Comment on hess-2021-536
Anonymous Referee #2

Understanding nutrient transport in rural catchments is important for managing water quality and protecting ecosystems. Detailed studies such as this are valuable in understanding the sources, fluxes, and transport mechanisms of nutrients. However, the paper needs revising before it is suitable for publication.

My main general criticism of the paper is that it does not place the results in context. The Introduction (L29-45) presents the global overview and discusses some of the important issues. However, the Section 5 is not very informative (as section 4 is also the Discussion, I presume that this is meant to be the Conclusions). For papers such as this to appeal to a broad international readership, those important issues need to be revisited at the end of the paper and the authors need to explain how their study informs work done elsewhere. Leaving the reader to work that out for themselves is not satisfactory. So, explain here what the implications are and/or how the work has advanced our understanding in general.

Some of the methodology is not well explained and it is difficult to follow the details from the figures and tables provided. More details are needed in places (better / additional figures and perhaps some supplementary tables). Moreover, where are the data? Even at the preprint stage, I would have expected the data to have been provided.

The English is understandable but idiomatic in places and would benefit from a final editing. The paper also is difficult to read in places due to the large number of
abbreviations. Mostly, they are introduced, but are easy to lose track of. Most variables need abbreviating, but other abbreviations (eg RDA) probably do not need to be there.

Abstract

The Abstract provides a good summary of the paper. However, as with the paper as a whole, provide one or two sentences at the end which explain why this is important.

Minor comments

L17-18. “Some metrics” is redundant, meaning of “overall dynamics” is unclear. Perhaps also specify what you mean by “nitrogen behaviour”.

L18. Sentence “The results showed...” is redundant as this is described in the next sentence

L19-20. Does TKN also show dilution, if so mention that here.

L22-23. This explains what you think is important but not how or why. Can you briefly expand on this?

Introduction

As noted above, the first paragraph of the introduction introduces some important general issues that need to be addressed throughout the paper, especially at the end.

The referencing in parts of the introduction can be improved. For example, several of the references in L33-45 are reports and Bieroza et al., 2018; D’Amario et al., 2021 deal with
techniques. Try to add a few key papers that discuss these general issues.

L46-47. Not clear what you mean here.

L50-54. Some of the concepts here could also use better referencing. Evans & Davies (1998: Water Resources Research, 34, 129-137) and Walling and Foster (1975: Journal of Hydrology, 26, 237-244) present some of the framework for these studies. Lloyd et al. (2016: Hydrology and Earth Systems Sciences, 20, 625-632) develop a framework for characterising hysteresis and also reference other literature. The recent paper by Knapp et al. (2020: Hydrology and Earth System Sciences, 24, 2561-2576) also develops methodology that is relevant here.

L59-65. This may be generally the case, but there are several studies that have looked at smaller catchments at high frequency. Some examples: Lloyd et al. (2016, Science of the Total Environment, 543, 388-404); Vaughan et al. (2017: Water Resources Research, 53, 5345-5363); Jiang et al. (2010: Soil Sci Plant Nutr, 56, 72-85). Other papers (eg Knapp et al., 2020) apply similar methodology to other solutes (including other nutrients such as P). The way that this is written implies that there is little work being done in this space, when there is a large body of work that needs acknowledging.

L48-58. You could add a schematic figure of hysteresis loops here to show differences in typology. This would make it clear exactly what you mean by rotation directions, slopes etc. You can also highlight what ΔC and ΔR represent. Alternatively, you could better annotate Fig. 2 to show these features.

L70-85. The objectives are very specific and parochial. While they describe what you have done and why it is locally important, can you reframe them so that they have a more general focus (ie understanding differences in the behaviour of TKN and NO3 that we do not understand in general)

L73-74. The studies cannot become increasingly rare – do you mean that there have not been many thus far?

L74-76. If understanding TKN is important, you could mention it in the main part of the introduction with a few more details rather than in your objectives section. It is a bit lost here.
Materials and Methods

The description of the Study Site (Section 2.1) is comprehensive.

L105-108. Is this the meteorology of the site or of the region (not sure if there are 10045 stations, which seems a lot, or if that is the station identifier and the sentence is slightly misworded).

L108. What do you mean by “pluvial” in this context?

L113. How was the hydrological year defined – specify the date / month when it starts.

Figure 1 only clearly shows landuse. Highlight the drainage features and the monitoring point(s).

L125-128. The preservation and storage of samples presumably is only after they are retrieved from the autosampler. How much of a delay between collection and storage was there and does this have an impact (I presume not).

L125-132. Minor point, but here and elsewhere be consistent with specifying valences or not.

L125-132. You should report the precision and lower detection limits of the analyses.

L135-139. For clarity, can you include a figure of a typical event showing rainfall, streamflow, and concentration data. That would help visualise the data and interpretation of events etc.

L140-151. These is some repetition here as you say that there are three groups of variables, describe broadly what they are, and then explain that in more detail. Some of these variables do not seem to have been explained – how did you calculate KE and I presume that WY is Q / catchment area? Some of the parameters associated with the Q-C loops would be clearer if they were on a figure (previous comment).
L145-146. Qmax-Qb will not give you a %

L151. Metal?

L154-159. There are probably better references. Yu & Schwartz (1999, Hydrol. Process., 13, 191–209) has an early general explanation. For these general statements, try to quote some of the early papers that develop the techniques or review-style papers.

L154-168. The use of EC in this way makes a range of assumptions (e.g., that pre-rainfall EC represents water from within the catchment, not a mix of that water and recent prior rainfall; that we know the EC of surface runoff; that the contrast in rainfall and catchment water EC is high). These are discussed in many papers that have used that technique (e.g. Miller et al., 2014, Water Resour. Res., 50, 6986–6999; Miller et al., 2016, Water Resour. Res., 52, 330–347; Riis et al., 2015, J. Hydrol. Reg. Stud., 4, 91–107; Rumsey et al., 2017, Hydrol. Process., 31, 4705–4718). Some comments are needed here if you are going to use that technique. Actually, I am not sure whether you really need this parameter – there is a little discussion in section 3.3 but not much else (?). Given the considerable uncertainties in using an EC mass balance, you probably could safely omit it.

Did you consider looking at the EC hysteresis? Notwithstanding the comments above, the EC hysteresis may be useful in understanding hydrology even if Qb is not calculated. In particular, if subsurface flow is important then that may show up.

L172-179. This could be more tightly worded. How close is “close to the peak” and does it vary with Q? Rotational directions can probably be defined by 5 samples (although a figure of eight might be hard to see), but what about the concentration and discharge differences?

L193 Delta (Δ) R not AR?

Table 1. What is V.C.?

L203 Linear not lineal

L206-210. This just says that these methods were used. In particular is there any reason that the Redundancy Analysis offers more than the correlations? Any details that we should know?
Results

Figure 2. Without some more details, it is difficult to interpret this diagram. I presume a & b have similar rotation but different slopes? How close to the start of the events are the first points and what time periods do these events depict (do the points within each graph and between graphs represent the same timesteps). More could be done to make it clear what is going on here.

L223-233. There are a lot of generalities here ("highs", "lows" etc) and Table 1 only shows summary statistics. Add a few more details to the text to explain and consider adding a Supplement Table with more details in it.

L235. It would be worth showing the TKN data on Fig. 2 also to illustrate this point.

L240-242. In the methods you introduced the +/-10% cut off for neutral loops, so you just use that here from the outset. So just note that 13% have DR values within the 10% limit and are classified as neutral. As written, it is not very clear how many of the loops you consider to be what type and whether you are being consistent in definitions.

L242-244. Not clear, needs rewording.

L244-250. Similar comments about the +/-10% apply here and again the text is not very clear.


L258-261. You should discuss that you are using a Pearson correlation matrix and any relevant details in the methods.

Discussion
This is a long section and a brief introduction at the start guiding the reader through what you intend to discuss would be good. There is also a tendency to interpret your data by reference to other studies (so on L304-305 you explain the results of others and then discuss your interpretations in the next few sentences). It would be preferable to discuss your interpretations and justify them using your data and then note whether they are similar or different to those elsewhere. Otherwise it looks like you are trying to fit your data into an existing framework, which I don’t think is the case.

L293. Section heading is confusing

L294-303. This seems to be off topic with the title of this section. Does it belong here? Perhaps it go be fore the sectiion heading and act as a general lead-in?

L304. What is an “accretion pattern”?

L310-321. There is a lot of speculation here (deep drainage, high NO3 in soils, rapid transport). Can you provide justification – there seems to be a number of prior studies on this area that may help.

L324-L330. In section 2, you say that overland flow is unusual, so how can that be?

L334-350. Similar to the comments above, there is a lot of speculation here. While studies elsewhere may help with that, is there evidence from this catchment that you could use to firm these ideas up.

L348-351. Not very convincing, what might those sources be?

L367-370. Very awkward sentence.

Discussion (Conclusions?)
As noted at the outset, this is where you should provide more of a global context. There are parts of Section 4 (e.g. L351-365 and L366-371) that are more general and which could form the basis of the Conclusions. Once a reader has gotten the basic idea of a paper, they may skip to the end to see what broader insights there are. This makes this last section important for communicating your ideas.