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The Jones *et al.* (2006) paper is an interesting contribution to Water Resources Research, highlighting the continued debate in hydrological science around the rapid mobilization of pre-event water to the stream. We agree that it is *very* important to assess the uncertainty in tracer-based estimates of pre-event water contributions to the stream and the role of dispersive processes on tracer based separation techniques. However, we believe that the conclusions that Jones *et al.* draw are misleading in some respects. In particular we would like to point out that (i) the use of the term "pre-event contribution" in Jones *et al*. is at odds with the accepted definition of pre-event water used by the catchment hydrology community, (ii) the "hydraulically based estimate" used by Jones *et al*. is *not* a measure of pre-event water contribution to stream flow, (iii) water itself will be subject to some form of dispersive process when flowing through a porous medium, and it is in no way realistic to 'switch off' this process in a modelling example, and (iv) oxygen isotope tracing, (which form the bulk of the examples given by Jones *et al.* in their Table 1 are techniques which exactly trace water molecules, and thus must, by their very nature, represent pre-event water. We elaborate these points further below.

(i) Pre-event water vs. groundwater

Jones *et al.* use the "rapid mobilization of old-water paradox" as defined by Kirchner (2003) as rationale for a modelling exercise which investigates the role of dispersive and diffusive fluxes to the contribution of pre-event or "old" water to stream flow. However, we feel that the quantities used in Jones *et al.* mix two very distinct attributes, namely the water origin or temporal water sources (new/old or event/pre-event) and the water flow pathways (overland or subsurface, saturated or unsaturated). It is critical for the hydrologic community that this distinction is made clearly and we strongly advocate that the term pre-event water be used when referring to the water stored anywhere in a catchment prior to a given rainfall event as it is self-explanatory.

Sklash and Farvolden (1979) wrote a benchmark paper for using tracers to separate the hydrograph into different water sources. It is now absolutely clear that what has been called *groundwater* in this paper is actually *pre-event* water. The methodology used was based on isotopic tracing (^{18}O, deuterium and tritium) which allowed the separation of the hydrograph "into its simple time components (pre-event and event water) by the simultaneous solution of the steady-state mass balance equation describing the fluxes of water and the tracer isotope at the stream" (Sklash and Farvolden, 1979, p48). Further emphasizing the fact that this paper is more about pre-event water than groundwater, they note that "during a moderate intensity storm on a very wet basin, both the overland flow and stream flow were dominated by groundwater" (Sklash and Farvolden, 1979, p64). This remark illustrates the fact that pre-event water can indeed reach the stream via overland-flow, which has been confirmed in many studies afterwards (e.g. Sklash et al. 1996). A likely reason for this confusion in the terminology is that most of the water stored in the catchment prior to a rainfall event is stored underground, hence the name *groundwater*. To the defence of Sklash and Farvolden, they strongly implied that the term groundwater was actually used for pre-event water. For instance, when describing the isotopic technique, their criteria (3) and (4) are particularly revealing:

(3) "The groundwater and vadose water are isotopically equivalent or vadose water contributions to runoff are negligible due to hydrogeologic constraints."

(4) "Surface storage contributes minimally to the runoff event."

10 years later, similar use of the term *groundwater* instead of pre-event water is still found in the literature, for instance McDonnell *et al* (1990, p455) wrote "old water

(groundwater and soil water)" and then "old water (often identified as groundwater)", maybe to suggest that they believed that the term *groundwater* was often misused? Today, the use of the term groundwater for pre-event water is becoming more uncommon. For example, in the most recent paper quoted by Jones *et al.* in their Table 1, McGlynn and McDonnell (2003, §17 on p7) state:

> "In this paper we use the following definitions for temporal and spatial sources of catchment runoff: For temporal sources, "new water" is rainfall associated with the current storm event and "old water" is resident catchment water prior to the current storm event. For spatial sources, "hillslope water" is water originating from hillslope zones (old and new) and "riparian water" is water originating from riparian zones (old and new)."

So McGlynn and McDonnell do explicitly differentiate between temporal water source and water pathways, which they call "spatial" sources of water. They also make clear that pre-event water can follow different pathways. Buttle (1994) provides an overview about these different pathways of pre-event water and he points out that groundwater flow is only one out of six processes that can deliver pre-event water to the stream.

We believe that now, 28 years after the benchmark Sklash and Farvolden paper, the bulk of the community distinguishes appropriately between pre-event water and groundwater contribution. However, some research still seems to imply that groundwater and pre-event water are the same thing, therefore confusing water pathways and water temporal sources. We believe this important distinction is unclear in Jones *et al.*.

(ii) "Hydraulically driven groundwater flow contributing to streamflow"

Central to the Jones *et al.* discussion is the definition of the "hydraulically driven groundwater flow contributing to streamflow" which they then use as a reference when comparing tracer based methods for different dispersion/diffusion values. This "hydraulically based estimate" is calculated by (1) setting the dispersion and diffusion values to zero in their numerical model and (2) integrating the tracer fluxes entering the stream from the unsaturated and saturated zone. By doing so this method discards the amount of pre-event water which could reach the stream via surface runoff. This is merely a "methodology to compute the actual Darcian subsurface flow contributing to stream flow generation" but not the pre-event water contribution itself as pre-event water can follow a variety of flow paths to reach the stream. For example, Jones *et al.* mention briefly the capillary fringe which can in some cases lift the water table creating exfiltration and "presents an opportunity for event and pre-event water to mix before reaching the stream channel". This process could not be quantified using Jones *et al.* "hydraulically based estimate".

When using conservative tracers in the field, both the subsurface water and rain water are sampled once to determine their respective tracer signature (geochemical or isotopic). Then multiple sampling is then done in the stream at regular time intervals during the storm event and usually for a while after it has ended. The proportion of event and pre-event water is eventually calculated from the ratios of the different concentrations in the stream water and a unit hydrograph derived from these. Hydrograph separation done this way can only separate between sources of water (pre-event/event) and cannot separate between pathways. Using this methodology, it is obvious to see that the hydraulically based estimate from Jones *et al.* is not comparable to pre-event water contributions from their Table 1.

(iii) Diffusion and dispersion coefficient vs. tracing water

Jones *et al.* underline the fact that in their computer simulations, the overland flow and groundwater flow volumes remain constant in their "hydraulically based estimate" because only tracer parameters are altered between simulations. However we argue that dispersivity coefficients are not linked to the tracers alone but also to the porous medium itself (e.g. Perfect *et al.*, 2002 for a relationship between soil moisture parameters and dispersivity) and therefore the "hydraulically based estimate" does not constitute a useful reference..

Let us for example consider a riparian zone containing pre-event water where any subsurface flow to the river is truly matrix flow, i.e. it can be represented with Darcy-

Richards' equation and preferential flow is negligible. This is similar to Figure 1 from Jones *et al.* This is of course a rather poor assumption for many real hillslope settings but it is a good analogue of situations where the InHM model used by Jones *et al*. can be applied reliably. After a rainfall event, subsurface flow initiates with pre-event water moving towards the stream channel. This subsurface flow is of course driven by hydraulic gradients, as Jones *et al.* rightly point out. However, the nature of flow through a porous medium dictates that water will undergo kinematic dispersion because of the tortuosity of the flow pathways and the geometry of the pores (e.g. Freeze and Cherry, 1979). The reason this process is not apparent in the Darcy-Richards' equation is that if a molecule of water is replaced by another molecule of water it does not change anything for the sake of pore water pressure calculations. However, when different types of water are considered, i.e. pre-event and event water, and if interested in the relative contributions of each type to the flow, kinematic dispersion *does* matter. The 'hydraulically based estimate' used by Jones *et al.* is achieved by 'switching off' kinematic dispersion in the solute transport module of the InHM model. This is not a realistic representation of the system and removes a major component of the mixing process. Any transport experiment and transport model recognizes and includes this process.

Jones *et al.* go on to compare (1) 'zero-dispersion' with (2) 'diffusion only' and (3) 'high dispersion' cases for stream discharge (Jones et al., figure 2). We disagree that this is a useful exercise. We have already pointed out that water itself will disperse when flowing through porous media. Therefore Jones et al. are *not* modelling the water parcels within the model in a 'zero-dispersion' case, but are merely integrating the Darcian flow streamlines.

We therefore believe that the "Hydraulically based pre-even contribution (model)" curve should *not* be included in the analysis of figures 11 to 15 in Jones *et al.* and that the conclusions drawn from these figures are misleading.

We would like to make it clear that we do agree that it is very important to assess the relative importance of dispersion in tracer based contributions to streamflow as well as the effect of tracer transfer within a watershed (e.g. Weiler et al., 2003). However, it would be more helpful to the argument of Jones *et al.* to compare different dispersion values in their modelling example, and to look at how this relates to pre-event water contribution estimates. This is in fact a critical exercise. If we are to model pre-event and event water effectively, we must parameterise the coefficients of diffusion and dispersion for the water molecules themselves in order to correctly represent their travel through the subsurface. In addition, as kinematic dispersion depends both on tracer properties *and* porous medium properties (Perfect *et al.,* 2002), both tracer and site dependant corrections should be considered.

(iv) Oxygen isotope tracing

One complicated issue when using conservative tracers is that of molecular diffusion. Due to concentration gradients, and even if the water is "still", a tracer in solution in the water will move towards zone of lower concentrations. This is illustrated by the "additional diffusion-only" case introduced by Jones *et al.* at the end of paragraph [15]; even if the two types of water do not mix, molecular diffusion will move the pre-event water tracer toward the surface and the event water toward the subsurface at rates dictated solely by the tracer characteristics, i.e. its coefficient of molecular diffusion in water at a given temperature. However, we believe that when using oxygen isotope water tracing this diffusive tracer flux is not an issue. Indeed when using isotope tracers, diffusion is linked to the actual motion of some the water molecules themselves (i.e. ^{18}O) rather than ions in solution in the water. If pre-event water with a ^{18}O water molecule signature diffuses from the underground to the surface it is indeed pre-event water that has moved to the surface rather than an ion that moved from the pre-event water to the event water flow. Therefore the associated flux should surely be taken into account when quantifying pre-event and event water components to stream flow.

Conclusion

Stream flow generation processes remain at the forefront of hydrological research as we still do not understand the spaces and times of operation of various processes. We therefore strongly advocate a multiple method approach to the assessment of pre-event water generation in the field, using a combination of geochemical, isotopic and other advanced tracing techniques, together with hydrometric monitoring and numerical modelling. When using tracer-based approaches as a substitute for direct tracing of pre-event water, the impact of dispersion and diffusion as well as transfer times within a watershed on hydrograph separation needs to be assessed, especially for the simulated water pathways to be trusted. However, when using numerical models and/or oxygen isotope techniques in the field, it is important to realise that due to the properties of the soil through which the water is flowing, water itself will *necessarily* undergo dispersion and diffusion processes and this should be born in mind when assessing streamflow generation processes.

In particular, Jones *et al.* advocate re-examining hydrograph separation techniques due to the conclusions they draw from the "hydraulically based estimate" derived from their numerical simulations. We think that this conclusion comes from a misunderstanding of what tracer based separations techniques actually do. Conservative tracers are used to identify the water origin and we strongly believe that current hydrograph separation techniques are fit for this purpose.

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