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Interactive comment on "Use of column experiments to investigate the fate of organic micropollutants – a review" *by* Stefan Banzhaf and Klaus H. Hebig

Anonymous Referee #1

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Overall this paper is fine and I have relatively minor suggestions and corrections below. The paper covers a lot of material outside my specific knowledge area so I cannot assess how truly comprehensive it is, but you will note that one of my comments suggests that the authors are missing some important areas that I am aware of relating to transport of organic compounds that cannot be well described by the equations and models presented here. While I do not expect a comprehensive coverage of this and it would perhaps be too long and deviate from the more focused and specific scope of this work, I do believe that some mention of it in the text, perhaps the conclusions or end of the introduction is warranted as it is important that people understand the limitations not just of column experiments, but of the very models used to interpret the

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data.

Comments

Page 4, L 20 – The reactions mentioned there are not what I would say change the rate of transport, but rather change the makeup of the porous medium, which in turn causes transport properties to change.

Figure 1 – I would strongly suggest than in pace of a cartoon , which it appears the authors have created, that the actual curves be plotted as solutions to the advection dispersion reaction equation. The reason I say this is that I am not convinced that the curves are equally comparable – for example it looks like the red one has undergone less dispersion than the blue, but it is further on in the column, which does not make sense unless you explain differences carefully. The curves as drawn qualitatively capture the mechanics, but would better convey them if they were also physically consistent with model predictions.

Page 6, L 15 – only under equilibrium assumption. If the solute is pumped through more quickly than sorption can take place this is not true.

Equation (3) – I don't believe that rho and theta have been defined.

First line Page 8 – degradation can include much more than this – seems way to specific to me.

Page 12 Line 34 – 'may lead to lower flow velocities. . .' I agree that the surface area will be different but lower flow velocities does not make sense. A well designed experiment will try to match dimensionless numbers (Peclet, Damkohler, Reynolds at least). I did not get a strong sense of this from the manuscript and this needs to be much clearer. An experiment that does not at least try to capture and match such quantities will have little relation to a real system, even if flow speed is matched. Dimensionless science is poorly understood and massively underutilized in column experiments and warrants discussion.

This last point is very important relative to one of the discussions the authors have on flow speeds in columns. Yes, it is true that if you have a high flow rate you can conduct a lot of experiments, but the information that you will obtain may be next to useless if the dimensionless numbers do not match, particularly if chemical reactions are involved since systems with high Peclet or Damkohler numbers can behave in fundamentally different ways than those with lower counterparts. Likewise Reynolds numbers can strongly influence the nature and structure of pore scale flows, which can strongly impact larger scale reactive transport.

Page 19, L 9. You mention field experiments, but then it gets no real focus. I would remove this altogether as the focus of this paper is column experiments and ultimately how such information can inform us on field like conditions.

Finally, one thing that is not touched upon at all is that, unlike many inorganic compounds, when discussing organic compounds these can often be made up of a mixture of molecules. The most classical example of this is Natural Organic Matter, which is ubiquitous in natural waters and is by its very definition a mixture of organic compounds of varying molecular size. This is an extreme example, but many other organic compounds have similar mixture properties. The reason I mention this is that when there is interest in understanding the transport of such substances models like the advection dispersion equation are not representative of the transport that actually occurs, even if highly uniform porous materials. The heterogeneity of the chemical properties of the mixture leads to so called anomalous transport behavior, which is due to fractionation, and has been documented in a variety of papers. The three papers that I am most familiar with that relate directly to column experiments are

- Dietrich, Lindsay A. Seders, et al. "Effect of polydispersity on natural organic matter transport." Water research 47.7 (2013): 2231-2240.

- McInnis, D.P et al, 2014. Natural organic matter transport modeling with a continuous time random walk approach. Environmental engineering science, 31(2), pp.98-106.

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- McInnis, Daniel P\et al. "Mobility of Dissolved Organic Matter from the Suwannee River (Georgia, USA) in Sand-Packed Columns." Environmental engineering science 32.1 (2015): 4-13.

There are several more, including in the references of the above articles. While the ADE is by far the most used equation to model transport in columns and I strongly believe that it is also one of the most useful, it is important that the community be aware of its limitations. It is not value when considering strongly chemically heterogeneous compounds and given that this can be true for many organic compounds I believe that mention of this is warranted. The ADE still provides useful information, but fails to model certain aspects accurately and such deficiencies can amplify when predictions are made at even larger scales.

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