

Referee comment #2

We thank the second referee for his constructive, useful and detailed comments and suggestions to our manuscript. Below, we reply to his questions and suggestions in detail.

Critical review of the paper's discussion on solute synchronies and end-member mixing

Introduction: The paper aims to determine the minimum number of end-members required to explain the variation of stream water solute concentrations during storm events based on the synchronous or asynchronous behaviour of different solute pairs. The authors propose a novel methodology that uses high-frequency solute synchronies to identify simple two-end-member mixing scenarios and more complex higher-order mixing scenarios. They apply this methodology to two French catchments with contrasting characteristics and analyse several major ion pairs on the event scale.

Event-scale concentration-concentration pattern: The authors present the results of their methodology for each catchment and each solute pair, using concentration-concentration plots and histograms of the slope and intercept of the linear regression between the solute concentrations. They classify the events into three categories: (1) events that can be explained by a simple two-end-member mixing model; (2) events that require a higher-order end-member mixing model; and (3) events that show no clear pattern or relationship between the solute concentrations. They discuss the possible causes and implications of these categories, such as the influence of precipitation amount and intensity, the spatial variability of solute sources and flow paths, the occurrence of biogeochemical processes, and the uncertainty of the end-member composition.

Strengths and weaknesses: The paper's discussion on the solute synchronies and end-member mixing is comprehensive and informative, as it provides a detailed description and interpretation of the results for each catchment and each solute pair. The authors also acknowledge the limitations and uncertainties of their methodology and data and suggest ways to improve them in future studies. However, the paper's discussion could be improved by comparing and contrasting the results with results obtained using EMMA.

We are pleased to hear that the reviewer finds our discussion comprehensive and informative. Concerning his last suggestion, we would like to highlight, that the objective of this manuscript and the presented methodology is to determine the minimum number of end-members that is required to explain the variation of a certain solute pair and not to identify the end-members and their chemical signature. The methodology we propose here can provide information to conduct an EMMA, particularly an inverse EMMA.

We have now tried to clarify this complementarity and possible link with the inverse EMMA in section 4.4.

Conclusion: The paper's discussion on solute synchronies and end-member mixing is a valuable contribution to the field of catchment hydrochemistry, as it introduces a new methodology that can help identify the minimum number of end-members and the hydro-biogeochemical processes that affect the stream water solute concentrations during storm events. However, the paper could benefit from a more extensive comparison with other studies that have addressed similar research questions in order to provide a broader perspective and context for the results and implications. A good example of current views on this topic is CHEMMA (Convex-Hull End-Member Mixing Analysis).

We now mentioned the use of CHEMMA in the introduction (Fei & Harman, 2022, HESS) and elaborate a bit further, what the “forward” and “inverse” EMMA and the CHEMMA can and cannot do. This leads to the introduction of our proposed methodology.

In the discussion, we re-take the main differences of the EMMA/CHEMMA on the one hand and our proposed methodology on the other hand and highlight what our methodology can add.

Minor revisions:

Given that both PCA in EMMA and the proposed methodology operate under the same assumptions of conservation of mass and non-reactivity of solutes and both interpret variance in solute concentrations as evidence of hydrodynamic mixing, could the authors elaborate on the unique contributions of their proposed methodology? Specifically, while PCA in EMMA not only identifies end members but also provides information about the main solutes contributing to each end member through the loadings of the principal components, it is not immediately clear what additional insights the proposed methodology offers. Could the authors provide further justification for the introduction of this new method?

The uniqueness of our proposed methodology is, that it does not require any prior assumptions, but that it is purely based on simple observations. In fact, the methodology does not necessarily require assumptions about conservation of mass or non-reactivity. To provide an example, first-order reactions also lead to a linear relationship on a concentration-concentration plot with two end-members. In addition, the proposed methodology does not require any prior knowledge about the catchment or additional measurements.

The PCA analysis, in contrast, requires a pre-selection of the variables, which are used in the PCA (in terms of the number and identity of the variables used). Choosing the right number of (conservative) variables to be used in the PCA can be challenging and can have an impact on the outcome (Barthold et al., 2011, Water Resours. Res.)

We have now strengthened this point in the introduction and the discussion.

In the figure 2 caption, it should just be mentioned that the colours of the data points correspond to different consecutive flood events.

We have now explained in the figure 2 caption, that the coloured data points are referring to individual measurement points.

The intext reference in line 200 showed an error.

Ok. Corrected.

I would suggest performing a PCA on the data in order to see if these interpretations discussed about solute behaviour makes sense in terms of the covariance of parameters.

We could perform a PCA with the four synchronous solutes at Kervidy-Naizin (Cl, Na, Mg, NO3), for example, to see if two end-members are sufficient even if all four solutes are taken together. However, we do not think that this would improve the understanding of our proposed methodology, but would rather make the manuscript more complex.

Instead, we now included in a paragraph about further extensions of this methodology (section 4.4.), that a PCA could be conducted on the synchronous ions to verify, if all synchronous solutes together also only require two end-members.

Suggestions

This technique is only relevant in specific cases of streamflow generation since it is based on the premise that there are only two end members, which is only true when the water sources are near the stream.

As mentioned above, the presented methodology is not based on any premises and does not require any prior assumptions, which is the main advantage of this methodology. As such, it can be applied to any case. Once the methodology is applied to a certain dataset, conclusions can be drawn about the minimum number of end-members required for a certain solute pair. A two end-member system, therefore, is not a requirement but the conclusion of the applied methodology.

We have now highlighted this point in the discussion, section 4.4.

The technique does not account for variance in the pre-event end member, which will most likely change as the system wets up and flowlines extend further away from the stream.

We agree with the referee, that in the currently presented form, the proposed methodology does not address the inter-event variance of the pre-event end-member explicitly, which could be easily added. However, fig. 4 hints at this variance, by showing the inter-event variances of the initial and peak molar ratios (red and green boxplots). In addition, this figure indicates whether the initial and peak molar ratios differ between each other despite their inter-event variance (grey boxplot).

However, analysing the variance of the pre-event end-member, as a function of time, season, hydrological conditions etc. are viable extensions of the proposed methodology. We have now added this potential extension in section 4.4.

Sensitivity of the classification:

Choice of Threshold: To address the arbitrariness of the threshold, the authors could conduct a sensitivity analysis. This would involve varying the threshold and observing how the classification results change. This could provide a more robust justification for the chosen threshold or suggest a different optimal value.

This is a good idea, which we covered to some degree, by presenting in table 1 the ranking for two different thresholds ($R^2 > 0.8$ or $R^2 > 0.9$). The table indicates that changing the threshold slightly would not change the classification of the variables.

This threshold is only used approximatively. As outlined in the discussion, other thresholds can be used, with a trade-off between the precision of the measurements (lower precisions requiring a lower threshold) and the ability to detect small contributions of a third end-member (requiring a higher threshold).

The thresholds used in this methodology therefore depend on the precision of the measurements and the willingness (or not) to detect (very) small contributions of a third end-member. We therefore think that the determination of the threshold values is best done manually by visually inspecting the measurement noise, for example.

Non-linearity: To account for non-linearity, the authors could consider using non-linear regression models or machine learning techniques that can capture complex relationships in the data. This would allow them to classify solute variations without assuming linearity.

The linearity is a central part of this methodology, because it is a consequence of a two end-member system. The methodology does not assume linearity. It allows to observe linearity and to draw conclusions about the number of required end-members.

It certainly would be possible to characterize the non-linear relationships in more detail. However, we do not think that this would add further information about the end-members or the catchment processes. We, therefore, do not address this point in the manuscript.

Overlap of Classification Types: To address the overlap of classification types, the authors could consider using a probabilistic classification scheme. Instead of assigning each solute to a single category, they could assign probabilities to each category, reflecting the degree of certainty in the classification. This would acknowledge the complexity of the system and the potential for solutes to exhibit characteristics of multiple categories.

This is an interesting idea. We would like to highlight, though, that the “invariant” category is based on individual solutes, whereas the “synchronous” and “complex” variation categories are based on pairs of solutes. Strictly speaking, we, therefore, cannot create a probabilistic classification scheme for each solute, but rather for solute pairs.

We now included in the SI a table (all 7 solutes in 7 rows and 7 columns), indicating for each pair the percentage of synchronous, complex and invariant relationships.

Case of Ca²⁺/Mg²⁺: For cases like Ca²⁺ and Mg²⁺, where there is evidence of synchronous variation but the relative variation is low, the authors could consider creating a separate category or sub-category. This would allow them to acknowledge the synchronous variation without contradicting their classification criteria.

This is a good idea. However, instead of creating sub-categories, we now consider ranking the relationships. Firstly, invariant solutes are removed from further analyses, because they do not provide additional information. Secondly, the remaining solutes are divided into synchronous or complex relationships based on solute pairs.

We now mention that point in section 4.3.1.

Meybeck and Moatar (2012) proposed a method for segmenting c Q curves based on the stream's median flow (q50), resulting in nine distinct c Q modalities. This method can be used to subset the chemistry data to find solute pairs that exhibit this synchronous behaviour. I am primarily interested in how the linear regression line was fitted to the data. There seem to be inflection points in the data suggesting a switching of the dominance of one end member over another. I believe fitting only one regression line may not be the best way to go about it.

This is an interesting point, which we investigated as well. One possibility, for example, is to separate the chemical variation during the rising discharge limb from the variation during the falling limb and evaluate the linearity for each part separately. We decided not to include this separation due to the clarity of the manuscript and due to the fact that it is not possible to synchronize the chemistry and discharge time series.

However, we added a paragraph in the discussion about potential extensions of the methodology (separating into rising and falling limb; varying the thresholds used; variability of the pre-event end-member etc.).

To answer the question of the referee, for each storm event and solute pair, we used the function `lm()` in R studio to calculate and `summary()` to extract the coefficient of determination. We added this information in the material and methods section, section 2.4.1.

“In addition, our methodology does not require the a priori assumption of conservative solutes, as it is required in the EMMA approach (Christophersen et al., 1990).” I do not completely agree with this statement. The interpretation of two end-members by looking at the co-variance of solutes very much relies on the fact that no chemical reaction takes place.

We try to explain this point in more detail: The methodology evaluates the existence of a linear relationship on a concentration-concentration plot. If a linear relationship exists, it can be concluded that only a two end-member system is required. This is independent of whether chemical reactions take place or not, because a linear relationship of a two end-member system is observed, even if first-order reactions take place ($C_{ion\ i,stream} = C_{ion\ i,end-member} \times k$; $k =$ reaction constant). Therefore, this methodology does not make prior assumptions about the conservativeness of the solutes. However, higher order reactions in a two end-member system lead to non-linear bivariate concentration relationships. The referee is right, though, that we interpret the results of the synchronous solutes as if they were conservative. We therefore extend the sentence by adding that we implicitly assume a conservative behaviour of the synchronous solutes for the interpretation of the results.

Adding c Q graphs of the solutes discussed will help to link this work to current work revisiting this concept. It will also give the reader a better conceptual feel of what is going on (flushing or chemostatic behaviour, for instance).

Due to the variable and unknown transfer time of the water to the analytical instrument, it is, unfortunately, not possible to synchronize the discharge with the ion concentration data. It is therefore not possible to plot accurate c-Q plots.

It would be interesting to see pH also added to the time series data.

Similar to our previous reply, the pH and ion concentration data cannot be synchronized easily and accurately. It is therefore difficult to add the pH data to the concentration time series.