EGUsphere, referee comment RC1
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Comment on egusphere-2022-205

Anonymous Referee #1

Referee comment on "Disentangling scatter in long-term concentration–discharge relationships: the role of event types" by Felipe A. Saavedra et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-205-RC1, 2022

General Comments:

This study presents a unique, spatially and temporally extensive dataset of nitrate C-Q relationships across 184 German catchments of varying size and land cover/land use from 2000-2015. The authors found that the degree of catchment hydrologic connectivity (and the closely related factor of runoff event type) strongly regulates the pattern of catchment nitrate export. Divergence of event-scale nitrate C-Q responses from the more generalized long-term response were attributed to a combination of catchment topographic properties and event type. The study dataset is impressive, providing a long-term view of catchment nitrate responses across gradients of event type, topography, and land use. The paper is very well written, making it both easy and enjoyable to read; there are only a few places in the manuscript where grammatical clarifications are needed. The statistical analyses presented in the paper are well-presented and wholly appropriate for the research questions that are being asked. Overall, this paper represents a meaningful addition to the existing C-Q literature and I recommend it for publication with only a few minor revisions. My main concern with the paper is that the potential influence of C-Q hysteresis on the observed patterns is not addressed anywhere in the paper. For example, if a particular catchment (or a particular event type) is characterized by a strong hysteresis signal, then the observed C-Q pattern (i.e., dilution or enrichment) would be highly influenced by the timing of sample collection. If a strong sampling bias exists where samples are more frequently collected on the rising limb relative to the falling limb (or vice versa), then the observed catchment or event C-Q signal might be confounded by the presence of hysteresis processes. I would not expect this to be an issue for the long-term C-Q pattern, but it may be an issue for the event-scale patterns and this would, in turn, cause a problem for the interpretation of the "Δres50" term presented in the paper. Given the low frequency of sample collection in this dataset (biweekly to monthly), it seems likely that a particular runoff event would be represented in the dataset by a sample collected either on the rising limb OR the falling limb but not both. It would be fascinating to see an additional analysis of this extensive dataset that incorporates the potential influence of sample timing on the hydrograph, but this is likely beyond the scope of this paper in its current form. However, I do think the authors need to include at least some discussion of the potential influence of this potential "hysteresis effect bias" associated with low-frequency event sampling.

Specific Comments:

Introduction: Very well-written and cited, providing a concise but informative review of the relevant C-Q literature. However, the Introduction focuses heavily (almost exclusively) on the hydrologic drivers of observed C-Q patterns, with little mention of the role of biogeochemical drivers. Particularly in the case of nitrate, biogeochemical drivers—emphasizing the "bio" aspect-- can also influence C-Q patterns. Because this paper focuses solely on nitrate concentrations, I think it is worth mentioning the potential role of biogeochemical processes as drivers of the observed C-Q patterns (this might fit well in the paragraph starting on L56 or after). For example, seasonality of microbial processes might influence soil nitrate concentrations and affect the observed patterns of C-Q especially during seasonal events (e.g., rain-on-snow). Similarly, one might expect the "C" side of the nitrate C-Q relationship to be strongly influenced by the timing of nitrogen fertilizer applications in agricultural catchments. In each of these two examples, the biogeochemical drivers exert as much (of not more) control on the C-Q relationship as the hydrologic drivers. Salli Thompson's 2011 paper "Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients" might be a useful paper to consider here.

Methods: If it is possible with your dataset to quantify the proportion of rising limb and falling limb samples, it would be good to include that quantitative information in the Methods section. If the proportions of the two are widely unbalanced, then the potential influence of that sampling bias on your results should be discussed in the Discussion. If it is not possible to determine the rising- or falling-limb status of samples in your dataset, then a brief acknowledgement of the implications of this should still be included in the Methods.

L134: What is meant here by "precipitation attribution"? Does this mean precipitation classification as rain or snow? Otherwise, I'm not sure what precipitation would be attributed to.

L243-247: For these correlation analyses, how did you account for the potential

interaction between catchment topographic characteristics and land use? For example, one would expect at least some of the flatter catchments to also be used for agriculture (indeed, Figure S4 seems to indicate this). Thus, a simple correlation between median catchment slope and nitrate C-Q response is not straightforward if it does not somehow control for potential biases due to land use effects on nitrate availability.

L253: "Instead, we *observed* strong..."? It seems like a word is missing here…

L264-266: It would provide useful context here to also provide the ranges around these median values, not only the medians themselves.

L276-296: These two paragraphs are basically invoking the same hydrologic driver for the observed C-Q patterns: catchment wetness status associated with a given event type. But catchment wetness also changes ***during*** events, and this is where the need to consider potential hysteresis effects / sampling biases becomes important. I am not sure where a discussion of this issue fits in best in the Discussion section, but it should be included somewhere.

L358: The word "wetness" is not needed here.

L373: "… controls of the variability *of* C-Q …" I think another "of" needs to be added here.

L414: The word “prompt” does not make sense here. I’m not sure what you’re trying to convey with that word, but “prompt” doesn’t work. Do you mean “prone”?

L432: Do you mean “increase” instead of “increment”?

L457-458: I generally agree, but it’s also important to consider that the Δres50 metric uses INDIVIDUAL grab sample deviations from the long-term C-Q pattern, whereas event-scale metrics like runoff coefficient integrate hydrologic conditions across an entire event. So accounting for potential biases due to the timing of sample collection and hysteresis become important to consider.

L464: Again, I’m not sure what you mean by “prompt” here.