Response to Referee #1

Xu Fei and Harman present a method to extend classical end-member mixing analysis by deriving end-members purely based on stream concentrations. By repeatedly delineating the convex-hull around stream concentrations and then classifying results using a k-means clustering approach the method includes an uncertainty assessment of the resulting end-members. The method is successfully applied to the Panola Mountain Research Watershed data.

I consider the outlined method a valuable addition to the end-member mixing literature and recommend publication in HESS after revisions are made that are outlined below. I must admit I am not a math expert and have not checked the given formulae.

Thank you for your concise summary and encouraging comment. We aim to provide a method that is both well-established in mathematical foundations and easy to understand for the general hydrology community. We have adopted some of your comments to improve the readability, particularly in the method section.

Current application of end-member mixing approaches involves the disentangling of stream water concentrations based on pre-conceived 'end-members', or origins of stream water. These end- members are sampled, and hopefully span the spread of stream water concentrations, thus enabling the calculation of flow route proportions. Xu Fei and Harman propose a method that calculates possible end-member concentrations from stream water alone. While this can indeed be very useful in practice, it also defies the purpose of an end-member mixing analysis to some extent: as a hydrologist, we are interested in where the water comes from that makes up the stream, not in its concentrations per se. I am sure the authors agree here, but I miss more discussion in the manuscript on the practical use of the proposed method in a hydrological analysis. Given the end-goal of finding water sources instead of end-member concentrations, where does their method come into play? As a first step, defining possible concentration profiles of end-members, after which you take to the field to 'find' these end-members? Or as a check of a more classical end-member mixing application: are end-members missed? Or vice-versa, as the proposed approach cannot handle end-members that are located outside the convex-hull of stream water concentrations.

We appreciate your suggestion in discussing practical applications of CHEMMA. In the revision, we also adopted the comment from Referee #2 and added a paragraph after l200:

"*For most hydrologists, end-member analysis is used to identify the water sources, and toward that purpose CHEMMA may be useful in the following ways: 1. CHEMMA may be used to reduce subjectivity when selecting from field-measured end-member candidates by comparing them to CHEMMA end-members; 2. CHEMMA may identify end-members that have not been sampled in the field, which may serve as a check for missing sources; 3. CHEMMA end-member compositions may help hydrologists ask better questions and provide guidance for field sampling by suggesting source characteristics; 4. CHEMMA can be used in conjunction with the Diagnostic Tool of Mixing Models (DTMM, developed by Hooper (2003)). DTMM is used to assess the tracer conservation, and mixture rank. CHEMMA can be enhanced by using DTMM analysis to select conserved tracers for analysis. The robustness of CHEMMA end-members also serve as a check for DTMM-determined rank of mixture.*"

Further, I would encourage the authors to provide more discussion of the uncertainty calculation of their method (how certain is the calculation of the convex hull), and how it relates to uncertainty in end-member mixing applications (how clearly defined is a single end-member, how time-variant is its concentration). On l197 you allude to some work you did on

this, but this did not make it to the manuscript?

Overall, the manuscript would benefit from a thorough spelling and grammar check.

Thank you for your suggestion. The uncertainty analysis within this technical note is limited to discuss the general intrinsic uncertainty introduced by the CH-NMF algorithm. However, much more work is required to dissect the total uncertainty arising from factors like the time-variability of the end-members and the algorithm's response to data uncertainty. We believe this is beyond the scope of a Technical Note introducing the approach. Therefore, we have decided to leave detailed analysis regarding uncertainty in practical applications for future work.

Minor comments:

l35: and each of which accounts. What which? You are referring to the columns of Y? Why not just speak of the principal components?

Thank you for pointing out this. "which" refers to Y_{obs}, which is the observation matrix projected onto the principal component space. The principal components are the rows of the projection matrix P.

l45: refer to diagnostic tools of (Hooper, 2003), as they propose a more formal analysis to assess the rank of the data. Hooper also finds evidence of a fourth end-member by the way… see around l173

Thank you for highlighting this. Hooper did not explicitly identify the composition of the fourth end-member (Hooper, 2003). We have edited the manuscript to reflect his speculation on its existence by adding the following sentence at l172:

"Hooper (2003) also suggested the existence of a fourth end-member."

l46: After thus subjectively determining the number of… Not sure what the purpose of this entire sentence is by the way, seems like it could be skipped altogether.

Here we intended to differentiate the rank of mixture idea from EMMA with the mathematically defined rank *d* (refer to comment l91) from CHEMMA.

l50: also: spatial and temporal variability in end-member concentrations

Thank you for the suggestion. We have added a fourth point to address this comment:

"4) uncertainties introduced by spatial and temporal variability in end-member concentrations cause extra difficulties."

l86: Only the top k PCs are retained? So while you criticize this subjectivity in lines 45-47, your method necessitates the same step? Please elaborate on this.

Thank you for identifying this confusion. We have added a sentence in the manuscript to acknowledge that the subjective selection of the number of end-members is not completely resolved by the proposed method:

"*The CHEMMA algorithm does not entirely avoid this subjective choice of the number of end-members retained, and so does not resolve this criticism of EMMA.*"

l87: Is there a reason why the analysis must be performed successively in 2D, and not in ND?

Thank you for noticing this technical detail. The search of finding the convex-hull is done in *all* 2D PC projections, not necessarily successive and limited to k retained PCs. The 2D search is a way to subsampling the vertices set and it gives the most "greedy" search result because one needs at least 2D to draw lines/planes (or other linear structures in higher dimension) and to find the linear intersections (candidate end-members) that bound the observation. In addition, searching in 2D subspaces not only preserves detailed structure of the convex hull for further simplification, but also is efficient in terms of computation cost (Thural et al., 2011). We currently have not added a detailed explanation of this into the manuscript but the issue is addressed in the literature cited (de Berg et al, 2000) .

l91: algorithm: also define k and d. And: how are they different?

Thank you. d is the rank of the observation covariance matrix, as defined in Step 2 of Algorithm 1, whereas k is the number of eigenvectors to retain (which is stated in l86 as last comment shown). We have added "where" before the definition of d to make it stand out more. We have also changed sentence a) at l93 to *"CH-NMF decomposes the correlation matrix of the observations to obtain at most d PCs (d is the maximum number of linearly uncorrelated variables)"*.

l123: This is quite a central drawback of the method. Can some directions/ideas already be given? Maybe a hybrid between chemma and field sampling for em signatures? Using the time-variance might also provide a way forward, searching for periods where certain end-members dominate and are thus better characterized from stream water concentrations.

Thank you for this insightful comment. It is certainly true that any method that relies exclusively on the stream water samples will face this challenge. We have shortly discussed this drawback both in the new added paragraph in l200 (in response to one of the above comments) and in the discussion part of the manuscript (l202 - l205). We have added a couple of sentences to address these suggestions in the discussion section.

After modified l199: "*The temporal end-member dominance may further deepen our understanding of stream water characterization.*"

After l206: "*4) using individual field end-member measurements to inform CHEMMA.*"

l144: Elaborate on 'uncertainty' versus spread of local minima of convex hull. are these really the same thing?

Thank you for your suggestion. Total uncertainty includes uncertainty due to the spread of local minima of convex hull as well as uncertainty due to sampling. Here we only examine the uncertainty arises from the algorithm. The complete examination of uncertainty is left for further work.

l149: What is a 'reasonable' variance? Is there a suitable metric? Provide guidance.

Thank you for this valuable comment. We have not identified a suitable metric at the stage. The current "reasonable" variance remains a subjective choice. We acknowledge the subjective here and we have modified the sentence in l202 from "*optimize the model complexity*" to "*eliminate the subjective choice of k*" for clarity.

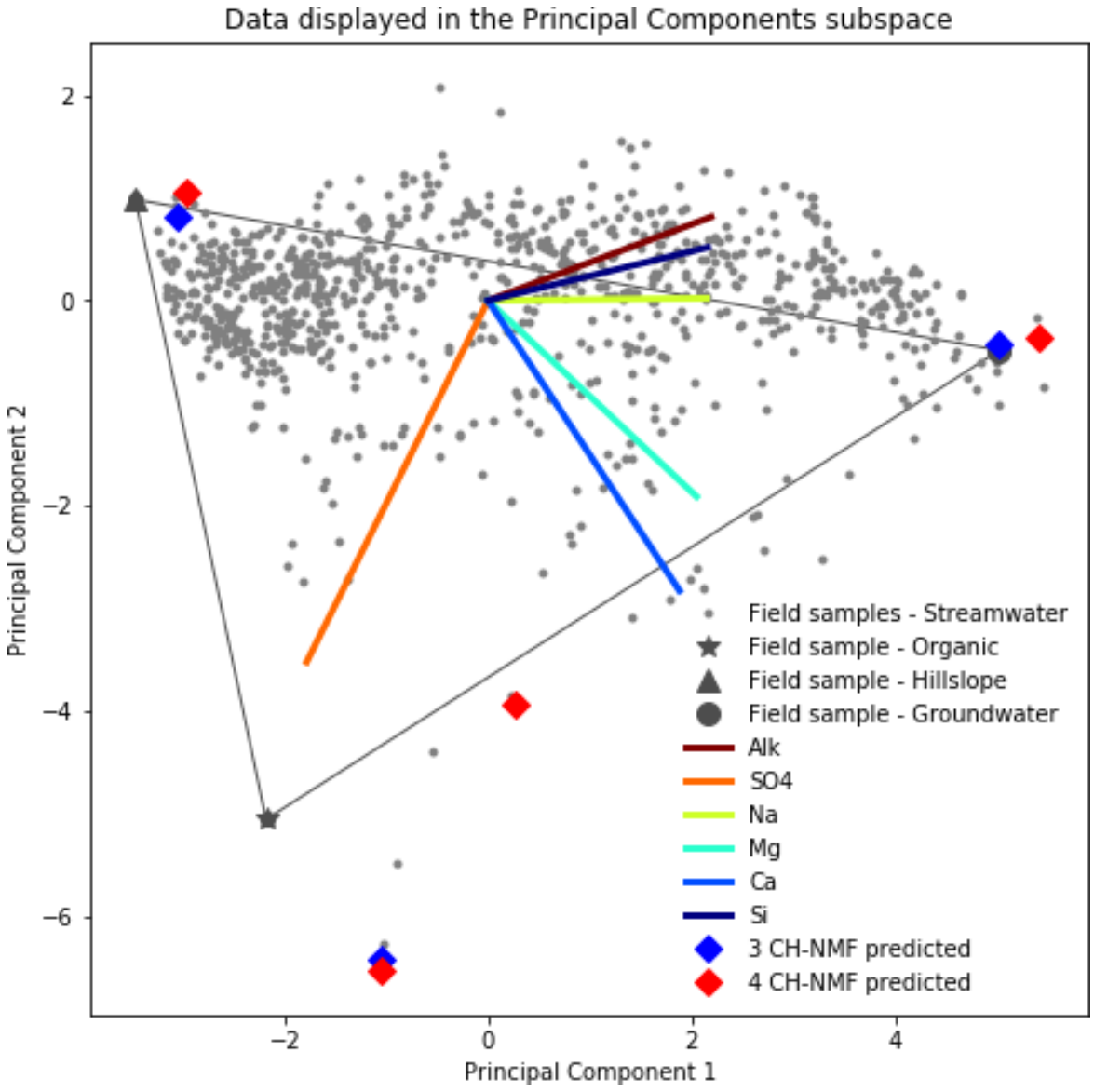
l197: “Fortunately, CHEMMA itself provides a tool for exploring some of these sources of uncertainty. By partitioning the dataset into time periods (or hydrologic state, etc), the temporal variability of end-members could be explored” What is this statement based on?

Thank you. This statement is intended to provide suggestion for ways to explore temporal variability. We have modified the sentence to clarify the intent:

“CHEMMA itself may provide a tool for exploring some of these sources of uncertainty. For example, by partitioning the dataset into time periods (or hydrologic state, etc), the temporal variability of end-members could be explored.”

On the python code:

Consider making your code available as an importable python module through pip and/or conda. Why is Figure 2 different on github code? location 4th endmember? accessed 1/7/2020:



References

Hooper, R. P. (2003). Diagnostic tools for mixing models of stream water chemistry. *Water*

Resources Research, *39*(3), 1–13. https://doi.org/10.1029/2002WR001528

Thank you for your suggestion. We will make a python module in the near future.

In the technical note, Figure 2 is made by using the centroids of the clusters from Figure 3 a and b. The Python code only shows one run of CH-NMF and what you saw is the algorithm find another 4th end-member in the space. By repeatedly run the CH-NMF and using the COP-Kmeans to classify the clusters, this occasional capture of "wrong" convex-hull vertex can be eliminated.

We will add a section in the Jupyter notebook to reproduce Figure 2.

Thank you for your careful reading. We have adopted the following grammatic comments.

l11: streamwater

l30: concentrations: what you mean is the concentration of different solutes are correlated

l33: dividing by the standard deviation. It doesn't require it per se, but yields better results

l34: transforms ~~the~~ from ~~the~~ observation space to ~~the~~ PC space

l55: In spite of EMMA's wide applications~~s~~

l81: to ~~the~~ end-member mixing

l89: "convex-hull": why here in quotes? This term has been used throughout the manuscript. Move its definition to its first use.

References

Christophersen, N., & Hooper, R. P. (1992). Multivariate analysis of stream water chemical data: The use of principal components analysis for the end-member mixing problem. Water Resources Research, 28(1), 99-107.

de Berg M, van Kreveld M, Overmars M, Schwarzkopf O (2000) Computational geometry. Springer, Berlin, Heidelberg

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