Response to Reviewer 1

We would like to thank reviewer 1 for their comments on the paper 'Bending of the concentration discharge relationship can inform about in-stream nitrate removal'. We address all the reviewer comments (in italic) one by one below with responses in normal font.

R1.1*: The paper aims to explain evolution of concentration-discharge patterns in a stream network using a modelling approach. This is an interesting topic, following observations from many systems, where the c-q patterns become homogenised downstream, i.e. from highly variable and positive c-q slopes in first order streams to more linear responses, near chemostatic responses in downstreams.*

The modelling approach adopted here explains one aspect of these previous observations, i.e. changes in curvature. The authors show that in 1st order streams curvature is larger than in higher order streams which can be explained by hydrological accumulation and homogenisation when moving downstream. Simply speaking, 1st order streams can have a larger variation in concentration sources compared to bigger streams. And/or activation/deactivation of these sources requires changes in flow discharge that can result in the 'bent' c-q relationship or simply speaking different slopes of the relationship for different flows.

We thank the reviewer for this comment and we generally agree here. The main aim of the paper is to examine if network scale nitrate uptake effects can be inferred from the bending of low frequency; multi-annual concentration (C) and discharge (Q) observations. Thereto 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(C)-log(Q) patterns (l.103-107).

We show that *Curvature* converges when moving from lower order to higher order streams in Fig. 3 where the spatial distribution of simulated Curvature in the Selke river network (Meisdorf) for a selected parameter set is shown (l.365-366). In this case, uptake and land to stream loading at the downstream grid cells have a decreasing local impact on the outgoing load due to the relatively larger upstream contributions that increase in the downstream direction (l.400-410). The convergence of *Curvature* in higher order streams is also shown in the results of the Monte Carlo simulations, where >10 000 parameter sets were applied to 13 German catchments (l.460-482). Here, simulated *Curvature* in lower order catchments 1, 5 and 11 has a higher variance and an overall lower mean value (higher bending) than the simulated *Curvature* in higher order catchments 4 and 6 (Table 4, l.414-417) . It is however clear that these differences between the catchments cannot be attributed to a single catchment property such as total network length or basin area (l.461-462)

R1.2: *The paper is heavy on modelling that can conceal the main findings of the paper, which is that 1) curvature is predominant in 1st order streams and 2) curvature is better explained by flow characteristics than nitrate uptake velocity. These findings can be explained by higher rate of biological processes in headwater streams (hypothesis investigated in this paper) but there are also other factors that can explain bending of the c-q curves, like stream morphology and flow-stage relationships, activation/deactivation of sources in relation to flow including presence of sewage pollution, drains etc. Thus, I am not convinced that the paper provides the one and only explanation for the observed patterns, rather than provides a plausible explanation for one of the possible explanations. This should be clearly communicated in the paper.*

In this paper, we indeed investigate a possible explanation for bent log(C)-log(Q) relationships, namely that log(C)-log(Q) bending can inform about in-stream NO_3^- removal. We don't aim to state that in-stream uptake is the only explanation for C-Q bending but rather that it is one possible explanation that is motivated from previous observation- and model driven studies (Moatar et al., 2017; Hall et al., 2009; Hensley et al., 2014; Wollheim et al., 2017, l.90-99). Note that flow stage relationships (and stream geomorphology in general) were accounted for in our modelling setup (l.176-177). We will make the point that we aim to investigate only one of the possible explanations for C-Q bending more explicit and clear in the revised version of the manuscript by adjusting the introduction, assumptions in the methods and conclusions. For example, we would edit line 313 to read: "Finally, we aim to determine if, **within this modelling framework**, C-Q bending at the catchment outlet (specifically *Curvature*) informs about the network wide in-stream uptake."

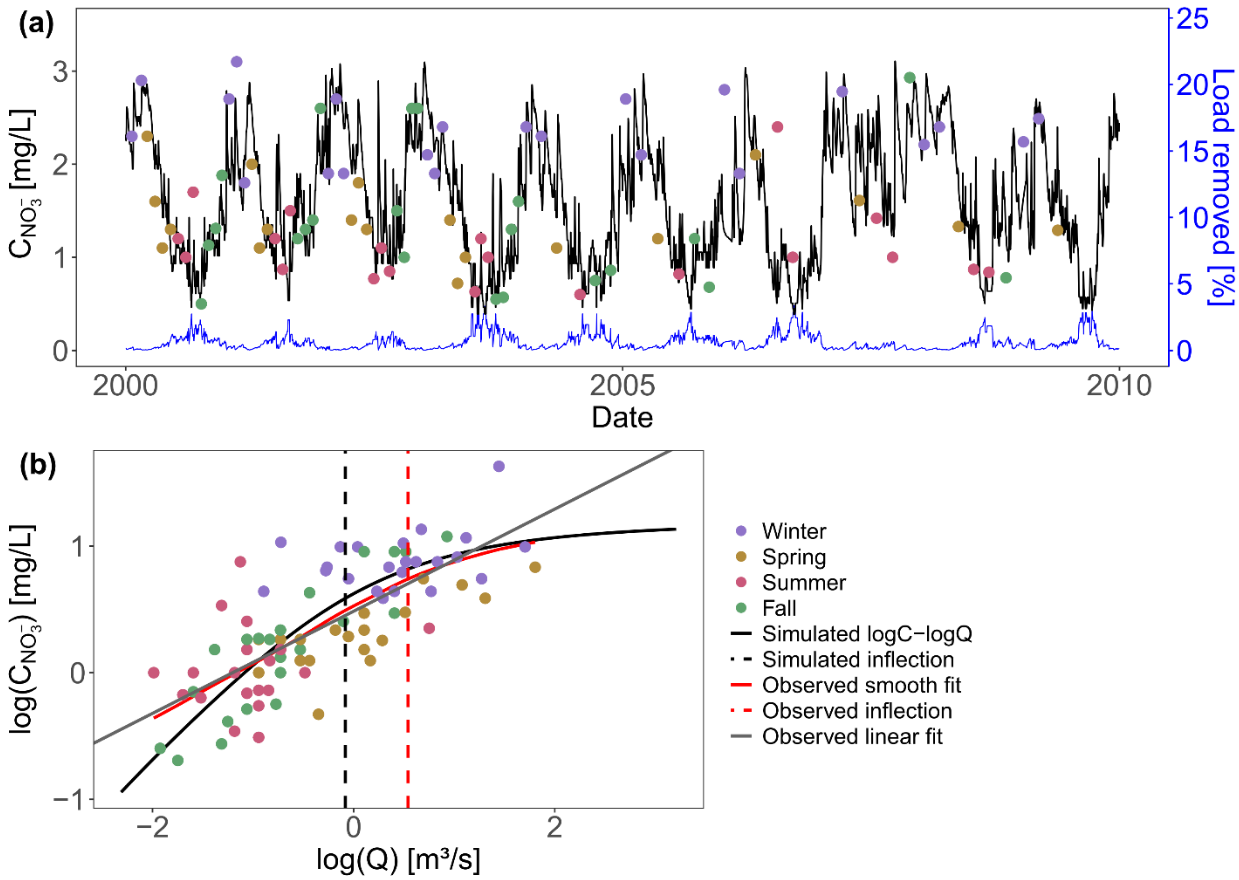
R1.3: *The modelling focus of the paper is, however, very dense and takes precedence over the problem – variations to c-q patterns and their controls. I would suggest 'moving' the modelling to the background of the paper and focusing more on the problem. This refocusing would make the paper easier to understand to a non-modelling reader and set it better in the previous research on the topic.*

We appreciate the reviewer's suggestion - however we would like to keep the modeling part entact, without losing the main focus of the paper. In this respect we believe that a thorough description of the Monte Carlo method and the uptake model are essential for the interpretation of the results as our study of the c-q patterns and their controls is modelling-based. However, we will revise the manuscript, and in particular the conclusion section, to ensure that the key findings can be understood by all the readers. We refer to comment WW.11 for the specific changes suggested to improve the conclusion.

R1.4: *Finally, the original concentration and flow data disappear in the paper convoluted in different models. E.g. linking curvature to other models with inherent uncertainty like Damköhler number or uptake velocity. Showing more raw data in the paper, e.g. providing traditional quantifications of the c-q slopes would be very useful for the reader to link their knowledge of the subject with the new findings of this paper. Also when showing variation in curvature, I would like to know how frequent are concave vs. convex shapes.*

Thank you again for your detailed suggestions. Our analysis relies on 'raw data'/ observations in the following instances; i) low frequency C and Q data for 444 French catchments that is used to validate the *Curvature* metric; ii) measured NO3- concentrations in the Selke Meisdorf station to validate the conceptual network model structure by comparing modelled observed NO3- at the network outlet (Fig. 2a and b); iii) measured daily Q time series for 13 German catchments (l.253) that were used as a direct input for the explorative model to simulate NO3- concentrations (and *Curvature*) for a range of parameter combinations. This latter point we will clarify in l.258 so this sentence would read: "All catchments had ~10 years of uninterrupted daily Q data available between 1995 and 2010 (Musolff, 2020) which was needed as an input for the network model." Also note that the Damköhler number (Da) and the uptake velocity (vf) are important metrics in the context of our study that we analyse to understand the relative importance of hydrological and biogeochemical processes (l.223-225 for Da) and define the uptake model (l.213-221 for vf) in the first place.

We aim to show how a time series of measured concentration (discharge is not shown here) is transferred to the C-Q space in Fig. 2 in the manuscript. In this figure the smoothed spline fits, used for calculating *Curvature*, are compared for the observed and simulated data. We already state the "classical" log-log linear slope in l. 345 but agree that it would be interesting to show the linear C-Q fit in Fig. 2b. Note that the simulation results in Table 4 report the log-log linear C-Q fit 'bout' at the catchment outlet for the different parameter combinations, next to the Curvature and the percentage load removed Lr among others.



In the French data that is used to validate the *Curvature* metric 77 % of the stations are characterized by Curvature ≤ 0 or a linear or concave shape (l.147). For the simulated *Curvatures* only concave shapes are generated as no point sources are considered in our approach (l.194-195 and comment R1.9).

R1.5: *General: Large number of studies show that high-freq and low-freq c-q relationships are governed by different factors. Please be clear in your paper based on which type of data you derive/base your assumptions on.*

With all due-respect to the reviewer efforts and time, we clearly mention several times in the manuscript that we consider low frequency log(C)-log(Q) relationships (l.10, 25, 99, 107, 131, 141, 151, 156, 640, 644, 669).. However, to further emphasize this point, we will add explicitly that the motivation for this study was a large-scale observational study based on low-frequency conventional monitoring (Moatar et al., 2017) so l.90 would read: “These studies identified distinct linear low-flow and high-flow NO3- log(C)-log(Q) regression slopes for a majority of the cases, **using low frequency monitoring data.**”

R1.6: *The title could be improved. I am not a big fan of bent c-q, maybe come up with a better term? For example curved c-q relationship as opposed to linear?*

We understand the reviewer's preference, but we believe that our chosen title is more informative of our work. At this junction, we would also like to recall some previous works - well accepted in the community - that mention non-linear C-Q relationships. For example, Moatar et al, 2017 uses the term 'nonlinear' to describe 'bent' C-Q relationships, while Diamond and Cohen, 2017 talk about 'slope breaks' and Marinos et al, 2020 'piecewise power law model'. Because the referenced terminology alludes to descriptive characteristics (linear or not) rather than quantitative (amount of nonlinearity) we chose the term 'bending'. As 'bending' is our key expression for that we would prefer to keep the title.

R1.7: *Line 13 not clear what you mean by more positive slopes. Be exact.*

Line 13 says: "...that more positive log(C)-log(Q) slopes under low flow conditions (than under high flows) are linked to biological NO3- uptake, …".

R1.8: *Lines 13-15 – what about point source pollution impact on low flow concentration?*

We thank the reviewer for addressing this point. Although for the explorative modelling approach proposed in this paper, additional NO_3^- sources such as incoming load resulting from point sources are not considered (similar to Bertuzzo et al., 2017; Wollheim et al., 2006) (l.194-195), we agree that point sources can have an impact on the in-stream N status. Therefore we will add the following sentences to Sect. 3.4 where we discuss the interpretation of C-Q bending at the catchment outlet: "For the parsimonious explorative modeling approach applied in this study, we mainly focused on the impacts of diffuse sources. Point source pollution, though not so significant as that of diffuse sources, can have impact during low-flow periods. Disentangling the contribution of NO3- from these two sources are challenging and remain open for further investigations."