**Responses to comments of Referee#2 on HESS-D paper hess-2010-65:**
"***Hydrochemical analysis of stream water in a tropical, mountainous headwater catchment in northern Thailand"***

We would like to express our gratitude to Referee#2. The referee is very skeptical if this paper can be published in HESS. Nevertheless, we hope to convince the referee with our response letter. We would like to emphasize that we are prepared to carry out a thorough revision of the manuscript. In the following, we give a short summary of the comments and address the raised concerns.

A technical note: References not yet included in the reference list of the manuscript are listed in Appendix 2 – References. New figures (A1 to A7) and tables (Table A1) are shown in Appendix 1.

## Response to Referee #2

## General Comments

**Comment 2)** Does the paper present novel concepts, ideas, tools, or data? NO.
**Reply 2)** We do not agree on this point. We present a new data set from a remote and rarely investigated tropical area. The motivation for the hydrograph separation came up from earlier studies at this experimental site. There, pesticide peaks were often detected during the recession limbs of the hydrograph (Kahl et al., 2007). According to these authors this finding is probably due to preferential transport with interflow, which could be proven by combining a pesticide transport experiment with a hydrograph separation. The present study aimed to investigate which hydrochemical tracers are suited to separate the different discharge components in this catchment.

**Comment 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.
**Reply 3)** We are aware that the number of events sampled is at the lower bound one needs for a robust interpretation. Meanwhile additional data, which were acquired for a master thesis, are available (Duffner et al. in preparation). We will add these data to the revised paper (if invited) (see Appendix 1, Figure A4 and A7). Further details on the data and how we selected the end-members are given in the specific comments below.

**Comment 4)** Are the scientific methods and assumptions valid and clearly outlined? NO.

**Comment 5)** Are the results sufficient to support the interpretations and conclusions? NO, see specific comments

**Comment 6)** Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists? NO.
**Reply 4-6)** We respond to the specific comments below.

**Comment 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.
**Reply 8)** The title will be changed in a revised manuscript.

**Comment 10)** Is the overall presentation well structured and clear? BARELY.
**Reply 10)** The structure of the revised paper will be substantially improved.

**Comment 11)** Is the language fluent and precise? NO.
**Reply 11)** The language will be improved in revised paper. The manuscript will be proofread by a native speaker.

**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:

**Comment S1) 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, 93-106. 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.
**Reply S1)** The data limitations are recognized and will be discussed more critical in a revised version. Data from two more events (see Appendix 1, Figure A4-A7) (Duffner et al., in preparation) are now available and the analysis of these data sets will be a part of the paper.
In general, we are sure that the referee agrees that it is difficult to satisfy all data demands, in particular if the experimental study is carried out in a developing country. Of course, the data availability of this work can not be compared with work carried out in such highly investigated watersheds like, e.g., the Panola Mountain Research Watershed. Considering this, we will re-focus the paper such that only interpretations/conclusion are drawn that are supported by observations and analysis. Furthermore, we would like to emphasize that this work is one of the first hydrochemical observations in northwestern Thailand focusing on stream flow generation Almost no information was available before, and this investigation was done to explore hydrological pattern for the first and to get ideas for further studies were pesticide transport pattern will be included.

**Comment S2) Which endmembers 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?).
**Reply S2)** The choice of the endmembers is based on the finding of pesticides along the recession limb of hydrographs in prior work at this study site (Kahl et al., 2008). The observation of pesticide peaks along the recession limb indicates transport mechanisms others than surface runoff and baseflow (because no peaks or base-concentration was detected during baseflow conditions).Therefore we wanted to test, if we could separate the interflow, which is considered to deliver these peaks along the recession limb. Surface runoff was chosen as an endmember as it is stated in literature (e.g., Ng and Clegg, 1997) to be an important pathway for pesticide losses. We agree on that, that the definition is not well understandable and we will give more details on this and describe it more precisely.
We cannot give detailed information on the infiltrability or permeability of the soils in the subbasin, but we have a detailed description of the soil properties on the hillslope close to the outlet, which might give an idea on infiltration properties. Up to a depth of 120 cm porosity and texture can be shown (Kahl et al 2007), furthermore, bulk density up to 100 cm depth can be given (Spohrer et al, 2005).
However, an EMMA as carried out by Burns et al. (2001), could not have been carried out and was not carried out, because the amount of data does not allow this concept for our case. The chemical mixing diagrams were used to check whether the stream water during the events was bound by the components we were observing. This was the case for silica and EC. Therefore we used these variables to carry out the hydrograph separation. All other major ions were not suitable based on the mixing diagrams.

**Comment S3) 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 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.
**Reply S3**) It is true that the spatial variability of the whole subbasin is not represented in our database. The measured stream flow before events, is considered as baseflow, which

is a mixture of delayed interflow and groundwater. This definition is justified by the fact, that there is frequent (several events per day) rainfall during the rainy season. Pure groundwater flow is most likely not possible. Based on that, we assume that the stream flow concentration prior the events represents baseflow concentration - the stream flow sustaining component in the rainy season. The endmembers shown in Figure 7 are averages of several samples collected during the time of observations. The bars indicate the standard deviation among these samples.
As mentioned above (Reply S2) the hydrochemcial mixing diagrams were used to test, if the available components were related with the stream flow during an event.

**Comment S4)** 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.
**Reply S4)** The mixing plots were done with all data, but silica and EC were chosen based on the quality of the mixing plots – the other mixing plots did not represent the stream flow concentration in the same manner as the plot with EC and silica does. A PCA was carried out for the data set from E1 and E2, resulting in an explanation of the variance of 92% (E1) and 91.0% (E2) by three components. However, we tried to focus on potassium, as it is known as a tracer for shallow sub-surface flow and surface runoff (Kinner and Stallard, 2004) and applied it as a tracer for these flow components. The problem which we faced applies to most of the tracers but silica and EC: the differences of concentrations among the components were not large enough. For example, the concentrations measured in stream before the event (shown in Table A1), are mostly not significantly different. For $Ca^{2+}$ the values are different among the components, but $Ca^{2+}$ is, based on literature, not commonly applied as a tracer. Therefore we decided that for this study site in particular most major ions are obviously not suitable to be applied for a hydrograph separation due to low concentrations and mainly non-significant differences.