, droughts prompt the accumulation of SON, but drying-wetting cycles can enhance the extensive transformation of SON. In-stream nitrate concentration dramatically elevates during the rewetting period after the drought. High mean rainfall intensity contributes not only to the transformation of N when mineralization is not limited by low temperatures, but also to the plant absorption of inorganic nitrogen in the growing season. There is merely small effect of mean rainfall intensity on stream water quality. Overall, the study clarifies the effect of rainfall variability on N dynamics in a small agricultural catchment, which provides theoretical support to formulate fertilization strategies and protect aquatic ecosystems under climate change in the future.

Key Points: N dynamics, HydroGeoSphere, Rainfall variability, Stochastic rainfall generator



44 **1 Introduction**

45 In the past decades, extreme climate events intensified by human-induced climate
46 change have frequently occurred globally [Pall et al., 2011; Min et al., 2011; Williams
47 et al., 2015; Hari et al., 2020] and caused socioeconomics, natural ecosystems, and crop
48 cultivation to suffer severely [European Commission, 2006; Wegren et al., 2011; Van
49 Lanen et al., 2016; BDF, 2019; Markonis et al., 2021; Black, 2023]. The hydrological
50 processes are susceptible to meteorological conditions on various spatial and temporal
51 scales [Ionita et al., 2017; Laaha et al., 2017; Zhang et al., 2021]. Most extreme climate
52 events tend to cause water scarcity and poor water quality at regional scales [Zwolsman
53 and van Bokhoven, 2007; Delpla et al., 2009; Whitehead et al., 2009; Stahl et al., 2016;
54 Ballard et al., 2019; Bauwe et al., 2020; Geris et al., 2022]. Under future global
55 warming scenarios, a higher frequency and intensification of extreme climate events
56 from daily to multiyear timescales will occur [O’Gorman et al., 2009; Dai et al., 2013;
57 Fischer and Knutti, 2014; Spinoni et al., 2018; Hari et al., 2020; Zhang et al., 2024].
58 Thus, their effect on water resources has attracted much attention around the world.

59 Heavy rainstorms and severe droughts being the predominant extreme climate events
60 around the globe share the common characteristic of rainfall variability [Trenberth et
61 al., 2011; Pendergrass et al., 2017; Hanel et al., 2018]. During heavy rainstorms,
62 extraordinary rainfall amounts and intensities cause large amounts of rainwater to
63 infiltrate into soils and trigger flash floods in a short time. Increased groundwater flow



64 and enhanced surface runoff stimulate the movement of solutes retained in the soil,
65 which thereby can lead to water quality degradation [Geris et al., 2022]. Different from
66 heavy rainstorms, severe droughts driven by precipitation deficits need to take several
67 months or potentially years to reach their full intensity [Otkin et al. 2018], from which
68 it takes 1-2 years for hydrological components to recover [Hanel et al., 2018]. Wilusz
69 et al. [2017] decomposed the relationship between rainfall variability and transit times,
70 a reflection of water velocities that control solute transport, and illustrated that climate
71 change may seasonally alter the ages of water in streams and thereby influence water
72 quality in the future. Nitrate (NO_3^- -N) is the major solute threatening the quality of
73 drinking water and destroying the structure and functions of aquatic ecosystems
74 [Vitousek et al., 2009; Alvarez-Cobelas et al., 2008; Dupas et al., 2017]. The nitrate
75 turnover processes established at the catchment scale are expected to change due to
76 climate change [Whitehead et al., 2009; Hesse and Krysanova, 2016; Mosley, 2015],
77 especially due to increasing drought events [Zwolsman and van Bokhoven, 2007;
78 Ballard et al., 2019; Zhou et al., 2022; Winter et al., 2023].

79 Several extreme climate events (extreme rainfall and droughts) occurred in Central
80 Europe during the last two decades, which has attracted worldwide attention. Extreme
81 rainfall in 2002, 2013, and 2021 cause a threat to humans and large damages to the
82 environment, economy, and infrastructure [Ulbrich et al., 2003; Thielen et al., 2016;
83 Voit, P. and Heistermann, M., 2024]. Three remarkable summer droughts occurred in



84 2003, 2015, and 2018–2019 (consecutive), driven by precipitation deficit in
85 conjunction with temperature anomalies during the vegetation growing period [Fink et
86 al., 2004; Schär et al., 2004; Ciais et al., 2005; Orth, Vogel, Luterbacher, Pfister, &
87 Seneviratne, 2016; Hanel et al., 2018; Hari et al., 2020; Camenisch et al., 2020], of
88 which the 2018 event caused unprecedented tree mortality in many species throughout
89 the Central European forests and unexpectedly strong drought-legacy effects [Schuldt
90 et al., 2020]. Zhou et al. [2022] detected higher soil N surplus (total N input with the
91 crop/plant uptake subtracted) and decreased the terrestrial N export in agricultural areas
92 located in Central Germany during the drought years (2015–2018). The same
93 phenomenon reported in the Nitrate Report 2020 of the Netherlands (RIVM, 2021)
94 indicates that more N was retained in the soil during the drought period compared to
95 the pre-drought period. However, by studying the 2018–2019 (consecutive) drought in
96 Central Germany, Winter et al. [2023] drew the conclusion that severe multi-year
97 droughts can reduce the nitrogen (N) retention capacity of catchments. It seems that the
98 opposite conclusions drawn from these studies can be attributed to the different
99 investigation timescales. The latter study considering the subsequent rewetting period
100 during which most nitrogen accumulated during the drought left the catchment. Leitner
101 et al. [2020] also found that in the year after a summer drought, NO_3^- leaching via soil
102 water seepage was significantly elevated compared to the long-term mean in a
103 temperate mixed forest on karst, an observation which was made in wetland-influenced
104 catchments as well [Watmough et al., 2004]. These prove that rainfall variability has a



105 profound impact on N dynamics. Therefore, it's imperative to shed light on the impact
106 of rainfall variability on water quality in terms of N dynamics.

107 A small agricultural catchment in Central Germany was selected as the study site, where
108 a hydrological model was previously established utilizing the fully coupled surface-
109 subsurface numerical simulator HydroGeoSphere [Yang et al., 2018]. The framework
110 of N dynamics was modified from the ELEMeNT approach [Yang et al., 2021]. Rainfall
111 time series with specific climatic characteristics were generated using a stochastic
112 rainfall generator [Robinson & Sivapalan, 1997] to take the place of the rainfall data in
113 the simulation period. The work is divided into two main components. First, we
114 explored the influence of inter-annual rainfall variability. Three representative years
115 (with high, normal, and low annual precipitation amounts, respectively) were chosen
116 from the past two decades in Central Germany as the target scenarios. A fourth scenario
117 with low annual precipitation amounts coupled with reduced plant uptake represents
118 the situation that vegetation is partially destroyed by extreme droughts. The statistical
119 analyses of nitrogen loads and fluxes and a comparison across different scenarios were
120 conducted. Second, we explored the impact of intra-annual rainfall variability. By
121 separately altering specific parameters, rainfall time series were generated by the
122 stochastic rainfall generator. Using these rainfall data, the flow and nitrogen transport
123 were simulated across hundreds of models. The responses of the N loads and fluxes to
124 the parameters (e.g., the amplitudes of the seasonal variations in the storm durations



125 and inter-storm period) were thoroughly analyzed subsequently.

126 **2 Data collection**

127 **2.1 Study Site**

128 The studied catchment, Schäfertal, is located on the lower reaches of the eastern Harz
129 Mountains, Central Germany, with an area of 1.44 km². Since 1968, this first-order
130 catchment has been subject to broad hydrogeological investigations, analyses, and
131 research [Altermann et al., 1970; Altermann et al., 1977; Borchardt et al., 1981;
132 Altermann et al., 1994; Wollschläger et al., 2016]. The valley bottom contains riparian
133 zones with pasture and a small channel (Figure 1a). The hillslopes on both sides of the
134 channel have an average slope of 11°, mostly used as farmland. The farmland undergoes
135 intensive agriculture, primarily winter wheat growing [Yang et al., 2018]. Two small
136 portions near the western edge are mostly forest. The types of land use in the catchment
137 do not generally convert until the economic and ecological goals vary between years,
138 e.g., shifting between planting and pasture [Wang et al., 2023]. A meteorological station,
139 which is 200 m from the catchment outlet, provides records of precipitation, air and soil
140 temperatures, radiation, and wind speed. The catchment outlet in the stream, where a
141 gauge station was built, is considered as the unique exit that allows water and solute to
142 leave the catchment and enter the downstream catchments. This is because a subsurface
143 wall (~55 m long and ~7 m deep) was erected across the valley to block subsurface
144 flow. The gauge station provides discharge data at 10-minute intervals, aggregated to



145 daily means in this study. Nitrate concentration data is measured by sampling near the
146 gauge station.

147 The aquifer is thin, with the thickness varying from ~5 m near the valley bottom to ~2
148 m at the top of the hillslopes (Figure 1a). Thirteen wells, each ~2 meters deep, were
149 constructed and fitted with automated data loggers to record groundwater levels. The
150 groundwater levels exhibit pronounced seasonal variations, rising to the land surface
151 during winter and receding to depths of ~3 meters below the ground during summer.
152 The groundwater storage is low (~500 mm, stored water volume divided by catchment
153 area). Most of the groundwater converges towards the channel vicinity, with the upper
154 sections of the hillslopes typically in an unsaturated state [Yang et al., 2018]. Luvisols
155 and Gleyic Cambisols are the aquifer materials of the hillslope. The valley bottom is
156 dominated by Gleysols and Fluvisols (Figure 1b) [Anis and Rode, 2015]. Generally, the
157 aquifer is comprised of two horizontal layers: a top layer of approximately 0.5 m
158 thickness, with higher permeability, higher porosity, and the developed root zone from
159 crops; and a base layer with less permeability due to the high loam content [Yang et al.,
160 2018]. The bedrock underlying the aquifer comprises greywacke and shale [Graeff et
161 al., 2009]. Owing to the aquifer material and unknown hydraulic properties, the bedrock
162 is often regarded as impermeable.

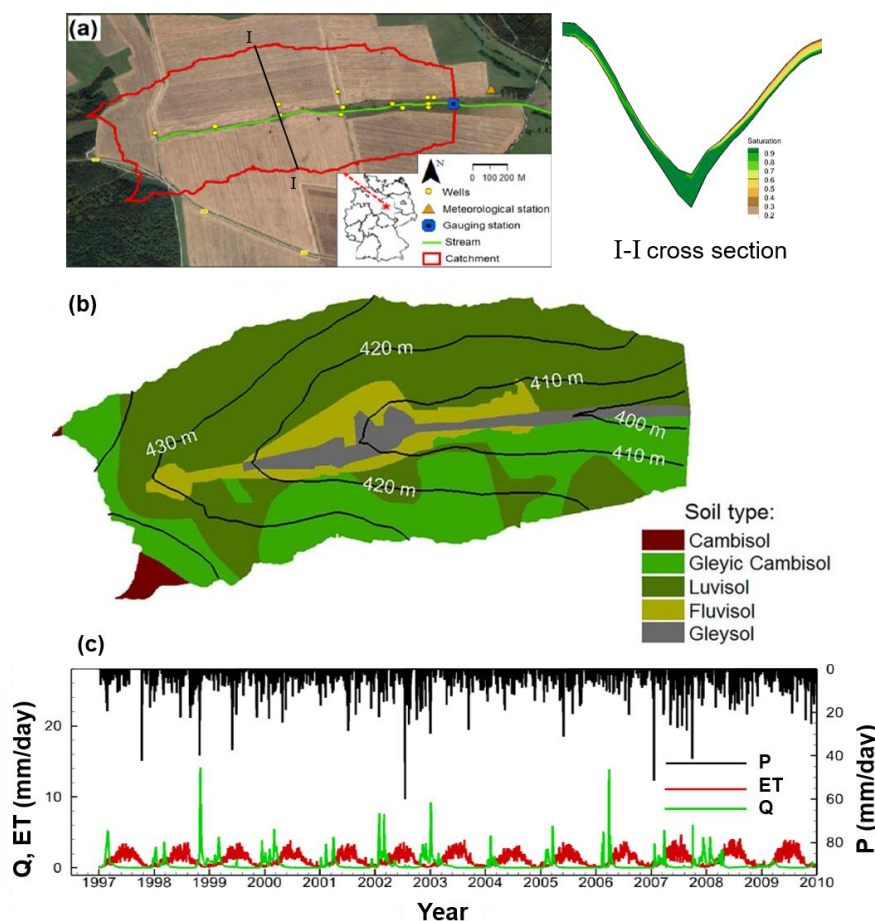


Figure 1. (a) The catchment ‘Schäfertal’ is located in Central Germany (background image from © Google Maps). The red line indicates the dividing ridge of the catchment [Anis and Rode, 2015]. I-I cross section shows the aquifer thickness variation. (b) The distribution of soil type in the catchment. (c) The measured daily precipitation (P), discharge (Q), and the simulated actual evapotranspiration (ET) [Yang *et al.*, 2018].

2.2 Measured data

The studied catchment exhibits a temperate and humid climate with pronounced seasonality. The humid climate in wet regions is quantified by an aridity index of 1.0. The ET is the main driver of the hydrologic seasonality, as the precipitation is uniformly



173 distributed across the year. According to the meteorological data records from 1997 to
174 2010, the mean annual precipitation (P) and discharge (Q) are 610 mm and 160 mm,
175 respectively (Figure 1c). Based on the 14-year water balance ($P = ET + Q$), the actual
176 mean annual evapotranspiration (ET) is 450 mm. The in-stream nitrate concentration
177 (C_Q) was measured at fortnightly to monthly intervals [Dupas et al., 2017], covering
178 the period 2001-2010. The N surplus, which is the annual amount of nitrogen remaining
179 in the soil after the consumption by plant uptake from the external N input, was
180 estimated as $48.8 \text{ kg N ha}^{-1} \text{ year}^{-1}$ during 1997–2010 for this catchment [Bach and
181 Frede, 1998; Bach et al., 2011]. Adequate data from numerous investigations and
182 previous research supports the exploration of N dynamics in the agricultural catchment.

183 **3 Methodology**

184 The hydrological model for the Schäfertal catchment was established using
185 HydroGeoSphere [Therrien et al., 2010] in the previous study [Yang et al., 2018]. The
186 framework of N dynamics [Yang et al., 2021] modified from the ELEMeNT modeling
187 approach [Exploration of Long-tErM Nutrient Trajectories, Van Meter et al., 2017] was
188 applied to track the fate of N in soil and groundwater in the present study. In order to
189 investigate the effect of rainfall variability on N dynamics, rainfall time series,
190 substituting for the precipitation data during the simulation period, were generated by
191 a stochastic rainfall generator [Robinson & Sivapalan, 1997; Wilusz et al., 2017]. These
192 models are described below in details.



193 **3.1 Flow modelling**

194 HydroGeoSphere is a 3D control volume finite element simulator that can model fully
195 coupled surface-subsurface hydrological processes by the dual nodes approach. It can
196 not only describe crucial hydrological processes such as dynamical evapotranspiration,
197 snow, sublimation, snowmelt, and freeze and melt of pore water, but also simulate 2D
198 overland flow by Manning's equation and the diffusive-wave approximation of the St.
199 Venant equations, 3D variably saturated underground flow by Richards' equation and
200 Darcy's law, flow in porous media, as well as the transport of reactive solutes. In
201 addition, HydroGeoSphere allows the simulation of 1D surface flow in a channel
202 network and water exchange flux between the channel domain and the subsurface
203 domain [Yang et al., 2015]. HydroGeoSphere has been frequently used to model
204 catchment hydrological processes and solute transport in many previous studies [e.g.,
205 Therrien et al., 2010; Yang et al., 2018]. Please refer to Therrien et al. [2010] for the
206 governing equations and technical details.

207 The hydrological model of Schäferfetal catchment is briefly recapitulated in the following.
208 More details are provided in Yang et al. [2018]. In the model, the subsurface domain
209 between the surface and bedrock was depicted using 3D prisms with side length ranging
210 from 30 m to 50 m. The surface domain was filled by the uppermost 2D triangles of the
211 generated 3D prismatic mesh, while the channel was delineated by 1D segments with
212 specified widths and depths. According to different aquifer materials and the difference



213 in their permeability in the vertical direction, the subsurface domain was separated into
214 ten property zones with zonal hydraulic conductivity and porosity values. The surface
215 domain and channel were parameterized with a Manning roughness coefficient
216 representing the land use. Spatially uniform and temporally variable precipitation
217 (Figure 1c) was applied to the entire surface domain. ET is computed as a combination
218 of plant transpiration from the root zone and evaporation down to the evaporation depth
219 [Therrien et al., 2010]. A critical depth boundary condition was assigned to the outlet
220 in the channel domain to simulate the discharge (Q) of the catchment. In order to
221 eliminate the influence of initial conditions, a preliminary model run was performed for
222 the period spanning 1997 to 2007. The simulated results at the end of the period were
223 taken as initial conditions for the actual simulations.

224 Key parameters that significantly influence the hydrological processes were selected
225 for the calibration [Anis & Rode, 2015; Graeff et al., 2009] using the software package
226 PEST [Doherty & Hunt, 2010]. PEST uses the Marquardt method to minimize a target
227 function by varying the values of a given set of parameters until the optimization
228 criterion is reached. The groundwater levels measured in groundwater wells and the
229 discharge measured at the gauging station were used as target variables. Considering
230 high CPU time (~1 day to run the model for the period for 14 year), the calibration
231 period spans 1 year, from October 2002 to October 2003. Subsequently, the calibrated
232 model was verified over the entire simulation period.



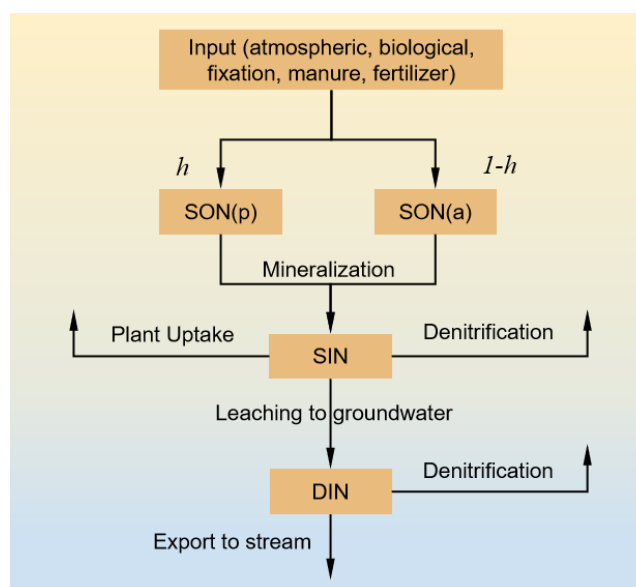
233 **3.2 Nitrogen transport in soil and groundwater**

234 The transformation and transport of nitrogen in the underground area are tracked by the
235 framework of N dynamics modified from ELEMeNT. ELEMeNT is a comprehensive
236 model maintaining a landscape memory, that is, considering the effect of not only
237 current conditions but also past land use and nutrient dynamics on current fluxes [Van
238 Meter et al., 2017]. The modification includes four parts in the framework. Firstly, the
239 N surplus is estimated by subtracting the plant uptake from external N input [Yang et
240 al., 2021]. Secondly, plant uptake was delineated corresponding to the reality. Thirdly,
241 denitrification was considered in both the N source zone in soil and groundwater. Lastly,
242 the process of transferring nitrogen from the source zone to groundwater was delineated
243 by leaching.

244 External nitrogen input goes through transformation and transport in the soil,
245 subsequently filters into groundwater and gets exported to the surface water body. In
246 route, every kind of nitrogen undergoes biogeochemical processes. The framework
247 includes a N source zone forming in shallow soil and a groundwater zone (Figure 2).
248 There are two assumptions in the N source zone: 1) the total N load in the N source
249 zone is comprised of an organic N (SON) pool and an inorganic N (SIN) pool; 2) the
250 external N input contributes only to the SON. The external N input represents
251 atmospheric deposition, biological fixation, animal manure from the pasture area, and
252 N fertilizer from the farmland. The SON is further distinguished as active SON with



253 faster reaction kinetics and protected SON with slower reaction kinetics. Both SON(a)
 254 and SON(p) are transformed into SIN by mineralization. SIN is further consumed by
 255 plant uptake and denitrification, and leaches from soil to groundwater as dissolved
 256 inorganic N (DIN), representing mainly nitrate in the studied catchment [Yang et al.,
 257 2018; Nguyen et al., 2021]. DIN can further undergo denitrification until being exported
 258 to the stream. The framework is considered to be acceptable based on the fact that most
 259 of the nitrate fluxes undergo biogeochemical transformation in the inorganic N pool
 260 [Haag and Kaupenjohann, 2001].



261
 262 **Figure 2.** The framework simulating the Nitrogen Transport in soil and groundwater, modified
 263 based on [Yang et al., 2021].

264 The governing equations to calculate N fluxes follow the ones of the framework in Yang
 265 et al. [2021]. The land-use dependent protection coefficient h [Van Meter et al., 2017]
 266 determines the amount of external N input that contributes to the protected SON



267 (SON(p)), and the residual contributes to the active SON (SON(a)). Mineralization and

268 denitrification are described as first-order processes. Based on the results of Wang et al.

269 [2023], the effect of wetness is considered in mineralization, using:

$$270 \quad MINE_a = k_a \cdot f(temp) \cdot f(wetness) \cdot SON_a \quad (1)$$

$$271 \quad MINE_p = k_p \cdot f(temp) \cdot f(wetness) \cdot SON_p \quad (2)$$

$$272 \quad DENI_s = \lambda_s \cdot SIN \quad (3)$$

$$273 \quad DENI_g = \lambda_g \cdot DIN \quad (4)$$

274 where $MINE_a$, $MINE_p$ (kg ha⁻¹ day⁻¹) are the mineralization rates for active SON and

275 protected SON, respectively. $DENI_s$ and $DENI_g$ (kg ha⁻¹ day⁻¹) are the

276 denitrification rates for SIN and DIN, respectively. k_a , k_p , and λ (day⁻¹) are

277 coefficients for the three first-order processes. $f(temp)$ and $f(wetness)$ are factors

278 representing the constraints by soil temperature and wetness [Lindström et al., 2010;

279 Wang et al., 2023], respectively. Plant uptake rate UPT follows the equation used in the

280 HYPE model [Lindström et al., 2010]:

$$281 \quad UPT = \min(UPT_p, 0.8 \cdot SIN) \quad (5)$$

$$282 \quad UPT_p = p1/p3 \cdot \left(\frac{p1-p2}{p2}\right) \cdot e^{-(DNO-p4)/p3} / \left(1 + \left(\frac{p1-p2}{p2}\right) \cdot e^{-(DNO-p4)/p3}\right)^2 \quad (6)$$

283 where UPT and UPT_p (kg ha⁻¹ day⁻¹) are the actual and potential uptake rates,

284 respectively. The logistic plant growth function is considered in the equation of

285 potential uptake rates. DNO is the day number within a year. $p1$, $p2$, $p3$ are three



parameters depending on the type of plants, whose units are (kg ha⁻¹), (kg ha⁻¹), and (day), respectively. $p4$ is the day number of the sowing date. The leaching rate adapts a first-order process considering soil saturation and groundwater velocity, using:

$$LEA = k_l \cdot f_w \cdot f_q \cdot SIN \quad (7)$$

$$f_w = \frac{S - S_r}{1 - S_r} \quad (8)$$

$$f_q = MIN\left(\frac{q}{q_{ref}}, 1\right) \quad (9)$$

where LEA is the leaching flux of SIN from the N source zone to the groundwater, k_l is a leaching coefficient (day⁻¹), f_w and f_q are two factors representing the constraints of soil saturation and groundwater velocity to the leaching process, respectively. S is the soil saturation, and S_r is the residual saturation. q (m day⁻¹) is the groundwater Darcy flow rate, q_{ref} (m day⁻¹) is a reference Darcy flow rate. This formulation of LEA is modified from the one used in Van Meter et al. [2017].

In these hydrogeochemical processes, a portion of N is retained in the catchment as the biogeochemical legacy in soil or the hydrological legacy in groundwater or permanently leaves catchments by denitrification, which does not degrade the water quality of the catchment during a certain period. Therefore, the N retention is used to quantify a catchment's capacity to prevent nitrogen from entering surface water bodies during a certain period [Wang et al., 2023], which is the fraction of the N retained in the catchment and consumed via denitrification to the total external N input, calculated using [Ehrhardt et al., 2021]:



306
$$\text{Retention} = 1 - \frac{N_{\text{out}}}{N_{\text{in}}} = 1 - \frac{\int_{t_1}^{t_2} N_{\text{outlet}}}{\int_{t_1}^{t_2} N_{\text{input}}} \quad (3)$$

307 where the N_{outlet} is the N mass leaving the catchment through the outlet during the
308 time period $(t_1 - t_2)$.

309 Due to the lack of spatiotemporal variation information of the external N input, its value
310 was fixed at $180 \text{ kg ha}^{-1} \text{ year}^{-1}$ according to Nguyen et al. [2021], where the N balance
311 was simulated in the upper Selke catchment covering the Schäfertal catchment. The
312 protection coefficient h was selected as 0.3 according to the values reported in Van
313 Meter et al. [2017]. p_4 as the sowing date of plant growth activities was set to 63 days
314 (early March) [Yang et al., 2018]. The DIN was transported in the coupled surface
315 water-groundwater system, with longitudinal and transverse dispersion coefficients of
316 8 and 0.8 m, respectively. Other parameters relative to N dynamics were calibrated by
317 PEST in empirical ranges. The measured C_Q at the gauge station and the N surplus of
318 $48.8 \text{ kg N ha}^{-1} \text{ year}^{-1}$ were used as the target variables. The calibration period spans
319 from March 2001 to August 2003, during which successive C_Q data was obtained. The
320 CPU time was $\sim 2 \text{ h}$ for a single iteration. The model validation was conducted over the
321 entire simulation period from 1997 to 2010 ($\sim 1 \text{ day}$ of CPU time). The calibrated best-
322 fit values for the transport parameters are listed in Table S1 [see in Supporting
323 Information]. For more details refer to Wang et al. [2023].

324 The N source zone serves as a boundary condition at the top of the aquifer for simulating
325 DIN transport in the groundwater. The bedrock is treated as impermeable for nitrate.



326 The catchment outlet is the only boundary allowing the exit of nitrate from the
327 catchment. In order to minimize the influence of the initial conditions, a preliminary
328 transport simulation (together with the flow simulation) was performed with zero load
329 in the SON and SIN pools and zero DIN concentration in the catchment, such that a
330 quasi-steady state for the SON and SIN pools can be reached at the end of the
331 preliminary simulation. The resulting data (N loads and concentrations) were used as
332 initial conditions for the actual simulations.

333 **3.3 Stochastic rainfall generator**

334 In order to investigate the effect of rainfall variability on N dynamics, rainfall time
335 series with different climatic characteristics were generated by a stochastic rainfall
336 generator. The stochastic rainfall generator is stochastic model of rainfall time series
337 originally created to investigate the timescales of flood frequency response to rainfall,
338 incorporating any combinations of storm, within-storm as well as between-storm, and
339 seasonal variabilities of rainfall intensity [Robinson & Sivapalan, 1997]. It can exhibit
340 a good performance of rainfall variability under climate change [Wilusz et al., 2017].
341 The identification of individual storms is based on the criterion of a specified minimum
342 dry period between events. Acreman [1990] noted the arbitrary nature of this criterion
343 in the selection of the minimum dry period. In this study, the minimum dry period was
344 set at 1 day (24 hours) due to the daily average meteorological data, which is consistent
345 with Wilusz et al. [2017].



346 The rainfall generator generates daily rainfall time series meeting the research
347 requirement in three steps. First, determine a series of alternating storm durations t_r and
348 inter-storm periods t_b over the simulation time that are independent of each other and
349 vary seasonally. Second, determine the average rainfall intensity i of each storm. It is
350 described as a random variable stochastically dependent on storm duration t_r . Third,
351 construct within-storm rainfall intensity variations using a normalized mass curve [Huff,
352 1967; Chow et al., 1988]. The detailed governing equations can be found in Sect. S1 of
353 the Supporting Information.

354 We adopted the source code in Python v2.7 of the rainfall generator from Wilusz et al.
355 [2017]. In the stochastic model, the seasonal averages (γ_s and δ_s), amplitudes (α_γ and
356 α_δ), and phases (τ_γ and τ_δ) are used to determine monthly average storm duration and
357 inter-storm period. $a_1^1 \sim a_1^4$, $b_1^1 \sim b_1^4$, a_2 and b_2 are the parameters characterizing the
358 dependence between average rainfall intensity and storm duration for the four seasons
359 (the first season (Jan - Mar), the second season (Apr - June), the third season (Jul - Sep),
360 and the fourth season (Oct - Dec)). In addition, there is an isolated parameter $P_{drizzle}$ in
361 the source code, a threshold of the identifiable storm. The storms with precipitation
362 greater than $P_{drizzle}$ can be identified as synoptic frontal events.

363 Rainfall time series representing different climate conditions were generated following
364 these steps below:

- 365 (i) Three representative years were selected according to historical
366 meteorological data, which are the wet year 2007 ($P = 916.3$ mm), the normal



367 year 2008 ($P = 588.7$ mm), and the dry year 2018 ($P = 444.1$ mm);

368 (ii) For each of the representative years, a set of parameters was determined so that

369 the generated rainfall time series can fit the actual rainfall data of this year best.

370 This inverse process was conducted using PEST;

371 (iii) The three sets of best-fit parameters (Table 1) were used again to generate 100

372 stochastic realizations (rainfall time series), for the wet, normal and dry year,

373 respectively. These realizations may deviate from the actual rainfall data in

374 terms of daily rainfall values, still being statistically identical with the rainfall

375 pattern of the representative years.

376



Table 1. Three parameter sets of the rainfall generator, for the wet, normal and dry year, respectively.

Parameter	Wet Year (2007)	Normal Year (2008)	Dry Year (2018)	Adjustable range	Note
$P(\text{mm})$	916.3	588.7	444.1	(400,1000)	Annual precipitation
$\gamma_s(\text{day})$	2.546	2.177	2.071	(0.1, 10)	Seasonally averaged storm duration
$\delta_s(\text{day})$	7.988	7.424	7.535	(0.1, 10)	Seasonally averaged inter-storm period
$\alpha_\gamma(\text{day})$	1.764	0.820	0.550	(-2.2, 2.2)	Amplitude of seasonal storm shift
$\alpha_\delta(\text{day})$	2.457	2.962	2.946	(-8, 8)	Amplitude of seasonal inter-storm shift
$(a_1, b_1)_1$	(0.875, 2.349)	(0.934, 1.802)	(0.909, 1.598)	(0.1, 5)	Coefficient 1 and 2 of the first season (Jan-Mar) for expected storm intensity
$(a_1, b_1)_2$	(1.015, 0.661)	(0.894, 0.538)	(0.857, 0.456)	(0.1, 5)	Coefficient 1 and 2 of the second season (Apr-Jun) for expected storm intensity
$(a_1, b_1)_3$	(0.917, 1.121)	(0.968, 0.845)	(0.947, 0.752)	(0.1, 5)	Coefficient 1 and 2 of the third season (Jul-Sep) for expected storm intensity
$(a_1, b_1)_4$	(1.666, 1.556)	(1.348, 1.341)	(1.392, 1.263)	(0.1, 5)	Coefficient 1 and 2 of the fourth season (Oct-Dec) for expected storm intensity
(a_2, b_2)	(0.658, 0.961)	(0.617, 1.057)	(0.632, 1.025)	(0.1, 5)	Coefficient 1 and 2 for expected storm variability
P_{drizzle}	0.137	0.146	0.140	(0.01, 0.99)	Probability of drizzle event
$\tau_\gamma(\text{day})$	105.760	100.297	100.474	/	Phase of seasonal storm shifts
$\tau_\delta(\text{day})$	120.665	124.044	124.161	/	Phase of seasonal inter-storm shifts



380 **3.4 Simulation scenarios**

381 **3.4.1 Inter-annual rainfall variability**

382 Wet Year (WY), Normal Year (NY), and Dry Year (DY) were set as the simulation
383 scenarios. In addition, a fourth scenario being similar to the Dry Year but coupled with
384 reduced plant uptake was considered as Extreme Dry Year (EDY). This EDY scenario
385 was used to account for the extreme drought occurring in 2018 that caused vegetation
386 to die back with lower plant uptake and impacted N dynamics to some extent [Winter
387 et al., 2023]. In the EDY scenario, the plant uptake was assumed to decrease down to
388 36% of the original value used in the DY scenario, according to the classification and
389 the occurrence period of the drought [Liu et al., 2010]. For each of the scenarios, the
390 water flow and N transport model was conducted 100 times by substituting the rainfall
391 data during the simulation period with the generated 100 stochastic rainfall time series
392 (Figure S1 in Supporting Information). Average annual N loads and fluxes under each
393 scenario can be calculated to ensure that they were not controlled by a single realization
394 and statistically meaningful. Additionally, we simulated the fluctuations of C_Q in each
395 scenario with time over three years. Finally, the average annual N loads, fluxes, and C_Q
396 as well as the variation of C_Q can be cross-compared and analyzed to elucidate the effect
397 of inter-annual rainfall variability on N dynamics.

398 **3.4.2 Intra-annual rainfall variability**

399 In order to explore the effect of intra-annual rainfall variability on N dynamics, the



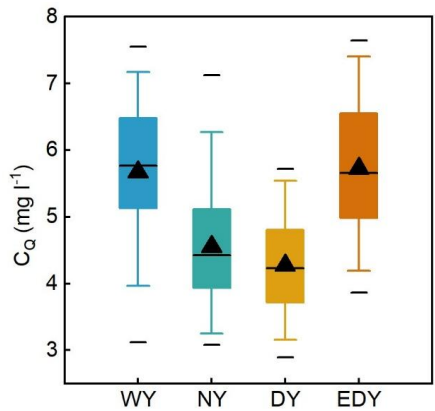
400 linear regression analyses between the parameters of the stochastic rainfall generator
401 and N loads, fluxes as well as C_Q were conducted based on the Normal Year (2008).
402 The seasonal averages of storm duration and inter-storm period (γ_s and δ_s), the
403 amplitudes of the seasonal variations in storm duration and inter-storm period (α_γ and
404 α_δ), the average rainfall intensity of four seasons ($E_1 \sim E_4$) and squared coefficient of
405 variation of the average rainfall intensity (CV^2), as well as the probability of drizzle
406 event ($P_{drizzle}$), were selected as the experimental parameters. $E_1 \sim E_4$ and CV^2 can be
407 approximately calculated by equation S5 & S6, using relative parameters and
408 seasonally averaged storm duration (γ_s). In total, 15 parameters (Table 1) were
409 subjected to the assessment of their effect on N dynamics.

410 For each of the experimental parameters, the rainfall generator generated 100 rainfall
411 time series randomly, whose annual precipitations are within the historical range, with
412 this experimental parameter varying randomly within the adjustable range but other
413 parameters being fixed to the best-fit values for the Normal Year. The ranges of the
414 experimental parameters used in the linear regression analyses are listed in Table 1.
415 Finally, the response of the average annual N loads, fluxes and C_Q to different rainfall
416 parameters can be analyzed.

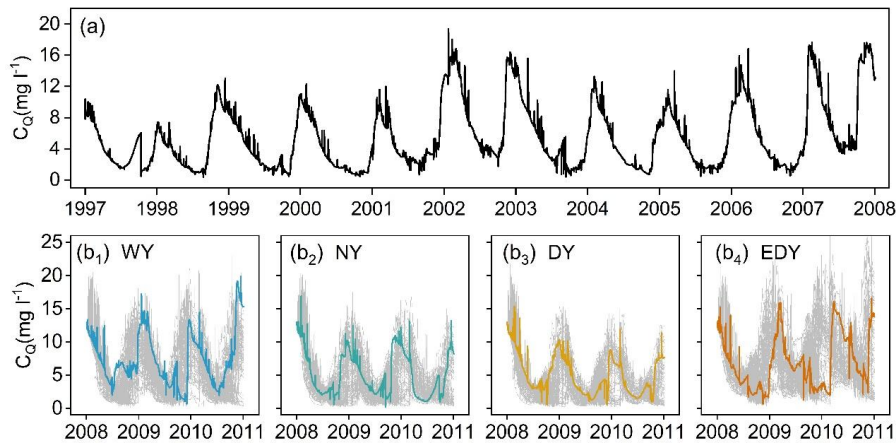


417 **4 Results**

418 **4.1 Effect of Inter-annual rainfall variability**



419
420 **Figure 3.** The simulated in-stream nitrate concentration (C_Q) for the scenarios of WY, NY, DY,
421 and EDY. The whisker represents the concentration ranges from 5th to 95th percentiles, with the
422 triangles indicating the median and the lines marking the maximum, average, and minimum of the
423 data set from top to bottom. The same as below.

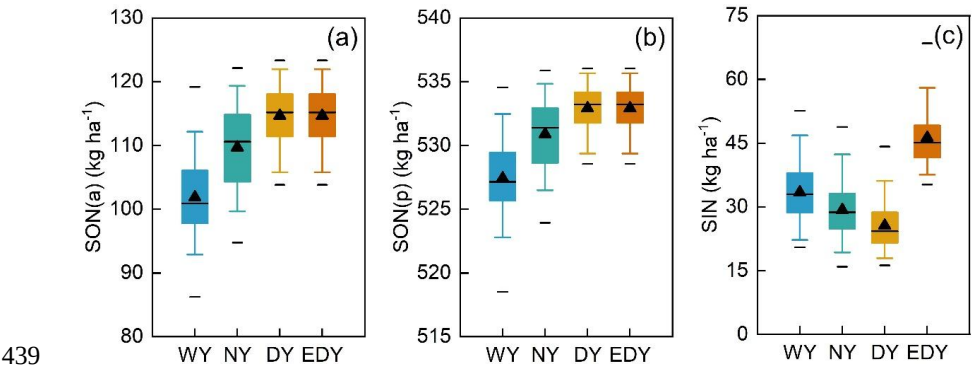


424
425 **Figure 4.** The fluctuations of simulated in-stream nitrate concentration (C_Q) under (a) the
426 historical rainfall (1997-2007) and the scenarios of (b₁) WY, (b₂) NY, (b₃) DY, and (b₄) EDY
427 (2008-2010). The grey areas are the simulation uncertainty generated by the acceptable
428 realizations.

429 Figure 3 shows the simulated in-stream nitrate concentration for the four scenarios. WY



430 produces high C_Q , with the median concentration almost being up to 6 mg l^{-1} . The
431 concentrations generally decrease when the rainfall pattern transforms from WY, via
432 NY, to DY. However, in EDY, when vegetation dying back occurs, concentrations as
433 high as the ones produced in WY can be observed again. The variations of C_Q in these
434 scenarios are exhibited in Figure 4(b₁) ~ (b₄). The range of C_Q generally decreases when
435 the rainfall pattern transforms from WY, via NY, to DY. But, the range of EDY is wider
436 than that of DY, and even similar with that of WY. These results generally suggest that
437 low C_Q are produced in dry years, but high concentrations can be produced in both wet
438 and extreme dry years.



440 **Figure 5.** The simulated loads of (a) active soil organic nitrogen (SON(a)), (b) protected soil
441 organic nitrogen (SON(p)), and (c) soil inorganic nitrogen (SIN) for the scenarios of WY, NY,
442 DY, and EDY.

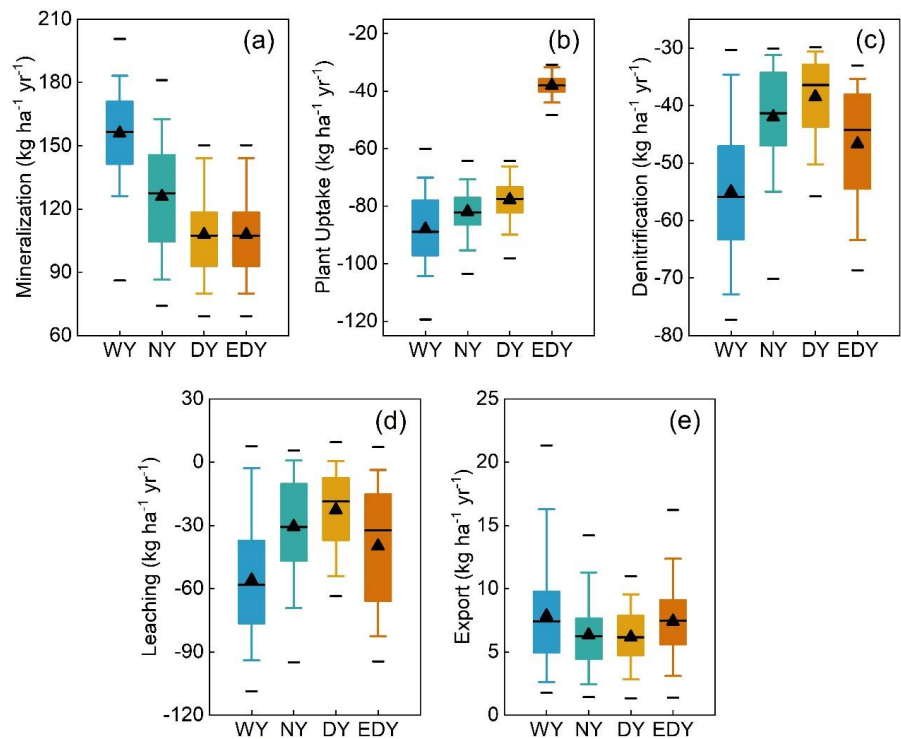
443 The soil organic nitrogen (SON) loads increase when the rainfall pattern turns from WY,
444 via NY, to DY/EDY (Figure 5a & b). The SON loads in DY and EDY are identical
445 because the vegetation dying back in EDY is not able to influence the transformation
446 of SON. The soil inorganic nitrogen load (SIN) is generally high in WY and low in DY



447 (Figure 5c). However, when vegetation dying back causes reduced plant uptake in EDY,
448 the SIN load can accumulate significantly to the highest level among the four scenarios.
449 The highest and the lowest N mineralization fluxes are produced in WY and DY,
450 respectively (Figure 6a). DY and EDY have the identical mineralization fluxes. It can
451 be attributed to the lower soil moisture content caused by decreased precipitation
452 constraining the mineralization process. Note that the fluxes of plant uptake,
453 denitrification, and leaching are negative values representing the sink term for the SIN
454 pool. For the plant uptake, the highest N fluxes are produced in WY (Figure 6b). Plant
455 uptake decreases when the rainfall pattern transforms from WY, via NY, to DY, induced
456 by the decreasing soil moisture. In EDY, due to vegetation dying back, plant uptake
457 significantly reduces to the lowest level. The fluxes of denitrification (in soil and
458 groundwater) and leaching (from soil to groundwater) both exhibit decreasing trends
459 when the rainfall pattern transforms from WY, via NY, to DY (Figure 6c & d). It can be
460 explained by the decreasing soil moisture inhibiting the biogeochemical activities, as
461 well as the N mobilization from soil to groundwater. However, for the EDY scenario,
462 large denitrification and leaching fluxes can still be observed even when soil moisture
463 content is small. This is because the plant uptake is significantly constrained in EDY,
464 such that more SIN is available for either consumption via denitrification or leaching
465 into groundwater. The N export flux to the stream generally follows the same patterns
466 as the leaching, with the relatively higher fluxes occurring in WY and EDY and lower
467 fluxes in NY and DY (Figure 6e). It demonstrates that in the catchment, leaching is a



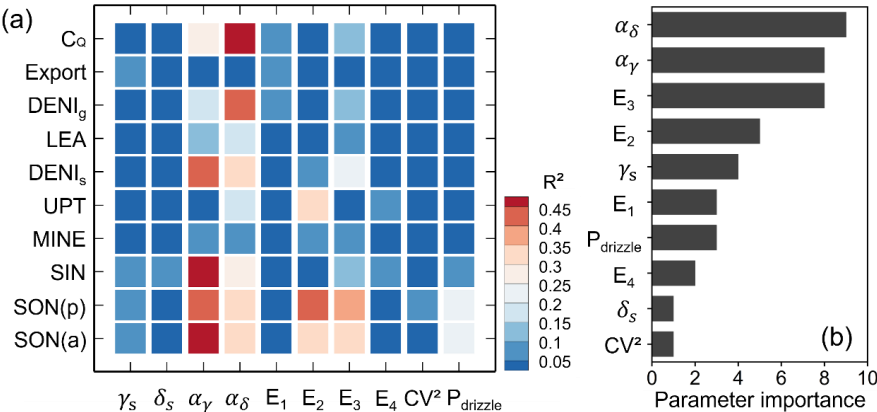
468 key factor to determine the N export from groundwater to stream water.



469
470 **Figure 6.** The simulated fluxes of (a) mineralization, (b) plant uptake, (c) denitrification (in
471 soil and groundwater), (d) leaching, and (e) export for the scenarios of WY, NY, DY, and EDY.

472 **4.2 Effect of Intra-annual rainfall variability**

473 The determination coefficients (R^2) of the linear regressions between the parameters of
474 the rainfall generator and the C_Q / N loads / fluxes are illustrated in Figure 7a. Lager R^2
475 values can be observed for the amplitude of the seasonal variations in the storm duration
476 and inter-storm period (α_γ & α_δ), the average rainfall intensity of the second season
477 and third season (E_2 & E_3). These parameters are the four most important parameters
478 (Figure 7b) that may influence N loads / fluxes, and are subjected to further discussion.



479

480 **Figure 7.** (a) The determination coefficients (R^2) of the linear regressions between the
481 parameters of the rainfall generator and in-stream nitrate concentration (C_Q), N loads, and
482 fluxes. (b) The importance of the parameters influencing the N dynamics.

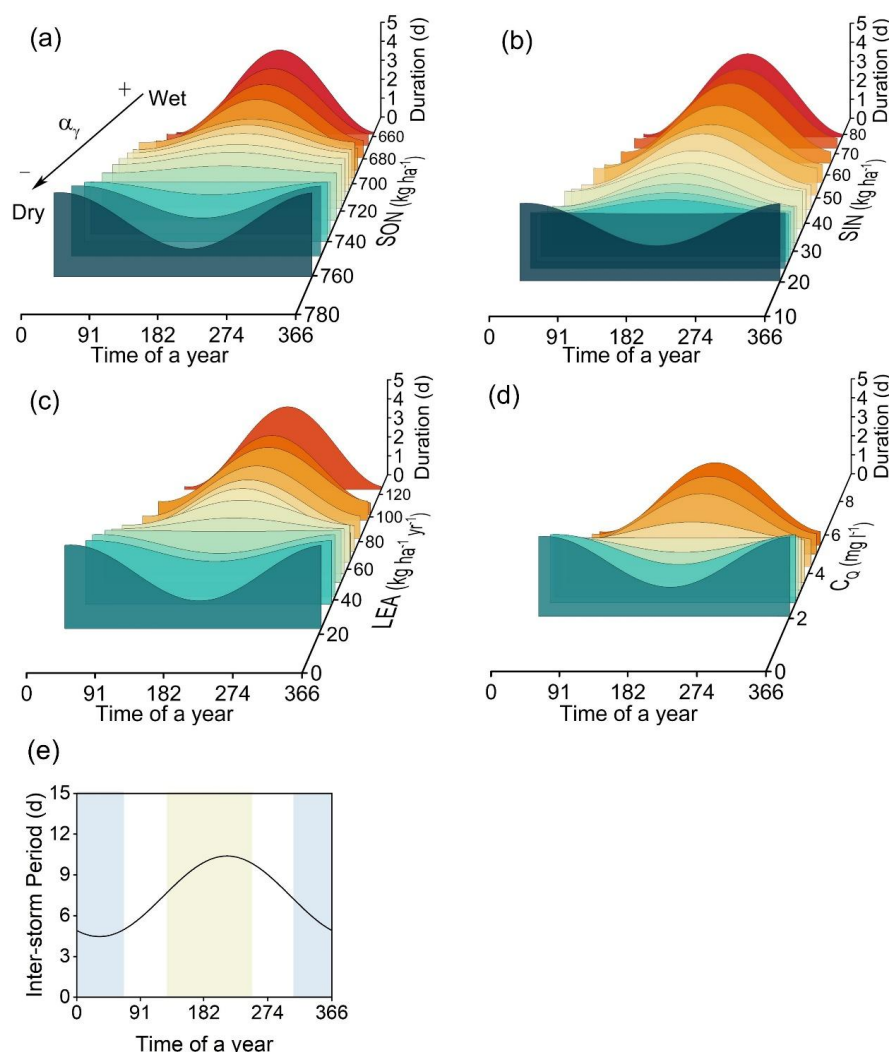
483 ***Storm duration***

484 The parameter α_γ determines how the average storm duration is distributed over the
485 course of a year (Figure 8a). Generally, larger α_γ values represent that storms with
486 longer duration are more likely to occur in mid-year, when ET is high and the inter-
487 storm duration is longer (yellow zone in Figure 8e). This pattern influences not only the
488 drying and rewetting cycles in summer time, but it also supplies more water in the
489 period thereby leading to an overall wet year (e.g., year 2007, $\alpha_\gamma=1.764$). The decrease
490 of α_γ causes that storms with longer durations are shifted towards the beginning / end
491 of the year (blue zone in Figure 8e), so that the year becomes drier (e.g., year 2018,
492 $\alpha_\gamma=0.55$).

493 Results suggest that the storm duration distribution during a year can significantly affect
494 the transformation and transport of N. Lower SON load (Figure 8a), but higher SIN



495 load (Figure 8b), can be observed when storms with longer duration occur mid-year.
496 This is due to the fact that the wetter conditions in the catchment can promote the
497 mineralization of SON into SIN, especially for warm periods when mineralization is
498 significantly constrained by soil moisture rather than by temperature. The wetter
499 condition associated with larger α_y increase the leaching flux of SIN from soil into
500 groundwater (Figure 8c), thereby increasing the average C_Q (Figure 8d). When storms
501 with shorter duration occur mid-year, the transformation and transport of N are subject
502 to retardation.



503

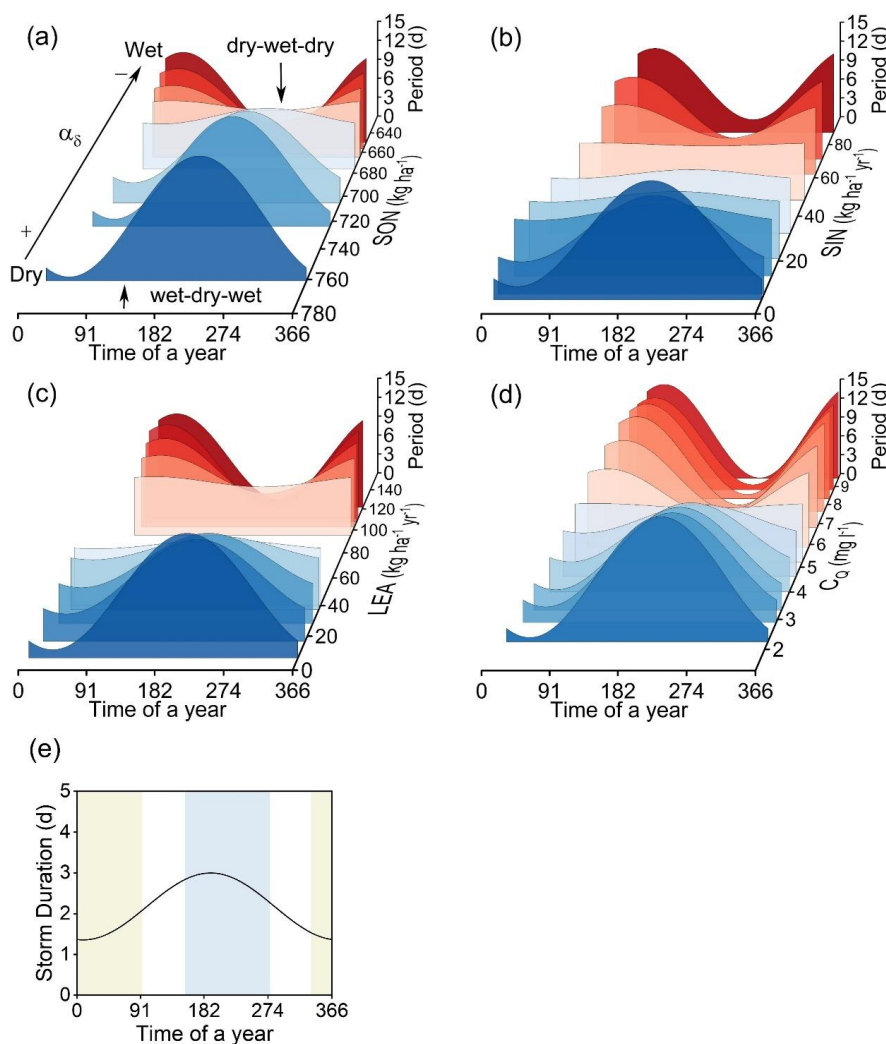
504 **Figure 8.** The effect of varied average storm duration distributions over the course of a year on
 505 (a) SON load, (b) SIN load, (c) leaching flux, and (d) in-stream nitrate concentration (C_Q). (e)
 506 The monthly average inter-storm period over the course of a year (kept constant when α_γ
 507 varies). As α_γ values decrease, storms with longer durations shift gradually from the period
 508 with high ET and longer inter-storm periods (yellow zone) to the period with low ET and shorter
 509 inter-storm periods (blue zone).

510 **Inter-storm duration**

511 α_δ regulates the variation of monthly average inter-storm periods throughout the



512 course of a year (Figure 9a). Large α_δ values imply that long inter-storm durations are
513 more likely to cluster in the middle of the year, which is associated with longer storm
514 durations (blue zone, Figure 9e), while short inter-storm durations occur at the
515 beginning / end of the year, associated with shorter storm durations (yellow zone,
516 Figure 9e). This forms a “wet-dry-wet” climate pattern which promotes the
517 accumulation of SON in the soil (Figure 9a), but reduces the SIN load (Figure 9b), the
518 leaching flux (Figure 9c), and the C_Q (Figure 9d). However, when α_δ decreases, long
519 inter-storm periods are shifted to the beginning / end of the year when the storm
520 durations are short (yellow zone, Figure 9e), forming a “dry-wet-dry” climate pattern
521 over a year. Such a climate pattern results in a lower SON load, but a higher SIN load.
522 This is because wet and warm conditions in the middle of the year promote the
523 mineralization of SON accumulated in the previous season. Consequently, a high
524 leaching flux and high C_Q are also observed.



525

526 **Figure 9.** The effect of varied average inter-storm period distributions over the course of a year
 527 on (a) SON load, (b) SIN load, (c) leaching flux, and (d) in-stream nitrate concentration (C_Q).
 528 (e) The monthly average storm duration over the course of a year (kept constant when α_δ
 529 varies). As α_δ values decrease, inter-storms with longer periods shift gradually from the
 530 period with longer storm durations (blue zone) to the period with shorter storm durations
 531 (yellow zone).

532 *Average Storm Intensity*

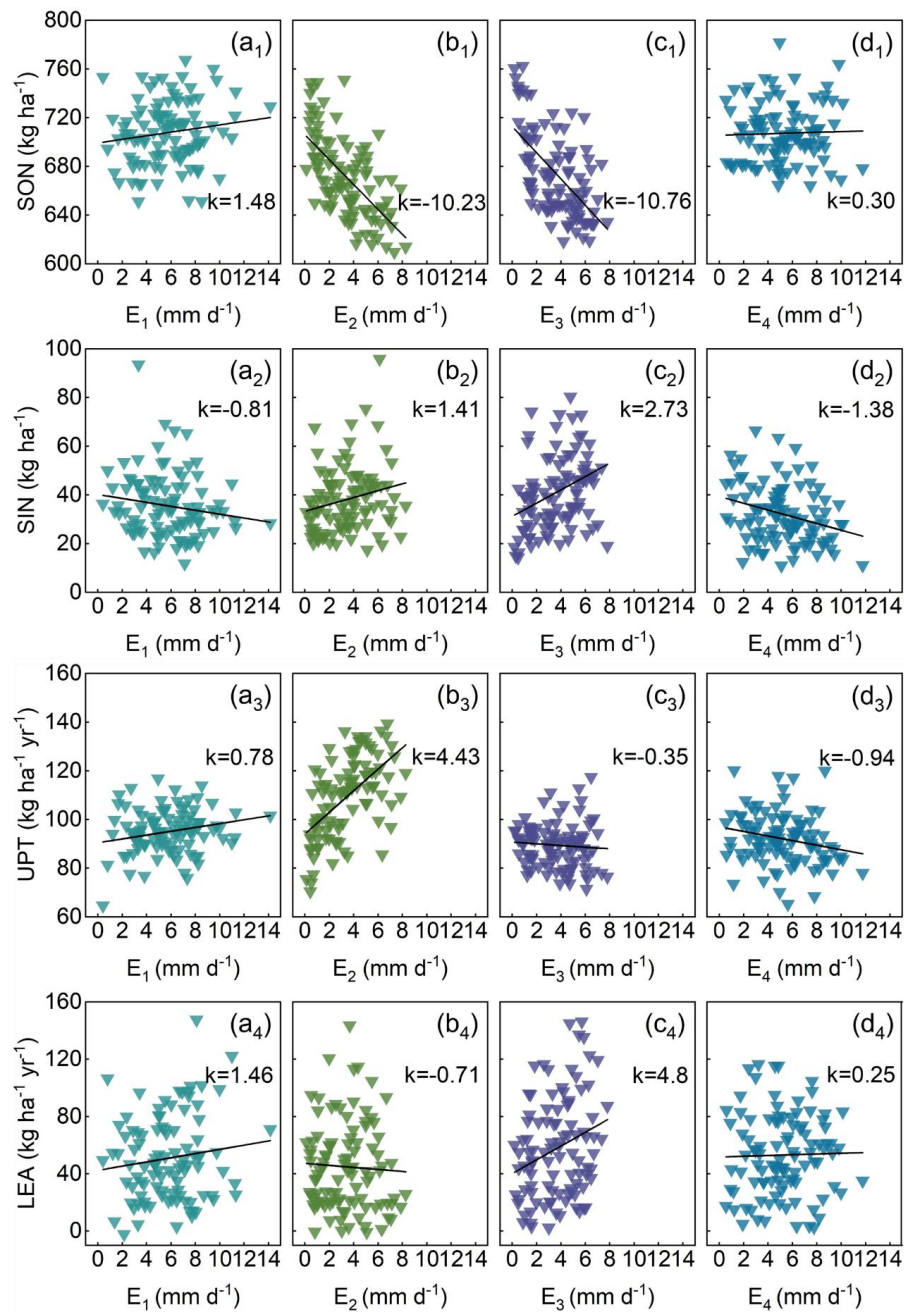
533 Figure 10 depicts the responses of SON, SIN, plant uptake, leaching, and C_Q to the



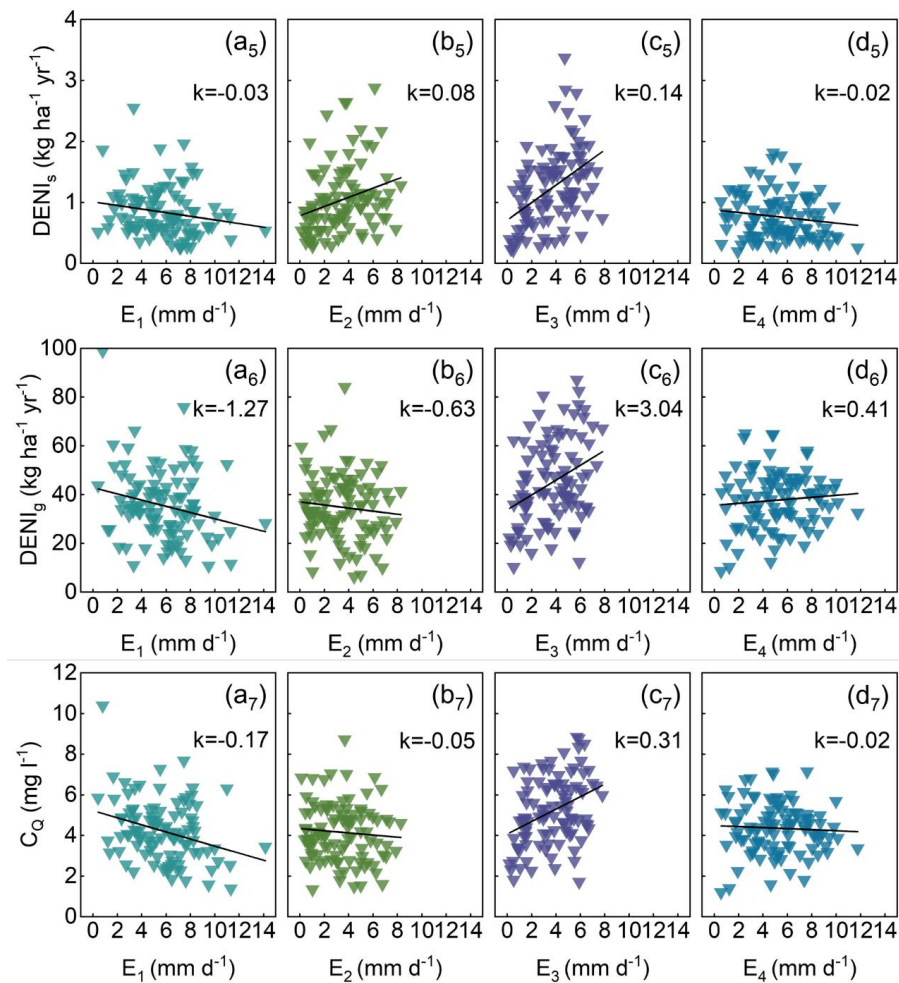
534 average rainfall intensity of the four seasons (E_1 , E_2 , E_3 , and E_4). Basically, increased
535 rainfall intensity creates a more humid catchment, intensifying the biogeochemical
536 processes (e.g., mineralization, plant-uptake). According to the slope of the linear
537 relationship (k), it is suggested that the increase of the rainfall intensity of the second
538 and third seasons (E_2 and E_3) can significantly reduce the SON load (Figure 10b₁ &
539 10c₁). Rainfall intensity in the first and last seasons (E_1 and E_4) has hardly an effect on
540 the SON loads and fluxes (Figure 10a₁ & 10d₁), probably because the mineralization of
541 SON is more restrained by the low temperature in these seasons. As the only sink of
542 SON, SIN load should theoretically increase with the increase of E_2 and E_3 , but a
543 relatively stronger response of SIN just occurs in the third season (Figure 10c₂). A
544 significant increase in the plant-uptake flux, concurrent with the increase of rainfall
545 intensity, is only observed in the second season when plant growth occurs (Figure 10b₃).
546 It follows that sufficient moisture contributes to intense absorption of nutrients by
547 vegetation, but just in the growing season. It can be inferred that extensive plant uptake
548 inhibits the response of SIN to the average rainfall intensity in the second season
549 (Figure 10b₂). In addition, leaching (Figure 10c₄) and denitrification fluxes (in soil,
550 Figure 10c₅) increase with the average storm intensity in the third season as well. The
551 response of the denitrification flux in groundwater to the change of average rainfall
552 intensity exhibits an obvious increase in the third season (Figure 10c₆), as well as a
553 slight decrease in the first season (Figure 10a₆). Finally, note that a change of the
554 average rainfall intensity only causes a minor increase or decrease of C_Q in the first and



555 third season (Figure 10a7 & c7), respectively.



556



557

558 **Figure 10.** The responses of soil nitrogen loads (SON & SIN), plant uptake and leaching fluxes
559 as well as in-stream nitrate concentration (C_Q) to the average rainfall intensity of the four
560 seasons (E_1 , E_2 , E_3 , and E_4). The symbol and magnitude of the slopes of these linear
561 relationships (k) represent the direction and the intensity of response of N dynamics to the
562 variations in average rainfall intensity, respectively.

563 5 Discussion

564 5.1 Increased rainfalls prompt N dynamics

565 The comparison of C_Q , N loads and N fluxes among the four scenarios of the inter-



566 annual rainfall variability reveals its effect on N dynamics. Mineralization, as the
567 unique process of the transformation from SON to SIN, is impacted by soil wetness and
568 temperatures. With the same soil temperatures assumed for all the scenarios, the
569 average level of mineralization corresponds to the annual wetness conditions. In WY,
570 the mineralization is increased. In contrast, the low mineralization in DY (EDY) leads
571 to the accumulation of SON. Apart from mineralization, the biogeochemical processes
572 relative to SIN, including plant uptake, denitrification, and leaching, are all influenced
573 by soil moisture as well [Yang et al., 2022; Yang et al., 2021]. Their average levels
574 decrease with decreasing wetness conditions from WY, via NY, to DY. In addition, the
575 transport of DIN relies on groundwater discharge and subsurface flow paths. Increased
576 discharge due to changes in precipitation may flush out more nitrogen to surface water
577 bodies [Mitchell et al., 1996; Creed and Band, 1998] by activating shallow preferential
578 flow paths with short transit times [Yang et al., 2018]. Thus, the changes of nitrogen
579 export and C_Q are consistent with the change of wetness conditions between WY, NY,
580 and DY as well. It can be concluded that high annual precipitation amounts can enhance
581 the transformation and transport of nitrogen while low annual precipitation amounts are
582 more conducive for N to be retained in the catchment. Our simulation results echo
583 previous findings that N retention is influenced by changes in precipitation [Dumont et
584 al., 2005; Howarth et al., 2006].



5.2 Stream water quality deteriorates during extreme droughts

In the EDY scenario, when the vegetation suffers from drought stress, SIN remarkably accumulates in soil [RIVM, 2021; Winter et al., 2023]. This is because in general plant uptake is the major sink for SIN [Yang et al., 2021; Zhou et al., 2022; Wang et al., 2023]. Due to the accumulation of SIN, denitrification and leaching in the EDY scenario are higher than those of the DY scenario as well. Subsequently, N export to the stream during the EDY scenario is higher than that during the DY scenario, even though the stream discharge is the same (Figure 11). This causes the in-stream nitrate concentration for the EDY scenario to be as high as that of the WY scenario.

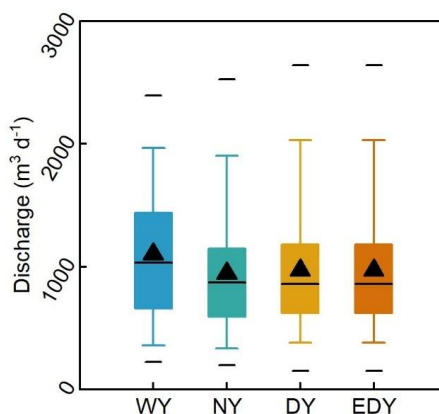
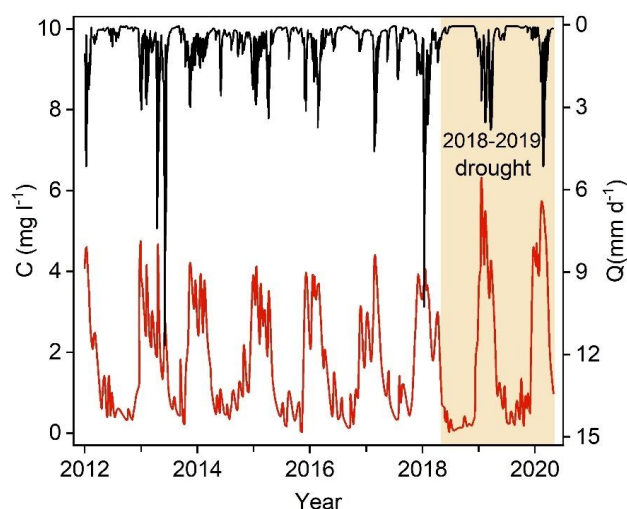


Figure 11. The simulated discharge for the scenarios of WY, NY, DY, and EDY.

During the 2018-2019 drought in central Europe, the observed peaks of in-stream nitrate concentration at a mesoscale catchment in central Germany were significantly higher than previous (Figure 12). Based on the data-driven analysis, Winter et al. [2023] indicated that nitrate loads in the 2018-2019 drought were up to 73% higher than the



600 long-term averaged loads. They demonstrated that such an increase was attributed to
 601 decreased plant uptake and subsequent flushing of accumulated nitrogen during the
 602 rewetting period. Our results confirmed their findings that reduced plant uptake in
 603 extreme droughts causes C_Q to increase (Figure 4(b4)), which suggests that vegetation
 604 plays a vital role in the increased risk of N pollution during extreme droughts. Thus,
 605 when vegetation suffers from drought stress, the N retention capacity can decline
 606 severely.



607
 608 **Figure 12.** Measured daily averaged nitrate concentrations (C, red line) and discharge (Q, black
 609 line) in the nearby Upper Selke catchment in central Germany [Winter et al., 2023]. The yellow
 610 area marks the 2018-2019 drought occurring across central Europe.

611 5.3 The distribution of storm durations controls the N loads

612 Our study indicates that the wet / dry conditions in the middle of a year are key to the
 613 transformation and transport of N throughout the whole year. The combination of longer
 614 storms and longer inter-storm periods mid-year represents an aspect of extreme climate



615 events that finds that intense rainfalls alternate with drought periods [Zhang et al., 2024].
616 Without temperature limitations, alternating longer storm durations and longer inter-
617 storm periods increase the extensive transformation of SON, which is consistent with
618 the results of laboratory studies that mineralization increased after successive drying
619 and rewetting cycles in soils [Cabrera, 1993]. It is concluded thereby that drying-
620 rewetting events induce the prominent changes in N dynamics [Fierer & Schimel, 2002].
621 However, the drier conditions induced by shortened storm durations and longer inter-
622 storm periods in mid-year cause the accumulation of SON, which is consistent with the
623 finding by Zhou et al. [2022] that droughts in the warm season contribute to nitrogen
624 retention in catchments. Thus, the distribution of storm duration within a year can
625 significantly affect N loads in a catchment.

626 **5.4 The distribution of inter-storm periods changes stream water** 627 **quality**

628 Different dry-wet patterns over the course of a year have an impact on N dynamics as
629 well, with a specifically intense focus on in-stream nitrate concentration. In the “dry-
630 wet-dry” pattern, the accumulation of SON during the previous dry season is
631 transformed and transported during the subsequent wetting period, which leads to
632 higher C_Q . In the 2018-2019 drought, accumulated N loads were flushed during the
633 rewetting period and thereby caused elevated nitrate loads (Figure 12). In the “wet-dry-
634 wet” pattern, wetter conditions but low temperatures in the beginning of the year and



635 warm droughts in mid-year both cause SON loads to accumulate throughout the entire
636 year and C_Q to decrease in general. The result that reduced C_Q may be attributed to
637 limited terrestrial export loading was proven by Zhou et al. [2022]. In summary, the
638 distribution of inter-storm periods during a year can cause noticeable variations in water
639 quality in terms of nitrate concentration.

640 **5.5 Average rainfall intensity has only a small effect on stream water** 641 **quality**

642 Wet conditions caused by high mean rainfall intensities contribute to the transformation
643 of SON to SIN [Knapp and Smith, 2001], if mineralization is not constrained by low
644 temperatures (Equation 1 & 2). The potential plant uptake is subject to the state of
645 vegetation (Equation 6), and the actual plant uptake is further limited by SIN load and
646 soil moisture content (Equation 5) [Yang et al., 2022; Cramer et al., 2009]. Thus, high
647 mean rainfall intensities increase plant absorption of inorganic nitrogen in the growing
648 season. Since plant uptake is the major sink of SIN, SIN flux hardly responds to the
649 variations of mean rainfall intensities in the season of growth. Leaching and
650 denitrification fluxes (in the soil) are determined by SIN load, soil saturation, and
651 groundwater velocity (Equation 3 & 7-9). As a result, the fluxes increase remarkably
652 when the average rainfall intensity in the third season increases. The denitrification
653 efficiency in groundwater depends on transit time. In the first season, increased
654 discharge caused by enhanced rainfall intensity (Figure S2a) accelerates the transport



655 of DIN and thus cuts down the denitrification flux [Wang et al., 2023]. However, due
656 to high ET in the third season, decreased discharge (Figure S2c) can prolong the transit
657 time of DIN and may increase denitrification. It is noteworthy that the unexpectedly
658 weak response of C_Q to the average rainfall intensity may be caused by the fact that
659 high-intensity precipitation events tend to have short durations and yield surface runoff.
660 It is less likely for the extreme precipitation to propagate to the groundwater zone and
661 impact the discharge and nitrate export (see Figure S2 in the supporting information).
662 On the whole, increased variations in precipitation can alter the transformation and
663 transport of nitrogen [Kane et al., 2008]. The results of the present study can help in
664 managing the water quality of agricultural catchments with prominent rainfall
665 variability and protect aquatic ecosystems during extreme rainfall and droughts in the
666 future. For instance, the formulation of a fertilization scheme for inter-storm periods to
667 avoid flushing in the rewetting periods after droughts. Also, increased fertilization in
668 the wet season of the growing season not only is conducive to vegetation absorption of
669 nutrients, but also does not cause pressure on soil and water bodies.

670 **5.6 Limitations and Outlook**

671 The contribution of high temperatures to extreme droughts has not been considered in
672 the present study. High temperatures induced several remarkable hydrological and
673 agricultural droughts in Central Germany, which even destroyed vegetation activities
674 [Fink et al., 2004; Camenisch et al., 2020; Liu et al., 2020; Schuldt et al., 2022; Winter



675 et al., 2022]. Considering the phenomenon, the present study indicates that vegetation
676 plays a quite significant role in N dynamics only by assuming reduced plant uptake.
677 Apart from that, both mineralization and denitrification are subject to temperature. For
678 instance, the biological activities of denitrifying bacteria are impacted by high
679 temperatures that can cause an increase in denitrification efficiency [Amatya et al.,
680 2009]. Thus, high temperatures can influence the nitrogen retention capacity of
681 catchments. The effect of rising temperatures on water quality and the environment in
682 terms of N dynamics should be investigated in detail.

683 In the future, the alteration of soil properties caused by rainfall variability should be
684 studied in the model. In the model, precipitation and solute enter the subsurface domain
685 with fixed soil porosity, ignoring the alteration of pores. Abundant microorganisms and
686 animals engage in extensive activities, and massive organic and inorganic matter
687 undergoes biochemical reactions in soil pores, which all change the physical and
688 chemical properties of porous media and thereby impact the process of seepage. These
689 biogeochemical processes are determined by several factors, such as
690 hydrometeorological conditions [Ondrasek et al., 2019]. For example, under drying
691 conditions, the activities of microorganisms and animals diminish which is not helpful
692 to the maintenance and improvement of soil structures. The severe deficit of soil
693 moisture causes the destruction of soil aggregates, more micropores replace macropores
694 and even compacted soil forms in the upper layer due to salt clusters, which thereby
695 decreases the porosity. What's more, extreme droughts may cause surface soil to crack,



696 which is adverse to plant growth and root development. Not to mention that changing
697 soil properties caused by complex and extreme climate patterns may have an effect on
698 the biogeochemical activities in soil. Consequently, the clarification of these
699 mechanisms will be conducive to exploring the more realistic response of solute
700 transport in groundwater to extreme rainfall and droughts.

701 **6. Conclusions**

702 In the context of climate change and the frequent occurrence of extreme rainfall and
703 droughts, the study adopted a stochastic rainfall generator (Robinson and Sivapalan,
704 1997) to explore the effects of inter-annual and intra-annual rainfall variability on N
705 dynamics for the first time in a small agricultural catchment in Central Germany. The
706 main conclusions of this study are:

707 (1) Higher annual precipitation amounts can enhance the transformation and transport
708 of nitrogen. Lower annual precipitation amounts are conducive to the nitrogen
709 retention capacity. Nonetheless, when vegetation suffers from drought stress, the
710 retention capacity will decline severely. Vegetation plays a vital role in N dynamics
711 under extreme droughts.

712 (2) Wet / dry conditions determined by the distribution of storm durations within a year
713 can significantly affect N loads within a catchment. Droughts can prompt the
714 accumulation of SON, but a drying-wetting cycle can enhance extensive
715 transformation of SON in the warm season.



716 (3) Different dry-wet patterns formed by the distribution of inter-storm periods during
717 a year can cause noticeable variations in water quality. In-stream nitrate
718 concentration prominently elevates during the rewetting period after the drought.

719 (4) High mean rainfall intensity contributes to the transformation of N when
720 mineralization is not limited by low temperatures, and to plant absorption of
721 inorganic nitrogen in the growing season. There is merely a small effect on stream
722 water quality.

723 Overall, the study clarifies the effect of rainfall variability on N dynamics in a small
724 agricultural catchment, which provides theoretical support to formulate fertilization
725 strategies and protect aquatic ecosystems under the context of climate change in the
726 future.

727 **Code availability.** All data used in this study are listed in the supporting information
728 and uploaded separately to HydroShare [Wang, 2024].

729 **Author contributions.** QW contributed to the conceptualization, methodology, software,
730 formal analysis, visualization, and writing (review and editing). JY contributed to the
731 conceptualization, methodology, formal analysis, and writing (review and editing). IH
732 contributed to the writing (review and editing). TX contributed to the conceptualization
733 and review and editing. CL contributed to the methodology, and review and editing.

734 **Competing interests.** The contact author has declared that none of the authors has any
735 competing interests.



736 **Disclaimer.** Publisher' note: Copernicus Publications remains neutral with regard to
 737 jurisdictional claims in published maps and institutional affiliations.

738 **Acknowledgements.** We thank Daniel C. Wilusz for the source code in Python v2.7 of
 739 the rainfall generator [Wilusz et al., 2017] and Min Yan and Huiqiang Wu for
 740 stimulating discussions.

741 **Financial support.** This research was supported by the National Key Research and
 742 Development Project, China (JY & CL: 2021YFC3200500), the National Natural
 743 Science Foundation of China, China (JY & CL: U2340212, JY: 52009032, TX:
 744 42377046, CL: 51879088), and the Natural Science Foundation of Jiangsu Province,
 745 China (CL: BK20190023).

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