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Interactive Comment

Interactive comment on "Contrasts between chemical and physical estimates of baseflow help discern multiple sources of water contributing to rivers" *by* I. Cartwright et al.

Anonymous Referee #6

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Having read the manuscript and the preceding comments, I am following the skepticism raised by referee # 2. The basic idea of the paper is to compare two different concepts of hydrograph separation: a "physical" one separating quickflow from baseflow and a "chemical" one separating event from pre-event water (using the problematic tracer EC). By the difference of these two concepts the authors try to obtain process insights, e.g. to assess the importance of bank storage. The entire approach has several weaknesses detailed as follows that limit its significance. Before these shortcomings are not dealt with I cannot recommend publication in HESS.

The underlying concepts of both separations have been known for a long time. None

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of them separates runoff components by source. Quickflow (direct runoff) and delayed flow (baseflow) have been separated by various methods using runoff data alone (e.g. the well known paper of Hewlett and Hibbert and many others). There is no method that is the "best", all have advantages and disadvantages. The other approach is the wellknown two component separation into event and pre-event water, because it uses a two-component mixing with two endmembers: the EC-signature of (1) rainfall and (2) low flow. Following the benchmark paper of Sklash et al. 1976, we know that pre-event water can be a major component of direct runoff. This result has stimulated research on runoff generation throughout the world to explain they high fraction of pre-event water in storm hydrographs. This pre-event water mainly originates from water from saturated zones on the surface or in the subsurface (riparian zones, hillslope groundwater, etc., which is quickly mobilized by piston flow processes. This is true for many catchments. This knowledge is ignored by the paper which becomes clear in the second paragraph of the introduction (ll21-22): "The quickflow component is dominated by event water but can also include older water displaced from soils or the unsaturated zone".

Moreover, it is not true that geochemical data sets are only measured at specific times, e.g. during low flow conditions (p 5947, second paragraph). Again there are many process studies that use the temporal variation of geochemical data and use them as hydrological tracers, e.g. for endmember mixing analysis. Also the obtained hysteresis effects are not new and can partly be explained by kinematic effects: A pressure wave travels along a river and causes the formation of a wave of old water before the new water arrives at the gauging station. How large is this effect in the present study?

How much general knowledge do we gain when we compare mathematically separated baseflow with chemically separated pre-event water? For sure the results will be site-specific and will assemble many processes: those that are responsible for pressure driven effects from saturated zones, and others, as stated in the paper, that delay event water, e.g. by bank storage. It is probably impossible to quantify a single process like the present paper attempts.

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Another point of concern is the use of EC as a chemical tracer. Other reviewers have raised this point already, but it needs to be strengthened once again: EC is NOT a conservative tracer, since it is a physical characteristic of the water and a summary tracer for all dissolved solids. Even when it is claimed that Na and Cl are main components of EC in the study basin, there is no major ion data given to support this statement. Is the dominance of these two ions really the same also at low EC values? It is also admitted in the paper that during times of stagnant water evaporation changes EC values: What is the difference between stagnant flow and the time when the highest EC value was measured? Have the mentioned Isotope samples that are used to exclude evaporation impacts been collected at extreme baseflow conditions? This is especially important, because this value is used as groundwater component for the CMB. During times of low flow also biological processes (primary production, etc.) might constantly change EC values.

Last but not least even more important is the limited representativity of the endmembers used for CMB. It is stated that spatially, groundwater EC covers an extremely wide range in the area (1000 – 20000 mikroS/cm). Despite this fact only one (constant) value (3200 mikroS/cm) is used to represent the baseflow "groundwater" component. Strictly speaking, this single value represents one specific mixture of groundwater components over time. This mixture will constantly change during events and during seasons and might change in both directions (not only in one as admitted in the paper). But the entire analysis of the paper is based on the assumption of this constant EC value. This uncertainty is enormous and calls the entire results (especially the seasonal baseflow values) into question. Moreover a similar effect is true for the surface endmember which is equated to rainfall EC. Already by the canopy, EC values are increased and this is more extreme when there is contact to the soil surface. This effects have been reported, data exist. So at least a range of values should be used to show the uncertainty of the separation. Probably this uncertainty will mask the influence of bank storage.

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