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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

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We appreciate the comments provided by Referee #1 on our manuscript and will first provide a reply to the more general comments and then one-by-one replies to the specific comments.

Reply to general comments

The referee claims that we are missing "some important areas [. . .] relating to transport of organic compounds that cannot be well described by the equations and models presented here ". We do, however, think that this does not apply too much to the topic of this manuscript as the literature suggested by the referee focusses on natural

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organic matter (NOM) and not so much on organic micropollutants, which are the topic of this review manuscript. The “mixture of molecules” that organic compounds can be made of is mostly not relevant for most laboratory column experiments as they do not investigate complex mixtures but usually single mechanisms. We do agree that complexity is a problem but we do not see that “many other organic compounds have similar mixture properties” as NOM, which is suggested by the referee without providing concrete examples. We therefore do not think that this topic needs to be brought up in this manuscript as NOM is simply out of our review focus, i.e. column experiments on organic micropollutants. Since we do not discuss “strongly chemically heterogeneous compounds” (i.e. NOM) we do not see a need for including the suggested material here.

Reply to specific comments

Comment 1: 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.

Reply: If the solubility of a compound is changing due to changing parameters, as ORP, T, etc., the compound may sorb or desorb. This does truly change the compound’s rate of transport, but not necessarily the aquifer’s properties (e.g. the porosity). In most cases the aquifer properties should not significantly be altered due to change of solubility, or redox- or other reactions of organic micropollutants, as they occur typically in the ng to μg-range.

Comment 2: 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

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drawn qualitatively capture the mechanics, but would better convey them if they were also physically consistent with model predictions.

Reply: The curves presented in Figure 1 are indeed modelled using the advection dispersion reaction equation, but are plotted at a constant distance (outlet of the column) and shifted for better illustration of the process. However, a strong retardation can deform the curve in a way that dispersion might look bigger than it actually is (i.e. that it looks as if the red curve has undergone less dispersion than the blue one). This is one reason for applying conservative tracers; since they allow for a separation of this effect. To avoid unclear interpretation of the figure we remodeled the figure and plotted the concentrations at a distinct time point (time step 100). The transport parameters used for the forward modelling of the curves are added to the caption: "Figure 1: Schematic representation of solute transport in groundwater, taking into account the main transport processes of advection, hydrodynamic dispersion, retardation, and degradation. BTCs were modelled using the CXTFIT code (Toride et al., 1999). Model was setup as Deterministic equilibrium CDE with flux-averaged concentration and dimensionless parameters. Characteristic length was set as 100. The initial values are: v = 1, D = 0.1*10-7, R = 1, μ = 0 (grey box, only advective transport); v = 1, D = 15, R = 1, μ = 0 (red curve, advective + dispersive transport); v = 1, D = 15, R = 3, μ = 0 (blue curve, retarded transport); v = 1, D = 15, R = 3, μ = 0.01 (green curve additional degradation). Breakthrough was modelled as multiple pulse input with a concentration of c = 1 between time step 10 to 50. The position of the curves within the column are plotted for the time step 100. "

Comment 3: 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.

Reply: The referee is right about this and we will change the text in this paragraph accordingly: "Under sufficiently low flow rates, equilibrium conditions between solid and fluid phase will establish. Then, a compound can only break through when all sorption places are filled according to the new equilibrium. When the system is flushed

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with compound-free water the opposite process takes place, the equilibrium shifts back, and the sorbed compounds are again released into the solution. The result is a delayed breakthrough curve at the observation point (blue curve in Fig. 1). However, under high flow regimes within the column, non-equilibrium conditions might prevail, which can significantly affect the described processes. “

Comment 4: Equation (3) – I don’t believe that rho and theta have been defined.

Reply: Rho and theta were defined in the text above the equation as bulk density and porosity. We will put the symbols in brackets for better identification: “If the distribution coefficient between a solid and liquid phase (Kd) of a specific compound is known, together with the bulk density (rho; " symbol will be added in the document as not supported here") and the porosity (Θ) of the substrate, the retardation factor of this compound can be approximated as follows (Stumm and Morgan, 1996): “

Comment 5: First line Page 8 – degradation can include much more than this – seems way to specific to me.

Reply: According to our knowledge the definition of degradation provided here is well describing the processes discussed in this manuscript.

Comment 6: 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

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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.

Reply: We oppose to the first statement as according to Darcy's law high effective porosities do result in lower flow velocities when the same hydraulic gradient is applied. We agree, however, that one could adapt the flow velocity by increasing the hydraulic gradient (i.e. the pumping rate in a column experiment) to achieve a higher flow velocity. As the referee points out, dimensionless science is poorly understood and hence not much is found on this in the literature on column experiments on organic micropollutants (which is what this review is about) and we therefore did not include this in our review. Furthermore, we do not argue that high flow velocities are desirable in column experiments, we state the opposite (p. 13 lines 5-8): "The flow velocity should ideally reproduce natural groundwater flow velocities, which one would normally expect to be between 1 cm d-1 and 1 m d-1. Using higher velocities allows experiments to be completed more quickly and hence many repetitions, but slow velocities are more likely to provide a realistic representation of natural processes, involving equilibration of solute and solid phases. "

Comment 7: 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.

Reply: We agree that field methods can be excluded here as we do not further discuss them in the manuscript and will therefore remove the respective text passage.

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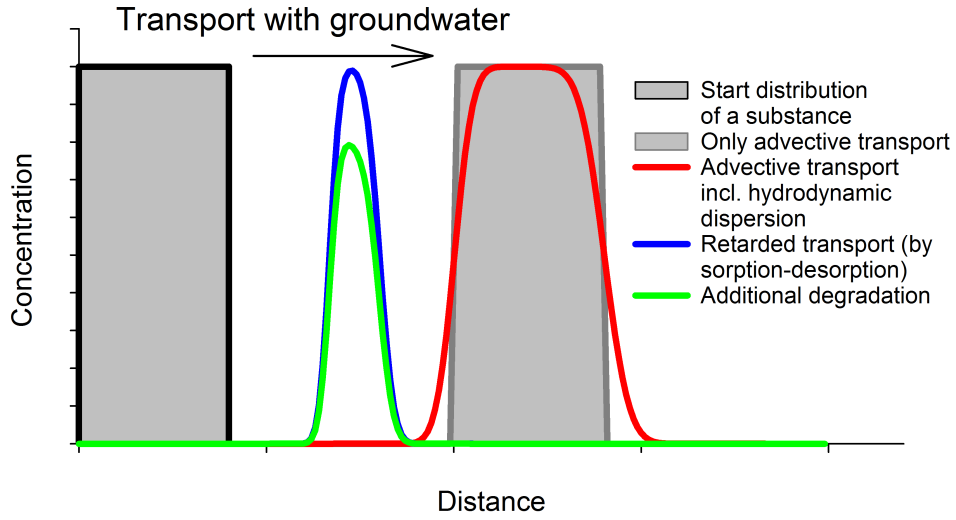

Fig. 1.

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