<u>Response to referee #2:</u>

The title of this paper "Transport behavior displayed by water isotopes and potential implications for assessment of catchment properties" is misleading, as it suggests the paper has something to say about water isotopes and their use in assessing catchment properties. I see no evidence of this whatsoever.

<u>RESPONSE:</u> The referee states that the title is misleading and makes a sweeping statement regarding the nature of our analysis and discussion regarding use of water isotopes for assessment of catchment properties. As we detail below, we respectfully disagree with this statement and provide explanations that justify the manuscript title and our analysis. The manuscript deals *explicitly* with transport behavior of water isotopes – presenting experiments and a quantitative discussion – and then makes *explicit* reference to catchment properties and a method of analysis, illustrating a quantitative implication regarding assessment of aquifer storage thickness. Nonetheless, we have introduced additional clarifications and explanations (as noted below) based on the referee's comments, where appropriate, in the revised manuscript.

The core claims of the paper rest on two points:

1. stable water isotopes behave similarly to inert tracers like Br-
2. The v_T parameter of a CTRW model fit to breakthrough curves showing non-fickian behavior is not the same as the value of v_W calculated from v_W=Q/(nA).

I have no major issue with either of these points, per se. However the authors then argue that there is some issue with using isotopes to understand water movement through catchments -- as though the movement of water molecules were somehow different from the movement of "water" itself.

<u>RESPONSE:</u> We are glad that the referee has no major issues with these two points, although regarding point 2, we explain below that the issue relates to a general question not limited to the CTRW analysis.

The referee's difficulty arises in the analysis and interpretations that follow these two points. Here the referee implicitly takes the position that there is no issue or difficulty in using water isotopes to understand water movement through catchments. Our line of argument requires elaboration on this point, which is given in the manuscript and expanded upon here. *The issue* *here is that Darcy's law does not actually identify and measure the velocities of* <u>*all*</u> *water molecules (e.g., including those that may be trapped in an immobile zone for extremely long or essentially infinite times); rather, Darcy's law offers a means to determine an "effective", continuum-scale, mean velocity of "water". Recognition of this difference between the definitions of the "mean water velocity" (given by Darcy's law), and the mean velocity of water isotopes or chemical tracers is a core feature of our analysis.* Briefly, we can define "movement of water itself" by using Darcy's law (as described in the manuscript, Section 3.2, paragraph 1). This is, indeed, the mean movement of "water".

Significantly, though, the catchment literature (citations given in the manuscript) often suggests or states that use of water isotopes to estimate travel times and, in particular, a mean travel time, yields a mean travel time of *water*. However, we demonstrate in the experiments presented in the manuscript that it this is in fact not the general case. Isotopes yield mean travel times similar to those of inert chemical tracers, as we show in experiments reported in the manuscript (and accepted by the referee). We thus show that v_T, the mean travel time of the isotope and the tracer, is distinct from the mean travel time of the "water" itself, as determined from Darcy's law. And as we explain further in the manuscript, this key point is often not recognized, so that frequent application of the classical ADE, in particular, to interpret breakthrough curves can be misleading and in fact incorrect. We then show that for the particular experiments under consideration, the ADE model is not adequate while a more general CTRW model (which encompasses the ADE as a special case) can interpret the data (Figure 3). Thus, with regard to the second point highlighted above by the referee, the fact that v_T is distinct from v_W is **not** specific only to the CTRW model. Significantly, it is equally relevant to the advection-dispersion equation (ADE) model, and similar approaches. We expand further on this point in the next comment/response below.

<u>DONE:</u> In light of the referee comments and our responses above, we have added a statement in the revised manuscript to clarify the arguments already provided therein. In Section 3.2., first paragraph, we have added the text highlighted above in *italics*. Additional text has been added related to v_W and v_T, and ADE and CTRW models; see the next comment/response /"DONE" text below.

To me the issue seems to rest entirely on the assumption that the v_T parameter that arises in CTRW theory is the 'true' mean velocity of the tracer, and that this ought to correspond with the value of v_W calculated as mentioned. Tf there is a mismatch between theory and observation then the issue is not with reality, it is with the theory . If the discrepancy between the two 'velocities' arises regardless of which tracer is used (which they themselves say their results support) then the use of isotopes as a tracer is not at issue. Rather it seems to me it highlights a theoretical confusion about what v_T and v_W actually mean in relation to one another. Does CTRW theory assert that they ought to be the same? Are the observations in agreement with the theory, or at odds with it? Where exactly does this difference come from? It certainly seems like a paper that disentangles that issue would be useful to the CTRW community.

RESPONSE: We do not claim that the v_T parameter in the CTRW should correspond to the value of v_W. In fact, we do not invoke v_W in the CTRW, and thus there is no "mismatch" or inconsistency between these two parameters in the CTRW framework. (These aspects are described in detail in CTRW literature cited in the manuscript; it seems inappropriate to review CTRW in great detail in the current manuscript.) Rather, we emphasize that the assessment and use of v_T and v_W is a matter of general interest, and of relevance to virtually any modelling approach.

In particular, we emphasize that the fundamental formulation of the ADE **requires** that the velocity term in the equation correspond to – i.e., be identical to – v_W. Every textbook development of the ADE immediately invokes the mean linear water velocity, v_W, based on Darcy's law. Thus, use of v_T, as estimated from a breakthrough curve, for example, as the value of "*v*" in the ADE is fundamentally incorrect. Otherwise, one is using a "circular argument", inserting a mean tracer velocity, which already takes into account the influences of dispersion and diffusion, into the ADE, and then attempting to fit a full breakthrough curve by solution of the ADE with an additional fitting parameter (dispersivity or dispersion coefficients). Even with this approach, we show in the manuscript that such a fitting approach with the ADE cannot match the measurements, particularly the long tailing behavior. It is at this point that we consider a CTRW anomalous transport interpretation of the system dynamics to successfully fit and interpret the measurements.

DONE: In light of the referee comments and our responses above, we have added a statement in the revised manuscript to clarify the arguments already provided therein. We added (Section 3.3., first paragraph): "It should be emphasized that the distinction between v_W and v_T holds regardless of the choice of model applied to interpret breakthrough curves. For example, the derivation of the classical ADE, and variants thereof, in particular, is predicated on v_W. In contrast, the continuous time random walk framework (CTRW) formulation discussed below is essentially founded on v_T."

Meanwhile, the community that uses isotopes to study catchment properties is moving on from the notion of 'mean travel time'. The leading-edge approaches do not require it, and it is reported less often in favor of other more reliable metrics, like those based on storage selection.

<u>RESPONSE:</u> We acknowledge that at least some portion of the community is now working more extensively with storage selection theory. However, another portion of the community continues to work with mean travel times in spatially 1D domains, as seen in the literature. We therefore believe it remains valuable and important to clearly report the discrepancies and inconsistencies that we address in the manuscript, and to illustrate the impact on assessment of aquifer storage thickness, which remains a key issue in catchment hydrology studies.

I would note in passing that the authors do not seem familiar with the storage selection approach. They seem to be under the impression that it is based on the collapse of the system to one spatial dimension (Line 331). This is not the case -- in storage selection theory the system is collapsed to zero spatial dimensions.

<u>RESPONSE:</u> Reference to 1D interpretations of catchment and aquifer conceptualizations was not intended to refer specifically to storage selection theory. In fact, we did not explicitly refer to the storage selection approach at any point in the manuscript; we certainly did not claim, nor intend to claim, that the storage selection approach collapses to one spatial dimension (according to the referee's reference to line 331). This latter approach is different, and we in fact do not refer to it explicitly in the manuscript.

<u>DONE:</u> In light of the above two referee comments, and our responses, we have added a note in the paragraph containing the reference to consideration of a system under one spatial dimension (Line 331 in the original manuscript). To add perspective, we now include the text: "An alternative approach employs storage selection theory, which involves collapsing the system to zero spatial dimensions and defining functions that interpret age-ranked release of water from storage and exit from the catchment, or in other words, defining functions that quantify the probability of water of a certain age being discharged at a given time."