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Interactive Comment

Interactive comment on "Hydrochemical analysis of stream water in a tropical, mountainous headwater catchment in northern Thailand" by C. Hugenschmidt et al.

Anonymous Referee #2

Received and published: 26 April 2010

General comments

- 1) Does the paper address relevant scientific questions within the scope of HESS? YES
- 2) Does the paper present novel concepts, ideas, tools, or data? NO.
- 3) Are substantial conclusions reached? NO. The overall sampling strategy (number of events sampled, selection of end-members, sample size of end-members) precludes substantial conclusions.
- 4) Are the scientific methods and assumptions valid and clearly outlined? NO.

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- 5) Are the results sufficient to support the interpretations and conclusions? NO, see specific comments
- 6) Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists? NO.
- 7) Do the authors give proper credit to related work and clearly indicate their own new/original contribution? YES.
- 8) Does the title clearly reflect the contents of the paper? NO. The title is completely misleading. It should read: An EMMA approach to deduce flowpaths in a headwater catchment in northern Thailand.
- 9) Does the abstract provide a concise and complete summary? YES.
- 10) Is the overall presentation well structured and clear? BARELY.
- 11) Is the language fluent and precise? NO.
- 12) Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? YES.
- 13) Should any parts of the paper be clarified, reduced, combined, or eliminated? N/A
- 14) Are the number and quality of references appropriate? YES.

Specific comments

How much information is needed to infer a catchment's hydrological functioning from its hydrochemical behaviour? If EMMA is the tool of choice, this question can be refined:

1) How many events should be sampled?

The authors based their conclusions on three events spread over two years. While this number may seem low, you can go lower and still get published: Grimaldi et al., 2004, got away with just one event, as implied by the title Behaviour of chemical solutes during a storm in a rainforested headwater catchment Hydrological Processes, 18, 93-

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106. Burns et al., 2001, derived flowpaths from the study of two events in Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA), Hydrological Processes, 15, 1903-1924. And so forth While the soundness of n=1 as the basis for hydrological inferences is debatable, it is obvious that the number of events per se is no indicator of quality. What several studies, including the ones listed above, with a low number of events share is ancillary hydrometric information to shore up the plausibility of hydrochemistry-based inferences. Unfortunately, this study is not among those: There is no information on soil moisture variations, or on soil water potentials, or on groundwater levels.

2) Which end members should be sampled?

In the absence of prior information, the extensive literature on EMMA provides reliable guidelines. Whatever the choice of end members is based on, it must be justified, and so does the omission of plausible potential end members. This study fails miserably in this respect: There is no rationale for either the selection or the omissions. In particular, ignoring that substantial source of water that goes by the name of soil water requires some in-depth explaining, as does the choice of surface runoff as an end member. Surface runoff may have a unique chemical signature if it is truly generated at the soil surface, but the authors do not provide pertinent information about infiltrability or permeability. In the absence of such information, it is more plausible to assume that surface runoff also bears a soil water imprint than to assume its chemical composition is unique. Similar arguments apply to the choice of interflow (strange terminology: why not throughflow, given the depth at which this process occurs?).

3) At how many sites should end members be sampled?

Unless a selected end member serves as a spatial integrator and as a proxy for a 'true' end member, such as baseflow instead of groundwater, the spatial variability of end member chemical composition must be accounted for by a sampling design that allows

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for the estimation of the spatial mean. Therefore, monitoring interflow and surface flow at just one site each (actually, the exact sampling locations are not even given) is hopelessly inadequate. In this sense, Fig. 7 is misleading and reflects the authors' misunderstanding of what EMMA is about. The end member 'BF' cannot possibly be uncertain: it is the chemical composition of just the one stream sample collected before it began to rain. The uncertainty attached to SF and IF is misleading at best because it does not represent the variability of these end members, given n=1.

4) How to compute end member contributions Regardless of the inadequate and unsubstantiated selection of end members, the final conclusions are based on two tracers — Si and EC -, although much more information is available, according to Fig 4. Why was all this information thrown away? How do these bivariate mixing plots look like for other choices of tracers? Given the flimsy data base, the authors could at least have extracted as much as possible by taking into account all the available information, possibly followed by data reduction (e.g., principal component analysis). The plain-vanilla approach to EMMA may have worked if more thought had been given to the sampling design (items 1-3 above), but this is not the case.

The fundamental flaws addressed above preclude an in-depth discussion of details, let alone of the way-too-many language errors. It is not clear how this manuscript can be rescued. Its reduction to a technical note does not make the design flaws go away, and hence can't yield a more plausible hydrological interpretation. If the objective was indeed to infer flowpaths from water chemistry, then no such inference is possible because the sampling design was incongruent with this objective.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 7, 2187, 2010.

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