HESS Opinions: Chemical transport modeling in subsurface hydrological systems – Space, time, and the holy grail of "upscaling"

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RC1: Anonymous Referee #1

Preliminary note: I like this opinion paper very much and rate it "very instructive", delivering a good piece of "food for thought" for both early career and advanced scientist and also an eye-opener for a number of more applied researchers and practitioners! The paper is rated as an "opinion" paper. As such I hope that is will provoke scientific debate and discussions and trigger other submission that critically dispute the opinion provided by the author. For that cause, I limit my review to aspects I think need to be clarified.

Response: The Author appreciates the reviewer's positive appraisal of the manuscript. The constructive comments are also most appreciated; they are addressed in detail below, and in the manuscript to be revised, where appropriate.

General comments

The term "holy grail" is a very fundamental claim. Yet, the scientific perspective on flow and transport is rather specific addressing primarily the domain heterogeneity with respect to porosity, hydraulic conductivity and geochemical properties (limited to partitioning and sorption).

Response: The term "holy grail" can have different connotations to different readers. It is used here in the context of the flow/transport perspective of the manuscript, as noted by the Reviewer. **Done:** In light of the comment on this point by both Reviewers, the text in the revised manuscript will be modified by using quotation marks in the title and first use of the term in the text. Also, on first use of the term, a clarification of the intended meaning of the term in the context of the discussion will be provided.

There are important other aspects, still unresolved and most frequently ignored in literature, of fluid flow and chemical transport conceptualisation, theory, and modelling. Among others, these include the role of temporally and spatially changing fluid (water) properties like the viscosity and surface tension, or spatially and temporally changing properties of the immobile surface like mechanical or wetting properties, the role of mobile interfaces, or the transport of other materials than solutes for chemical transport. Importance arise from the fact that these factors have different spatial and temporal heterogeneity patterns that are incompatible with the ones addressed in this opinion paper. A fundamental and rigorous theoretical analysis is lacking. At time being, it is unclear whether an "explicit accounting of temporal information" will be enough to provide a way out.

Response: The Reviewer points out that other factors, such as viscosity, surface tension, wettability and transport of materials, can influence modeling of fluid and chemical transport. The

Author agrees, but notes that these factors are generally significant for multiphase flows, non-Newtonian fluid flow, and other scenarios; they are less relevant to the scenarios of flow and transport considered in the manuscript.
The Reviewer suggests that these other factors have spatial and temporal heterogeneity patterns that are incompatible with the ones addressed in this opinion paper. This point is certainly worth considering, but it is beyond the scope of the manuscript.
Given that the intent and scope of the manuscript appear clear, and in the interests of not expanding the text even further, the Author prefers not to include this discussion in the manuscript.
Done: In the revised manuscript, a brief statement will be included noting that these additional factors that are beyond the scope of the manuscript.

This holds also for the statement (L57 and on) on the relative effectiveness of upscaling approaches for "fluid flow". The "success" is limited to situations with fluids having the fluid properties of "pure water". I am not aware of any study that addresses temporal and spatial variation of the fluid viscosity. Once viscosity is considered no longer constant, even taking into account temporal effects, will not be sufficient to correctly represent "chemical transport".

Response: Agreed, although the ubiquity of non-constant viscosity scenarios in general groundwater systems might be considered limited.
Done: In the revised manuscript, the L57 statement will specify that constant fluid viscosity is assumed.

So "upscaling" with respect to heterogeneity in porosity, conductivity or geochemical properties fortified by an explicit accounting of temporal information is, admittedly, a grand challenge, but at least from my point of view, not the "holy grail".

Even when the attempt "to develop and apply chemical transport equations at large (length) scales, based on measurements and model parameter values obtained at significantly smaller length scales" would be successful, we must suppliantly recognize that we are still very far away from a "holistic" explanation (understanding) of transport in natural systems like soils and aquifers across scales. Thus, I recommend to "tone done" the paper by taking out the "holy grail".

Response: As noted in a Comment/Response above, the term "holy grail" is used in a specific context in the manuscript. The Reviewer suggests here that we are still very far from a full explanation of transport across scales. This comment would appear to agree with the Author's perspective, and specific use of the "holy grail" term.
Done: In the revised manuscript, as noted previously, the text will be modified by using quotation marks in the title and first use of the "holy grail" term in the text. Also, on first use of the term, a clarification of the intended meaning of the term in the context of the discussion is provided.

At the very beginning, the paper should point out that the presented examples on "chemical transport" are limited to situation of chemical transport of inert, i.e., non-reactive solutes. Although the author touches "reactive transport" in section 3.3.2, his paper does not elaborate this case.

Response: Agreed.
Done: In the revised manuscript, this point will be stated explicitly.

Even though the paper is an "opinion paper", I recommend eliminate the „Disclaimer". I strongly recommend to add the respective literature and references. It is good scientific conduct and will help the non-experts to navigate and reproduce the authors opinion by mirroring those with the existing "philosophies".

Response: The original manuscript included 42 references citing a range of author groups. Moreover, the manuscript is an "Opinion", rather than a "Review", the latter of which would indeed necessarily include at least 100-200 papers to fully survey and support consideration of all of the concepts and perspectives contained here.
Done: In the revised manuscript, and in light of the other reviewer's recommendation, ~20 additional citations will be included that expand on CTRW and other (non-time-centered) approaches ("philosophies"). The Author prefers to retain the "Disclaimer" in the Introduction, as the manuscript is not developed as a comprehensive review that surveys hundreds of papers.

Line 109 and section 1.3 Approach – Outline.: A graphical sketch of the hierarchy would help improve the perceivability.

Response: It is not clear to the Author how to present the hierarchy in graphical form, nor that doing so would add clarity. It appears that the text is sufficient to introduce the approach that is developed in the text that follows.

L116 and further: I recommend to detail what is meant "by measurements at similar scales of interest" and what type of "observational techniques" could/should be employed. It remains at this point quite unclear how this may be achieved in practice in the field. While structural features governing the permeability can eventually be measured at the same scale by, e.g., non-invasive geophysical methods, this is definitely not possible for the "geochemical heterogeneity" that controls retention and release. Most of the information on "reactive chemical transport" at the field scale regional scale has still to be delineated from - integrating - well measurements.

Response: Agreed.
Done: In the revised manuscript, these important clarifications will be introduced in a straightforward manner.

To a certain degree I feel that the examples used to illustrate the "opinion" are somewhat inconsistent. The paper motivates with natural porous media like "soil layers" and "subsurface geologic formations" and aquifers (see Abstract; L37-38). However, e.g. section 2.1 and Figure 1 are far from an even stochastic correct representation of natural subsurface geologic formations. Are the presented effects to expected as relevant or significant if more realistic "permeability" domains are considered?

Response: The Author understands the Reviewer's point. Figure 1 is an introductory, first example that focuses specifically on *pore-scale* flow behavior. There is no claim that this figure represents soil or aquifers, nor a stochastic representation of them.
Done: In the revised manuscript, text will be introduced to clarify the purpose of Figure 1 and the discussion associated with it, and to place it in perspective relative to the text that subsequently that focuses on soils and subsurface geological formations.

Specific comments

I recommend to reduce the relative clauses and commenting statements (e.g., the parenthesis) as these interrupt the "reading flow".

Response: Agreed.
Done: In the revised manuscript, the text will be modified throughout to improve the flow.

It is a single author paper. So, I recommend that the author refers to this by als writing "I" rather than "we".

Response: The use of "I" and "we" remains a subject of debate and writing style. Many statements are accepted by the community, so that "we" is in many contexts "more correct". Moreover, some statements are made based on results of multi-author studies, which again suggests that "we" is preferred, giving credit others who contributed to the cited paper(s). The Author therefore prefers to retain use of "we" throughout the manuscript.

Section 2 Fluid Flow: I am missing more recent approaches to resemble "connectivity" that are based on topology.

Response: OK.
Done: In the revised manuscript, brief mention of topology-based connectivity with citations will be included.

L496-497: Heterogeneities exist at all scales. Yet, AFM allows the resolution of small scale heterogeneities at resolutions; that prohibit to consider water still as a continuum fluid phase and the molecular properties of water govern dynamics and interactions with the porous medium. So, I suggest to eliminate the AFM example.

Response: OK. AFM was included only parenthetically.
Done: In the revised manuscript, this example will be deleted.

L645-647: Of course, at time being, a very detailed - in the sense of resolution - knowledge (measurement) on the spatial variability of the reactive surfaces is necessary to reconstruct "reactive" chemical transport.

Response: Agreed, but the text here is not referring at all to "reactive" chemical transport, which is mentioned later in the text.
Done: In the revised manuscript, in line with a Comment/Response above, clarifications will be introduced when referring to conservative and reactive chemical transport scenarios.

Minor comments

Chapter 3: Chemical transport. One may wonder in as far the observable effects (given in figures remain relevant or significant once the transport of an even only slightly "reactive" component is considered.

Response: The figures shown in Chapter 3 relate to conservative tracers. Chemical reactions introduce additional effects on transport patterns.
Done: In the revised manuscript, clear distinction between conservative and reactive transport situations will be made, with reference to the figures and discussion throughout the Chapter 3.

Figures 4 and 5: To what extent might the "non-Fickian" behaviour be due to the fact that the chemically inertness of the dye is not correct (due to sligth sorption of the dye to chemical impurities of the quartz sand).

Response: These figures are discussed in detail in the paper from which they were reproduced. Dye sorption was negligible. The text introducing these figures states explicitly that the red dye was inert.

Technical corrections (non exhaustive)

Response: The Author thanks the Reviewer for catching these typos, which the Author unfortunately missed.
Done: In the revised manuscript, the Author will make these corrections and others that were found.

L37 and on: replace „soil layers" by „soil"
L73: "case" instead of "Case"
L160: erase "is"
L174: replace "to not" by "do not"
L323: second "Path" change upper to lower case

L327: erase second “cause“ in “does not cause necessarily cause a potential“
L371: erase first “only” in “knowledge only of only the flow”
L393: replace “show” by “shown”
L813; replace “dues” by “due”
L836: add a comma to “too”.
L1060-1064: Revise. This sentence is confusing.
L1080: replace “many” by “may”
