

Manuscript Egusphere-2022-205

Disentangling Scatter in Long-Term Concentration-Discharge Relationships: the Role of Event Types

We acknowledge the Editor and two Reviewers for providing detailed and constructive comments to our manuscript in the present and previous rounds of review. This document provides our point-by-point replies (black color) to the reviewer comments (blue color). In addition, we enclosed a revised manuscript with track changes in our response.

Reply to Editor comments

Thank you for thoroughly addressing the comments raised by reviewers in the last round of review. In the present round, one reviewer raised additional comments, so I am returning your manuscript for minor revision. I look forward to receiving your revised manuscript.

Thank you very much for managing the review process. In the following lines, we address all the new comments of the reviewers.

Reply to Reviewer #2

General comments

Saavedra et al. provide a comprehensive study on nitrate concentration-discharge relationships. With an original methodology, they successfully identify key relationships between C-Q patterns and hydrological event types. The approach is sound, the results and interpretations are well conducted and interesting for the readership of HESS. I have raised some relatively minor issues, which must be properly addressed prior to publication.

We appreciate the reviewer's constructive comments and suggestions. We address all your comments in the following lines.

Major comments:

L139: could you please represent these 4 regions on the map (Fig 2a)? For someone outside Germany, this could be useful to better understand the interpretation from Fig 5a.

Thanks for the insightful comment. We added in Fig. 2 the four natural regions of Germany.

L177: "neutral ($b \sim 0$) indicates a weak dependency of C and Q." This could also be because the long-term CQ relationship is the combination of different opposing events or seasonal patterns vs storm events: for instance, at the seasonal scale there is a dilution pattern, which combines with enrichment during storm events. Since the entire study here has for objective to disentangle the scatter in C-Q plots, we expect from the authors to carefully chose their words in this particular case. Please, consider rephrasing.

We agree with the comment and we rephrased the sentence. Please refer to line 176 in the revised manuscript.

L187-197: this methodological approach is absolutely key for the robustness of the entire study, because a different choice (for instance compute deviation from CQ relationship from non-event observations) would likely lead to different outcomes. It is unclear to me where to find the results from this important bootstrapping analysis. Please make the result from this analysis much clearer as the reader shouldn't have any doubt about your methodological choices.

Thanks for the insightful comment. We added bootstrapping results to supplementary material. Please refer to Figure S2 and lines 193 in the revised manuscript.

L312: "Event runoff coefficients exhibit a larger variability across event types than across catchments for most of the catchments.". Please place this sentence after the following one "Catchment median event runoff coefficients exhibit a coefficient of variation of 41% across catchments. Nevertheless, median runoff coefficients of event types exhibit coefficients of variation in different catchments from 12% to 118%, with a median value of 67% across catchment" as it is very hard to get as it is now.

We agree with the comment and we rephrased the sentence. Please refer to lines 309-313 in the revised manuscript.

L344-346: "Lower nitrate concentration during runoff events with dry antecedent conditions can be explained by low pre-event conditions linked to hydrological and biogeochemical drivers in addition to possible dilution during runoff events.". What are exactly these "hydrological and biogeochemical drivers" being mentioned? Please be specific and name directly these processes.

Thanks for the insightful comment. We specified each driver and rephrased the whole paragraph. Please refer to lines 337-355 in the revised manuscript.

L353: "due to a more efficient removal". Please explain the driver behind, because a more efficient removal necessarily removes more nitrate! Please be more specific with the name of the processes behind (e.g. denitrification, biological uptake, ... etc).

Thanks for the insightful comment. We rephrased the whole paragraph to be more specific. Please refer to lines 337-355 in the revised manuscript.

L378-379: "Most of nitrate samples during no event conditions coincide with low rates of discharge (Fig. 4a) as well as Rainfall events with dry antecedent conditions (i.e., Rain.dry.patchy and Rain.dry.uniform)". How could a sample taken under no-event condition coincide with some rainfall events? Please clarify or revise.

We thank the reviewer for pointing this out. We explain in this sentence that samples taken during Rainfall events with dry antecedent conditions and samples taken during no-event conditions are taken at relatively low discharge levels. We rephrased the paragraph for clarification. Please refer to lines 365-369 in the revised manuscript.

L439-440: "We acknowledge that catchment characteristics might be highly correlated (Fig. S4)". It is indeed needed to do so, but this sentence seems lost in the paragraph, although one can understand with the end of the paragraph what was meant. Please revise this sentence, because the reader should not have to read the end of the paragraph to understand the meaning of the sentences found mid-paragraph.

Thank you for the comment. We modified and reorganized the paragraphs to improve readability. Please refer to lines 436-450 in the revised manuscript.

Minor comments:

L29: I'm not native English speaker, but are you sure "portend" is appropriate in this sentence?

We changed the sentence. Please refer to line 29 in the revised manuscript.

L30: “particularly of nitrate”. I agree excessive nitrate concentrations are partly responsible, but please, temper this statement as P is in general the main driver for eutrophication in freshwater-ecosystems.

We modified the sentence. Please refer to line 30 in the revised manuscript.

L55: “The time of fertilizer”. Consider “timing” instead of “time”

Revised as suggested. Please refer to line 55 in the revised manuscript.

L57: “On the other hand,” Please remove

Removed. Please refer to line 57 in the revised manuscript.

L83: “C-Q relationships are more positive due to the accumulation in soil during dry periods of nitrate from atmospheric deposition”. Consider rephrasing to “C-Q relationships are more positive due to the accumulation of nitrate in the soil during dry periods by atmospheric deposition”

Revised as suggested. Please refer to line 82 in the revised manuscript.

L84: “Eurpe,” Typo. Please correct

Corrected. Please refer to line 83 in the revised manuscript.

L167: “This implies that only events longer than 1 day are captured.”. Can we reliably detect a hydrological event of 2 days with daily data? Is there a minimum number of daily observations needed to detect an “event”?

We thank the reviewer for pointing this out. The event identification procedure consider events only if there is an inducing snowmelt or rainfall event occurring before the event (using seasonal basin lag times as searching window prior the runoff event) and if the increase in discharge is at least 10% compared to the baseflow discharge rate. The minimum event duration is therefore 1 day. For further information, please refer to Tarasova et al., 2018. Moreover, in our dataset the 95% of the identified events exhibit a duration of 3 or more days. We included this information in the revised manuscript, please refer to lines 155-156.

L248: Please insert a “the” in between “considerable scatter in” and “regressions”

Corrected. Please refer to line 247 in the revised manuscript.

L276: Please guide the reader, this paragraph is a bit lost in between two bigger paragraphs and the reader needs to read the end of it to understand what it is about (i.e. the timing of sampling during rising/falling limb of the hydrograph).

Thank you for the comment. We modified and reorganized the paragraph to improve readability. Please refer to lines 272-277 in the revised manuscript.

L277: “Fig. S6b” Please sort the figures numbering from SI accordingly to their appearance in the text.

Thanks for the insightful comment. We sorted the figures numbering from Supplementary Material in the revised manuscript.

L278-281: this sentence is very long and difficult to read. Please simplify to help the reader.

Thank you for the comment. We rephrased the paragraph. Please refer to lines 272-277 in the revised manuscript.

L285-286: maybe give numbers to make it clearer?

Thank you for the comment. We added the values of interquartile ranges in the revised manuscript. Please revise lines 279-282 in the revised manuscript.

L295: "however the last feature shows" which feature is being mentioned? Please be more specific.

Thank you for the comment, corrected as suggested. Please refer to line 291 in the revised manuscript.

L308: "A nitrate surplus is strongly related only to Rain.wet residuals." Please revise to "Nitrate surplus is significantly related only to Rain.wet residuals."

Corrected. Please refer to line 305 in the revised manuscript.

L338: "movilized". Please revise

Corrected. Please refer to line 334 in the revised manuscript.

L339: "In addition, the movilized water during this events is less affected by biogeochemical processes due to lower microbial activity induced by low temperature during snow-impacted events.". Could you add at least 1 reference to support this statement?

We added a reference. Please refer to line 335 in the revised manuscript.

L341-374: could you make this a single paragraph? Splitting the discussion in so many short paragraphs makes it difficult to follow.

We merged the paragraphs. Please refer to lines 337-363.

L355-356: "Moreover, during runoff events with dry antecedent conditions nitrate concentrations can decrease below pre-event concentration level.". Isn't it redundant with previous statements in previous paragraph?

We agree with the comment we rephrased the paragraph. Please refer to lines 337-363.

L449-454: these sentences are a repetition of the lines 439-444. Please delete and make sure this paragraph still makes sense.

We agree with the comment. We modified the paragraph. Please refer to lines 436-450.

L481: "a substantial decline in seasonal snowpack accumulation and earlier snowmelt onset in Central Europe". Yes but wouldn't the frequency of rain on snow events increase? Please make sure of this aspect, which would completely change the interpretation of the outcome paragraph.

Thanks for pointing this out. To the best of our knowledge, there is a consensus in future and present negative trends in snow accumulation in the study region. This negative trend is consistent with a decreasing trend observed in the frequency of rain-on-snow events (Cohen et al., 2015). We added references and modified the text. Please refer to lines 461-466 in the revised manuscript.

L519-520: "Moreover, we inferred using catchment descriptors physical mechanisms that explain the spatial variability of this scatter.". Please reorder or revise, something is missing or misplaced in this sentence.

We agree with the reviewer. We deleted the sentence for readability.

References:

Cohen, J., Ye, H., & Jones, J. (2015). Trends and variability in rain-on-snow events. *Geophysical Research Letters*, 42(17), 7115–7122. <https://doi.org/10.1002/2015GL065320>

Tarasova, L., Basso, S., Zink, M., & Merz, R. (2018). Exploring Controls on Rainfall-Runoff Events: 1. Time Series-Based Event Separation and Temporal Dynamics of Event Runoff Response in Germany. *Water Resources Research*, 54(10), 7711–7732. <https://doi.org/10.1029/2018WR022587>