

***Interactive comment on* “Technical Note: Improved mathematical representation of concentration-discharge relationships” by José Manuel Tunqui Neira et al.**

Anonymous Referee #2

Received and published: 12 September 2019

Dear authors and editor,

I saw there were reviewer’s comments submitted in Aug 2019, which has been replied by the authors. However, to independently and subjectively review this paper, I did not read their comments and reply on purpose. I am sorry for the potential repeat of the comments with the other referee.

This paper, Technical Note: Improved mathematical representation of concentration-discharge relationships, presents an improved mathematical representation of the empirical relationships between discharge and ions concentrations (C-Q relationship). The core improvement is to modify the log-transformed relationship by the Box and

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Cox transformation. Although the topic is of great interest among multi-disciplinary groups, i.e. hydrology, biogeochemistry, agriculture, etc., there exist many pieces of critical confusion and missing information, including the scientific significance and rational, the quality of presentation and the potential impacts on the existing scientific study. Therefore, I do NOT recommend this manuscript to be published in this journal.

Major comments: 1. It seems that the abstract might require more work to gain attentions from potential audiences.

2. It is true that the C-Q relationship has been intensively studied for a very long time. However, the history and existing processes are not thoroughly reviewed in this manuscript. For exempling, in addition to the straightforward power-transformation of C-Q relationship (Eq. 1 in Ln 25), Moarar et al., 2017 proposed a segmented C-Q relationship to detect the change point in long-term C-Q relationships for different ions; Hirsch et al., 2010 and Zhang 2018 utilized Weighted Regressions on Time, Discharge and Season (WRTDS) models to analyze the nutrients export to rivers; Bieroza et al., 2019 evaluated the variations of slopes in C-Q relationships from low-frequency data. It is suggested to provide a more thorough review of current literature and the research gap.

3. There is a missing but critical part in the introduction: the scientific importance and rational of this study. Some questions need to be answered to proceed the manuscript, including: "What is the research gap?" "What is the research question in this area?" "What is the proposed method or approach to fill the gap and to address the research question?" "Why does the proposed method have the potential accordingly?" "What are the potential impacts and output that the proposed method will generate?"

4. It is very rare to see a figure in the introduction. Please justify the significant importance to include a figure here (Ln 36, Figure 1).

5. It might make more sense if section 2-5 to be re-organized. Some of the descrip-

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tion of log-transformed C-Q relationship needs to go to Introduction, and some of the materials need to re-organized as Materials and Methods. A considerable amount of materials needs to go to Results and Discussion.

6. Although this technical note focuses on the development of a method, it is still necessary to briefly introduce the dataset used in this note. It is acceptable to provide a brief summary and a citation to the dataset.

7. With all due respect, the reviewer did NOT see significant differences among $n = 3$ to $n \Rightarrow \infty$ in Figure 3 and Figure 4. Please first define what the optimal scenario is and then clearly indicate how to identify the optimal scenario, either visually or numerically.

8. For the multi-objective identification, the authors involved load in the statement. Generally, C-Q relationship only involves the flow (Q) and solute concentration (C). Some researchers also investigated the relationships between Q and load (Basu et al., 2010). Please clarify the definition of C-Q relationship in the manuscript. Please also justify the reason(s) to include load in this relationship.

9. The algorithms of multi-objective identification are not clear. The authors need to provide more narratives to explain why the average of two NSEB would help achieve the optimal goal considering multiple objectives.

10. It seems that the authors considered the two transformation methods as models. For instance, the authors used obs and cal to denote concentration in Eq. 4-8. In addition, the NSE is a widely used indicator to test the performances of numerical models. Please clarify if these transformations are treated as models or not. If so, please discuss the benefits and potential output of numerical modeling of C-Q relationships.

11. There are some potential improvements in the figures. A figure must be able to be interpreted independently without further information in the content or somewhere else. It is disappointing that nearly all the figures fail to meet this requirement. Examples include: The labels and extent of axis should not be removed (Figure 1-4); The

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units of flow and concentrations are very important (Figure 1-5); The denotation of symbols needs to be explained. For instance, what is the meaning of [Q] and [C] in Figure 2? The reviewer saw some people utilized [Ca²⁺] to indicate the concentration of Ca²⁺. However, the meaning of [Q] and [C] is very confusing.

12. The result section seems somehow weak. If the authors intended to prove that the proposed method performances better, it is required to also present the results for the existing log-transform methods. The editor, reviewers and audience can justify the performances and thus make conclusions. However, in this manuscript, only proposed method is presented.

13. For Figure 6, it is not easy to understand the objective of this figure. If the figure tries to quantify the performance of two-sided power transformation model, there are NO quantitative indicators to show the performances. Additionally, there is no demonstration of the data set for the audience to interpret the results.

14. Due the confusions and missing parts listed above, the conclusions could not be drawn according to the current version of manuscript.

15. It is suggested that the authors should review more publications regarding C-Q relationship.

16. The authors need to make it consistent with the terms used in this manuscript. For example, what are the differences between log-log transformation, power transformation, B-C transformation, logarithm transformation? It is quite difficult to understand so many similar but slightly different terms at different places.

Specific comments: Ln 15: what are the differences between log-log transformation and power transformation?

Ln 23: "... give an exhaustive view of the current work on this relationship...". Did the authors imply that there is NO research gap given the exhaustive research?

Ln 24: please explain what is "a one-sided power relationship".

Ln 26: generally, no equation is written in the introduction.

Ln 31-33: please discuss the reasons that might cause the differences in clear and unclear relationships for different ions.

Ln 33: please explain why the authors choose to use the data from Neal et al., 2013a and 2013b. Does this phenomenon only appear in their dataset? Or is this phenomenon widely reported by other studies?

Ln 41-42: “For many years, since the size of the C-Q datasets was limited by the cost of chemical analyses, it was difficult to analyze in much detail the precise shape of the C-Q relationship.” This statement is NOT correct. By comparing the C-Q relationships between a 3-year high-frequency data and weekly measurements, Duncan et al., 2017 reported that, “. . .The sensor data corresponding to the 3 years of data overlap (2013–2015) display essentially the same $\ln Q$ slope as the weekly $\ln Q$ data, even though the number of sensor data points is more than two orders of magnitude greater than the number of weekly points per year. “ The reviewer agree with the previous values of high-frequency measurements. However, the value of long-term, low-frequency dataset should also be recognized.

Ln 45: “. . .all the extremes of the relationship can now be included in the analysis.” In this case, please justify how the propose method, B-C transformation, could take the advantage of the appearances of extremes.

Ln 49-50: The statement of “. . . which provides . . .” is irrelevant. Please consider removing it.

Ln 53: please explain what is “RiverLab”.

Ln 53: “logarithm transformation” Please make it consistent with “log-log transformation”.

Ln 60-62: “. . .This slightly different shape may be due to the high frequency of the time series (Moatar and Meybeck, 2007) or to catchment dynamics (Kirchner, 2009),. . .” As

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this journal is Hydrology and Earth System Sciences, please discuss further how the hydrological processes, i.e. rainfall, runoff generation, infiltration, might influence the shape of C-Q relationship, for example chloride (Cl⁻).

Ln 64: please explain "...a continuous alternative...".

Ln 65: please explain the differences between "a progressive alternative" and "a continuous alternative".

Ln 71-73: it is suggested to put this section in Appendix.

Ln 74: please try to avoid using the term "clearly". The audience can be easily confused, as they don't share the same expertise and experiences with the authors.

Ln 79: "...Chloride ions concentrations measured on the Oracle-Orgeval observatory ("RiverLab")..." Repeated information with Ln 53. Please remove it.

Ln 82-83: "To our knowledge, there is no physical or mathematical reason why all ionic species should have a C-Q relationship of the same shape." Actually, there are physical reasons that all ionic species should NOT have a C-Q relationship of the same shape, because the hydro-biogeochemical processes that control the transport and reaction of ions are different. For example, chloride (Cl⁻) is mostly treated as a non-reactive ion, which indicates that the hydrological processes are the critical factors for C-Q relationship. In contrast, nitrate (NO₃) is highly soluble and reactive, which means the interactions of all the hydro-biogeochemical processes control the C-Q relationships.

Ln 83: "...and EC (Electrical conductivity)..." should be "... and Electrical Conductivity (EC)..."

Ln 85-86: "...but we first followed the advice of Box et al. (2016, p. 331) and did it visually." Please clarify how to visually identify the optimal shape.

Ln 86-87: "Figure 4 shows the most adapted power transformation..." Please clarify what a power transformation is.

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Ln 97-103: it seems that the optimal shape was identified based on the greatest value of R2. Please include this information in the content and discuss why the greatest R2 will help identify the best shape.

Ln 108-110: it is very confusing. The reviewer has some difficulties to understand this part.

Ln 104-146: The whole multi-objective identification section is not well-organized and the reviewer has some difficulties to understand it. Please consider re-organized it and clearly state the objective of this section.

Ln 150: “..the entire calibration dataset. . .” If the transformation is treated as a model, please separate the whole dataset independently into calibration and validation sub-dataset. And then report the numerical indicators (i.e. R2) for both calibration and validation sub-dataset.

Ln 150-151: Given the obvious and intensive noise in the scatter-plot for each ion in Figure 6, the statement of “..fit very well..” is quite questionable.

Ln 151-152: “On can only mention. . .” Please double check the language.

Ln 164-165: “The two-sided power transformation we proposed is a valid and progressive alternative” The current results and discussion cannot support this statement.

Ln 167-168: “The simulated concentrations for the 3 ions and the EC show a good performance.” Further evaluation of model performances is required to draw this conclusion.

References

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