



Bending of the concentration discharge relationship can inform about in-stream nitrate removal

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Abstract. Nitrate (NO_3^-) excess in rivers harms aquatic ecosystems and can induce detrimental algae growths in coastal areas. Riverine NO_3^- uptake is a crucial element of the catchment scale nitrogen balance and can be measured at small spatiotemporal scales while at the scale of entire river networks, uptake measurements are rarely available. Concurrent, low frequency NO_3^- concentration and stream flow (Q) observations at a basin outlet, however, are commonly monitored and can be analyzed in terms of concentration discharge (C-Q) relationships. Previous studies suggest that more positive $\log(\text{C})-\log(\text{Q})$ slopes under low flow conditions (than under high flows) are linked to biological NO_3^- uptake, creating a bent rather than linear $\log(\text{C})-\log(\text{Q})$ relationship. Here we explore if network scale NO_3^- uptake creates bent $\log(\text{C})-\log(\text{Q})$ relationships and when in turn uptake can be quantified from observed low frequency C-Q data. To this end we apply a parsimonious mass balance based river network uptake model in 13 mesoscale German catchments (21-1450 km²) and explore the linkages between $\log(\text{C})-\log(\text{Q})$ bending and different model-parameter combinations. The modelling results show that uptake and transport in the river network can create bent $\log(\text{C})-\log(\text{Q})$ relationships at the basin outlet from log-log linear C-Q relationships describing the NO_3^- land to stream transfer. We find that the bending is mainly shaped by geomorphological parameters that control the channel reactive surface area rather than by the biological uptake velocity itself. Further we show that in this exploratory modelling environment, bending is positively correlated to percentage NO_3^- load removed in the network ($L_{r,perc}$) but that network wide flow velocities should be taken into account when interpreting $\log(\text{C})-\log(\text{Q})$ bending. Classification trees, finally, can successfully predict classes of low (~4 %), intermediate (~32 %) and high (~68 %) $L_{r,perc}$ using information on water velocity and $\log(\text{C})-\log(\text{Q})$ bending. These results can help to identify stream networks that efficiently attenuate NO_3^- loads based on low frequency NO_3^- and Q observations and generally show the importance of the channel geomorphology on the emerging $\log(\text{C})-\log(\text{Q})$ bending at network scales.

1 Introduction

Transport and transformation of nitrate (NO_3^-) in river networks are major controls of downstream exports to receiving lakes, reservoirs and coastal systems (Alexander et al., 2000; Billen et al., 1991; Peterson et al., 2001; Seitzinger et al., 2002; Seybold



30 and McGlynn, 2018). Increased NO_3^- concentrations in surface waters can induce detrimental algae growths (Beusen et al.,
2016; Canfield et al., 2010; Galloway et al., 1995), compromise river ecosystem health and jeopardize drinking water supplies.
Since the beginning of the 20th century, human activities such as agricultural expansion and fossil fuel burning have mobilized
additional reactive nitrogen (N), initiating and later exacerbating this problem (Seitzinger et al., 2002). In arable landscapes,
which include large parts of Europe, the efficient management of aquatic NO_3^- at network scales is complicated by the
35 spatiotemporal variability of loading patterns and hydrologic regimes as well as the lack of understanding of nutrient pathways,
connected transit times and removal processes from input to export. Nevertheless, nitrate concentration and load variability
can be predicted at catchment scales when relying on detailed process understanding regarding transport and biogeochemical
processing (Alexander et al., 2009; Schlesinger et al., 2006; Wollheim et al., 2008). Moving beyond small scale variability and
characterizing nitrate processing at the catchment scale however remains a challenge (McDonnell et al., 2007; Li et al., 2020).

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Within river reaches and streams, reactive solutes like NO_3^- are affected by complex interactions of physical, biological and
chemical processes. Physical transport is driven by local discharge and channel geomorphology and dictates the NO_3^- residence
time in a reach, thus influencing the timescales at which biogeochemical processing can take place (Kirchner et al., 2000;
Runkel and Bencala, 1995; Zarnetske et al., 2011). NO_3^- is removed and transformed by denitrifying bacteria in the anoxic
45 river sediment (Birgand et al., 2007; Peterson et al., 2001), ammonified or retained through assimilation processes in the oxic
or anoxic river compartments by bacteria, fungi and primary producers such as algae and macrophytes, potentially entering
higher trophic levels. In the latter case, N in the form of DON (dissolved organic nitrogen) and more commonly DIN (dissolved
inorganic nitrogen), together with phosphorus (P) may be released to the water column later on (Durand et al., 2011; Vanni,
2002; Vanni and McIntyre, 2016). The nutrient spiraling model (Newbold et al., 1981; Stream Solute Workshop, 1990) that
50 formally describes these processes has been used to quantify and compare NO_3^- transport and uptake (the net result of all
removal and release processes) in river reaches (Peterson et al., 2001; Mulholland et al., 2008; Hall et al., 2009) and stream
networks (Ensign et al., 2006; Doyle, 2005; Marce and Armengol, 2009). Quantifying in situ NO_3^- uptake is labor intensive
and may involve local nutrient additions, potentially altering the ambient uptake rate (Hensley et al., 2014; Mulholland and
Tank, 2002). Other methods require high frequency measurements (Jarvie et al., 2018; Kunz et al., 2017) that are mostly
55 limited to small spatial scales (i.e. reach scale) and can vary considerably between measuring points (Boyer et al., 2006). At
the scale of entire river networks contrarily, uptake measurements are rarely available (but see Wollheim et al., 2017; Hansen
et al 2018) and models are applied instead to predict spatiotemporal uptake patterns (Boyer et al., 2006; Yang et al., 2018).
These models account for the spatial configuration of the stream network, an important aspect for stream biogeochemistry that
is often ignored in small scale experimental approaches (Fisher et al., 2004). Spatially distributed models however, require
60 calibration of uncertain spatiotemporal parameters and may not reflect the essential features of the system despite fitting
observed data well (Klemes, 1986).



River networks link terrestrial source zones to coastal areas and integrate biogeochemical and hydrological catchment functions across scales (Bouwman et al., 2012; Helton et al., 2018). Small streams (usually headwaters) are known to influence the export signal disproportionately because of their overall (high) contribution to total stream length and effective NO_3^- removal capacity (Alexander et al., 2000; Horton, 1945), explained by high sediment surface to water volume ratios. Generally, high removal efficiencies have been reported for river network areas with lower specific discharges (Hall et al., 2009; Hensley et al., 2014), under favorable circumstances such as high light availability, heavy in-stream vegetation (Hensley et al., 2014; Rode et al., 2016) and for streams with a high capacity for lateral and hyporheic exchange (Gomez-Velez et al., 2015; Kiel and Cardenas, 2014). The scaling of in-stream uptake processes beyond the river reach has been approached by combined experimental-modelling studies with defined explicit scaling relationships (e.g. Basu et al., 2011; Aguilera et al., 2013; Bertuzzo et al., 2017; Lindgren and Destouni, 2004) and theoretical frameworks explaining how the river network capacity regulates solute export (e.g. Wollheim et al., 2018). Abbott et al. (2018) shows how spatially heterogeneous patterns of water chemistry stabilize while the temporal variability of nutrient concentrations persists when moving downstream, facilitating the temporal scaling of headwater measurements. Nevertheless, insights into linking the interplay of nitrate removal processes at the network scale to downstream export patterns in space and time are largely missing.

Concentrations (C) for in-stream solutes such as carbon, major ions, particulates and nutrients are commonly monitored concurrently with discharge (Q) at the basin outlet. C-Q relationships integrate the effect of biogeochemical and hydrological processes within the catchment and have mainly been discussed in terms of land-stream transfer and source configuration in catchments as well as subsurface retention processes (Godsey et al., 2009; Musolff et al., 2017, Bierozza et al., 2018). The shape of long term (multiple years) C-Q relationships in the log-log space is typically described by the slope of a linear regression model (Godsey et al., 2009). Here, three archetypes have been distinguished; (i) a positive $\log(C)$ - $\log(Q)$ slope, indicating enrichment, occurs when an increasing discharge additionally mobilizes solutes, (ii) a negative C-Q slope or dilution pattern is commonly linked with source limitations and (iii) a neutral or chemostatic slope implies low variability in in-stream concentrations across a high range of discharges, a pattern observed for example for solutes derived from weathering bedrock (Ameli et al., 2017; Godsey et al., 2009). The potential information loss associated with linear and monotonic NO_3^- $\log(C)$ - $\log(Q)$ analysis was addressed by Moatar et al. (2017) and Minaudo et al. (2019) for more than 200 French catchments and by Diamond and Cohen (2018) for 44 rivers in Florida, USA. These studies identified distinct linear low-flow and high-flow NO_3^- $\log(C)$ - $\log(Q)$ regression slopes for a majority of the cases. Moatar et al. (2017) found that stronger positive slopes under low flow conditions correlate positively with chlorophyll-a concentrations (associated with biological processes) and attributed this condition to biological NO_3^- concentration mediation in the stream. This is consistent with the findings of Hall et al. (2009) and Hensley et al. (2014) among others that in-stream uptake is more efficient under low-flow than under high-flow. Furthermore, Wollheim et al. (2017) illustrates non-linear NO_3^- C-Q relationships conceptually for storm flow dynamics in a river network, showing high retention capacities in the headwater catchments that decrease under increasing flows, changing the slope of C-Q relationships from dilution to enrichment. Based on these studies we hypothesize that the magnitude (or



100 efficiency) of in-stream NO_3^- uptake is encoded within observed C-Q relationships, and their analysis therefore can improve our understanding of in-stream uptake processes through providing an alternative to elaborate field and modelling work aimed at quantifying NO_3^- removal in stream networks. Low frequency NO_3^- observations are widely available (e.g. biweekly to monthly grab sampling, Ebeling et al., 2020 rev; Minaudo et al., 2019; Moatar et al., 2017) but if and how this data can be utilized to characterize catchment scale in-stream processing has yet to be investigated.

105 In this paper, it is postulated that network-scale uptake effects can be inferred from the non-linearity or bending of low-frequency, multi-annual concentration (C) and discharge (Q) observations. To test this hypothesis, we apply a parsimonious river network model (similar to Bertuzzo et al., 2017; Helton et al., 2018; Helton et al., 2010; Mulholland et al., 2008) in 13 German catchments to explore the catchment scale transport and uptake processes that influence downstream $\log(\text{C})$ - $\log(\text{Q})$ patterns. The specific objectives are to (i) introduce *Curvature* as a robust metric to quantify bending of low frequency C-Q time series in the log-log space; (ii) explore the sensitivity of C-Q bending to hydrological and in-stream biogeochemical parameters (e.g. channel shape, water velocity and biological NO_3^- uptake velocity); (iii) explore how C-Q bending is linked to network scale in-stream uptake; (iv) provide guidelines if and on under what circumstances the C-Q bending can offer
110 conclusive information on effective in-stream uptake. In this proof of concept exploratory study, we demonstrate how (existing) low-frequency monitoring data can be effectively utilized to quantify nitrate uptake in river networks and show how small scale uptake processes shape emerging patterns at catchment scales.

2 Methods

115 2.1 Curvature

The shape of C-Q relationships are often described as linear (Bierozza et al., 2018; Godsey et al., 2009; Musolff et al., 2017) or segmented linear (Meybeck and Moatar, 2012; Moatar et al., 2017; Marinos et al., 2020), implying a limit on the possible C-Q shapes and setting assumptions such as 'fixed breaking points'. Here, we introduce the concept of *Curvature* to quantify rather than describe the shape of "broken-stick" C-Q relationships, without the assumption of a fixed form. In a strict
120 geometrical sense the curvature ($-\infty$; $+\infty$) is the instantaneous rate of change of direction of a point that moves on a curve. A straight line for example has a curvature of zero and a large circle has a smaller curvature than a small circle (Pressley, 2010) (Fig. B1). Here, *Curvature* identifies the magnitude and direction of the $\log(\text{C})$ - $\log(\text{Q})$ section with the largest instantaneous change. To calculate *Curvature* for an observed (noisy) C-Q relationship, a smoothed spline, f , is iteratively fitted with increasing degrees of freedom (df) to capture the general $\log(\text{C})$ - $\log(\text{Q})$ shape accurately but avoid overfitting. Initially, $\text{df} =$
125 3 and the $\log(\text{Q})$ region of the largest instantaneous change is identified as $Q_m \pm 0.05$ with $Q_m = \underset{\log Q}{\text{argmax}} |f''|$. Then, df is increased until, at $\text{df}=i$, the $\log(\text{Q})$ corresponding to the largest instantaneous change is not within the initial Q_m region



any more. Consequently, *Curvature* is calculated for a smoothed spline fit, f , with $df = i-1$ as
$$\begin{cases} \max_{\log Q} f'' \text{ if } \left| \max_{\log Q} f'' \right| \geq \left| \min_{\log Q} f'' \right| \\ \min_{\log Q} f'' \text{ if } \left| \max_{\log Q} f'' \right| < \left| \min_{\log Q} f'' \right| \end{cases}$$

Curvature of a log(C)-log(Q) relationship could be considered as a complementary metric to the slope of the linear regression model (Godsey et al., 2009) and could serve as an alternative for segmented linear regression fits (Meybeck and Moatar, 2012; Moatar et al., 2017; Marinos et al., 2020) (Fig. B2) as it quantifies bending.

We assume here that a multi-annual (6 to 15 years) low frequency (biweekly to monthly) C-Q relationship without temporal (significant) trends in a given station has one *Curvature*. To verify this assumption in a realistic setting, *Curvature* was computed for observed nitrate (C) and Q data (1995-2010) of French water quality stations with biweekly to monthly sampling frequencies (Dupas et al., 2019). Following the removal of C outliers (falling outside of $\mu \pm 3.5\sigma$ in the log space, with μ and σ representing the sample mean and standard deviation, respectively) 444 stations were selected that satisfy the following four criteria: (i) the station should have at least 70 coupled C and Q observations (total number of samples, $n \in [70; 402]$); (ii) a minimum of 6 years of data are represented; (iii) there is no bias in the intra annual distribution of the data (i.e. never less than 10% of the C-Q observations in one season); and (iv) the station C observations had no significant temporal trends (Mann Kendall test, $p\text{-value} > 0.05$) (Ebeling et al., 2020 rev). We then assessed the robustness of *Curvature* to the low frequency C-Q observations in a time series by selecting different subsamples of C-Q data from the entire available time series for a given station. More specifically, 100 random time series subsamples (each with a minimum length of 70) without replacement but with overlap were taken for each station, with the subsamples passing the four criteria above, and *Curvature* was calculated for each subsampled time series. On average, the subsamples represented nearly 80% of the complete time series for a station.

The estimated *Curvature* for the observed NO_3^- log(C)-log(Q) data ranges between -5.25 and 3.88 (median is -0.23, Fig. B3) and 77% of the stations are characterized by *Curvature* ≤ 0 or a linear or concave shape (similar to Moatar et al. 2017). The time series subsamples for each station generally had a small *Curvature* variability (Interquartile Range, IQR for a given station below 1) for 93% of the stations with some exceptions demonstrating a larger IQR up to 8. This indicates *Curvature* quantification for most low frequency C-Q time series is robust. The Spearman rank correlation ($\rho = 0.53$, $p\text{-value} < 2.2e-16$) between the absolute observed *Curvature* and IQR for each station is significant and positive, implying that C-Q relationships with a higher absolute *Curvature* have a higher uncertainty when quantifying the C-Q bending. However, *Curvature* variability (IQR) in the subsamples for each station has no significant correlation with the number of data points available for one station. This implies that *Curvature* tends to be temporally robust when the C-Q data obeys the four above criteria so that the length of the low frequency time series length does not impact the estimated *Curvature*. Overall, the proposed *Curvature* metric – quantifying the C-Q bending- is suitable to describe bending in multiannual, temporally stable log(C)-log(Q) relationships.



2.2 Network Model

In this work an explorative grid based (100 m x 100 m) mass balance network model (comparable to Bertuzzo et al., 2017; Helton et al., 2018; Helton et al., 2010; Mulholland et al., 2008 and conceptually shown in Fig. B4) was used to simulate in-stream nitrate transport and biological removal on a daily basis. The model was developed in R (R Core Team, 2013).

2.2.1 Stream network and hydrological properties

Following Bertuzzo et al. (2017) and Helton et al. (2018), each river network node (i.e. grid cell) i ($1 \leq i \leq N$) has a drainage area A_i [m²] that is calculated as the sum of the total upstream drainage area $\sum_j W_{ji} A_j$ [m²] and the direct drainage area a_i [m²] (e.g. laterally contributing drainage area) to grid cell i (Eq. (1)):

$$A_i = \underbrace{\sum_j W_{ji} A_j}_{\text{Upstream Drainage Areas}} + \underbrace{a_i}_{\text{Direct Drainage Area}} \quad (1)$$

where W_{ji} [-] is an element in the connectivity matrix W ($N \times N$) such that $W_{ji} = 1$ if j is directly neighboring and flowing into i and $W_{ji} = 0$ otherwise. A_j [m²] is the total drainage area to node j .

The total local discharge Q_i at a given grid cell i is proportional to the total drainage area at that grid cell, A_i , [m³ s⁻¹] (following Bergstrom et al., 2016 and Bertuzzo et al., 2017) (Eq. (2)), which in turn dictates the downstream hydraulic geometry relationships of river geomorphic parameters channel width, w_i [m], and average channel depth, d_i [m] (Leopold and Maddock, 1953) (Eq. (2.1) and Eq. (2.2)). The local velocity in a grid cell v_i [m s⁻¹] is calculated according to Eq. (2.3) and the corresponding travel time, T_i [days] is computed in Eq. (2.4):

$$Q_i = Q_{t.sp} * A_i \quad (2)$$

$$w_i = K_w * Q_i^{a_w} \quad (2.1)$$

$$d_i = K_d * Q_i^{a_d} \quad (2.2)$$

$$v_i = \frac{Q_i}{w_i * d_i} \quad (2.3)$$

$$T_i = \frac{l_i}{v_i} \quad (2.4)$$

where $Q_{t.sp}$ [m³ s⁻¹] is the specific discharge that is calculated as the ratio of the daily discharge at the outlet and the total number of catchment grid cells, consequently varying in time. Parameters a_w [-] and K_w [-] are the respective exponent and coefficient parameters in the river width-discharge relationship (Eq. (2.1)); while a_d [-] and K_d [-] compose the exponent and coefficient parameters of the depth-discharge relationship (Eq. (2.2)), respectively. The flow length through a grid cell i , l_i [m], equals 100 or $100\sqrt{2}$ m for horizontal/vertical or diagonal flow directions, respectively. The ratio of a_d to a_w corresponds to a parameter r [-] $\in \mathbb{R}^+$ which prescribes the cross section geometry relation such that a triangular channel cross section is represented by $r = 1$, a parabolic channel cross section by $r = 2$ and channel cross sections with progressively flatter



bottoms and steeper banks by increasing values of r (Dingman, 2007). The width-discharge relation in Eq. (2.1) is conceptually illustrated in Fig. B5 for two sets of a_w and K_w .

2.2.2 Nitrate uptake

Similar to Eq. (1) the incoming load, $L_{in,i}$ [mg s^{-1}], to a river network grid cell i is the sum of upstream load contributions
 190 $L_{in,up,i}$ [mg s^{-1}] and direct land to stream loading $L_{in,ls,i}$ [mg s^{-1}], given that $L = CQ$ (Eq. (3)). The contribution of direct land
 to stream loading concentration can be expressed as a power law (Musolff et al. 2017) with the exponent b [-], the slope in the
 $\log(C)$ - $\log(Q)$ relationship that is an indicator of the C-Q archetype (Godsey et al., 2009) and coefficient c [-]. Following
 Jawitz and Mitchell (2011), the coefficient c is calculated to yield the long-term mean in-stream input concentration C_{mean}
 [mg L^{-1}] (Eq. (A1)). Additional NO_3^- sources such as the load resulting from NO_3^- release within the stream network as point
 195 sources are not considered here (similar to Bertuzzo et al., 2017; Wollheim et al., 2006), so that only concave or linear $\log(C)$ -
 $\log(Q)$ patterns ($Curvature \leq 0$) can be simulated. Also, we do not consider other loading processes that may create bending
 at the catchment outlet (e.g., shifts in transport pathways and solute sources, Marinos et al. 2020).

$$L_{in,i} = \underbrace{L_{in,up,i}}_{\text{Upstream Loads}} + \underbrace{L_{in,ls,i}}_{\text{Direct Land to stream Loading}} = \sum_j W_{ji} L_j + c * (Q_{t.sp} * a_i)^{b+1} \quad (3)$$

The modelled in-stream NO_3^- uptake follows first order removal kinetics (Alexander et al., 2000; Boyer et al., 2006; Ensign
 200 and Doyle, 2006), such that the outgoing load from grid cell i , L_i [mg s^{-1}] is a fraction of the incoming load $L_{in,i}$ (Eq. (4)) and
 the absolute removed load $L_{r,i}$ [mg s^{-1}] can be described as (Eq. (5)) with the in-stream processing chiefly occurring at the
 sediments and biofilm at the benthic-pelagic interface (Wollheim et al., 2006). Here, $L_{r,i}$ is influenced by separate hydrological
 ($\frac{P_i * l_i}{Q_i}$) and biological (v_f) components (similar to Bertuzzo et al., 2017).

$$L_i = L_{in,i} * e^{-\frac{v_f * P_i * l_i}{Q_i}} \quad (4)$$

$$205 \quad L_{r,i} = L_{in,i} - L_i = L_{in,i} * (1 - e^{-\frac{v_f * P_i * l_i}{Q_i}}) \quad (5)$$

where P_i is the cross section wetted perimeter calculated from the Manning equation (using the bed slope S_i and assuming a
 fixed roughness coefficient = 0.03 [m m^{-1}]) in open channels (Eq. (A2)). The uptake velocity parameter v_f [m day^{-1}] indicates
 the rivers total biological nutrient demand (areal uptake, U [$\text{mg m}^{-2} \text{day}^{-1}$]) relative to in-stream concentration C_{mean} [mg L^{-1}]
 with $v_f = k_i d_i$ and k_i the first order removal constant (Ensign and Doyle, 2006; Wollheim et al., 2006). The parameter v_f
 210 accounts for the processes altering the rate and form of downstream NO_3^- delivery (Doyle, 2005) and is therefore not limited
 to denitrification only. We assume that v_f is independent of the in-stream NO_3^- concentration C_{mean} (Pennino et al., 2014;
 O'Brien et al., 2007) such that the areal uptake rate $U = v_f * C_{mean}$ is tightly linked with C_{mean} in a first order relationship.
 Others (e.g., Hensley et al., 2014; Mulholland et al., 2008; O'Brien et al., 2007) contrarily found explicit scaling relationships
 where v_f decreases non-linearly for increasing C_{mean} ($10^{-4} - 10^1 \text{ mg L}^{-1}$) when considering distinct catchments. However, in



215 Germany, the NO_3^- concentration range across a range of catchments is small ($10^{-1} - 10^1 \text{ mg L}^{-1}$ according to Ebeling et al., 2020 rev) and rivers generally have minor longitudinal concentration variability (Hensley et al., 2014; Ensign and Doyle, 2006) which suggest independent definitions of v_f and C_{mean} .

The Damköhler number Da [-] is calculated as the ratio between transport (τ_T) and reaction (τ_R) timescales and is often used to characterize the relative importance of hydrological and biogeochemical processes in hydrological connected systems (Oldham et al., 2013; Kumar et al., 2020):

$$Da = \frac{\tau_T}{\tau_R} = \frac{TT}{k^{-1}} \quad (6)$$

where, τ_T represents as the effective travel time, TT [days] or the exposure time scale under advective conditions. We estimated the catchment wide TT as the spatiotemporal median of the sum of all downstream T_i (Eq. (2.4)) for a grid cell in the network ($\sum_i^{out} T_i$) (similar to Bergstrom et al., 2016). Whereas τ_R represents the reactive time scale of biological processes. It is approximated as k^{-1} [days $^{-1}$] with the effective catchment wide k estimated as the spatiotemporal median of the grid-scale first order reaction constant $k_i = d_i/v_f$.

2.3 Exploring *Curvature* with Monte Carlo Simulations

Monte Carlo simulations are performed to explore how *Curvature* evolves from a range of model input parameter combinations in a variety of catchments (Sect 2.3.1 below). These simulations utilize the same set of 11107 unique parameter combinations in each of study catchments that, during one model run, are each kept constant in time and uniform in space for simplicity. The unique parameter combinations are generated by Latin Hypercube sampling from uniform parameter ranges that are set according to literature values (Table 1). Some physical constraints were also imposed such that the channel geometry parameters a_w and a_d must obey continuity principles ($a_w + a_d < 1$ and $a_w > a_d$, following Leopold and Maddock, 1953). The main simulation results are i) *Curvature* [-], deduced from simulated $\log(C)$ - $\log(Q)$ relationships when minimum 80 % of the C data is above the ‘detection limit’ of $0.002 \text{ mg L}^{-1} \text{ NO}_3^-$; and ii) the network wide percentage load removed $L_{r,perc}$ [%]. The latter is calculated as the median of the ratio between the daily absolute removed load and the daily absolute incoming load in the river network. While all outputs can be spatially and temporally explicit on a daily time step, *Curvature* is examined at the catchment outlet, integrating both spatial and temporal aspects. The Monte Carlo results are subsequently subjected to a global sensitivity analysis with the PAWN method (Pianosi and Wagener; 2015) to elucidate influential model parameters. Furthermore a correlation analysis is conducted to explore how these influential parameters impact simulated *Curvature*. Finally, a Classification and Regression Tree algorithm (CART, Breiman et al., 1984) allowed us to visualize parameter interactions as detailed in Sect. 2.3.2 below.

245 **Table 1: Network model parameter ranges for the Monte Carlo simulations.**

Parameter	Unit	Description	Range	References
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v_f	[m day ⁻¹]	Uptake velocity	10 ⁻⁴ ; 0.25	Marce and Armengol, 2009
b	[-]	Slope b lin. regress. log(C)-log(Q)	-1.5; 1.5	Musolff et al., 2017, Ebeling, 2020b
C_{mean}	[mg L ⁻¹]	Land to stream concentration	10 ⁻⁴ ; 20	Ebeling, 2020b
K_w	[-]	Coefficient width-Q function	2.6; 20.2	Andreadis et al., 2013
a_w	[-]	Exponent width-Q function	0.01; 0.54	Andreadis et al., 2013; Dingman, 2007
K_d	[-]	Coefficient depth-Q function	0.12; 0.63	Andreadis et al., 2013
a_d	[-]	Exponent depth-Q function	0.28; 0.667	Andreadis et al., 2013; Dingman, 2007

2.3.1 Catchment selection

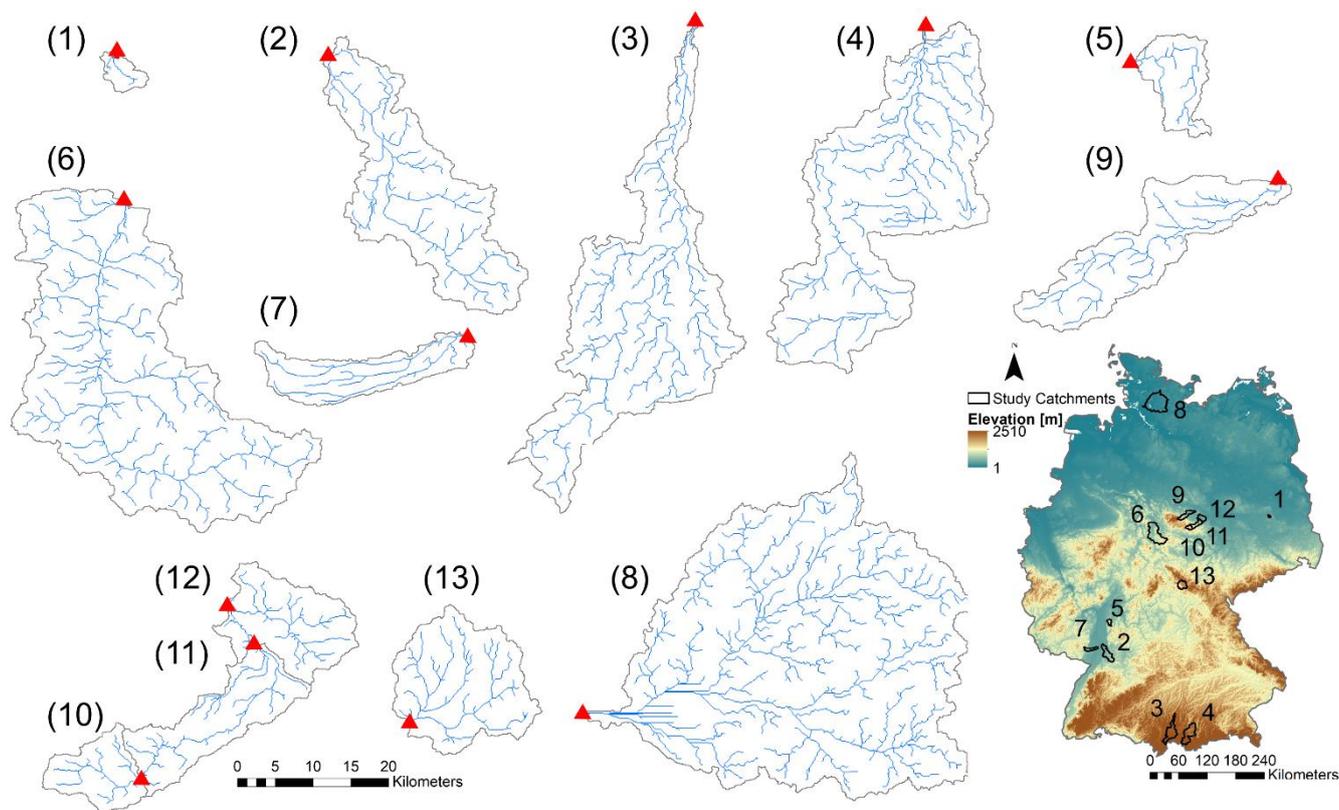
We applied the network model in 13 mesoscale catchments across Germany with varying sizes (21-1450 km²) and distinct geophysical settings as stream order, median discharge and catchment shape (quantified with the Horton form factor; Horton, 1945) (Table 2). The catchments were selected based on a database of water quality and catchment characteristics within Germany (Ebeling, 2020a). Three nested sub-catchments for the Selke as well as the Holtemme river system, both part of the Bode, a well-studied river system near the Harz Mountains in central Germany were included additionally (Fig. 1) (Ehrhardt et al., 2019; Rode et al., 2016; Winter et al., 2020; Mueller et al., 2018). All catchments had ~10 years of uninterrupted daily Q data available between 1995 and 2010 (Musolff, 2020). The selected catchments were delineated in ArcMap (ESRI, 2011) from a 100 m x 100 m DEM (EEA, 2013; Ebeling et al., 2020 rev). A flow direction, flow accumulation and valley slope grid in the same resolution were established. The channel threshold drainage area for the network delineation was set to 150 grid cells (1.5 km²), which agreed well with the observed river network, resulting in a tree shaped river network with N grid cells or nodes.

Table 2: Catchment properties summary: Catchment Area, median Elevation, Slope and Topographical Wetness Index (TWI), maximum Strahler Stream Order, Horton form factor, Drainage Density, median discharge (Q) and the coefficient of variation of the discharge (CV Q).

ID	River	Area [km ²]	Med. elevation [m]	Med. slope [°]	Med. TWI [-]	Stream order [-]	Network length [km]	Horton form factor [-]	Drainage density [km km ⁻²]	Med. Q [m ³ s ⁻¹]	CV Q [-]
1	Dahme	20.9	105	1.50	10.08	2	11	0.67	0.52	0.02	1.13
2	Kraichbach	422.5	164	2.84	9.45	4	228	0.23	0.54	0.85	0.47
3	Wertach	658.1	833	4.30	9.17	4	391	0.14	0.59	10.60	0.96
4	Ammer	713.7	858	8.34	8.80	4	416	0.29	0.58	14.98	0.84
5	Modau	88.6	272	5.61	8.47	3	47	0.42	0.53	0.52	0.80
6	Leine	993.2	276	4.40	8.95	4	525	0.45	0.53	6.22	0.85
7	Speyerbach	142.0	187	3.58	9.84	3	104	0.17	0.73	0.66	0.64
8	Stör	1452.2	25	0.90	10.63	5	905	0.46	0.62	14.10	0.76
9	Holtemme	272.5	258	3.58	9.49	4	145	0.17	0.53	1.04	1.01
10	Selke Silberhütte	94.5	456	4.02	8.72	3	49	0.27	0.51	0.56	1.34



11	<i>Selke Meisdorf</i>	282.1	342	3.94	9.03	3	160	0.35	0.57	0.70	1.34
12	<i>Selke Hausneindorf</i>	460.1	263	2.90	9.60	4	256	0.37	0.56	0.65	1.50
13	<i>Schleuse</i>	263.2	597	9.12	7.92	4	139	0.79	0.53	2.88	1.07



265 **Figure 1: Germany DEM with the location and outline (shape) of selected catchments, along with their drainage networks (in blue) and outlet location (red triangle). See Table 2 for catchment ID's and properties.**

To verify the model's ability to reproduce realistic concentration time series and *Curvature*, modeled and simulated data were compared in the Selke catchment (at Meisdorf gauging station; 282 km², Table 2) where extensive field campaigns and modelling studies have been conducted related to in-stream processes (Rode et al., 2016; Dupas et al., 2017; Yang et al., 2019; Yang et al., 2018). This relatively homogeneous upstream part of the Selke consists of forest and cropland and is characterized by consistent export regimes (Winter et al., 2020). For an input parameter combination (Table C1) set to reasonable values for this catchment (Rode et al., 2016), the land to stream NO₃⁻ inputs averaged 1.2 kg N day⁻¹ km⁻² which is similar to the 1.9 kg N day⁻¹ km⁻² reported by Winter et al. (2020) for the Selke River (Meisdorf); and it is well within the general 0.001 to 100 kg N day⁻¹ km⁻² range established by Mulholland et al. (2008). Flow velocity had a spatiotemporal median value of 0.47 m s⁻¹, which is also comparable with measured flow velocities (Risse-Buhl et al., 2017). Furthermore, daily discharge data, monthly



nitrate concentrations (Winter et al., 2020) and integrated uptake measurements (Rode et al., 2016; Yang et al., 2019) were available for the Selke River (Meisdorf) between 2000 and 2012. Also, the spatially explicit nature of the network model was exploited here for the set input parameter combination (Table C1) to gain an insight into how the interplay of transport and uptake processes at every network grid cell can result in a curved C-Q pattern at the catchment outlet.

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2.3.2 PAWN sensitivity analysis and correlation analysis

We performed a global sensitivity analysis (GSA) using the moment independent PAWN method (Pianosi and Wagener (2015)). The method allowed for estimating the effect of the parameter inputs on the entire model output distribution and can be applied to rank the inputs and identify the uninfluential ones. The resulting PAWN sensitivity indices were estimated from generic input-output samples created with the numerical approximation strategy proposed by Pianosi and Wagener (2018). With this strategy, the range of variation of each input x_i is partitioned into a number n_i of equally probable ‘conditioning’ intervals ($I_{i,k}$, $k = 1, \dots, n_i$), i.e. each interval contains the same number of data points. Given a scalar model output y (here *Curvature*), the PAWN method compares the output conditional Cumulative Distribution Function (CDF) ($F_y(y)$), computed by concurrently varying all the inputs, and the n_i conditional CDFs for that input ($F_{y|x_i}(y|x_i \in I_{i,k})$). Each conditional CDF is obtained by varying all inputs within their entire range except for x_i , whose values are contained within one of the n_i conditioning intervals. The Kolmogorov-Smirnov statistic (KS) is then calculated as the maximum vertical distance between the conditional and unconditional CDFs, while the PAWN sensitivity index (S_i) for input x_i aggregates the results over all conditional CDFs through a summary statistic as presented in Eq. (7):

$$S_i = \text{stat}_{k=1 \dots n_i} KS(I_{i,k}) \quad (7)$$

295 where $KS(I_{i,k}) = \max_y |F_y(y) - F_{y|x_i}(y|x_i \in I_{i,k})|$

In this study, we applied Eq. (7) using $n_i = 10$ conditioning intervals for each input parameter and the maximum KS value, KS_{max} , as summary statistics, which is an appropriate metric for screening non-influential input parameters. We estimated confidence intervals of the sensitivity indices using 15000 bootstrap resamples and checked the robustness of the results. The PAWN analysis was carried out using the Python version of the SAFE toolbox for global sensitivity analysis (Pianosi et al., 2015).

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To explore the direction of change in the C-Q bending at the catchment outlet resulting from variations in the model parameters and the catchment in-stream uptake, a Spearman rank correlation analysis was performed including all the simulated catchment responses and parameter combinations. These correlations were visualized in a correlation matrix using the ‘corrplot’ package in R (Wei and Simko, 2020).

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2.3.3 Identify parameter and model output interactions with classification tree



Finally, we aim to determine if C-Q bending at the catchment outlet (specifically *Curvature*) informs about the network wide in-stream uptake. Thereto, a recursive modelling approach is proposed, using the Classification and Regression Trees algorithm (CART, Breiman et al., 1984) which allows for the identification of non-linear synergistic interactions among model parameters and output variables. This non-parametric method segregates classes for a response variable by progressively splitting selected predictor variables in a binary way. The resulting decision tree is simple and intuitive to interpret and can facilitate the fast characterization of river networks. The response variables include the effective catchment wide removal efficiency L_r , the Damköhler number Da and the uptake velocity v_f , while the predictors are *Curvature*, the median network velocity v and all of the model input parameters except for v_f (Table 1). For each response variable, three classes are defined representing low, intermediate and high ranges found in the literature (Table 3) that each contain 5 % of the simulation outputs (obtained by distributing the non-missing model simulations over 20 percentiles). The overall CART accuracy for each response variable is assessed by attributing 80 % of the simulation outputs in the low, intermediate and high classes to a training sample and assigning the remaining 20 % to a test sample. The training sample is then used to construct the classification tree while the test sample is needed to assess the prediction accuracy and calculating the performance statistics for each class. The CART analysis was performed using the ‘caret’ package in R with the Gini impurity measure as splitting criterion (Kuhn, 2020).

Table 3: Classes containing low, medium and high values for response variables v_f (uptake velocity), $L_{r,perc}$ (percentage load removed) and Da (Damköhler number) are used for the CART training and testing samples. Similar classes are obtained for model output *Curvature*. These classes stem from distributing the non-missing simulation data over 20 percentiles and selecting the percentiles corresponding to low, medium and high literature values with the respective percentile number (1-20) indicated in brackets. The training sample for constructing the CART model was then allocated 80% of this data and the test sample 20 %.

Variable	Units	Low	Medium	High	References
v_f	$[m\ day^{-1}]$	10^{-4} -0.01 (1)	0.10-0.11 (10)	0.23-0.24 (20)	Birgand et al., 2007, Marce and Armengol, 2009
$L_{r,perc}$	$[\%]$	3.8-5.2 (7)	28.7-35.1 (15)	63.0-75.3 (19)	Birgand et al., 2007
Da	$[-]$	0.17-0.25 (3)	0.88-1.02 (10)	3.25-4.19 (18)	Oldham et al., 2013
<i>Curvature</i>	$[-]$	-0.70;-0.51 (3)	-0.25;-0.22 (9)	-0.03;-0.01 (18)	Dupas et al., 2019

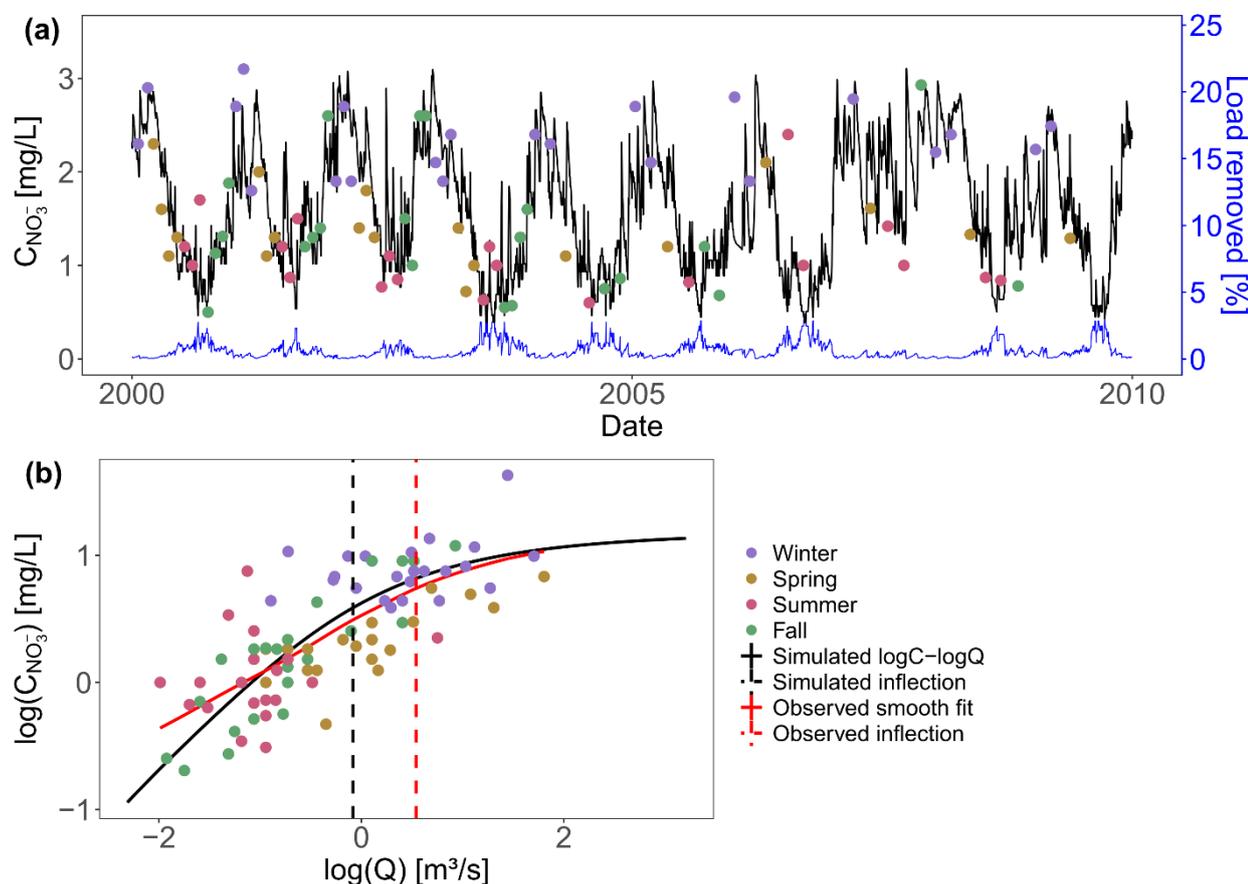
330 3 Results and Discussion

3.1 Model validation in the Selke River (Meisdorf)

To evaluate the network model performance in a realistic setting, we implemented the model with a fixed parameter combination (Table C1) in the Selke catchment and aimed to capture C-Q dynamics at the basin outlet. The simulated NO_3^- concentration time series for the Meisdorf station in Fig. 2a shows a seasonal pattern that follows the observation concentration data reasonably well (Nash-Sutcliffe Efficiency; NSE = 0.50, percent bias; pbias = -0.4 %). This seasonality is also reflected in simulated daily percentage of load removed (the ratio between the daily total removed load and the daily total incoming



load in the river network); and ranges from almost 0 % to 3.4 % in this case, with the median $L_{r,perc}$ value equal to 0.41 %. The highest removal efficiencies are simulated in fall and summer and coincide with low simulated NO_3^- concentrations at the catchment outlet. The observed nitrate concentrations generally show an enrichment export pattern in the $\log(C)$ - $\log(Q)$ space (b = 0.40, $R^2 = 0.56$) and a *Curvature* of -0.35 which agrees well with the simulated *Curvature* of -0.28 (Fig. 2b). The observed low nitrate concentrations coincide with low discharges in fall and summer, while high concentrations occur mainly in winter when discharges are higher.



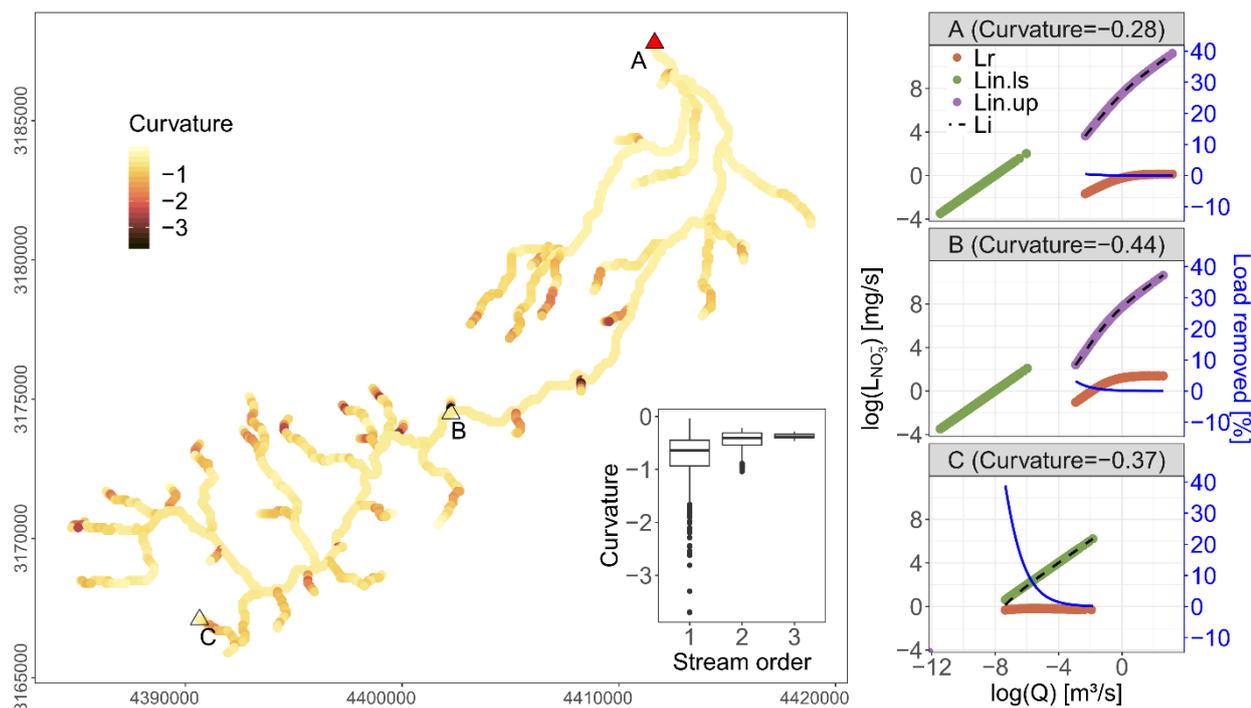
345 **Figure 2:** (a) Simulated and observed NO_3^- concentrations at the Selke Meisdorf gauging station for a 10 year simulation period (2000-2010; $\text{NSE}=0.50$). One data point ($C \sim 5 \text{ mg L}^{-1}$) is not shown here. The simulated median percentage of load removed in the stream network (blue line) is given during the same time period. (b) The observed NO_3^- concentrations and Q are log transformed and plotted together with the simulated C-Q data for 2000-2010. A smoothed spline is fitted to the observed and simulated C-Q data; and *Curvatures* of -0.35 and -0.28 are calculated at the respective discharges of $1.72 \text{ m}^3 \text{ s}^{-1}$ and $0.92 \text{ m}^3 \text{ s}^{-1}$, indicating the smoothed spline inflection points.

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Within the Selke Meisdorf river network the simulated *Curvature* is largely contained within -1.12 to -0.29 (10th and 90th quantiles respectively) for the given parameter combination (Table C1, Fig. 3). High *Curvatures* (< -1.12) are found



exclusively at grid cells with a low total drainage area ($A_i < 9 \text{ km}^2$) and *Curvature* becomes stable with increasing drainage areas (inset Fig. 3, Fig. B5). The incoming ($L_{in.ls}$ and $L_{in.up}$; Eq. (3)), removed (L_r ; Eq. (5)) and outgoing absolute load (L_i ; Eq. (4) with $L = CQ$) as function of Q in the log-log space are shown in Fig. 3 for three selected grid cells on the main river stem with low (C), intermediate (B) and high (A) drainage areas. The corresponding log(C)-log(Q) relationship for the outgoing load (L_i) at the outlet (A) is presented in Fig. 2b. Note that *Curvature* is calculated from log(C)-log(Q) relationships rather than log(L)-log(Q). The loads in grid cell A, B and C generally increase with discharge while the load removal efficiency decreases with discharge. The highest removal efficiencies are found in the headwater grid cell C (39 % for low discharge), followed by mid-stream grid cell B (3 % for low discharge) and the outlet A (0.5 % for low discharge). However, the total absolute load removed (L_r , sum per year) is largest for the mid-stream grid cell B (66.2 kg N year⁻¹), followed by the headwater cell C (25.6 kg N year⁻¹) and the outlet A (21.0 kg N km⁻² year⁻¹). Finally, the total yearly incoming load ($L_{in.ls} + L_{in.up}$) increases in the downstream direction from 658 kg N year⁻¹ in the headwaters to 72716 kg N year⁻¹ at the basin outlet.



365 **Figure 3:** Spatial distribution of simulated *Curvature* in the Selke river network (Meisdorf) for a selected parameter set (see Table C1). Three representative grid cells covering low (A), intermediate (B) and high (C) total drainage areas show the incoming land to stream load as $L_{in.ls}$ (Eq. (3)), the incoming load from upstream as $L_{in.up}$ (Eq. (3)), the removed load as L_r (Eq. (5)) and the outgoing load as L_i (Eq. (4)) in the log(L)-log(Q) space. The load removed as a percentage of the incoming load is presented on the secondary axis. The corresponding *Curvatures* for these grid cells are calculated from the log(C)-log(Q) relationships rather than log(L)-log(Q).

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With uniform, constant parameters the network model does not account for a spatiotemporal parameter variability. Nevertheless, it successfully (see NSE and pbias) reproduces the seasonality of the observed concentrations over the 2000-2010 period for the Selke Meisdorf catchment (Fig. 2a). For comparison, Yang et al. (2018) found a similar performance (NSE = 0.47, pbias = -3.35 %) when applying a fully distributed model with 16 calibrated parameters in this catchment between
375 1997 and 2009. The uptake velocity v_f for our simulation was set to 0.098 m day^{-1} to closely match the observed (assimilatory) uptake range of 0.009 to 0.103 m day^{-1} for the Selke Meisdorf river network (Rode et al., 2016), the annual percentage load removed equals 4.7 % which is within a comparable range reported in prior studies (Rode et al., (2016) and Yang et al., (2018) found annual means of 4.8 and 7.6 % respectively). Yang et al. (2018) reported very high uptake efficiencies (up to 75 %) for
380 in our model simulation (the lowest simulated NO_3^- concentration equaled 0.4 mg N L^{-1}). Additionally, due to the parsimonious structure of the proposed model, we did not account for the temporally changing effects of environmental factors like temperature and light availability that might (seasonally) influence uptake efficiencies in the river network. Nevertheless, these reported high low flow uptake efficiencies in summer are not a main contributor to the annual percentage load removed that is dominated by high flows, generally recorded during winter. Thus for the Monte Carlo simulations (Sect. 3.2 below) we
385 calculated $L_{r,perc}$ as the median of the daily percentage load removed rather than the total removal efficiency for the entire simulated time period to better represent an effective long term network wide removal capacity.

The interplay of incoming, removed and outgoing load at each network grid cell shapes the $\log(L)$ and $\log(C)$ - $\log(Q)$ relationships; and thus the estimated *Curvature* at the catchment outlet (Fig. 3). Land to stream loading ($L_{in,ls}$) that varies
390 linearly with direct incoming discharge at a given grid cell (Eq. (3) with $L = CQ$) in the log space (*Curvature* = 0) can lead to a bent outgoing $\log(C)$ - $\log(Q)$ relationship where concentration or load (L_i) varies non-linearly with discharge (*Curvature* \neq 0). The onset of a bent $\log(C)$ - $\log(Q)$ pattern (*Curvature* = -0.37) is illustrated in the headwater grid cell C in Fig. 3 where $L_{in,ls}$ is the only incoming load (upstream incoming load, $L_{in,up}$ equals 0 in this case). The absolute removed load is higher under increasing Q while the percentage load removed is lower, which explains observed C-Q patterns with higher $\log(C)$ -
395 $\log(Q)$ slopes for low flows than for high flows (Moatar et al., 2017; Wollheim et al., 2008; Doyle, 2005; Wollheim et al., 2017; Basu et al., 2011). This decreased NO_3^- load removal efficiency at the basin outlet (spatial scale) or during events (temporal scale) can arise because stream morphology characteristics such as depth and water velocity, that correlate with varying discharge, constitute higher surface-to-volume ratios at the headwaters (generally low flows) than at the outlet (higher flows) (Peterson et al 2001; Hensley et al 2014). In the Selke Meisdorf case, uptake and land to stream loading at the
400 downstream grid cells (B and A in Fig. 3) have a decreasing local impact on the outgoing load due to the large upstream contributions that increase in the downstream direction (see explicit scaling relationship for input flux in Bertuzzo et al., 2017). This is also explained by Wollheim et al. (2018) who suggests that the river network saturates as supply exceeds biological ‘demand’. Dupas et al. (2017) on the other hand shows how NO_3^- uptake effects are decreasingly visible in C-Q observations



405 downstream and concentrations largely matched those estimated by a conservative mixing model. The saturation effect with
the accumulation of large load is reflected in the *Curvature* converging to a constant value when moving from upstream to
downstream or from a lower order to a higher order river reach (Fig. 3, B6). This also corroborates the recent findings of
Abbott et al. (2018) who found that the temporal variability (here reflected in the C-Q relationship) of nutrients is preserved
moving downstream in a river network. Overall the Selke example shows that the network model can realistically reproduce
the bending of observed NO_3^- C-Q relationships that evolve from the decreasing removal efficiency at higher discharges.

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3.2 Monte Carlo simulation results

To elucidate how *Curvature* at the catchment outlet is shaped by in-stream transport and removal, a Monte Carlo simulation
was run for the same 11107 model input parameter combinations (Table 1) in each of the 13 German catchments (Fig. 1). The
overview of the model outputs for each study catchment in Table 4 shows that catchments 1, 5 and 11 display the smallest 10th
415 quantile *Curvature* values of -1.61, -1.40 and -1.24 (highest bending) while the catchments 4 and 6 registered higher (lowest
bending) and less variable *Curvature* (10th quantiles at -0.31 and -0.35) (Fig. B7). Catchments 3, 4 and 8 are characterized by
high discharges (Table 2) at the catchment outlet and demonstrate low percentages of load removed, $L_{r,perc}$ (90th quantile at
29.8, 32.1 and 19.3 % respectively). The highest $L_{r,perc}$ are found in catchments 1 and 10 (98.4 and 95.1 % for the respective
90th quantiles). The regression slope of the log(C)-log(Q) relationship at the basin outlet, b_{out} , is positively skewed for all
420 catchments compared to the slope b of the land-to stream loading function that had no positive or negative preference (Table
1, Eq. (3)) with the most positive slopes found in catchment 5. The distribution of the concentrations at the catchment outlet,
 C_{out} , are generally similar across all catchments (10th and 90th percentiles within 0 to 6.2 mg L⁻¹) and are significantly less
variable than the land-to-stream incoming concentration (parameter C_{mean}) that varied from 10⁻⁴ to 20 mg L⁻¹ across all the
simulations (Table 1). The highest C_{out} are found in the largest catchment 8. The median water velocity v (Eq. (2.3)) is
425 between 0.01 and 0.5 m s⁻¹ for the 10th and 90th quantiles of all the study catchments. With the largest v simulated for
catchments 3 and 4 that also have the highest discharge. The median river network travel time, TT , for all simulations and
catchments ranges from 0.1 to 4 days between their respective 10th and 90th quantiles and remarkably have no clear relationship
with catchment properties as the total river network length (Table 2). Finally, the Damköhler number, Da (Eq. (6)), is variable
around 1 with the highest values, indicating reaction driven conditions, found for catchments 2 and 12 that respectively range
430 from 0.6 to 10.3 and 0.7 to 10.8 for the 10th and 90th quantiles. The lowest Da values are found for catchments 4 and 10 (90th
quantile < 2) implying more transport driven conditions.

**Table 4: 10th and 90th quantiles of model outputs *Curvature*, percentage load removed, $L_{r,perc}$, Damköhler number Da , regression
slope of the log(C)-log(Q) relationship at the basin outlet, b_{out} , the median concentration at the basin outlet, C_{out} , the median water
435 velocity, v , that is calculated with the channel shape parameters a_w , a_d , K_w and K_d and discharge (Eq. (2.3)) and median river
network travel times, TT , for each of the 13 German catchments.**



Catch. ID	<i>Curvature</i> [-]		$L_{r,perc}$ [%]		Da [-]		b_{out} [-]		C_{out} [mg L ⁻¹]		v [m s ⁻¹]		TT [days]	
	10 th	90 th	10 th	90 th	10 th	90 th	10 th	90 th	10 th	90 th	10 th	90 th	10 th	90 th
1	-1.61	-0.01	2.6	98.4	0.3	6.4	-0.65	2.22	<10 ⁻⁴	4.68	0.01	0.25	0.1	1.8
2	-1.04	-0.01	0.9	78.5	0.6	10.3	-0.42	2.31	<10 ⁻⁴	2.36	0.02	0.29	0.6	3.9
3	-0.43	-0.02	0.2	29.8	0.2	2.8	-0.54	1.96	0.01	5.27	0.07	0.48	0.5	3.3
4	-0.33	-0.01	0.2	32.1	0.1	1.5	-0.60	1.85	0.03	5.56	0.07	0.50	0.3	1.9
5	-1.40	-0.01	1.3	85.1	0.1	2.0	-0.49	2.43	0.01	3.76	0.04	0.38	0.2	1.5
6	-0.35	-0.02	0.5	54.6	0.3	4.3	-0.58	1.84	0.02	3.75	0.04	0.36	0.4	2.7
7	-0.44	-0.01	0.8	72.6	0.2	3.6	-0.52	2.09	0.01	4.4	0.04	0.38	0.4	2.8
8	-0.63	-0.01	0.1	19.3	0.2	4.1	-0.71	1.70	0.07	6.24	0.05	0.39	0.5	3.0
9	-0.68	-0.01	0.8	70.4	0.3	5.3	-0.53	1.99	0.01	3.43	0.04	0.35	0.5	3.1
10	-0.79	-0.01	1.9	95.1	0.1	1.9	-0.45	2.33	0.01	3.88	0.04	0.36	0.2	1.2
11	-1.21	-0.01	1.6	85.6	0.5	7.4	-0.48	2.35	<10 ⁻⁴	2.41	0.03	0.32	0.5	3.5
12	-0.97	-0.01	1.5	83.2	0.7	10.8	-0.49	2.07	<10 ⁻⁴	2.43	0.02	0.29	0.5	4.1
13	-0.46	-0.01	1.3	72.9	0.1	1.5	-0.72	1.69	0.05	4.35	0.05	0.42	0.2	1.4

The Monte Carlo output in Table 4 shows reasonable results, as simulated *Curvatures* for all catchments and all parameter combinations (80 % of the values between -0.70 and -0.012, Table 4 and Fig. B7) are comparable with the *Curvatures* from NO₃⁻ log(C)-log(Q) relationships in the French catchments (80% of the values between -0.41 and -0.067, Fig. B3) (Dupas et al., 2019). Note that simulated *Curvature* can only be smaller than and equal to zero as the model takes into consideration in-stream uptake (no release) and a uniform land to stream loading function. For the model output $L_{r,perc}$, a wide range of uptake efficiencies were captured from almost 0 to near to 100 % (Mulholland et al., 2008) for some simulations and a median value of 14.4 % across simulations. This simulated range however exceeds the proposed range by Birgand et al. (2007) of 10 to 70% of N removal for agricultural drainage networks at annual time scales. High removal percentages (median over the simulated time period of daily percentage load removed in the network exceeding 95 %) are registered for 3.4 % of all simulations while very limited load removal ($L_{r,perc} < 5$ %) occurred for 32.1 % of all the simulations. Other simulation outputs such as the effective velocity v surprisingly rendered similar distributions across the catchments (Table 4) given that the median Q varied for almost three orders of magnitude at the basin outlet (Table 2). Their specific discharges (Sect. 2.2.1) were similar and by taking the spatiotemporal median v as an effective catchment value for each simulation the (more numerous) headwater grid cells were better represented than the grid cells close to the basin outlet. A similar effect is found for the range of the effective travel time TT . Generally these similar v and TT distributions from model simulations between catchments align with the notion of Langbein and Leopold (1964) that drainage networks evolve naturally to transport water (and sediment) most efficiently such that an equilibrium between channel form and water and sediment load is imposed (Leopold and Maddock, 1953). Finally, also Damköhler numbers Da exhibited realistic ranges, mostly distributed around 1 (Oldham et al., 2013;



Ocampo et al., 2006), with 36.5 % of the simulations < 0.8 and 50.8 % > 1.2 indicating that more simulations reaction driven than transport driven. Note that here Da only takes into account in-stream transport and uptake.

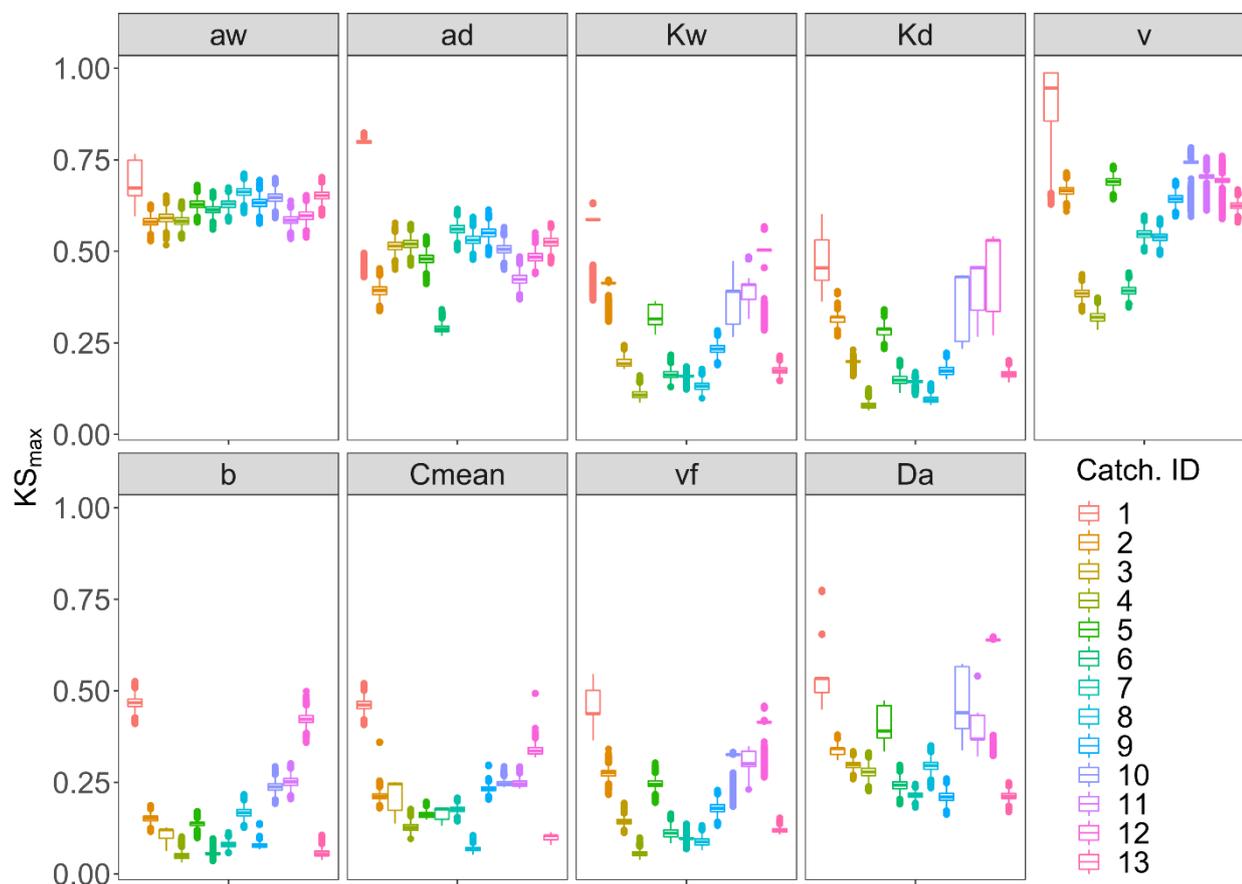
As for the simulations, the same parameter input set is applied in each catchment, differences in model outputs between the catchments result from the combination of distinct transport and uptake processes in each river network. From Table 4 and Table 2 it is clear that differences in these three model outputs (i.e. $Curvature$, $L_{r.perc}$ and Da) between the catchments cannot be attributed to a single catchment property such as total network length or basin area. This could be due to a number of factors, for example $Curvature$ has the highest variability between simulations in the smallest catchment 1, compared to the other catchments, which could be due to variability in local loading and uptake patterns in the network driven by Q that are still visible at the catchment outlet. Following the simulated Selke Meisdorf example in Sect. 3.1 (Fig. 3, Fig. B6), it is shown that $Curvature$ tends to converge to a constant value with increasing drainage areas (similar to Abbott et al., 2018 for nutrient concentrations, Dupas et al., 2017 for nutrient uptake and Bertuzzo et al., 2017 for DOC removal). Drainage area is however not the only catchment property influencing $Curvature$ at the outlet. For example, catchment 6 is the second largest catchment (Table 2) and has the least bent (and least variable) $\log(C)$ - $\log(Q)$ relationships. The network structure could possibly play a role here as the largest catchment 8 has some large tributaries near the basin outlet (Fig. 1), which could bypass removal and transport high load during events, introducing a more variable $Curvature$ (Mineau et al., 2015; Helton et al., 2018). The percentage load removed, $L_{r.perc}$, is notably lower catchments with high Q – like 3, 4 and 8 (Table 4) which follows the narrative in Sect. 3.1 that uptake efficiency decreases with increasing Q because of increasing loads to the system (Wollheim et al., 2018; Mulholland et al., 2008) that also result in less efficient uptake within the reactive surface area (Peterson et al., 2001; Hensley et al., 2014). The high $L_{r.perc}$ in small catchments 1 and 10 could then be attributed to their low Q , however why the small catchment 5 does not have similar uptake performance is less clear. Similarly, differences for the third output variable, Da , between the catchments are hard to pin down based on certain properties. Generally the model output variability between the catchments (as a result of different catchment properties) is minor compared to the output variability within the catchments (due to the effect of the chosen input parameter set). Nevertheless catchment properties as the drainage area and the network structure might influence observed $Curvature$ in a way that cannot be disentangled with our approach and should be taken into consideration when interpreting $\log(C)$ - $\log(Q)$ relationships for a given catchment.

3.3 $Curvature$ sensitivity analysis and model parameter correlation

The PAWN sensitivity analysis clarifies the influence of each of the independent input parameters (Table 1), a variable derived from these input parameters, the median water velocity v (Eq. (2.3)), and an output variable, the Damköhler number, Da (Eq. (6)) on $Curvature$. The sensitivity index KS_{max} in Fig. 4 and Table C2 shows that across all catchments $Curvature$ is most sensitive to the exponents in the width- Q relation a_w ($KS_{max} = 0.62$) and depth- Q relation a_d ($KS_{max} = 0.51$) with little variability between the catchments (KS_{max} has a low Coefficient of Variation, CV, of 0.06 and 0.22 respectively). The slope



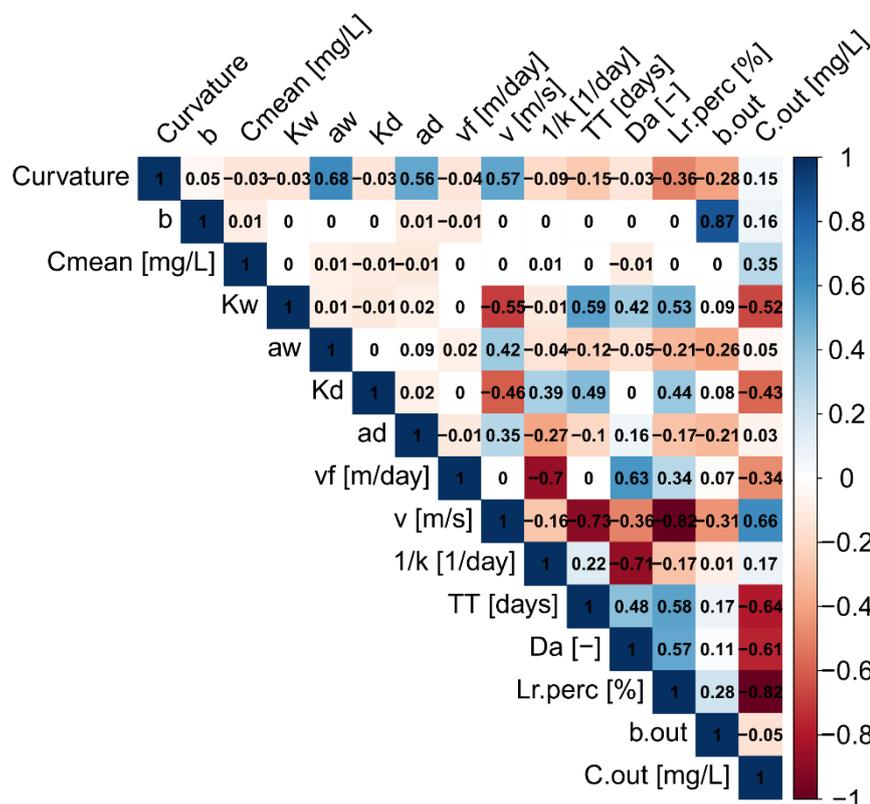
of the linear loading function, b , is least important in shaping *Curvature* ($KS_{max} = 0.14$) however a high variability of KS_{max} is observed (CV = 0.76) that is caused by larger sensitivities for catchments 1 and 12 (KS_{max} near 0.45). *Curvature* is equally sensitive to v_f and C_{mean} (KS_{max} 0.18 and 0.19) but v_f exhibits higher variability in KS_{max} than C_{mean} (CV 0.59 and 0.47), caused by catchments 12 and 1. Furthermore, over all the catchments *Curvature* is sensitive to the median velocity v and the Damköhler number Da (KS_{max} equals 0.64 and 0.31 respectively, CV 0.26 and 0.38). When considering the catchments individually, basin 1 with smallest discharge has the highest median KS_{max} (0.59) across all input parameters, while catchment 495 4 that has the highest discharge exhibits the lowest median KS_{max} (0.13). Additionally, *Curvature* is very sensitive to the velocity v in catchment 1 ($KS_{max} = 0.95$), while it is least sensitive to v in catchment 4. Overall, the results indicate that *Curvature* more sensitive to the model parameters in the low Q catchment 1 compared to the large Q catchment 4, while the other catchments show no clear order in *Curvature* sensitivity according to their catchment properties. For example in nested catchments 10, 11 and 12 (Fig. 1), the largest catchment 12 has the highest KS_{max} (0.50) and lowest CV (0.26) over all the 500 input parameters, indicating that here *Curvature* is more sensitive to the input parameters here than in the smaller sub-catchments 10 and 11.





505 **Figure 4: The KS_{max} sensitivity index for each of the model input parameters and each of the 13 simulated catchments. The input parameters related to the channel geometry (a_d , a_w , K_d and K_w), land-to-stream loading (b and C_{mean}) and biogeochemistry (v_f) are shown together with two variables derived from some of the input parameters: the median velocity v and the Damköhler number Da . Each boxplot displays 15000 bootstrapped estimates of KS_{max} for each of the 13 simulated catchments.**

In a next step the estimated *Curvature* across all simulations is correlated to the model input parameters as well as to output variables like the percentage load removed, $L_{r.perc}$, the log(C)-log(Q) slope at the catchment outlet, b_{out} , the median concentration at the basin outlet C_{out} and the uptake constant k to identify the strength and direction of their relationship. The resulting Spearman correlation matrix (Fig. 5) reflects the PAWN sensitivity findings, with the highest *Curvature* correlation found with parameters a_w ($\rho = 0.68$) and a_d ($\rho = 0.56$) and input variable v ($\rho = 0.57$). *Curvature* is independent of v_f ($\rho = -0.04$) but shows a negative correlation with $L_{r.perc}$ ($\rho = -0.36$), suggesting that lower *Curvature* (higher bending) is related to a higher $L_{r.perc}$. Furthermore, *Curvature* is negatively correlated to the log(C)-log(Q) regression slope at the catchment outlet b_{out} ($\rho = -0.28$) such that higher bending coincides with more positive b_{out} . The variable v is additionally strongly negatively correlated with $L_{r.perc}$ ($\rho = -0.87$) so high percentage load removed occurs at low velocities. Da on the other hand is positively correlated to $L_{r.perc}$ ($\rho = 0.58$) which indicates that higher Da are occurring together with higher load removed. Da , thereby seems to be controlled more tightly by variation in k^{-1} ($\rho = -0.71$) than by TT ($\rho = 0.48$). Finally C_{out} is negatively correlated with $L_{r.perc}$ ($\rho = -0.82$) and Da ($\rho = -0.61$).



520

Figure 5: Correlation matrix for the model parameter inputs: channel depth and width exponents a_d , a_w and coefficients K_d , K_w , slope of the land-to-stream loading, b , concentration of the land-to-stream load C_{mean} , uptake velocity v_f and outputs: The bending of the log(C)-log(Q) relationship at the catchment outlet, $Curvature$, effective stream velocity v , first order uptake constant k , travel time TT , Damköhler number Da , daily percentage load removed $L_{r.perc}$ and slope of the log(C)-log(Q) relationship and median concentration at the outlet b_{out} and C_{out} . The Spearman rank correlation coefficients (ρ) are given for each combination.

525

The PAWN and correlation analysis results suggest the input parameters dictating the channel morphology a_w and a_d (Sect. 2.3), are controlling factors for the magnitude of the bending in log(C)-log(Q) curves at the catchment outlet. Parameters a_w and a_d are the exponents in the respective width-Q and depth-Q relationships (Eq. (2.1) and (2.2)) and influence the response of the wetted perimeter (P_i , Eq. (A2)) in a given reach in the network and thus the reactive surface area ($P_i * l_i$) to changes in discharge. This is conceptually illustrated in Fig. B5. The correlation analysis outcomes imply that low $Curvature$ (high bending) and low a_w and a_d occur together (Fig. 5). This is evident from the underlying model parameterizations, wherein the absolute load removed $L_{r,i}$ (Eq. (5)) is related with the width and depth exponents explicitly (Eq. (A3)) where a_w and a_d constitute the exponent of $Q(1 - a_w - a_d)$. When the latter term is large (small a_w and a_d) there is a larger difference between

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535 the effect of low and high Q 's on the local absolute removed load and which can lead to a higher *Curvature* (Sect. 3.1, Fig. B5). Network based modelling studies often set the width exponent a_w to a value of 0.5 that was found to be representative for rivers globally (Bertuzzo et al., 2017; Rode et al., 2016; Wollheim et al., 2018). This a-priori fixed a_w may, however, strongly affect the simulated C-Q dynamics at the basin outlet as is demonstrated here. *Curvature* finally shows the lowest sensitivity to the loading parameters b and C_{mean} that influence the incoming load to a grid cell (Eq. (3)) and thus impact the local absolute load removed $L_{r,i}$ (Eq. (5)) rather than the percentage removed load $L_{r,perc}$. This indicates that the contribution of local incoming load in the downstream direction has a limited impact on the log(C)-log(Q) bending at the catchment outlet. Much like in the example shown for the Selke Meisdorf catchment in Sect. 3.1 where the locally contributing Q 's are generally smaller (or equal for the headwaters) than the total Q in a given network reach so that the influence of the loading parameters b and C_{mean} on the total load decreases in more downstream reaches (Sect. 3.1, Fig. 3). Generally, for the entire river network, whether parameter b has an enriching ($b > 0$), chemostatic ($b \sim 0$) or diluting ($b < 0$) character or whether the land to stream loading concentration C_{mean} is small or large has little influence on the observed bending at the outlet.

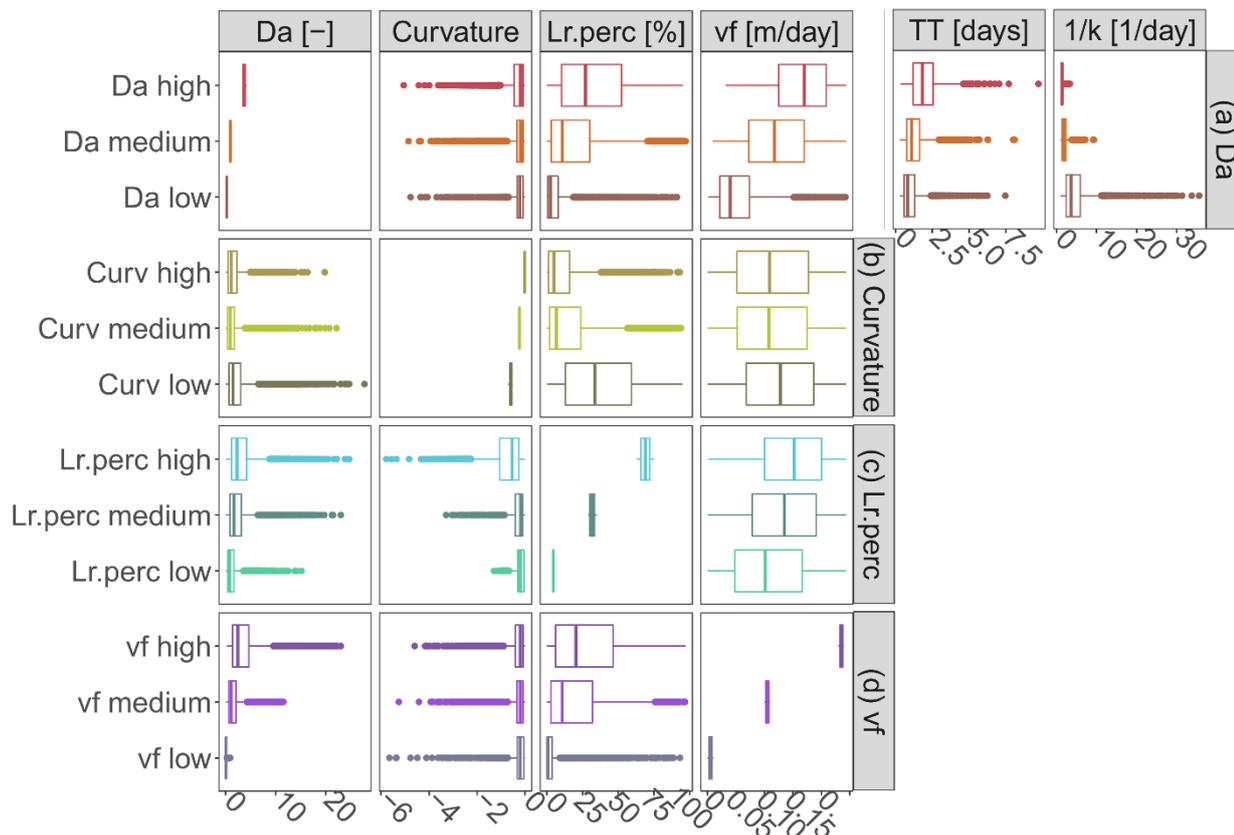
Although *Curvature* only has an intermediate sensitivity to the uptake velocity v_f and they don't correlate well, v_f is an important 'boundary condition' for log(C)-log(Q) bending at the catchment outlet. No biological demand (low v_f) would mean that none of the incoming load would be removed from the river network. The outlet signal would in this case be solely driven by the discharge controlled transport processes and no bending would be observed (*Curvature* = 0). Because v_f is defined as a constant within one simulation that is independent of the local nutrient concentration (Sect. 2.2.2), the percentage of load removed in the network is mainly controlled by the varying hydrological conditions here represented by the effective network wide velocity v ($L_{r,perc}$ and v , $\rho = -0.82$). This confirms that discharge and channel morphology are among the most important predictors of removal (Alexander et al., 2000; Seitzinger et al., 2002; Wollheim et al., 2006). The role of v was further examined in the context of restored and channelized streams (Kunz et al., 2017) and agree with our findings that decreased v influences N cycling (Peterson et al., 2001). Nevertheless, by examining a range of v_f in the Monte Carlo simulations, the positive correlation between the percentage load removed and the biogeochemical uptake velocity is clear ($\rho = 0.32$).

560 The PAWN and correlation analysis results show that *Curvature* is sensitive to the Damköhler number Da ($KS_{max} = 0.31$ Fig. 4, Table C2) that has a high positive correlation with the percentage load removed $L_{r,perc}$ ($\rho = 0.58$; Fig. 5). This indicates that high Da occur concurrently with more efficient removal and is in line with others (Ocampo et al., 2006) who found sometimes almost 100 % NO_3^- removal in the riparian zones of an agricultural catchment with Da exceeding 2. The transport timescale TT that makes up Da ($\rho = 0.48$; Fig. 5) together with the inverse of the first order uptake constant k^{-1} ($\rho = -0.71$; Eq. (6)) are examined for classes of low, median and high Da (defined in Table 3) in Fig. 6a to disentangle which values of k^{-1} and TT occur together and can constitute a certain Da range (each class contains 5 % of all simulations). It is shown here that low Da are driven by both low TT and high, variable k^{-1} implying a transport driven system with limited NO_3^- removal



(median $L_{r.perc}$ equals 2.4 % in Fig. 6a for low Da). High Da , contrarily, have high TT and low k^{-1} , fostering intermediate uptake percentages (median $L_{r.perc} = 27.1$ %). Although also v_f clearly differentiates for classes of low, medium and high Da in Fig. 6a, the corresponding *Curvature* values are similar in their range and mean. Nevertheless, this does not mean that Da is not influencing *Curvature* at the basin outlet as there could be interactions with other inputs that are not captured here (which is supported by the PAWN findings, where Da appears to be influential).

From the *Curvature* perspective (Fig. 6b) we identify model output ranges of $L_{r.perc}$, Da and input variable v_f that constitute low, median and high *Curvature* classes (Table 3). High *Curvature* (~ -0.02) is thereby linked to low $L_{r.perc}$ (median 4.8 %), while low *Curvature* (~ -0.60) is connected to higher and more variable $L_{r.perc}$ (median 33.6 %), generally indicating that more bent systems are more efficient in terms of removal and vice-versa. To explore some cases when this latter statement might not be true, we examine the input parameter ranges where high bending simulations (*Curvature* < -0.51 , 13.1 % of all simulations) occur concurrently with low percentage removal ($L_{r.perc} < 5.2$ %, 0.9 % of all simulations) on the one hand and high percentage removal ($L_{r.perc} > 63.0$ %, 4.9 % of all simulations) on the other hand in Fig. B8a. Here, it is seen that high bending, low uptake cases mainly occur for simulations with a high effective velocity v (driven by lower values for the channel shape parameters K_w , K_d , a_w and a_d). As discussed before, low a_w and a_d are correlated with a high bending (low *Curvature*) and *Curvature* is most sensitive to these parameters. However, we show here that these low a_w and a_d do not lead to a more efficient NO_3^- uptake if the other channel shape parameters cause relatively high velocities (median $v > 0.1 \text{ m s}^{-1}$), throughout the network. Although the latter case is shown to be true for a minor percentage of all simulations (0.9 %), it still explains why low *Curvature* (high bending) can be connected to a wider range of $L_{r.perc}$. A similar analysis in Fig. B8b for low bending (*Curvature* > -0.03) shows that concurrent high removal simulations ($L_{r.perc} > 63.0$ %) are even rarer (0.1 % of all simulations) compared to concurrent low removal ($L_{r.perc} > 5.2$ %; 7.4 % of all simulations). Deviations from the expected ‘high *Curvature* - low $L_{r.perc}$ ’ pattern are also here driven by (very low) v . In this case however, a_w and a_d are generally high in both cases (leading to high *Curvature*) and the different v stem from coefficients K_w and K_d that are higher in high removal simulations. Finally, Fig. 6d illustrates that low medium and high uptake velocities v_f lead to distinct Da and $L_{r.perc}$ but do not show up in the bent signal at the catchment outlet.



595 **Figure 6: The corresponding simulated ranges for high, median and low values (Table 3) of the main simulation outputs: (a) Damköhler number Da , (b) *Curvature*, (c) Percentage load removed $L_{r.perc}$ and (d) uptake velocity v_f are shown for the same variables (in the columns). The median travel time, TT , and the inverse of the first order uptake constant, k^{-1} are given additionally for low medium and high Da .**

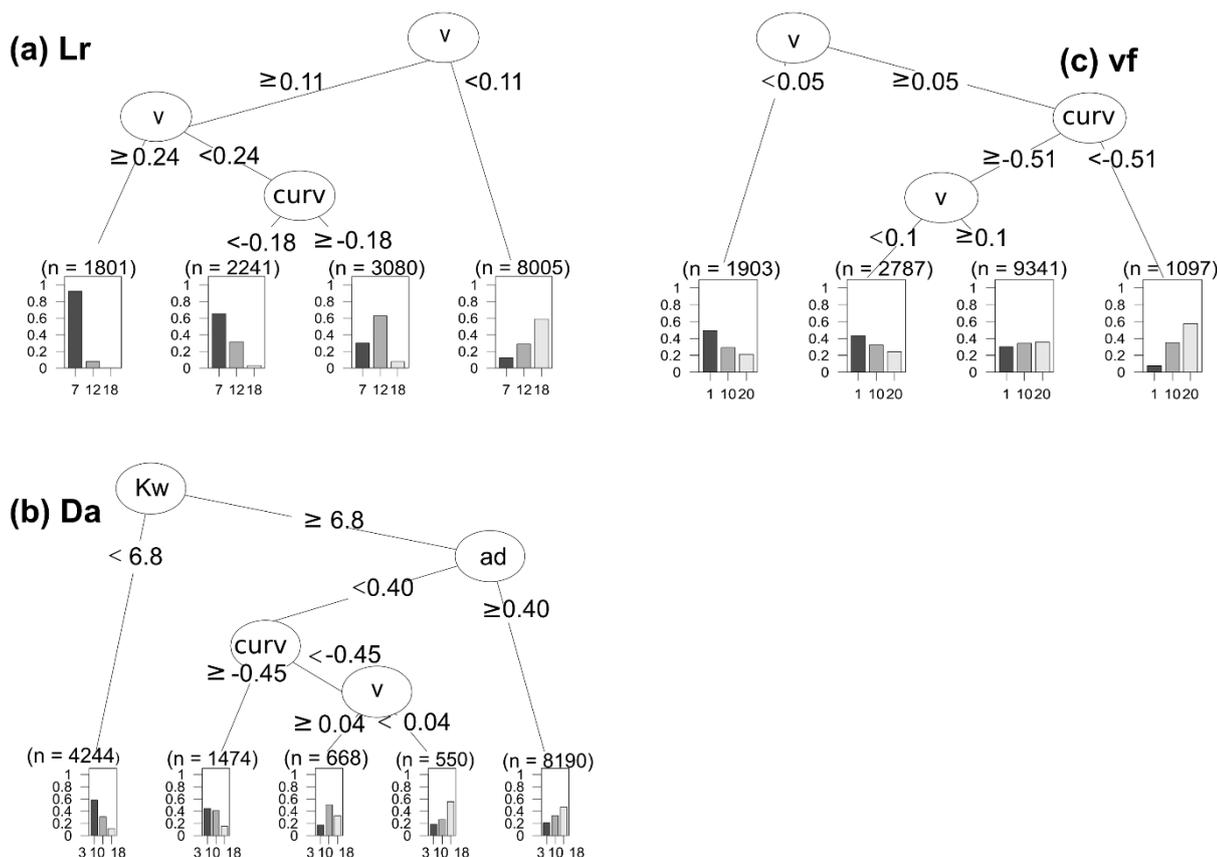
3.4 Predicting in-stream processing with *Curvature*

600 To determine if observed C-Q bending at the catchment outlet (here *Curvature*) can be utilized to quantify in-stream uptake in the upstream river network and to visualize model parameter interactions, a classification tree was established for low, medium and high values (Table 3, Fig. 6) of the response variables $L_{r.perc}$, Da and v_f (Fig. 7a, b and c respectively). The prediction accuracy metrics in Table C3 and the probability histograms in Fig. 7 show that $L_{r.perc}$ can be predicted relatively well (overall accuracy of 0.66) compared to the other response variables Da (accuracy 0.51) and v_f (accuracy 0.40). The fitted CART models all perform significantly better than a random allocation of simulation results to each class for each response variable (Accuracy > No Information Rate, p-value < 2.2e-16). While the classes for $L_{r.perc}$ and v_f are partitioned using only the network effective velocity v and *Curvature*, predicting Da in our case requires information on the channel geomorphology parameters the width coefficient K_w and the depth exponent a_d . The histograms for each of the response variables in Fig. 7

605



indicate the probability of a test sample to be of a certain class when following the partition rules in the respective decision tree. For example, for $L_{r.perc}$ the probability that the daily percentage load removed is small (around 8%) exceeds 0.95 when the effective velocity v in the catchment is larger than 0.22 m s^{-1} ; while the probability that $L_{r.perc}$ is high (around 70%) in this case is close to 0 (Fig. 7a). For v_f the lowermost (1) and highest (20) classes are predicted most accurately (0.58 and 0.56 respectively, Table C3) and indicate that when the velocity is not very small and $Curvature$ is smaller than -0.51 (more bent), v_f is most likely high (probability 0.59). For Da , the lower and higher classes can be predicted most accurately (0.69 and 0.68 respectively), for example, Da is small with a probability of 0.58 when K_w is relatively low (< 6.8). When on the other hand K_w exceeds 6.8 and a_d is larger than 0.4 or when a_d is smaller than 0.4 but $Curvature$ is smaller than -0.45 and v is very small ($< 0.04 \text{ m s}^{-1}$) it is most likely that Da is large.



620 **Figure 7: CART decision tree for the response variables $L_{r.perc}$ (accuracy = 0.66), Da (accuracy = 0.51) and v_f (accuracy = 0.40). The classes of each response variable are defined in Table 3 and the prediction metrics for these classes are stated in Table C3. The histograms illustrate the probability of a test sample to be from a certain class when following the binary splits of the decision tree.**



625 These findings demonstrate that $\log(C)$ - $\log(Q)$ bending at the catchment outlet, together with the median velocity and the
response of the width and the depth of a channel to discharge (parameters K_w , K_d , a_w and a_d) can help to classify the in-stream
daily percentage load removed $L_{r.perc}$, the Damköhler number Da and to a certain extent the uptake velocity v_f . The velocity
may be concluded from the channel shape, discharge (Eq. (2.3)) and the topography with the channel shape parameters
sometimes available from rating curve information or detectable from high resolution satellite pictures. The CART models
could help obtain an initial probability of NO_3^- removal efficiency in a river network, especially in a context where network
630 wide uptake measurements are scarce (Wollheim et al., 2017; Hensley et al., 2014) and physical, fully distributed models are
not always feasible to apply (Boyer et al., 2006; Klemes, 1986). Although the CART models are developed using ‘only’ the
13 German catchments included in the Monte Carlo analysis, in Sect. 3.2 and Table 4 we shown that the output variability
between the catchments (as a result of different catchment properties) is minor compared to the output variability within the
catchments (due to the effect of the input parameter set). Nevertheless, the prediction performance of these CART models
635 might be influenced in unknown ways when applied to catchments with dissimilar catchment sizes, network structures or
hydrological regimes.

4 Conclusions

640 In this study, we explore how NO_3^- $\log(C)$ - $\log(Q)$ relationships, observed at a basin outlet, can display bending as a result of
network scale in-stream uptake processes. We established a parsimonious grid based river network model for 13 distinct
German catchments and investigated the influence of in-stream loading, transport and uptake parameters on the bending of
 $\log(C)$ - $\log(Q)$ relationships. Based on our exploratory analysis we conclude that:

- Noisy, multi-annual and low frequency NO_3^- $\log(C)$ - $\log(Q)$ relationships at a basin outlet can be described as bent
and this bending can be robustly quantified with the new *Curvature* metric. *Curvature* tends to converge with
645 increasing drainages areas and is temporally stable on multi-annual time scales.
- A bent $\log(C)$ - $\log(Q)$ relationship (*Curvature* < 0) at the basin outlet can arise from log-log linear land to stream C-
Q relationships and uptake within the river network. This supports the hypothesis that more positive slopes under low
flow (bended $\log(C)$ - $\log(Q)$ curves) are linked to biological NO_3^- concentration mediation in the stream (Moatar et
al., 2017); and connects *Curvature* (as a quantitative measure) to observations of increased removal efficiency under
650 low flows (Wollheim et al., 2017).
- The bending at the catchment outlet is primarily shaped by the channel geomorphological parameters, a_w and a_d
(exponents in the respective stream width and depth to discharge relationships; with *Curvature* sensitivity indices
 KS_{max} equal to 0.62 and 0.51; and Spearman correlation coefficient, ρ , equaling 0.68 and 0.56 respectively) and less
by the uptake velocity v_f ($KS_{max} = 0.18$, $\rho = -0.04$), given that v_f differs from zero. In that case *Curvature* would
655 equal zero and the $\log(C)$ - $\log(Q)$ relationship would be solely shaped by the accumulation of upstream load. Thus,
the change of reactive channel bed area with discharge (mediated by a_w and a_d) has a greater influence on the bending



at the outlet than the biological removal capacity (here v_f). Additionally we demonstrate that an a-priori fixed a_w might strongly affect the simulated C-Q dynamics at the basin outlet.

- *Curvature* at the basin outlet can be linked to the network-wide removal efficiency $L_{r.perc}$ ($\rho = -0.36$), indicating that systems with more bending in their log(C)-log(Q)-relationship are more efficient in terms of removal and vice-versa. It is, however, clear that also cases with high bending ($Curvature < -0.51$) and low removal ($L_{r.perc} < 5.2\%$, 0.9 % of all simulations) or low bending ($Curvature > -0.03$) with high removal ($L_{r.perc} > 63.0\%$, 0.1 % of all simulations) exist that are imposed by respective higher and lower network wide median velocities. This shows how the velocity, v , (calculated from the channel shape parameters a_w , a_d , K_w and K_d) may mediate the connection between $L_{r.perc}$ and *Curvature* and stresses that v should be considered when interpreting log(C)-log(Q) bending.
- Simple classification trees - like CART - can be useful for predicting low, median and high classes of response variables $L_{r.perc}$, the Damköhler number Da and v_f . They provide useful insights on how catchments with low frequency concentration and discharge time series (that are generally available) can reveal information on the upstream river network uptake performance.

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To evaluate the generality of the results presented here, *Curvature* should be calculated for NO_3^- concentration observations of a larger range of catchments and linked to the respective catchment properties. Properties such as light and stream ecological state can serve as proxies for uptake performance and for example topographic gradient can be a proxy for network transport velocity. Such a data-driven exploration would further elucidate the linkages between nutrient uptake efficiency and low-frequency C and Q observations.

675



Appendix A

c calculation (Jawitz and Mitchell, 2011)

$$c = e^{\mu_c - b * \mu_q} \quad (\text{Eq. A1})$$

680 With

$$\mu_q = \text{mean}(\log Q_{t.sp} * a_i)$$

$$\mu_c = \log \text{mean} C - \frac{\sigma_c^2}{2}$$

$$\sigma_c = \sqrt{b^2 * \sigma_q^2}$$

$$\sigma_q = \sqrt{\text{var}(\log Q_{t.sp} * a_i)}$$

685

Stream channel wetted perimeter P_i [L], where A is the cross-sectional area [L²], R_H [L] is the hydraulic radius and w_i [L], d_i [L] and v_i [L/T] are the local stream width, average depth and velocity respectively. S_i [L/L] is the stream bed slope and n [-] is the Manning roughness coefficient that is equal to 0.03 for all simulations.

$$P_i = \frac{A}{R_H} = \frac{w_i * d_i * S_i^{\frac{3}{2}}}{(v_i * n)^{\frac{3}{2}}} \quad (\text{Eq. A2})$$

690

The load removed in a grid cell (Eq. (5)) with the width and depth exponents, a_w and a_d , stated explicitly.

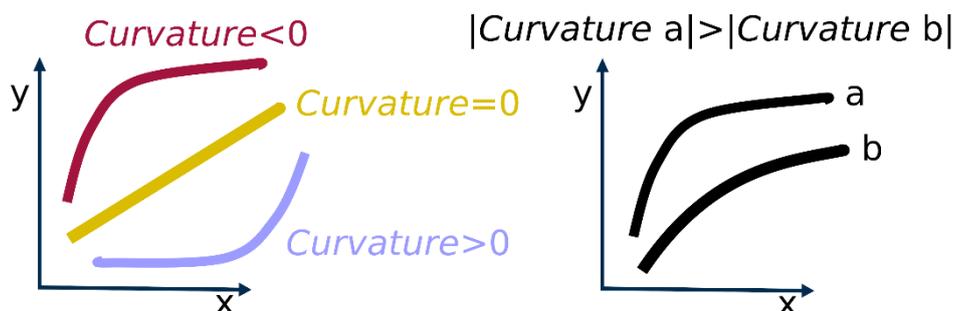
$$L_{r,i} = L_{in,i} * \left(1 - e^{-\frac{v_f * (K_w * K_d)^{\frac{5}{2}} * S_i^{\frac{3}{2}} * n^{\frac{3}{2}}}{Q_i^{1-a_w-a_d}}} \right) \quad (\text{Eq. A3})$$

The velocity in a grid cell (Eq. (2.3)) with the width and depth exponents, a_w and a_d , stated explicitly.

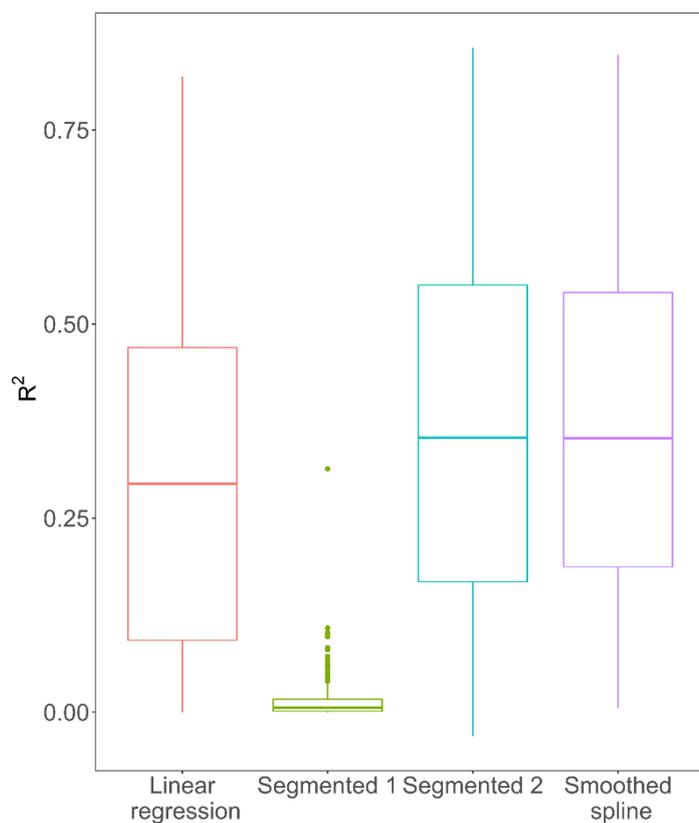
$$695 \quad v_i = \frac{Q^{1-a_w-a_d}}{K_w * K_d} \quad (\text{Eq. A4})$$



Appendix B



700 **Figure B1:** Conceptual figure explaining *Curvature*. *Curvature* is calculated as the largest instantaneous rate of change of direction of a point that moves on a curve. When *Curvature* < 0 the curve is concave, for *Curvature* > 0 the curve is convex.



705 **Figure B2:** R^2 for four models fit to $\log(C)$ - $\log(Q)$ data of 444 French stations (Dupas et al., 2019). The smoothed spline method used for calculating curvature is compared to a simple linear regression fit, a segmented linear regression (Segmented 1) with a fixed breakpoint at the median Q (Meybeck and Moatar, 2012) and a segmented regression without a fixed breakpoint as described in Marinos et al. (2020).

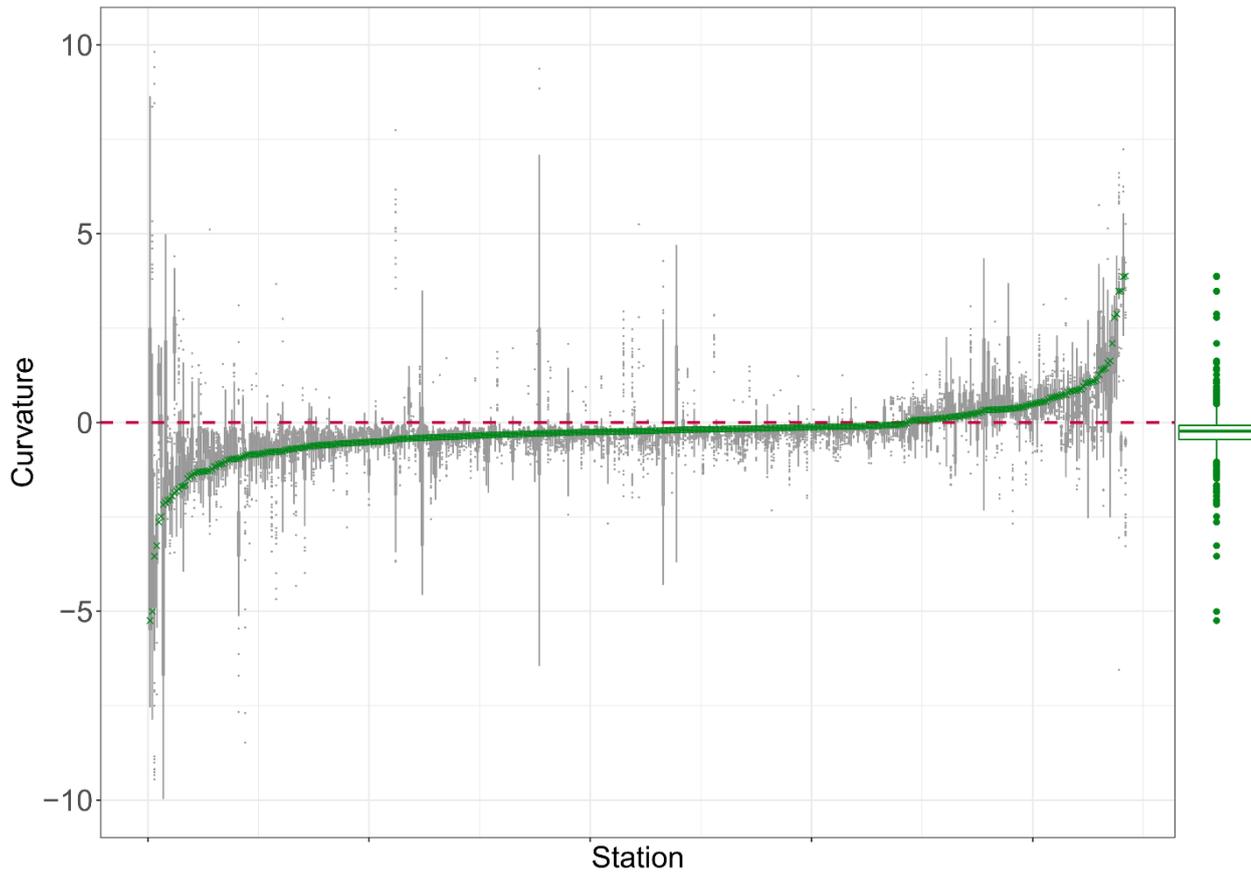


Figure B3: *Curvature* of nitrate $\log(C)$ - $\log(Q)$ data for 442 French monitoring stations arranged from left to right with increasing *Curvature* (green crosses). For a given station, the grey boxplot represents the temporal robustness of this metric by subsampling 100 times from the original time series. The green boxplot indicates the range and distribution of all observed station *Curvature* values.

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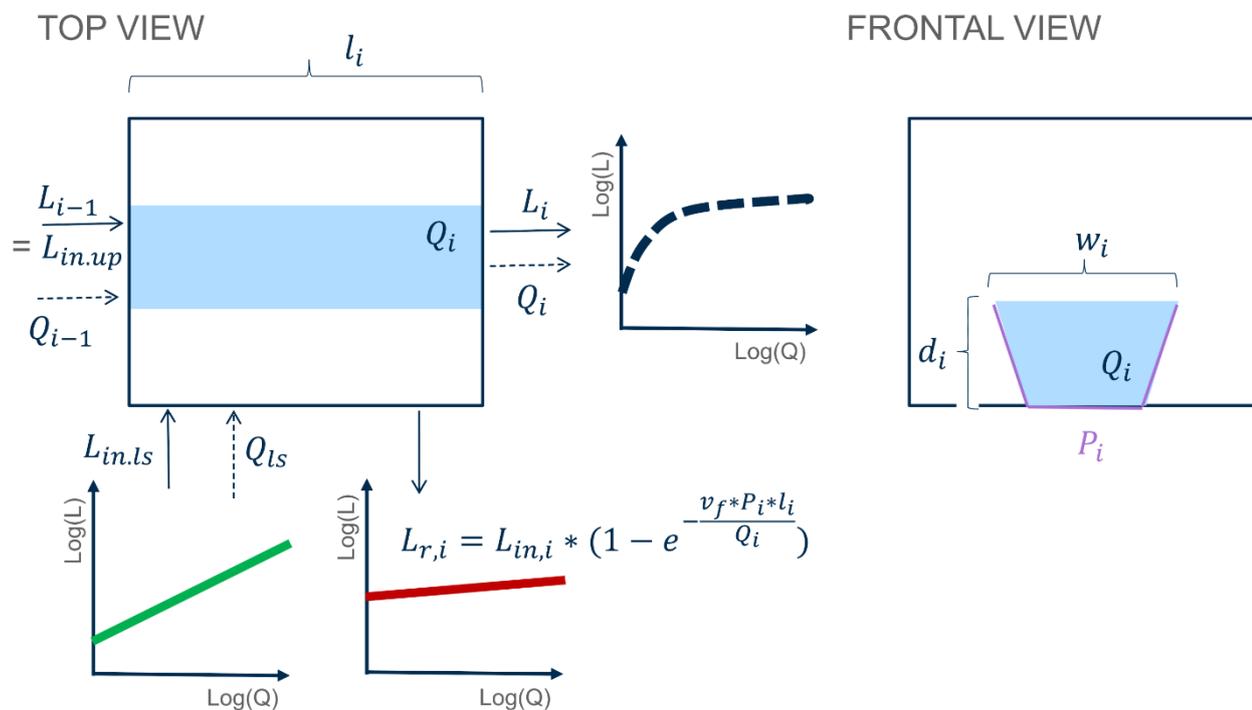


Figure B4: Network model, illustrated for one grid cell.

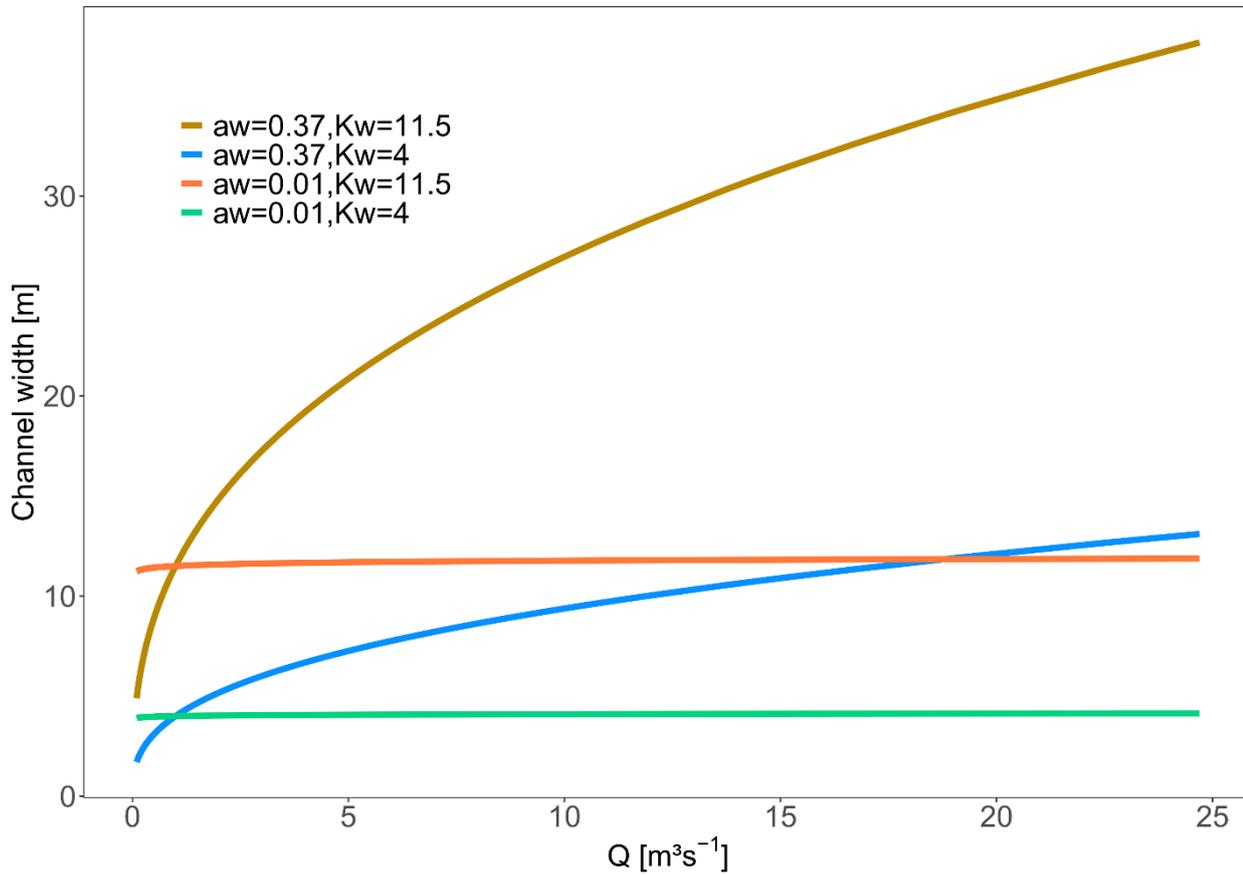


Figure B5: The effect of parameters a_w and K_w on the channel width illustrated for the Q timeseries at the Selke Meisdorf station.



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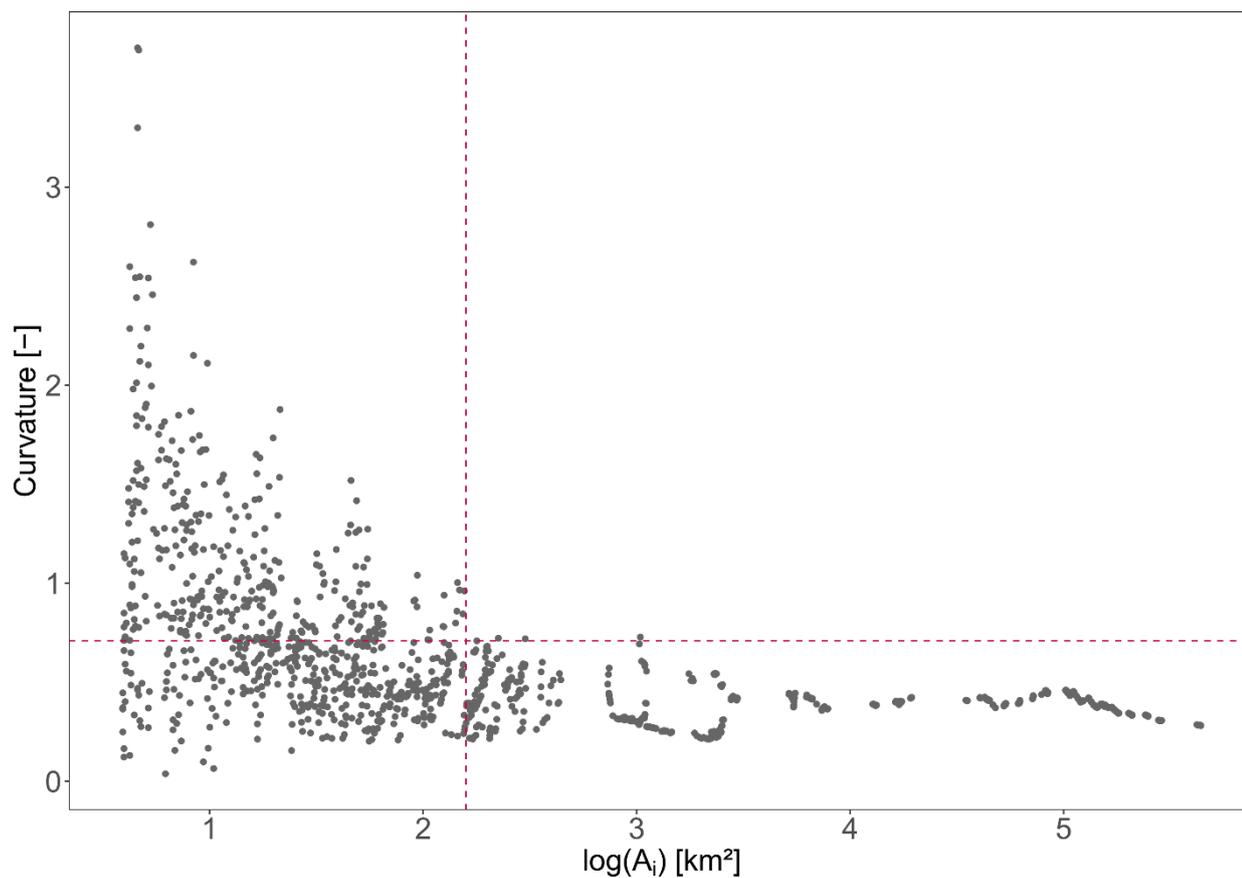


Figure B6: *Curvature* as a function of total drainage area A_i (Eq. (2)) for each gridcell of the Selke Meisdorf validation run with one uniform and constant parameter set (Table C1).

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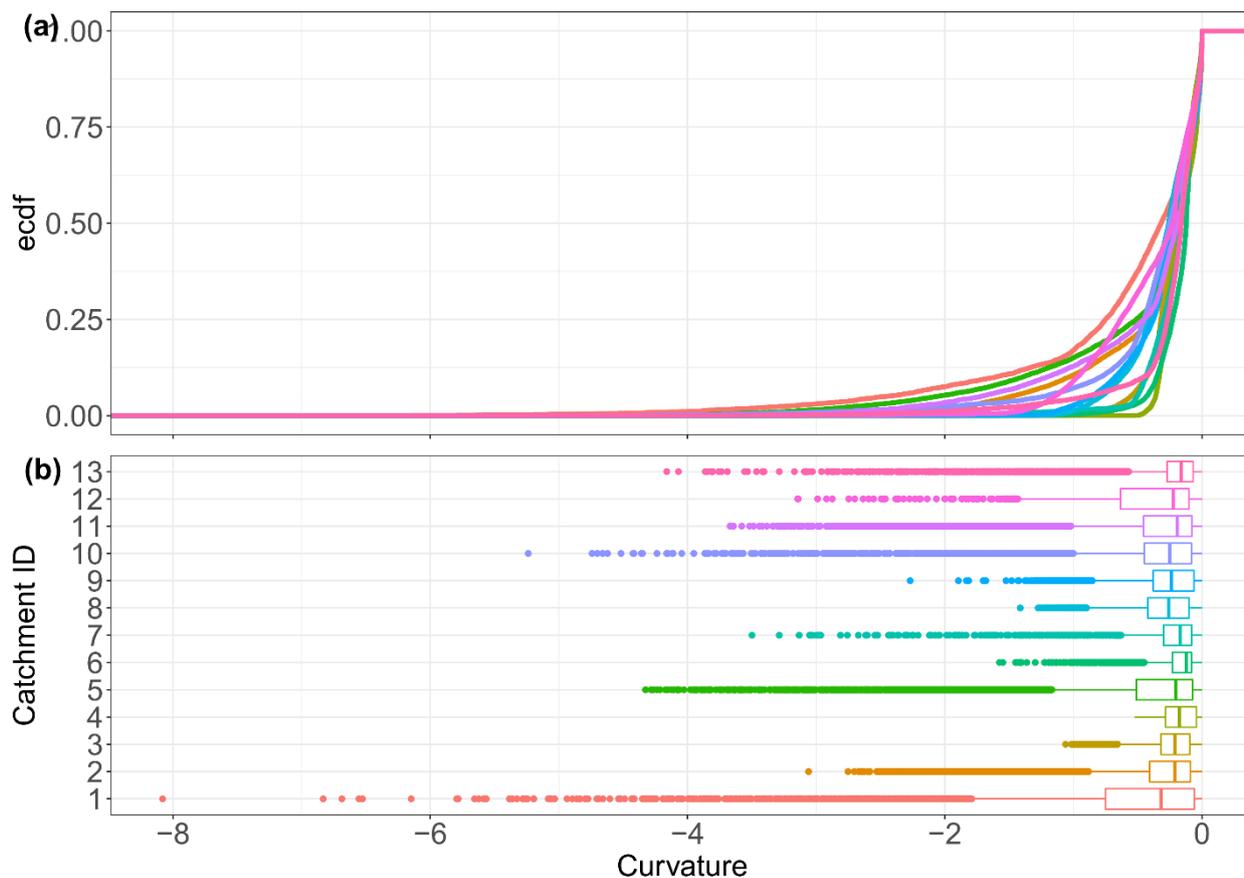
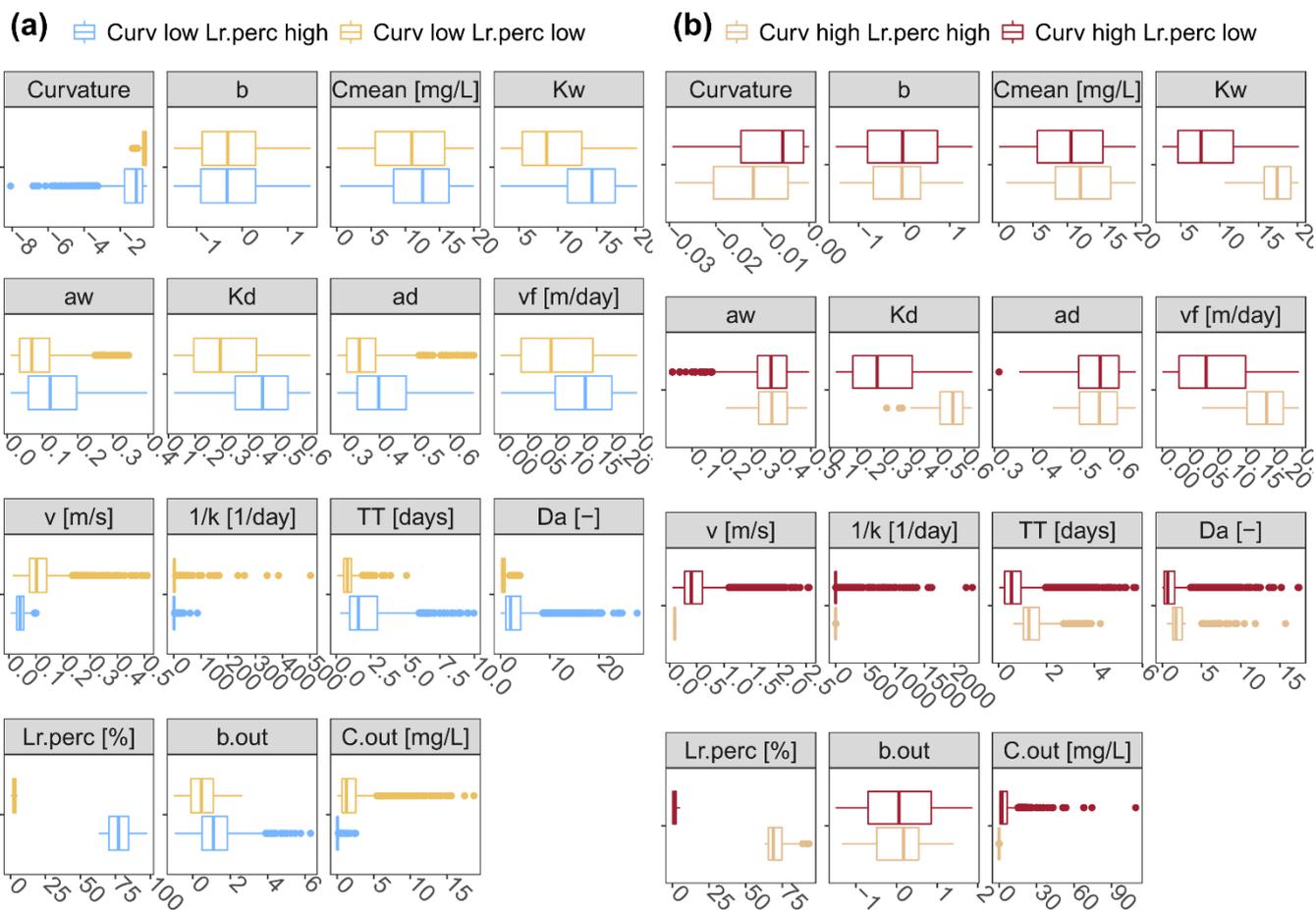


Figure B7: *Curvature* distributions resulting from running the same 11107 input parameter combinations in each of the 13 catchments (a) shows the elemental cumulative distribution and (b) boxplots. None of the catchments have a normally distributed *Curvature* set according to the Kruskal-wallis ($p < 0.05$) test.



735 **Figure B8:** Two specific cases of Fig. 6, (a) when *Curvature* is low (high bending) and $L_r.perc$ is low opposed to high and (b) when *Curvature* is high (low bending) and $L_r.perc$ is high opposed to low.



Appendix C

740 **Table C1: Validation range for all parameters**

Parameter	Validation Value Selke
v_f	0.098
b	0.014
C_{mean}	3.014
K_w	2.75
a_w	0.09
K_d	0.17
a_d	0.49

Table C2: PAWN sensitivity indices KS_{max} for all the parameters and all the catchments, together with median and coefficients of variation (CV).

Parameter	Catchment ID													Median	CV
	1	2	3	4	5	6	7	8	9	10	11	12	13		
v_f	0.44	0.28	0.14	0.06	0.24	0.11	0.10	0.09	0.18	0.33	0.30	0.41	0.12	0.18	0.59
b	0.47	0.15	0.12	0.05	0.14	0.05	0.08	0.17	0.08	0.24	0.25	0.42	0.05	0.14	0.76
C_{mean}	0.46	0.21	0.25	0.13	0.16	0.18	0.18	0.07	0.23	0.25	0.25	0.34	0.10	0.19	0.47
K_w	0.59	0.41	0.19	0.11	0.32	0.16	0.16	0.13	0.23	0.39	0.41	0.50	0.17	0.23	0.51
a_w	0.75	0.58	0.59	0.58	0.63	0.61	0.63	0.66	0.63	0.65	0.58	0.60	0.65	0.62	0.06
K_d	0.45	0.32	0.20	0.08	0.29	0.15	0.14	0.09	0.17	0.46	0.43	0.53	0.16	0.20	0.55
a_d	0.80	0.39	0.52	0.52	0.48	0.29	0.56	0.53	0.55	0.51	0.42	0.48	0.53	0.51	0.22
Median	0.59	0.39	0.25	0.13	0.33	0.18	0.18	0.17	0.24	0.43	0.42	0.50	0.18		
CV	0.31	0.46	0.53	0.81	0.53	0.65	0.67	0.76	0.58	0.45	0.41	0.26	0.74		
Variable															
Da	0.53	0.34	0.30	0.28	0.39	0.24	0.22	0.30	0.21	0.44	0.37	0.64	0.21	0.31	0.38
v	0.95	0.67	0.39	0.32	0.69	0.39	0.55	0.54	0.64	0.74	0.70	0.69	0.62	0.64	0.26

745 **Table C3: Performance statistics for each of the classes for the variables $L_{r,perc}$, Da and v_f predicted by CART.**

	$L_{r,perc}$			v_f			Da		
	class 7	class 12	class 18	class 1	class 10	class 20	class 3	class 10	class 18
Sensitivity	0.63	0.38	0.94	0.43	0.00	0.77	0.63	0.07	0.82
Specificity	0.91	0.89	0.69	0.74	1.00	0.36	0.75	0.97	0.54
Pos Pred Value	0.77	0.62	0.61	0.45	NA	0.38	0.56	0.54	0.47
Neg Pred Value	0.83	0.75	0.96	0.72	0.67	0.76	0.80	0.68	0.86
Prevalence	0.34	0.32	0.34	0.34	0.33	0.33	0.34	0.33	0.33
Detection Rate	0.21	0.12	0.32	0.14	0.00	0.26	0.21	0.02	0.27



Detection Prevalence	0.28	0.12	0.32	0.32	0.00	0.68	0.38	0.04	0.58
Balanced Accuracy	0.77	0.63	0.82	0.58	0.50	0.56	0.69	0.52	0.68

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Author contributions JD and AM designed the study together with RK. JD developed the model code, carried out the simulations and interpreted them. FS provided help with the PAWN method. JD and AM prepared the manuscript draft and all co-authors contributed to reviewing and editing the manuscript.

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