

## ***Interactive comment on “Quantification of pore-size spectrums by solute breakthrough curves” by S. Erşahin***

**Anonymous Referee #2**

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The manuscript aims to quantify pore-size spectra (not “spectrums”) based on examination of breakthrough curves (BTCs) from a conservative solute. More specifically, as stated on page 8376: “The objectives of this study were (i) to develop a procedure to utilize breakthrough curves of conservative tracers to calculate effective pore-size spectrum for entire range of effective pore-size and (ii) to calculate corresponding pore water velocity spectrum in a porous medium.”

It is debatable whether or not these objectives were met; I am not convinced, based on my comments below. I have several main concerns:

(1) The analysis is based on experiments in which sand columns only 5 cm in length were employed. This is a very short distance, and as demonstrated extensively in the

C4806

literature, not generally sufficient to reach uniform flow conditions, nor to allow a solute front to become fully established. Preferential flow and solute transport patterns will generally dominate. Moreover, the author provides essentially no information on the inlet and outlet boundaries, and no indication of how uniformly the fluid and solute entered and exited the columns. Given the short column length, I have serious reservations as to the real utility of the measured BTCs, especially in the context of the current analysis, which relies on the critical assumption of uniform flow and transport.

(2) Further to (1), a main conclusion is that (e.g., as stated in the Abstract) “The results revealed that size distribution of effective pores could be quite different even in replicates of small sand columns, which are highly similar in particle-size and total porosity.” This result is certainly already well-known, and is rooted at least partly in the short length of the columns.

(3) The analysis of the BTCs is based on a highly simplified theory (page 8378), which employs an empirical “mean pore tortuosity” ( $\tau$ ), and an idealized definition of pore radii. The manuscript should provide more background on the statement: “Radii of capillaries in a size-class can be calculated by (Jury et al., 1991). . .” – does this conceptual picture perceive the pore space as a bundle of capillary tubes? If so, how relevant is an estimated distribution of radii for real flow and transport problems? This approach completely neglects pore \*connectivity\*, which is absolutely critical. The use of expression (5) requires explanation and justification. The analysis in the manuscript also introduces dispersion effects in a highly simplified manner (equation 3), which again assumes uniformity in flow and solute transport patterns that are not likely established in 5 cm columns.

(4) Further to (3), no sensitivity analysis is provided to test different flow rates, to determine “robustness” of estimates of parameter values. It is likely that parameters will vary, given that (fluid and solute) sampling of the pore space varies over time and rate. Also, for example, the value of the empirical “mean tortuosity of the pores” ( $\tau$ ) is not fit to the BTCs, and a value of 1.1 is assumed. What is the sensitivity to the choice

C4807

of this parameter? No analysis was done to test also the sensitivity in the number of segments chosen to analyze the BTCs.

(5) As noted on page 8382, the author observes a right-shift in BTCs with decreasing particle size, stating that “Nielsen and Biggar (1961) attributed the right-shift in their study to amount of water not displaced during the miscible displacement. Figures 1–4 show that considerable amount water was not displaced in the columns and that calculated values of mobile water fraction (beta) in the columns were not correlated to particle-size.” These findings confirm the above comments, that the flow and transport patterns are not uniform (required for the theoretical analysis employed in the manuscript), which can be due to the short column length and the inherent heterogeneity of the porous medium, as well as to the nature of the inlet and outlet boundary conditions. Also, introducing fluid and solute into a vertical column, from above, may lead to instabilities and density-dependent flow.

(6) Further to the above-mentioned concerns regarding variability – Figures 1-4 demonstrate very significant variability. I do not agree with the author’s statements regarding reproducibility and similarity among the replicates. The BTCs are not symmetrical (which is required in the theory underlying the analysis), and vary considerably from one replicate to the next. The plots for pore water velocity and pore radii are given on different vertical and horizontal scales – the scales should be unified – but this will show huge variability among replicates.

(7) On page 8383, the authors states that “In general, the model under predicted mean pore water velocity particularly for greater vbm values (Fig. 5) (those values for 2–1 and 1–0.5mm sand sizes). However, in overall, the measured and predicted vb values were highly associated as indicated by high correlation coefficient ( $r = 0.89$ ,  $P < 0.01$ ) calculated between measured and predicted values.” First, the plot shows a different P value ( $P < 0.001$ ). Regardless of the  $r$  and  $P$  values, which do not appear to be correct, the correlation is not particularly good, showing systematic deviation below the line.

C4808

(8) As a minor note, the manuscript contains many typographical errors which require careful attention.

To conclude: On the basis of my comments above, I cannot recommend publication of this manuscript. Major revision (at the very least) is required – and even then, the experimental setup and use of an inconsistent theory suggest that the manuscript is seriously flawed and should be rejected. I note that on page 8388, last sentence of conclusions, the author states that: “Another study is currently underway to evaluate the proposed model on disturbed and undisturbed soil columns (30 cm long and 8.5 cm id) to extend its use to more complicated conditions.” Use of a 30 cm long column is more appropriate; it might be best to wait until these newer results are available and combine whatever can be justified from the current manuscript.

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C4809