Referee #2

When I read the manuscript on the first time, I was thrilled, as this is something I have been waiting for many years to come out. If we could determine the chemical composition of end-members using streamflow chemistry alone, end-member mixing analysis would be significantly improved and revived. After I read it for a couple of times, I found the fundamental idea is still intriguing, but the assumptions the main method, namely CHEMMA, is based on may be flawed and cause significant uncertainties on the modeling results. A conceptual set-up of why and how this modeling would work could be strengthened. Readability could be improved as well, particularly in regard to some mathematical details and their connection/implication with/in the hydrologic questions being investigated. Remember that most of readers who are interested in this study are hydrologists not mathematicians.

Thank you for recognizing the value of our work and providing suggestions on improving the quality of this manuscript. We will improve the readability in methodology section to strengthen the conceptual set-up.

Major Comments:

The main approach is to use Convex-Hull Non-negative Matrix Factorization (CH-NMF) to infer possible end-member compositions by searching for a simplex that optimally encloses the stream water observations. The assumption for this is, based on authors, that end-members are located near the most extreme points that bound the observations in "mixing" space. From this assumption, it is clear that a simplex is basically determined by the data structure of observations, in other words, the shape of the sample cloud. What if one or more extreme points are missing in our observations? This could happen if samples are collected sparsely or only on certain hydrologic conditions/seasons that do not contain extreme samples (samples with extreme concentrations for at least one solute). The number of samples could also change how samples are distributed. With the same data set, can similar results (with reasonable uncertainties) be obtained from subsets of samples with varying number of samples that are randomly selected?

Thank you for your insightful comment. This is indeed a drawback, and we have mentioned briefly in the manuscript that CHEMMA can only identify end-members that are well-sampled in the data. We will expand on this point in the revised manuscript by highlighting this issue in both abstract and introduction. We acknowledge that some of the fundamental assumptions could limit the CHEMMA application. Improvements that overcome these limitations are left in future work.

There is a lack of conceptual setup where this study came from and where it goes in relation to existing tools in EMMA, particularly the diagnostic tools of mixing models (DTMM; Hooper, WRR, 2003). In one study, Christopherson and Hooper (WRR, 1992) specifically concluded that “Unambiguous identification of the source solution compositions from the mixture alone is impossible; thus, it is necessary that potential source solutions be derived from independent measurements.” I do not mean this conclusion cannot be challenged, but the rationale must be stated clearly and explicitly, possibly using a conceptual set-up. Also, what is its relation with DTMM? Will the current study be supplemental or a substitute to DTMM in regard to the number of end-members? Can DTMM actually help to enhance CHEMMA and how?

The study used data collected in late 1980s. That is okay but what I am concerned is about the conservativity of all six solutes. How can we be convinced if all six solutes are conservative? If any of those is not conservative, the results of CHEMMA would be different. In my opinion, this is where DTMM may be able to help. Also, isn’t it interesting to compare the number of end-members acquired using CHEMMA to DTMM?

We appreciate your suggestion on improving the understanding of practicing CHEMMA. We agree that the conceptual set-up is not clearly stated in the paper. In the revision, we will modify the last paragraph of the introduction (l55 – l65). We have added a sentence in l65 to clarify the conceptual setup:

"Christophersen and Hooper (1992) suggested that "[u]nambiguous identification of the source solution compositions from the mixture alone is impossible". In a strict sense this is likely true, since the underlying assumption (streamflow as a conservative mixture of invariant sources) is unlikely to be adhered to in a real watershed. However, we believe there may be utility in developing tools that can seek some insights (perhaps not free of ambiguity) into the potential source solution composition from the observed mixture. We propose CHEMMA as an attempt to push this boundary and to see how far we can get."

As we said to Referee #1's comment, we have added a paragraph after l200, and discussed DTMM in point 4:

"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."

Minor Comments:

L18: Before the first reference, add "e.g.,". Many classical references on EMMA were not actually cited.

Thank you for this suggestion. We have added "e.g.", and also added two new references mentioned in your comment (Liu et al., 2008 and 2017) as applications of EMMA under different climatic settings.

L24: This statement should refer to conservative solutes.

Thank you for bringing up this confusion. We added a word "solute" between "chemical composition" to clarify that the sentence is talking about solute conservation.

L30: "Streamwater concentration are naturally correlated." It is true if you refer to conservative solutes; otherwise it is an ill statement. Use two words "stream water" instead of one word "streamwater". Also, use plural for "concentration".

Thank you for your suggestion. We changed "streamwater" to "stream water" for this manuscript. We also adopted Referee #1's suggestion and changed this sentence to:

"Stream water concentrations of different conservative solutes tend to be correlated."

L28: The second one is no longer a hypothesis or assumption because of the diagnostic tools of mixing models by Hooper (2003); See Liu et al. (WRR, 2008) for a demonstration and how this was addressed.

L45: True traditionally but not after DTMM is developed. See Liu et al. (WRR, 2008, 2017) as examples.

L51-52: Not true with DTMM.

L52-53: True but DTMM can help identify conservative solutes so that users can use only conservative ones. I mention this because I think your study is also based on mixing of conservative solutes. This should be stated/defined earlier in your text.

L186-206: Need to indicate where this modeling will lead to and how it may work together with DTMM.

We would like to response to these five comments collectively. Thank you for your recommendation about DTMM and related application papers. We agree that DTMM workflow is a good complement to both EMMA and CHEMMA. And we added a paragraph to clarify how DTMM and CHEMMA can potentially work together. Please refer to the response to the last major comment above for more details.

L33-35: Multiple issues here. (1) Is Pobs actually eigenvectors? If so, use a parenthesis to annotate so; otherwise explain what it is and how to calculate it. (2) Get rid of the redundant “the”. (3) My understanding is that once a standardized data set is used, a correlation matrix is decomposed rather than covariance matrix. Check if this is correct.

Thank you for carefully checking the mathematical details. The rows of P_{obs} are the eigenvectors of the correlation/covariance matrix X_{obs}. We have added a parenthesis segment: *(rows of which are eigenvectors of the correlation matrix)*, and we have deleted the redundant “the” appearing later. Because X_{obs} is standardized observation, the correlation matrix and the covariance matrix are essential the same. Performing eigendecomposition on both matrices yields the same results. We have adopted your comment to change the covariance matrix to correlation matrix to make it clear.

L36: If P are indeed eigenvectors, cite Christopherson and Hooper (1992) for the equation.

Thank you. P are eigenvectors. We have cited Christophersen and Hooper (1992).

Result 2: Eigenvectors and PCs are different. PCs are calculated based on eigenvectors and observed concentrations.

Thank you. We adopted a terminology in this manuscript consistent with usage in applied mathematics literature, such as Jolliffe (2002). In our understanding, eigenvectors are derived from the correlation matrix of the observed concentrations by performing eigendecomposition (as used for this manuscript) or singular value decomposition. Resulting eigenvectors are orthogonal bases as known as Principal Components (PCs) (Jolliffe, 2002). Loadings are the coefficient calculated based on eigenvectors (PCs) and observed concentrations (Jolliffe, 2002), and are referred as contributions (of end-members) in this manuscript.

L93: I still think it is correlation matrix not covariance matrix. Also, what you mean here is eigenvectors not PCs.

Thank you. As we responded before, in the revised manuscript we have changed covariance matrix to correlation matrix for clarity. We used eigenvectors and PCs

interchangeably according to our reference of PCA terminology (Jolliffe, 2002).

Result 3: Is it specified anywhere how to project mathematically?

Thank you for finding this confusing part. Projecting a matrix A to another space through a projection matrix P^T to get projected matrix B is defined as $B = AP^T$, just as Equation 1 and 2 show. We added a parenthesis fragment: *(similar form as Eqn. 1 & 2).*

Result 4: Will the dimension of S differs from one projection plane to another?

Thank you for noticing this technical detail. Yes. S records all boundary points in each projection plane and the number of recorded points at each plane can be different.

Result 5: Is X expression actually [[xem1], [xem2], . . ., [xemk]], as each xemi has a dimension of n by 1?

Thank you for noticing the dimension consistency. Yes, x_{emi} has dimension of n by 1. We have checked the consistency of dimensions in Algorithm 1 a couple of time before submitted the manuscript.

L125: I think "equifinality" is part of your talking here. Why not citing "equifinality" directly? It is a common term that hydrologists are very familiar with.

Thank you for your comment. The concept here is slightly different from equifinality. This paragraph particularly talked about limitation of an optimization problem on minimizing the objective function in Step/Result 5.

Thank you for pointing out style problems. We have adopted the following comments.

L31: Need at least one reference (e.g., Christopherson and Hooper, 1992).

L41-42: Cite Hooper (WRR, 2003).

L60: Need to specify "extreme points". I think you refer to "extreme points of stream water samples".

L64: I think you mean "end-members' composition".

L94: Spell out PCA as it appears for the first time.

L102: Specify the constraints, each between 0 and 1 with sum of all to be 1.

References

Liu, F., Bales, R. C., Conklin, M. H., & Conrad, M. E. (2008). Streamflow generation from snowmelt in semi-arid, seasonally snow-covered, forested catchments, Valles

Caldera, New Mexico. Water Resources Research, 44(12).

Liu, F., Conklin, M. H., & Shaw, G. D. (2017). Insights into hydrologic and hydrochemical processes based on concentration-discharge and end-member mixing analyses in the mid-Merced River Basin, Sierra Nevada, California. Water Resources Research, 53(1), 832-850.

Jolliffe, I. T. (2002). Mathematical and Statistical Properties of Population Principal Components. In Principal Component Analysis (pp. 8-22). Springer, New York, NY. https://doi.org/10.1007/b98835