Bayesian hierarchical modelling of nitrate concentration in a forest stream affected by large-scale forest dieback

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Abstract

The ecosystem function of vegetation to attenuate riverine export of nutrients is of substantial importance for securing water quality. This ecosystem function is at risk of deterioration due to an increasing risk of large-scale forest dieback under climate change. The present study explores the response of the nitrogen (N) cycle of a forest catchment in the Bavarian Forest National Park, Germany, in the face of a severe bark beetle () outbreak and resulting large-scale forest dieback. Outbreaks of bark beetle killed the dominant tree species Norway spruce () in up to 55 % of the area. A Bayesian hierarchical model that predicts stream NO concentration (C) with discharge (Q) and water temperature (T) as predictors (C-Q-T relationship) was found as the best fitting model. This informed top-down development of a catchment model to explain the C-Q-T relationship so that the annually-varying model parameter estimates provide mechanistic interpretations of the catchment processes. NO concentration increased after the dieback because N was released from the decaying fine litter of trees beyond the capacity of the terrestrial vegetation and riparian zone to regulate the nutrient export. Within a decade after the dieback, the released N was flushed out and nutrient retention capacity was restored with the regrowth of the vegetation. Greater understanding of canopy mortality due to climate change and other anthropogenic impacts are required to mitigate the deterioration of nutrient retention and prevent nutrient loss.

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12	
13	Key Points:
14 15	• Pulse of nitrate export from a forest catchment in response to bark beetle infestation followed by recovery of nutrient retention capacity
16 17	• Bayesian hierarchical model predicting stream nitrate concentration dynamics with discharge and water temperature
18 19 20	• Mechanistic explanation of concentration-discharge-temperature relationship to assist interpretation of the regression analysis

21 Abstract

22 The ecosystem function of vegetation to attenuate riverine export of nutrients is of substantial importance for securing water quality. This ecosystem function is at risk of 23 deterioration due to an increasing risk of large-scale forest dieback under climate change. The 24 present study explores the response of the nitrogen (N) cycle of a forest catchment in the 25 26 Bavarian Forest National Park, Germany, in the face of a severe bark beetle (*Ips typographus*) outbreak and resulting large-scale forest dieback. Outbreaks of bark beetle killed the dominant 27 tree species Norway spruce (Picea abies) in up to 55 % of the area. A Bayesian hierarchical 28 model that predicts stream NO₃ concentration (C) with discharge (Q) and water temperature (T) 29 as predictors (C-O-T relationship) was found as the best fitting model. This informed top-down 30 development of a catchment model to explain the C-Q-T relationship so that the annually-31 32 varying model parameter estimates provide mechanistic interpretations of the catchment processes. NO3 concentration increased after the dieback because N was released from the 33 decaying fine litter of trees beyond the capacity of the terrestrial vegetation and riparian zone to 34 regulate the nutrient export. Within a decade after the dieback, the released N was flushed out 35 and nutrient retention capacity was restored with the regrowth of the vegetation. Greater 36 understanding of canopy mortality due to climate change and other anthropogenic impacts are 37 required to mitigate the deterioration of nutrient retention and prevent nutrient loss. 38

39

40 **1 Introduction**

Water is important in the global nutrient cycle, both as a transport agent and as a medium 41 for biogeochemical reactions in soil, ground and surface waters. Large aquatic ecosystems rely 42 43 on the nutrient supply via hydrological pathways. However, when nutrients are present in water at excessive concentrations, they can cause environmental harm such as eutrophication and 44 hypoxia, leading to deterioration of water quality for ecosystems and human use [Hilton et al., 45 2006; Xu et al., 2014]. Vegetation is a crucial mediating agent in the cycling of water as it 46 intercepts precipitation, and transpires and regulates evaporation and groundwater flow [Harman 47 et al., 2011; Adams et al., 2012]. Nutrient exports are also regulated by vegetation growth which 48 assists in biogeochemical processes that retain nutrients in soils or release them [Botter et al., 49 2010; Gall et al., 2013]. 50

51 Forest catchments, whose hillslopes and riparian areas are covered largely by vegetation, are especially effective at regulating nutrient exports. Since forests account for approximately 30 52 % of global land cover [Hansen et al., 2013], the nutrient regulation of forest catchments 53 provides a crucial ecosystem function for the conservation of water resources and ecosystems 54 worldwide. In recent decades, concerns have grown about large-scale pulses of forest dieback 55 due to drought and insect infestation [Allen et al., 2010; Seidl et al., 2017]. Although tree 56 mortality and pulses of increased mortality are natural processes, large-scale forest diebacks can 57 undermine the nutrient regulating function of forests and thus threaten ecosystem and drinking 58 water quality. 59

In a catchment experiencing pulses of increased forest mortality, export of nitrogen (N) is of key concern since inorganic N is leached easily [*Gundersen et al.*, 2006] and hence in-stream concentrations respond drastically to diebacks [*Hartmann et al.*, 2016]. *Vitousek and Reiners* [1975] were among the first to explain that an ecosystem loses nutrients after a forest dieback, 64 but then retains them more effectively than before the dieback as biomass accumulates again

during the following succession. Several studies have since observed increases of inorganic N

66 exports in forest catchments affected by forest diebacks caused by bark beetle infestation

67 [Biederman et al., 2016], wildfire [Betts and Jones Jr., 2009], windthrow [Hartmann et al., 2016]

and also in watersheds affected by clear-cut harvest [*Pardo et al.*, 1995].

69 Outbreaks of the European spruce bark beetle (Ips typographus Linnaeus) have increased in frequency and magnitude in Central Europe over recent decades due to the combined effects 70 of past land use legacies and climate change [Seidl et al., 2011; Senf et al., 2017], leading to an 71 observable increase in canopy mortality [Senf et al., 2018]. For instance, the Bavarian Forest 72 National Park, Germany, experienced two large-scale bark beetle outbreaks between 1990 and 73 2010 [Kautz et al., 2011], which led to the dieback of most of the bark beetle's host tree Norway 74 75 spruce (Picea abies (L.) H.Karst.). The dieback of Spruce caused an increase in the export of nitrate (NO₃), while at the same time benefitting biodiversity since the mortality of this dominant 76 tree species created canopy gaps and provided new niches (i.e., deadwood) for many forest 77 dwelling species [Gundersen et al., 2006; Beudert et al., 2014]. While the forest dieback has 78 79 been unprecedented, recent studies have shown the high resilience of the system, with the forest returning after several years post dieback [Zeppenfeld et al., 2015; Senf et al., 2019]. Further, 80 unlike most forests of Europe that are intensively managed, the bark beetle outbreak within the 81 82 core zone of the National Park was protected without any management measure, leading to a unique opportunity for research on the effects of forest diebacks on ecosystem processes, such as 83 the responses of the N cycle of a whole forest catchment to natural bark beetle induced forest 84 diebacks. 85

Nutrient export from a catchment is complicated by heterogeneous sources, dynamic 86 pathways and variable biogeochemical processes [Basu et al., 2011; Musolff et al., 2015]. It is 87 challenging to monitor the relevant processes in hillslopes and streams across an entire 88 catchment. In practice, nutrient concentration is most often monitored in streams representing 89 90 integrated effects of catchment processes and enabling quantification of downstream export. The relationship of solute concentration with discharge (C-Q relationship) and its variation in space 91 and time has proven a particularly useful indicator of catchment processes [Musolff et al., 2015; 92 93 Rose et al., 2018; Zhi et al., 2019]. Previous studies showed that the C-Q relationship relies on 94 the reactivity of the solute and spatial correspondence between the source areas and discharge [Seibert et al., 2009; Basu et al., 2011; Thompson et al., 2011]. These studies have followed a 95 96 data-driven, or 'top-down' modelling approach [Sivapalan et al., 2003] that aims at accounting for the dominant catchment processes using parsimonious model structures that are 97 commensurate with the often limited availability of data [Krueger et al., 2007]. 98

Regression models have proven particularly efficient in screening and investigating the 99 relationships of nutrient concentrations with other environmental variables [Chavez and Service, 100 1996; Clark et al., 2004b; a; Exner-Kittridge et al., 2016]. Where these data and relationships 101 relate to disparate scales then an hierarchical model is called for, with the Bayesian hierarchical 102 framework being the most flexible and coherent. Bayesian hierarchical modeling has been 103 applied to hydrochemical data to predict the behavior of aquatic environments such as nutrient 104 concentrations [Xia et al., 2016], algal blooms [Obenour et al., 2014; Cha et al., 2016; Cha et al., 105 2017], dissolved oxygen [Borsuk et al., 2001; Stow and Scavia, 2008] and salinity [Webb et al., 106 2010]. Borsuk et al. [2001] and Stow and Scavia [2008] applied mechanistic models in a 107 Bayesian hierarchical framework combining the strengths of mechanistic and statistical modeling; 108

making predictions based on process knowledge while estimating parameters empirically fromdata.

The aim of this study was to investigate the response of the N cycle of a catchment within 111 the Bavarian Forest National Park, the Grosse Ohe catchment, to the bark beetle induced forest 112 dieback using in-stream monitoring data and Bayesian hierarchical modeling in top-down 113 114 fashion. We hypothesized: (1) that NO₃ concentrations in forest streams would increase due to the loss of nutrient retention capacity in forests affected by large-scale mortality; (2) that the 115 nutrient retention would recover after dieback due to the regrowth of vegetation, indicating an 116 overall resilient ecosystem. To test those hypotheses, we first developed a Bayesian hierarchical 117 model through model comparison to investigate temporally variant relationships between stream 118 NO₃ concentration and other environmental variables. Second, the resultant model structure 119 inspired a parsimonious catchment model that provides mechanistic interpretations of catchment 120 dynamics across sites and years for specifically addressing the hypotheses. The derivation of the 121 parsimonious catchment model, resulting from the initial Bayesian hierarchical model, will be 122 described in the results section. We conclude our analysis by correlating model parameters with 123 an independent remote sensing based proxy of vegetation activity, the normalized difference 124 vegetation index (NDVI) in order to guide parameter interpretation and independently evaluate 125 the plausibility of the mechanistic model. 126 127

128

129 **2 Materials and Methods**

130 2.1 Study Area and Measurements

Grosse Ohe is a headwater catchment located in the Bavarian Forest National Park, 131 Germany, with a size of 19.1 km² and a mountainous topography with 11.1° mean slope at 132 altitudes of 770 – 1447 m above sea level. 98 % of the catchment area is forested, and human 133 management was excluded since at least the 1970s (i.e., since establishment of the National 134 Park). Norway spruce dominated forests cover approximately 70 % of area, with the remaining 135 136 area being dominated by European beech (Fagus sylvatica L.). Stream hydrochemistry was monitored at the outlets of Grosse Ohe (48°56'17.99" N, 13°24'45.13" E) and its two nested 137 subcatchments Markungsgraben (48°57'20.89" N, 13°25'35.8" E, 1.1 km²) and Forellenbach 138 (48°56'33.61" N, 13°25'10.63" E, 0.7 km²). The forest dieback was most severe in 139 Markungsgraben (mortality on approximately 82 % of the catchment area) compared to 140 Forellenbach (mortality on approximately 57 % of the area) and the entire catchment Grosse Ohe 141 (mortality on approximately 55 % of the area). A map displaying the study catchment with the 142 forest dieback, the streams and the monitoring stations can be found in Figure S1 of the 143 Supporting Information. 144

The hydrochemical measurements include water level and concentrations of nitrogen (N), phosphorus, organic carbon and dissolved oxygen (DO), pH, conductivity and water temperature. Water levels were measured quasi-continuously (every 15 minutes) and converted to discharges via rating curves. Baseflow was separated from the discharge with a digital filter algorithm available in the R package 'EcoHydRology' [*Fuka et al.*, 2018]. The baseflow index was computed as the proportion of baseflow relative to discharge. Temperature, pH, DO and electric conductivity were measured every minute. All sub-daily data were aggregated to daily means to

match the instantaneous sampling. Instantaneous samples for chemical analyses were taken 152

- manually every two weeks at Grosse Ohe and Markungsgraben and weekly at Forellenbach. The 153
- samples were analyzed monthly in the laboratory to determine nutrient concentrations according 154
- to DIN/EN/ISO. The monitoring programs started in 1977 for Grosse Ohe, 1988 for 155 Markungsgraben and 1990 for Forellenbach. Water temperature was only available from 2002
- 156 and DO was not available at Forellenbach. Further details of the geographical and
- 157
- hydrometeorological characteristics and monitoring of the area are described in *Beudert and* 158
- Gietl [2015]. 159

The annual percent of forest canopy experiencing dieback was manually identified via 160 airborne image analysis (see Heurich et al. [2010] for details). We further acquired annual NDVI 161 time series from the United States Geological Survey Landsat satellite archive for the years 1986 162 to 2016 (see Senf et al. [2017] for details on image processing). We used the NDVI time series as 163 independent proxy of vegetation activity, i.e., indicating the loss and subsequent recovery of 164 photosynthetic activity during and after the bark beetle outbreak. We averaged annual NDVI 165 observations at the catchment level and applied a smoothing model (generalized additive model) 166 to account for variable phenology between Landsat acquisitions that potentially overshadow the 167

- more subtle longer-term trends associated with forest dieback and recovery [Senf et al., 2019]. 168
- 169
- 170

2.2 Bayesian Hierarchical Regression Model

The concentrations of NO₃ in the streams of Grosse Ohe and its nested subcatchments 171 were predicted by regression models in a Bayesian hierarchical framework. Candidate regression 172 models with different sets of predictors were compared (see below). The slopes and intercepts of 173 174 the regression models were allowed to vary each hydrological year (starting in November):

175
$$\log(C_i) = \beta_{0,j} + \beta_{1,j} X_{1,i} + \beta_{2,j} X_{2,i} + \dots + \beta_{P,j} X_{P,i} + \varepsilon_i$$
(1)

where C_i and $X_{\{1, 2, ..., P\},i}$ are *i*th measurements of stream NO₃ concentration and the 176 corresponding values of the P predictors, respectively. $\beta_{0,i}$ and $\beta_{\{1,2,\dots,P\},i}$ are the intercept and 177 slope parameters for the *P* predictors, respectively, for the *i*th year. ε_i is the residual error. By 178 modelling ε_i as a normal distribution and taking the logarithm of the response C_i, NO₃ 179 concentration was effectively modelled as a lognormal distribution. The model parameters $\beta_{0,i}$ 180 $\beta_{\{1, 2, \dots, P\}, j}$ and ε_i were partially pooled across the hydrological years to control over-fitting. That 181 is, these parameters were modelled as realizations of common distributions, whose parameters 182

were simultaneously inferred from the data: 183

184
$$\beta_{m,j} \sim Normal(\mu_{\beta_m}, \sigma_{\beta_m}^2)$$
, for $m = 0, 1, 2, ..., P$ (2)

185
$$\varepsilon_i \sim \text{Normal}(0, \sigma_{\varepsilon_j}^2)$$
 (3)

186
$$\sigma_{\varepsilon_i} \sim \operatorname{Normal}(\mu_{\sigma_{\varepsilon}}, \sigma_{\sigma_{\varepsilon}}^2)$$
 (4)

where $\mu_{\beta m}$ is the mean of the regression parameter β_m and $\sigma^2_{\beta_m}$ is the variance of the "random 187 effect" that models the variability of β_m between years. 188

The residual error for the jth year ε_i is considered normally distributed with mean zero 189 and variance $\sigma_{\epsilon_i}^2$, which varies between years according to a normal distribution with mean $\mu_{\sigma_{\epsilon}}$ 190 and variance $\sigma_{\sigma_{\epsilon}}^2$. Weakly informative Normal(0,5) prior distributions were assigned to μ_{β_m} with 191

192 m = 0, 1, 2, ..., P. Weakly informative Inverse-gamma(0.01, 0.01) priors were assigned to σ_{β_m} , 193 μ_{σ_s} and σ_{β_s} as these parameters are bound to be positive [*Gelman*, 2006]. Allowing the

parameters and residual error term to vary temporally in the Bayesian hierarchical framework

reflects the possibility that the processes that regulate stream NO_3 vary over time, but shrunk

196 towards a common mean so as to avoid over-fitting. From this temporal variation of model

197 parameters we hope to extract information on catchment dynamics in top-down fashion (see 2.3).

The partially-pooled models were compared with pooled and non-pooled models. In the 198 pooled version, the parameters were constant over the years. In the non-pooled version, the 199 parameters were estimated individually for each year, without common prior distributions. The 200 joint posterior distribution of the parameters was simulated using Markov Chain Monte Carlo 201 (MCMC) methods available in Stan [Carpenter et al., 2017] and implemented in the R 202 environment [R Core Team, 2018; Stan Development Team, 2018]. 1000 realizations of the 203 model parameters and predicted NO₃ were generated from their posterior distributions after 1000 204 burn-in samples in four parallel chains. Code files of the partially pooled, non-pooled and pooled 205 models are provided in the Supporting Information. 206

The candidate regression models with different sets of predictors were compared for their predictive accuracy by means of k-fold cross validation. The data sets of each site were randomly divided into 10 subsets y_k , for k = 1, 2, ..., 10, with even numbers of data point. The models were fit to a training data set $y_{(-k)}$ and subsequently used for predicting the NO₃ concentrations of the validation set y_k . This process was repeated for each subset and the posterior distributions of the predictions were used to calculate the expected log pointwise predictive density (ELPD), a relative measure of predictive performance under out-of-sample conditions [*Vehtari et al.*, 2017].

214

215 2.3 Top-down Catchment Model

In a second step, the regression analysis (2.2) was interpreted with a parsimonious 216 process-based model of NO₃ export at the catchment scale in top-down fashion [Sivapalan et al., 217 2003]. Equations describing the processes of nutrient export were defined using the predictor 218 variables of the best fit regression model and based on the literature. In this way, mechanistic 219 220 implications of the regression model could be derived. As a first step towards explaining the temporal variation of the parameters in relation to the bark beetle induced forest dieback, 221 222 correlations between annual parameter estimates and the NDVI as independent proxy of vegetation activity were quantified using Spearman's rank correlation coefficient (ρ). 223

224

225 **3 Results**

2263.1 Temporal Variations of Vegetation Canopies and Hydrochemical Responses

Over the entire catchment, Grosse Ohe, the bark beetle infestation occurred in two waves
between 1994 and 2009, killing Norway spruce trees with annual mortality rates peaking in 1999
(12 % of area) and 2006 (5 % of the area). The infestation occurred in Forellenbach in 1994 –
2000 and 2002 – 2008 with maximum annual mortalities of 12 % (1999) and 7 % (2006),
respectively. The bark beetle outbreak led to highest mortality rates in the Markungsgraben

catchment between 1995 and 2001, where a maximum annual mortality rate of 39 % was

recorded in 1997 (Figure 1a). The annual NDVI time series well fitted the recorded mortality,

- with largest negative deviations in annual NDVI (i.e., annual vegetation activity) for
- 235 Markusgraben (Figure 1a), but with rapid recovery of vegetation activity after the main mortality
- waves for all catchments. The rapid return of vegetation including spruce trees is also well
 documented in other studies, suggesting that the forests recovered from the bark beetle induced
- spruce dieback [*Svoboda et al.*, 2010; *Zeppenfeld et al.*, 2015; *Senf et al.*, 2019].
- Discharge was highly variable over the course of the bark beetle outbreaks (Figure 1b), 239 with a discharge yield of 0.40 - 58.5 mm day⁻¹ across all sites and over the entire monitoring 240 period. In volumetric terms, the largest flux occurred at the most downstream monitoring station 241 of Grosse Ohe ($0.59 \pm 0.66 \text{ m}^3 \text{ s}^{-1}$ (mean \pm standard deviation)), followed by the upstream 242 stations Markungsgraben $(0.05 \pm 0.06 \text{ m}^3 \text{ s}^{-1})$ and Forellenbach $(0.02 \pm 0.02 \text{ m}^3 \text{ s}^{-1})$. The 243 baseflow indices were 49 %, 64 % and 54 % in Markungsgraben, Forellenbach and Grosse Ohe, 244 respectively. The baseflow contribution decreased with mean slope $(16.1^{\circ} \text{ in Markungsgraben},$ 245 8.4° in Forellenbach and 11.1° in Grosse Ohe). 246
- 247 Annual mean stream NO₃ concentration increased until 2000 at Markungsgraben, 2003 at Forellenbach and 2002 at Grosse Ohe, during the first halves of the dieback periods (Figure 1c). 248 Correlation coefficients ρ between annual mean NO₃ and NDVI were -0.82 – -0.88 across the 249 sites, meaning that stream NO_3 decreased when the vegetation was active (compare Figure 1a 250 and c). NO₃ showed minima in the growing season (May - September) and maxima in the 251 dormant season. However, under elevated NO₃ concentrations during the dieback, the seasonal 252 253 pattern vanished in 2004 at Forellenbach and 1998 and 2003 at Markungsgraben. We define the years with decreased NDVI and elevated NO₃ (1995 - 2003 at Markungsgraben, 1997 - 2009 at 254 255 Forellenbach and Grosse Ohe) as dieback phase and the preceding and following years as pre-256 and post-dieback phases, respectively.
- The water temperature ranged between -0.01 and 20.1 °C, while 95 % of the values were within 0.03 - 13.0 °C, with means increasing above 5 °C in May – October (Figure 1d). Temperature measurements at the three sites were highly correlated (p < 0.01, r² 0.83 – 0.96), meaning that the water temperature reflects the regional climate of the area. Annual mean temperatures showed clear and steady increasing trends across the sites (Mann-Kendall test p < 0.05).
- 262 263





265

Figure 1. (a) Normalized difference vegetation index (NDVI), mortality, (b) discharge, (c)

nitrate concentration (NO₃) and (d) water temperature of Markungsgraben, Forellenbach and
 Grosse Ohe.

270 3.2 Selection of Regression Model

271 The regression models with different sets of predictors and pooling setups were compared using ELPD, with greater values signifying better predictive performance. Both original and log-272 transformed data were tested, and the ELPDs of the best fitting models are presented in Table S1. 273 274 C-Q-T (concentration-discharge-temperature) model with partially pooled parameters showed the greatest ELPD values across the sites, outperforming even models with three predictors. The 275 C-Q-DO model (concentration-discharge-dissolved oxygen) was more accurate than the C-Q-T 276 model at Grosse Ohe but the enhancement in ELPD was low (0.01). DO was correlated with 277 water temperature with $\rho = -0.72$ at Markungsgraben and $\rho = -0.97$ at Grosse Ohe because of the 278 increased solubility of oxygen in water at low temperatures [Wetzel, 2001]. No DO data were 279 available for Forellenbach. 280

As a result, the C-Q-T model was selected for further analysis. The equation can be written as

283
$$\log(C_i) = \beta_{0,i} + \beta_{1,i} \cdot \log Q_i + \beta_{2,i} \cdot T_i + \varepsilon_i$$
(5)

285 3.3 Development of Top-down Catchment Model

A mechanistic model explaining the variation of in-stream NO₃ with discharge and water temperature was developed based on the relationships between the variables suggested by the selected regression model. This mechanistic model is a lumped model that conceptualizes the processes within the catchment as a single unit. Hence the parameters of this model represent the characteristics of the entire catchment without spatial heterogeneity; they are so called "effective" parameters.

292 The relationship of $log(NO_3)$ and water temperature in the regression model suggests that 293 NO₃ is processed in first-order reactions with rates affected by water temperature. In the riparian zone, the NO₃ is either removed by assimilation of plants and microorganisms or by 294 denitrification, or produced from organic N via mineralization and nitrification [Stoddard, 1994; 295 296 Zheng et al., 2016]. Among different possibilities of defining the riparian zone, we define it as the soil adjacent to the stream and in the hyporheic zone, where nutrients are retained actively 297 via biogeochemical processes [Lowrence et al., 1983; Parkyn, 2004]. The vertical concentration 298 profile of NO₃ in the riparian zone is shaped by heterogeneous inputs from the hillslope soils and 299 biogeochemical reactions. It can be expressed as a function of depth z and temperature T as 300

301
$$c(z,T) = c_{s0} \cdot e^{kt_r T + fz}$$
 (6)

where c_{s0} is the initial concentration of NO₃ at the surface layer [mg N L⁻¹], k [C^{o-1} s⁻¹] is a rate constant, t_r [s] is the NO₃ residence time and f [m⁻¹] is a shape parameter of the vertical distribution. The biogeochemical processes were assumed to alter the NO₃ concentration in the riparian zone instantaneously or at least within the residence time t_r before the nutrient enters the stream [*Seibert et al.*, 2009] based on literature reviews of rates of N uptake and denitrification [*Stoddard*, 1994; *Masclaux-Daubresse et al.*, 2010].

NO₃ is assumed to be transported laterally from upslope sources through the riparian zone to reach the stream. Lateral water flux at depth z (q) $[m^2 s^{-1}]$ was modeled to decline exponentially [*Seibert et al.*, 2009]:

$$q = q_0 \cdot e^{\lambda z} \tag{7}$$

where λ [m⁻¹] is a shape parameter of the water flux profile and q₀ [m² s⁻¹] is the transmissivity at the top of the riparian zone. The hydraulic conductivity of the soil was assumed to be little affected by the forest dieback and thus did not change over the years.

Integration of equation 7 results in an equation for discharge $[m^3 s^{-1}]$ governed by groundwater depth, or depth of the saturated zone below the soil surface:

317
$$Q = q_0 / \lambda \cdot e^{\lambda z}$$
(8)

 $q_0/\lambda \text{ [m}^3 \text{ s}^{-1}\text{]}$ represents the maximum discharge when the soil is saturated (groundwater depth z = 0 m), neglecting overland and preferential flows.

Modifying the model by *Seibert et al.* [2009], averaging the NO₃ flux (concentration times lateral water flux) over depth results in a governing equation of in-stream NO₃

322 concentration as a function of upslope inputs (represented by c_{s0}), discharge (Q) and water

323 temperature (T):

325

324
$$C = \frac{L}{Q} = \frac{\int_{-\infty}^{z_t} qcdz}{\int_{-\infty}^{z_t} qdz}$$
(9)

$$\log C = \log[c_{s0}(1+b)^{-1}\left(\frac{\lambda}{q_0}\right)^{D}] + b \cdot \log Q + kt_r T$$
$$= \log S + b \cdot \log Q + kt_r T$$
(10)

where z_t is ground water depth at time t, b is f/λ [-] and S is $c_{s0}(1 + b)^{-1}(\lambda/q_0)^b$. This equation combines the C-Q and C-T relationships into the C-Q-T relationship revealed by the best fit regression model. The rationale of the current model explains the mechanism of the empirical C-Q-T relationship. More details on the derivation and assumptions of equation 6 and 10 can be found in the Supporting Information (Text S1 and S2, respectively).

331 From the definition of **S** it follows that

332
$$c_{s0} = S(1+b)(q_0/\lambda)^b$$

This equation can be used for estimating c_{s0} , which is affected by the dynamics of the vegetation and hence potentially sensitive to the bark beetle outbreak.

(11)

335 It is important to note that equations 5 and 10 are analogous to each other. The intercept of the regression model is logS, a compound of four mechanistic parameters; c_{s0} , b, λ and q_0 . The 336 slopes of equation 5, β_1 and β_2 , correspond to b (= f/ λ) and the product of k and t_r of equation 10 337 (kt_r) , respectively. In our hierarchical setup, the soil input c_{s0} can be inferred from the annual 338 estimates of S and b given values of q_0 and λ . The C-Q slope b signifies the vertical profile of 339 NO₃ transport through the riparian zone shaped by hydraulic conductivity (λ) and availability of 340 341 the nutrient (f). A positive k indicates that the riparian zone is a source of NO_3 and a negative k indicates a sink, while t_r is always equal to or larger than zero. Accordingly, the parameter kt_r 342 represents the rate of removal ($kt_r < 0 C^{\circ^{-1}}$) or production ($kt_r > 0 C^{\circ^{-1}}$) of NO₃ in the riparian 343 zone. The magnitude of net removal/production is determined both by the biogeochemical 344 reaction (k) and the residence time (t_r). With $kt_r < 0 C^{\circ-1}$, NO₃ is lower in summer creating a 345 seasonal pattern because high temperature enhances net NO₃ removal [Christensen et al., 1990; 346 *Clark et al.*, 2004a; *Huber*, 2005]. The seasonal pattern is reversed if $k_r > 0 C^{\circ-1}$ with net NO₃ 347 production magnified by a temperature increase. 348

349

350 3.4 Prediction of Nitrate

The stream NO₃ concentrations predicted by the C-O-T model corresponded well to the 351 observed concentrations (Figure 2). The root mean square errors (RMSE) were 0.36 [0.33 - 0.40]352 (mean [95 % credible interval]) mg N L⁻¹, 0.20 [0.19 – 0.22] mg N L⁻¹ and 0.18 [0.17 – 0.19] mg 353 $N L^{-1}$ across the years at Markungsgraben, Forellenbach and Grosse Ohe, respectively. The 354 model predicted the seasonal pattern of NO_3 correctly, as well as the disappearance of the 355 seasonal pattern in the dieback phase at Markungsgraben (1997-2001) and Forellenbach (2002). 356 In these years, the two predictors were insufficient to explain the NO₃ dynamics, showing higher 357 RMSEs (0.68 [0.58, 0.80] mg N L^{-1} at Markungsgraben and 1.10 [0.98, 1.19] mg N L^{-1} at 358

359 Forellenbach). NO₃ at Forellenbach was greatly controlled by discharge, where the concentration

performed before 2002 at Forellenbach due to the limited availability of temperature data.



363

Figure 2. Predicted and observed in-stream nitrate concentrations at the outlets of (a)
Markungsgraben, (b) Forellenbach and (c) Grosse Ohe.

366

367

Plotting predicted and observed in-stream NO₃ against each other verified the high predictive accuracy of our model (Figure 3). The RMSE normalized by the mean of observed NO₃ indicated that the deviation between the predicted and observed NO₃ was lowest at Forellenbach, followed by Grosse Ohe and Markungsgraben. The model tended to underestimate NO₃ in the years when the nutrient concentration peaked and the predictors did not explain sufficiently the variation (showing high RMSE) across sites.



Figure 3. Predicted vs. observed in-stream nitrate (NO₃) concentration of (a) Markungsgraben,
(b) Forellenbach and (c) Grosse Ohe. Posterior distributions and medians of predicted NO₃ are
displayed. Blue points are random draws from the posterior distribution. 1:1 lines and
normalized root mean square errors (median [95 % credible interval]) are indicated.

381

3.5 Temporal Variations of Model Parameters

The parameter S was estimated for each year by exponentiating the intercept of the 382 regression model based on equation 10 (Figure 4a). S was greatest at Markungsgraben (median 383 of $0.08 - 5.15 \text{ mg N L}^{-1}$), where the NO₃ concentration was generally highest, compared to the 384 medians of 0.05 - 1.97 mg N L⁻¹ at Forellenbach and 0.40 - 1.80 mg N L⁻¹ at Grosse Ohe. S 385 showed a temporal pattern similar to that of annual mean in-stream NO₃ across the sites with the 386 median ρ of 0.77 – 0.94, increasing in the dieback phase and decreasing in the post-dieback 387 phase. Since S is a complex of multiple parameters (equation 10), we will describe the temporal 388 dynamics further in terms of c_{s0} below (see Equation 11). 389

390 The parameter kt_r was significantly (P($kt_r > 0 C^{\circ -1}$) < 0.05) below zero in the pre- and post-

dieback phases. kt_r increased close to zero in some years in the middle of the dieback phase (Markungsgraben in 1997 – 1999, Forellenbach in 2003 – 2004 and 2007) (Figure 4b). At Grosse

Ohe, the 95 % credible intervals of kt_r remained below zero throughout the study period. The

medians of kt_r at Forellenbach and Grosse Ohe remained in the ranges of $-0.06 - 0.00 \,^{\circ}\text{C}^{-1}$ and -

 $0.04 - -0.02 \,^{\circ}C^{-1}$, respectively. The kt_r at Markungsgraben showed a larger temporal variation

compared to those of the other sites. From 2006 onwards, the k_r at Markungsgraben was -0.10 –

- $-0.05 \, {}^{\circ}\text{C}^{-1}$ (range of medians), considerably lower than at the other sites. The estimate of kt_r was
- very uncertain in 2012 (-0.07 [-0.13 -0.02] $^{\circ}$ C⁻¹) because only three data points were available in this year.

The estimates of the C-Q slope b fluctuated near or above zero at Markungsgraben and Grosse Ohe (median -0.08 - 0.21) in their respective pre-dieback and dieback phases (Figure 4c). Medians of the parameter b decreased below zero in the post-dieback phase from 2004 at Markungsgraben and 2012 at Grosse Ohe, although its 95 % credible interval overlapped with zero in some years. At Forellenbach, b was clearly negative in all the years investigated except for 2007 – 2009. These years, in which b was estimated near or above zero (median -0.05 -0.03), are the last years of the dieback phase at this site.

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Figure 4. 95 % credible intervals of model parameters (a) S, (b) kt_r and (c) b estimated for each year at Markungsgraben (Mark), Forellenbach (Forelle) and Grosse Ohe (Grosse)

The dynamics of S were broken down into dynamics of c_{s0} using equation 11 given the 411 annual estimations of S and b and for various values of q_0/λ as this ratio was not explicitly 412 estimated (Figure 5). Reasonable values for q_0/λ were chosen based on the range of discharges 413 observed at our study sites. The specific runoff maxima at the study sites were 23.8 - 58.3 mm 414 day⁻¹ across the years. Hence, the q_0/λ values were chosen as 20, 40 and 60 mm day⁻¹ multiplied 415 by the area of the individual (sub-) catchment. The chosen values of the q_0/λ represent a 416 conservatively wide range of probable maximum discharge. The parameter c_{s0} is positively 417 related with q_0/λ when b > 0 and negatively related when b < 0 as equation 11 implies. Although 418 419 c_{s0} varied with different assumptions of q_0/λ (differences in median 0.00 – 1.61 mg N L⁻¹), the general temporal pattern of c_{s0} was not affected by these assumptions. 420

The parameter c_{s0} showed a steep increase at the onset of the dieback in Markungsgraben and less alterations in Forellenbach and Grosse Ohe. At Markungsgraben, c_{s0} rose up to 2.66 – 11.62 mg N L⁻¹ in 1998 depending on the assumed q_0/λ . At Forellenbach and Grosse Ohe, c_{s0} remained in the ranges of 0.01 - 3.27 mg N L⁻¹ and 0.01 - 9.60 mg N L⁻¹, respectively. The c_{s0} estimates of Forellenbach were the lowest among the monitored sites.

The estimated c_{s0} peaked in 1998 at Markungsgraben and Grosse Ohe, preceding the peak of in-stream NO₃ (2000 at Markungsgraben and 2003 at Grosse Ohe). Then, c_{s0} decreased below the pre-dieback levels from 2005, 2010 and 2012 onwards at Markungsgraben, Forellenbach and Grosse Ohe, respectively, as the vegetation recovered (Figure 1a). c_{s0} of Markungsgraben showed an especially drastic decrease below pre-dieback levels and even below that of Grosse Ohe.

The c_{s0} estimated with $q_0/\lambda = 40$, as an example, was correlated with the annual mean of in-stream NO₃ with a ρ of 0.88 [0.81, 0.92] at Markungsgraben, 0.77 [0.74, 0.80] at Forellenbach and 0.70 [0.61, 0.79] at Grosse Ohe. c_{s0} tented to be higher than in-stream NO₃ until 2004 at Markungsgraben and until 2012 at Grosse Ohe and was similar or lower afterwards at both sites. At Forellenbach, c_{s0} was lower than in-stream NO₃ for most of the research period except in 2007 – 2009, when they were comparable to each other.

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Forellenbach and (c) Grosse Ohe. Three c_{s0} scenarios are shown and all convey a similar pattern.

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3.6 Correlations between Model Parameters and NDVI

446 The NDVI was negatively correlated with the annual model parameters, most notably c_{s0} , 447 with correlation coefficients ρ of -0.67 [-0.74, -0.59], -0.81 [-0.85, -0.77] and -0.62 [-0.72, -0.51] 448 at Markungsgraben, Forellenbach and Grosse Ohe, respectively (Figure 6a). The parameter kt_r 449 was negatively related with NDVI at Markungsgraben and Forellenbach with ρ of -0.70 [-0.78 – 450 -0.58] and -0.45 [-0.62 – -0.26], respectively (Figure 6b). At Grosse Ohe, the terrestrial 451 vegetation dynamics did not significantly impact kt_r (ρ of -0.10 [-0.34 – 0.16], with the credible

- 452 interval including zero). The correlation between the C-Q slope b and NDVI was -0.31 [-0.45 -
- 453 0.11], -0.81 [-0.86 -0.74] and -0.41 [-0.53 -0.28] at Markungsgraben, Forellenbach and
- 454 Grosse Ohe, respectively, with the strongest correlation at Forellenbach (Figure 6c).
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Figure 6. Annual model parameter estimates (a) c_{s0} , (b) b and (c) kt_r for Markungsgraben (Mark), Forellenbach (Forelle) and Grosse Ohe (Grosse) plotted against NDVI. Error bars signify the 95 %

- 460 credible intervals of the parameters.
- 461

462 4 Discussion

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4.1 Dynamics of Catchment Processes Inferred via Time-Varying Model Parameters

- 464
- 4.1.1 Nitrate Inputs to the Riparian Zone

The soil NO₃ (c_{s0}) increased as N was released from the dead trees in the dieback phase and decreased in the post-dieback phase again below pre-dieback levels (Figure 1a,c). c_{s0} showed negative correlation with NDVI (Figure 6a). These results suggest that the soil NO₃ input was affected by the vegetation dynamics. Furthermore, c_{s0} showed high correlations with the annual mean NO₃ concentration (section 3.5), implying that the NO₃ input from the soil governed strongly the in-stream NO₃ concentration.

471 The reduction of c_{s0} in the post-dieback phase indicates that removal of NO₃ (hydrological export and biological retention) outran supply of NO₃ (decay of the dead trees and 472 atmospheric deposition). Export of NO₃ via stream discharge depleted the nutrient over 7 - 10473 years after the diebacks. Additionally, regrowth of young vegetation enhanced net retention of 474 NO₃ as it shed little amounts of litter compared to mature vegetation [Covington, 1979; Bormann 475 and Likens, 1994]. The strongest dieback in Markungsgraben created large openings and allowed 476 477 for the establishment and growth of understory vegetation communities [Niemelä, 1999], which led to the most active regrowth of the vegetation (Figure 1a) and reduction of c_{s0} (Figure 5). 478

For comparison, the NO₃ concentration in soil water measured in the Forellenbach catchment by *Beudert and Breit* [2004] rose in 1997 – 2000 up to approximately 45 mg N L⁻¹, 12-fold higher than the maximum c_{s0} estimated at this site (Figure 5). Soil water in that study was collected from a plot with a dead spruce stand upslope of the stream, while c_{s0} in this study 483 conceptually represents the NO_3 concentration at the soil surface of the whole of the riparian

zone. The NO₃ concentration in the riparian zone was reduced compared to the upslope soil

485 water by biogeochemical retention in the unsaturated zone and dilution with groundwater during

transit to the riparian zone [*Beudert and Klöcking*, 2007]. Biogeochemical and hydrological
 processes in the hillslopes also played important roles in the NO₃ export [*Verseveld et al.*, 2009;

Chadwick and Asner, 2016; *Harms and Ludwig*, 2016], although the catchment model in this

- study does not explain those processes.
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4.1.2 Rates of Biogeochemical Processes in the Riparian Zone

The temporal evolution of NO₃ concentrations and the parameter kt_r in our study catchment reflects how its N budget evolved during the bark beetle outbreak and the subsequent succession. The parameter kt_r was negative in the pre-dieback period, indicating that the riparian zone was a net sink of NO₃. With the dieback, NO₃ was produced at a rate comparable to that of its retention in the riparian zone (kt_r $\approx 0 \text{ C}^{\circ-1}$). The riparian zone started to retain NO₃ effectively again in the post-dieback phase, showing negative kt_r.

Vegetation controls N export not only by taking up the nutrient for growth but also by 498 providing a carbon energy source via exudation or litterfall for microbial denitrification [Scaglia 499 et al., 1985; Mulholland et al., 2008; Dosskey et al., 2010; Zhai et al., 2013]. Both processes 500 could have been impaired by the mortality of the trees and recovered with the forest recovery, 501 supported by the correlation between kt_r and NDVI especially in the strongly affected 502 Markungsgraben. While denitrification has been reported as the primary process of NO₃ removal 503 in soil-water systems [Bachand and Horne, 1999; Mulholland et al., 2008], Huber [2005] 504 505 attributed the seasonal pattern of NO₃ in our catchment to the active vegetation uptake during summer. However, it was not possible to separate the two pathways of retention with the data 506 available for this study; this will be subject of future research. 507

508 With marginal changes in annual precipitation, evapotranspiration was reduced while the 509 runoff coefficient increased in the catchments following the dieback, most remarkable in 510 Markungsgraben [*Beudert and Klöcking*, 2007; *Bernsteinová et al.*, 2015]. The increased runoff 511 coefficient suggests that canopy mortality could have altered the residence time of the nutrient (t_r) 512 and affected the N retention capacity [*Hill et al.*, 1998]. However, this effect could not be 513 separated from the parameter kt_r.

514 During the dieback phase, organic N and ammonium (NH₄) released from the killed trees were available for mineralization and nitrification, from which more NO₃ was produced in the 515 growing season at high temperatures [Arheimer et al., 1996; Kaiser et al., 2011]. This result 516 supports the first hypothesis that the riparian zone did not act as a net sink of NO_3 and the 517 518 nutrient export was not retained effectively when the trees were killed. When kt_r was near zero across the sites, the production and retention of NO₃ were of comparable rates so the in-stream 519 520 NO₃ concentration did not show a seasonal pattern. Such disappearance or even reversal of the seasonal pattern after severe dieback has frequently been observed in forest catchments [Pardo et 521 al., 1995; Yeakley et al., 2003; Kaňa et al., 2015]. 522

523 In Markungsgraben, NO₃ was depleted thus less available for export in the post-dieback 524 phase (c_{s0} in Figure 5a) and retention was enhanced (Figure 4b) with the recovery of the 525 vegetation (Figure 6c). Thus, we maintain partly the second hypothesis that the nutrient retention 526 was recovered with the post-dieback regrowth of the forest. In addition, the N input via

atmospheric deposition showed a reduction over time in our catchment [*Beudert and Gietl*,

528 2015], which could have contributed to the decrease in stream NO₃ but was not evaluated in this

- 529 study.
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4.1.3 Hydrological Pathways of Nitrate Export

The C-Q relationship has been interpreted by heterogeneous nutrient sources within a 532 catchment that are variously connected to the stream by dynamic transport pathways [Seibert et 533 534 al., 2009; Basu et al., 2010]. In a mechanistic sense, the solute is mainly transported via nearsurface layers when b > 0 or via sub-surface layers when b < 0 [Seibert et al., 2009]. The in-535 536 stream solute concentration increases at high flows (b > 0) as ground water intersects nearsurface layers rich in the nutrient (flushing pattern) (see equations 10 and 11). Conversely, when 537 b < 0, then the solute concentration decreases at high flows as the water flux in near-surface 538 layers does not flush a high concentration of solute (dilution pattern). A value for b near zero 539 540 indicates that the solute transport is homogeneous over the depth of the riparian zone and does not vary with discharge (chemostasis). However, Musolff et al. [2015] found empirically that 541 chemostatic solute export has b values in the range of [-0.2, 0.2]. The C-Q relationship can vary 542 if the dominant pathway of nutrient export is switched [Zhi et al., 2019]. In our catchment, the 543 temporal variations of b and c_{s0} suggest that the NO₃ export was chemostatic in the pre-dieback 544 and dieback phases and shifted to a dilution pattern in the post-dieback period. 545

The parameter b was in the range of [-0.2, 0.2] at Markungsgraben and Grosse Ohe in the 546 pre-dieback phase (Figure 4c) indicating chemostasis of the NO₃ export. Several studies 547 observed that chemostasis of NO₃ is a sign of N-saturation with the nutrient homogeneously 548 distributed [Basu et al., 2010; Van Meter and Basu, 2015; Bieroza et al., 2018]. The parameter b 549 was near zero when the parameter c_{s0} was estimated comparable to in-stream NO₃, supporting 550 indirectly the homogeneous distribution of NO_3 in the soil profile of the riparian zone (Figure 5). 551 Conversely, b was slightly above zero when c_{s0} was higher than in-stream NO₃. The parameters b 552 and c_{s0} were especially high in the dieback phase (Figure 4a,c) showing high correlations with 553 NDVI (Figure 6c). In these years, NO₃ released from the killed trees accumulated in the near-554 surface layer inducing a flushing effect and hence steep increases in c_{s0} . 555

The parameter b decreased below zero (Figure 4) and c_{s0} was lower than the stream NO₃ (Figure 5) in the post-dieback phase (after 2014 at Markungsgraben and after 2013 at Grosse Ohe). By that time, the NO₃ concentration in the near-surface layer had been depleted by the flushing and the biological retention. It is also likely that the NO₃ had been leaching into deeper groundwater over time after the diebacks [*Jury and Nielsen*, 1989]. The water flux through the near-surface layer at high flows then diluted the stream NO₃, resulting in the negative C-Q slopes observed.

The parameter b was lowest at Forellenbach and clearly negative in the pre- and postdieback periods, signifying a strong dilution effect in this sub-catchment. Indeed, the NO₃ concentration decreased sharply in storm events. This dilution effect is supported by the high baseflow index of 64 % possibly caused by flat topography (section 3.1). In 2007 – 2009, during the second dieback (Figure 1a), b was near zero and c_{s0} was comparable to in-stream NO₃, likely because the released nutrient was distributed homogeneously along the soil profile. In the postdieback phase, NO₃ was depleted in the near-surface layer, thus b was decreased below zero and pre-dieback levels and c_{s0} was much lower than in-stream NO₃.

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4.2 Concentration-Discharge-Temperature Relationship

573 Regression modeling predicting NO₃ concentrations in streams from air or water temperature as a single predictor has been used elsewhere [e.g. Clark et al., 2004a; Exner-574 Kittridge et al., 2016]. A negative C-T relationship is attributed to reduced microbial and plant 575 uptake of the nutrient at low temperatures [*Clark et al.*, 2004a]. However, more common by far 576 577 is the C-Q model, which is often interpreted by the variability of solute exports coming from spatially heterogeneous sources and mobilized through temporally varying pathways [e.g. Seibert 578 579 et al., 2009; Basu et al., 2010; Musolff et al., 2015; Moatar et al., 2017; Zhi et al., 2019]. 580 Winterdahl et al. [2011] revealed that soil temperature was an important factor responsible for the residuals of a C-Q model for DOC (dissolved organic carbon). They modified the C-Q model 581 by Seibert et al. [2009] to allow the profile of concentration to vary as a function of soil 582 583 temperature. The current study found that the C-Q-T model predicted NO₃ export more accurately than either the C-T or the C-Q model (Table S1). The rationale of the model 584 developed in this study (section 3.3) explains the mechanism of the empirical C-Q-T relationship, 585 complementing the attempt by Winterdahl et al. [2011]. 586

Basu et al. [2011] and Thompson et al. [2011] classified solute export from a catchment 587 into source-limited and transport-limited states. Previous studies suggested different metrics for 588 verifying the state of solute export such as the parameter b, coefficients of variance (CV) and r^2 589 of the load-discharge regression [Godsey et al., 2009; Basu et al., 2010; Musolff et al., 2015]. In 590 591 our study, shifts between these states were verified based on the annual estimates of the parameters kt_r, b and c_{s0} of the C-Q-T model. The NO₃ export was in a transport-limited state in 592 the pre-dieback phase, revealed by its chemostasis ($-0.2 \le b \le 0.2$). However, the riparian zone 593 acted as a net sink of NO₃ (kt_r < 0 C^{\circ -1}; c_{s0} higher than in-stream NO₃), and in-stream NO₃ was 594 stagnant, indicating an equilibrium between export and retention of NO₃. In the dieback phase, 595 the nutrient export was exacerbated with the release of the N from the killed trees (increased c_{s0}) 596 without net retention (kt_r $\approx 0 \text{ C}^{\circ^{-1}}$). As the N was depleted and the forest recovered in the post-597 dieback phase, the nutrient export was shifted to a source-limited state with strong N retention 598 (low negative $kt_r < 0 C^{\circ-1}$), and the lowered NO₃ transport in the near-surface layer (b < 0; 599 lowered c_{s0}). 600

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- 4.3 Efficacy of Bayesian Hierarchical Modelling

Previous studies of the C-Q model revealed that its parameters vary temporally [Köhler et 603 al., 2008; Seibert et al., 2009]. The C-Q-T model of our study was fit to the data in a Bayesian 604 hierarchical framework to allow for the temporal variability of its parameters, which explained 605 the temporal changes in the catchment processes caused by the forest dieback. The partially 606 pooled model captured the variations in the relationships between the variables and showed an 607 enhancement in accuracy compared to the pooled regression models (Table 1) [Simpson, 1951; 608 Cha et al., 2016]. A next level of model development would be the prediction of parameter 609 variations, as Cha et al. [2017] demonstrated, with data of vegetation dynamics, for instance 610

611 NDVI in our case.

A Bayesian hierarchical model is capable of predicting the response variable and parameters by sharing information across hierarchical levels and at the same time avoiding

overfitting [Borsuk et al., 2001]. At Markungsgraben, NO₃ and the parameters for 2012 were

615 predicted with three data points only, albeit yielding low precision in the parameter estimates.

Had the model been applied in a non-pooling approach, the estimations would have been over-

617 confident given the little amount of the data.

618

619 5 Conclusions

In our case study, the best fitting regression model predicted stream NO₃ concentration (C) with discharge (Q) and water temperature (T). This C-Q-T relationship adds to the widely acknowledged C-Q relationship the effect of water temperature on the variability of solutes in streams. The C-Q-T relationship could be applicable to other non-conservative solutes that are regulated by biogeochemical reactions in streams, and hence are sensitive to water temperature. It would be worthwhile to investigate the applicability of the C-Q-T model to different solutes and types of catchments.

The top-down modeling approach yielded mechanistic interpretations of soil N inputs, main transport pathways and rates of biogeochemical processes in a parsimonious way that is commensurate with the data availability. Due to its flexibility, Bayesian hierarchical modeling is especially suited for top-down modelling via time-varying parameters. Partial pooling maintains flexibility of model parameters while avoiding over-fitting. The next step following the topdown route would be to explicitly model the annual variation of parameters by auxiliary data, such as NDVI as indicated in our study.

The temporal trends of the parameters led us to maintain our first hypothesis that the NO_3 634 released through tree mortality (increased c_{s0}) was not effectively retained in the riparian zone 635 during the dieback phase ($kt_r \ge 0 C^{\circ^{-1}}$). In the post-dieback phase, NO₃ was depleted (decreased 636 c_{s0}) and young re-growing vegetation retained more NO₃ than it released N via litter shedding 637 $(kt_r < 0 C^{\circ^{-1}})$, thus we partly maintain our second hypothesis. We attribute the changes in the 638 NO₃ budget to the alteration in the nutrient retention capacity of the riparian zone but also to 639 abrupt release and depletion of the nutrient. The hypotheses could be tested robustly by means of 640 the parameters estimated as probability distributions in the Bayesian hierarchical framework. 641

Although the bark beetle induced forest dieback observed in our study catchment 642 impaired the water quality by releasing N from the forest, the system turned out resilient in the 643 sense of a rapid recovery of ecosystem functions (i.e., retaining nutrients). It is important to note 644 here that the system was not managed at all. Stream NO₃ concentrations were reduced 10 years 645 after the dieback in the most severely affected upper sub-catchments and showed a general high 646 resistance in the most downstream reach (Figure 2). Moreover, the biodiversity in our forest 647 catchment was improved after the diebacks with the emergence of new habitats provided by 648 649 standing and lying deadwood [Beudert et al., 2014]. Hence, our study supports that European montane spruce forests are in fact highly resilient to the current disturbance regime [Zeppenfeld 650 et al., 2015; Senf et al., 2019]; we here complement these studies by showing that this resilience 651 also includes the key ecosystem function of water purification. 652

The water temperature in our catchment showed a constantly increasing trend presumably as a manifestation of climate change [*Beudert et al.*, 2018]. An increase in forest mortality is

expected under climate change [Allen et al., 2010; Seidl et al., 2017], with more frequent forest 655

diebacks that might also increase in severity. Hence, under climate change more nutrients might 656

be released. A portion of the released N would be denitrified and released into the atmosphere as 657

nitrous oxide (N_2O) [Norton et al., 2015], a potent greenhouse gas. It would be shortsighted to 658 limit N cycling studies to water quality effects ignoring the climate change potential of N₂O 659

emissions. Further studies are needed to explore the response of the N cycle of forest catchments 660

- to changing mortality patterns under climate change. 661
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Acknowledgments and Data Availability 664

665 BB designed and performed the hydrochemical monitoring program of Forellenbach and coordinated the related programs of Grosse Ohe catchment in the Bavarian Forest National Park. 666 CS contrived the methods for the statistical analyses of the data. HJ formulated research 667 questions, developed the codes for the statistical analyses and performed the analysis. HJ and TK 668 developed the mechanistic catchment model. HJ led the writing of the paper which all co-authors 669 contributed to. The work of HJ was part of his doctoral research at IRI THESys of Humboldt-670 Universität zu Berlin, enrolled at the Geography Departed of the same university. IRI THESys 671 was funded by the German Excellence Initiative. The hydrochemical data were provided from 672 the Bavarian Environment Agency (LFU) and the German Federal Environment Agency (UBA) 673 and are available online in Zenodo repository (https://doi.org/10.5281/zenodo.3703070) [Beudert 674 et al., 2020]. 675

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