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Comment on hess-2021-536

Anonymous Referee #1

Referee comment on "Improving the understanding of N transport in a rural catchment under Atlantic climate conditions from the analysis of the concentration–discharge relationship derived from a high-frequency data set" by María Luz Rodríguez-Blanco et al., Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2021-536-RC1>, 2022

Review of the manuscript „Improving the understanding of N transport in rural catchments under Atlantic climate conditions from analysis of the concentration-discharge relationship derived from a high frequency data set “

This manuscript analyzes event characteristics and nitrate and TKN hysteresis patterns of 173 runoff events in a rural catchment in the North-West of Spain. The strength of relation between event characteristics and nitrate and TKN dynamics during events are examined by means of correlation and redundancy analysis to understand relative importance of different hydrological processes in the mobilization of these substances.

Increasing nitrate concentrations in the headwater catchments is a pressing environmental issue and additional insights from high-frequency datasets on the controls of nitrate dynamics during events can be valuable information for informed water quality management. However, the novelty of this study is not clear. Particularly, it is difficult to evaluate its additional value as the Introduction fails to present a comprehensive overview of previous studies on the possible controls of nitrate dynamics. Moreover, there are several methodological ambiguities and subjective choices in the analysis that make it difficult to evaluate the reliability of the results. Finally, more effort is needed to improve the manuscript's structure and writing, especially in the Introduction and Discussion Sections. Therefore, I recommend major revisions. Below I provide my detailed comments.

General comments:

- The novelty of the study is not sufficiently highlighted. The additional value of the performed analysis is not clear because the Introduction does not provide a sufficient

overview of findings on the controls of nitrate hysteresis from the existing high-frequency studies. Particularly, the Introduction should clearly indicate what is known so far about the role of event characteristics on the hysteresis patterns and what is the additional value of the analysis performed in this study. Moreover, it should be indicated what kind of additional information the analysis of TKN might provide compared to the analysis of nitrate concentrations alone.

- There are several methodological ambiguities and subjective choices that have to be clarified, particularly concerning the necessity and additional value of redundancy analysis (see detailed comments to Lines 206-210), separation of event and pre-event water that was performed but was not further analyzed (see detailed comments to Lines 159-168), the choice of subjective manual techniques for event identification and hysteresis classification (see detailed comments to Lines 135-139 and Lines 174, respectively).
- The rationale for the analysis of two selected substances should be clearly stated, as well as the rationale for the choice of event characteristics. Why are particularly these event characteristics expected to be decisive for hysteresis patterns? A more hypothesis-oriented choice of these characteristics might also be helpful to highlight the novelty and the additional value of this study compared to the previous literature.
- The connections of different hysteresis patterns to the particular runoff generation processes in the Discussion Section are rather speculative and need more in-depth clarifications and evidence from related field studies or own observations.
- There is little discussion provided on the identified relations between event characteristics and nitrate and TKN hysteresis patterns in the Discussion Section, although it appears to be the central topic of the manuscript.

Detailed comments

Line 12: The title implies the analysis of several catchments, although in fact the analysis was performed in a single catchment. Please revise.

Line 17: Not clear what is meant here by the overall dynamics of hysteresis. Please clarify.

Line 18: Not clear what is meant here by "parameters". Please clarify.

Line 19: Please be more cautious with such statements. It is rather difficult to infer particular runoff generation processes directly from hysteresis patterns. Please revise.

Lines 19-21: Consider providing here an explanation why there are such considerable differences in the hysteresis patterns of NO₃ and TKN.

Line 22: Consider providing more details on how exactly different event characteristics affect corresponding hysteresis patterns. Moreover, please clarify what is the difference

between "runoff" and "discharge" here.

Lines 29-31: This is rather general, the Introduction can benefit from a more specific opening sentence.

Lines 46-47, 50-53, 53-54, 56-57, 62-64: These statements require a reference.

Lines 59-60: I cannot agree with this statement. The analysis of nitrate hysteresis are rather often performed in the headwater catchments since high frequency observations are usually only available from local research observatories (see e.g., Knapp et al., 2020; Winter et al., 2020; Mussolf et al, 2021; Koenig et al., 2010; Vaughan et al., 2017 among many others).

Line 62: What is meant here by "clean" rural catchment? Please clarify.

Lines 71-72: What these drivers can be? This part of the Introduction should provide a clear rationale on selecting event characteristics for the analysis based on findings from previous studies and/or own hypothesis on which characteristics might be potentially important for the hysteresis of NO₃ and TKN concentrations.

Lines 72-74: Are such studies becoming increasingly rare? I would argue that CQ studies become increasingly frequent as the density of observations has increased in the past decades. Please clarify.

Line 74: Please clarify why there is a particular interest in the concentrations of TKN and how its analysis complements NO₃ investigations.

Lines 69-85: The structure of the Introduction and especially of this last paragraph is rather confusing. The Introduction has to be streamlined and clearly present the current state of the art on the topic of nitrate hysteresis and its potential controls, indicate the knowledge gap and provide clear objectives of this study that strive to close this gap.

Line 90: What is meant here by relief? The difference between max and min elevation? Please clarify.

Figure 1: Please indicate river outlet and river network on this Figure. Please clarify the

title of the legend. What is shown by the solid line within the catchment? Please clarify.

Line 106: This number of meteorological stations does not seem very plausible to me. Please correct and consider displaying the locations of the considered meteorological stations in Figure 1.

Line 113: Please clarify which N concentrations exactly were measured.

Lines 112-115: Please indicate how many gauges were actually used for interpolation, consider indicating their location in Figure 1.

Lines 121-122: Please clarify how the start of the rainfall event was identified.

Lines 123-124: Please clarify how exactly sampling frequency was defined based on magnitude and duration of the event? Were the forecasted values used? If so, please indicate that and provide details on the type and the accuracy of the forecast.

Lines 135-137: Does this threshold correspond to the rule described in the Line 121-122? Moreover, please indicate if any minimal interarrival time between rainfall events was used for event definition.

Lines 137-138: Please clarify how the inflection point is identified.

Lines 138-139: Please clarify how baseflow conditions were identified. Was baseflow separated? Which method was used for that? How is the start of the next event defined?

Lines 142-148: The choice of these particular event characteristics has to be clarified. Why exactly these characteristics? What do authors expect to find by investigating them? Moreover, some of the characteristics e.g., water yield, rainfall kinetic energy have to be introduced in more detail, i.e., source, definition etc.

Line 145: This definition of delta Q will not result in % units. Please revise.

Line 146: Why the duration of the events is in days when the observations are performed

every 10 min? Please clarify.

Line 147: How was the initial phase of the falling limb identified? Please clarify.

Line 151: Please clarify what is meant here by "metal load".

Lines 159-168: Please notice that EC is not always applicable for pre-event and event water separation (see e.g., Musolff et al. 2015; Musolff et al., 2020). Please indicate if implemented assumptions are expected to be valid in the study area. Moreover, the results of this separation were barely mentioned in the Results section and are absent from the Discussion altogether. Consider either removing this separation or including it more distinctly in the analysis of hysteresis patterns. Generally, it is not clear what additional insights about the controls of hysteresis patterns can be gained from this analysis.

Lines 171-172: Please clarify why multiple-peak events cannot be considered.

Line 172: Please define exactly how close to the peak discharge the observation should be.

Lines 173-175: Please clarify why visual examination was preferred to the automated approaches. How can the robustness of the performed classification be verified?

Line 177: Please indicate what is exactly meant by "figure of eight".

Table 1: Please explain what is V.C.? Consider including Δt to the "antecedent conditions" group, as it rather represents pre-event than event conditions. Moreover, please clarify why it has units of days when the observations are available on much finer resolution? Is that the reason for its min value being equal to zero? This is rather confusing as it makes an impression that a consecutive event can start at the same time step when the previous event finishes.

Line 192: Please clarify what AR stands for? Generally, the manuscript is oversaturated with many not very intuitive acronyms. Consider using full terms instead.

Line 195: Please clarify how standardization is performed here. Was any standardization

applied for Ah?

Lines 200-204: This part is rather confusing and hard to understand, consider revising. Moreover, please indicate if the selected thresholds are in line with previous hysteresis classifications in the literature.

Lines 209-210, 285: From this description, it is not clear what is the additional value of the redundancy analysis compared to correlation. Please clarify.

Figure 2: Please clearly state in the caption what these four panels show (i.e., time of event, type of hysteresis). Please add a-d labels to the panels. Please clarify why four different hysteresis are displayed when only three types were considered? Do the two plots on the top correspond to the same type or not? Please indicate the starting point of the event in each subplot.

Lines 217-219: It is not clear how the authors are able to define that the entire range of rainfall and antecedent rainfall is covered without examining what their actual range is. Please clarify.

Lines 224-226, 232-233: Seasons are not indicated on Figure 2 making it impossible to verify statements in these sentences. Please add corresponding information to Figure 2 or revise these sentences.

Line 227: Please indicate what is considered here by "long duration"

Line 244 and Figure 3: Do these type numbers correspond to Figure 3? Please indicate this in the text and in the caption of Figure 3.

Line 246: In case of NO₃, only 62% of events have positive delta C. This is not very similar to 93% for TKN. Please revise.

Line 246: Compared to baseflow or to the pre-event values? Baseflow was not formally separated (at least the Method section provides no indication of such analysis). Please revise.

Lines 296: Please clarify what kind of information is provided in the parenthesis.

Lines 305-307: Anticlockwise hysteresis was also linked previously to a particular spatial distribution of sources (see e.g., Vaughan et al., 2017). Please indicate if this can also be the case in this study catchment.

Lines 312-315: Please indicate how the point with maximum contribution of subsurface flow can be identified here.

Line 315-316 : Such a statement requires references. Please add.

Lines 319-321: Please clarify why particularly in these years such conditions have arisen. Moreover, this sentence is rather confusing, please revise.

Lines 326-328: Is there any evidence of surface runoff presence in this particular study catchment? Please clarify.

Lines 329-330: This seems like a description of the "eight" hysteresis shape that was not considered in the classification in this paper. Please revise,

Lines 331: Please indicate clearly which event from Figure 2 is meant here.

Lines 332-333: It is not clear how this confirms the control by subsurface flow. Please be cautious with your conclusions if they cannot be directly supported by your own findings. Please revise.

Line 336: Please clarify what kind of findings or observations support rapid exhaustion in this case?

Lines 349-351: This sentence is rather confusing. Which event characteristics point this out? What can be a possible source of this additional nitrogen? Please clarify and revise.

Lines 355: What is the difference here between runoff and discharge. Please clarify.

Line 354-356: The dominant role of event characteristics, particularly of rainfall intensity and by extension its connection with the activation of fast flow paths, stated in these sentences in my opinion contradicts the previous statement in Line 332-333 about the dominant control of subsurface flow. Please clarify.

Lines 356-357: The relation between rainfall intensity, discharge rates and nitrogen loss is not clear from this description. Please provide more process-oriented hypotheses on how event characteristics might affect hysteresis.

Line 359-361: This rather contradicts earlier statements (Line 232-233) that nitrate concentration in winter (wet season) is higher than in any other season. Please clarify.

Line 363: What is meant here by "strength of the event". Please clarify.

Line 368: What do you mean here by "losses" here? Consider using a more conventional term here.

Lines 368-370: This statement would be much more clear if the main sources of TKN were introduced earlier. This is the first time they are mentioned in the manuscript. Please revise.

Lines 377-379: Be cautious providing statements that are not directly inferable from your own results. It is rather difficult to identify dominant runoff generation processes from hysteresis patterns alone.

Editorial comments

Lines 14,19,69 and elsewhere: Consider using the correct chemical "NO₃⁻" notation.

Line 150: Consider using "initial" instead of "0".

Line 182: Consider using hysteresis "characteristics" instead of "parameters".

Lines 183, 190: The term "trend" is not clear here. Consider using the term "slope"

instead.

Line 185: Please add " $\Delta C =$ " on the left side of equation 2

Line 199, 203: consider using "classes" instead of "regions" as these cases do not have any spatial aspect.

Line 229: word order: "with discharge" should be before "were observed"

Line 238: than before the event

Line 239: an increase in NO₃

Line 253: repetition "10%"

Table 2: In the caption "bold" instead of "both". Consider transforming this table into a correlation matrix to improve visualization of the results.

Line 301: due to increased nitrogen concentrations

Line 304: they are

Line 305: it should be Winter et al. 2021

Line 314: contribution of subsurface flow

Line 325: runoff events with short interarrival time

Line 349: distant sources

Line 359: under wet antecedent conditions?

Line 372: Conclusion or Concluding remarks

Line 375: C-Q

References

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