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Hydrology and Earth System Sciences Discussions

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

S. Ersahin

acapsu@gmail.com

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The author appreciates Referee2 for her/his evaluation of this manuscript. Some of his/her suggestions were highly esteemed while others were found negotiable. The author's responses to the referee's critics/concerns are listed below.

1. The referee criticizes length of the columns (5.0 cm) used for the tests, stating that the length of the columns are generally not sufficient to reach uniform flow conditions, nor to allow a uniform solute to become fully established, and preferential flow and solute transport patterns will generally dominate. The column experiments have been used for over 300 years to study hydrogeological properties. However, no attempts have been made to standardize or compile best practices to construct a soil column

and literature shows a bewildering array of technical approaches. “Some of the smallest columns reported in the literature measure 1 cm in diameter and 1.4 cm in length” (Lewis and Sjöstrom, 2010). Perfect et al. (2002) used 6 cm long undisturbed soil columns to investigate relation between the coefficient of lateral mass exchange and water retention curve. Selim et al. (1989) used disturbed soil columns with 4.4 cm id and 6.35 cm long disturbed soil columns to investigate chromium mobility and interactions in six different soils. In undisturbed aggregated soil columns, short columns may not be appropriate due to preferential flow effect while for uniformly repacked columns, as used in this study, short columns can be appropriate (Fried and Combarnous, 1971). Preferential flow effect in transport of a noreactive chemical is characterized by early appearance and slow approach to relative concentration of unity. Inspection of BTCs reveals that neither of these conditions existed in the columns. This suggests that it’s hard to consider a preferential flow effect in these columns. In sand, preferential flow occurs as fingering. Fingering occurs when instability develops in the wetting as through coarse unsaturated sand. It has been demonstrated that the fingers doesn’t form in very dry and saturated sand (Lewis and Sjöstrom, 2010). Since this study was conducted in completely saturated conditions, preferential flow was not likely to occur. As it’s is well known, the hydrodynamic dispersion (HD) is the combined effects of diffusion of transported solute at the front, and mechanical dispersion. According to Roberts et al. (1987), HD is thought to have governed the front shape in experiments at low pore water velocity. Moreover, Han et al. (1985) stated that longitudinal dispersivities were smaller in uniform particle case. Unless the fluid is nearly immobile, mechanical dispersion dominates and molecular diffusion effect can be neglected (Lewis and Sjöstrom, 2010). In the present experiment, the columns were packed with uniform sand, and pore water velocity is high enough to establish a relatively uniform solute front. Shapes of the BTCs also indicate that a uniform solute front was established during test. The referee states that the theory applied in this experiment assumes uniform transport conditions. However, there is no such assumption stated explicitly in the manuscript. Theory can be applied to both uniform non-uniform transport conditions. The column diameter is also important. Lewis and Sjöstrom (2010) reported that columns with diameter <7.59 cm have grater dispersivity than column with diameter<7.59 cm. Also, Bromly et al. (2007) reported that columns longer that 10.7 cm produced dispersivities grater than columns shorter than 10.7 cm. In the case of non-ideal solute input, the column length is important to attenuate the input heterogeneity. In the present studuy, the solute input was highly uniform as it was supplied uniformly on the column surface by a disk infiltrometer.

2. Again, I disagree with the referee's conclusions that size distribution of effective pores is quite different in uniform sand columns is partly rooted to in the short length of the columns. The size distribution of effective pores could be highly different from that total pores (effective + noneffective pores). During the packing, slight differences in packed lenses of sand particles may result in considerable differences in continuity, conductivity, tourtuousity, and so on of the effective pores even in uniformly packed columns (Lewis and Sjöstrom, 2010). For example, inclined micro-layers may form during the packing in one column while no such conditions exist in another, resulting in differences in the flow conditions and corresponding size-distribution of effective pores between two columns. Mechanical dispersion is caused by microscopic flow velocity caused by differences in the pore size and geometrices, creating localized dilutions (Lewis and Sjöstrom, 2010). Therefore, differences caused during packing of the columns would result in the differences among replicates.

3. The theory used in this study was applied to BTCs of a nonreactive solute (Cl). The correlation coefficient calculated between masured and calulcated values of saturated pore water velocity values was 0.89, suggesting that there is still an 11% of uncertainty between measured and calculated values. This uncertainty would be resulted form the conditions that could not be accounted by the model and/or error from the experimental setup and laboratory analysis of the effluent collected. Coming to pore connectivity, the Eq. (5) in the manuscript calculates narrowest mean radius of the pores in an effective capillary class. The model not only accounts for hydrodynamic

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dispersion in the mobile region but also accounts for mass exchange between mobile and immobile regions and between mobile domains. The model accounts for the connectivity intrinsically since it calculates the narrowest mean radius for a given capillary class. However, accounting pore connectivity explicitly may require use of results from some other techniques (such as CP, three dimensional visualization techniques, and so on) of pore size analysis together with the model used in this study. Also, pore connectivity may be parameterized using fractal dimension of the pores size distribibuiton in the system. However, all these make the model more complicated while improving it. Literature was sited for expression (5). I am not sure what kind of explanation and justification is needed for this expression. Should I restate the information in the cited literature?

4. The referee criticizes that no sensitivy analysis was conducted to test different flow rates to determine robustness of estimates of different parameters. The model used in this study determines of pore size distribution using amont of water needed to transport a known amount of solute and within a known length of time, in which the solute traveled along a known distance. Conducting this experimet under strained flow rates would be intervining the system that contradicts with the stated theory. I am not sure whether the referee meant conducting the experiment under different matric heads to eliminate contribution of given pores from the system. If he/she meant this, it has been stated already in the manuscript that condcuting an experiment even under a slightly low matric head takes very long time, and therefore, the validation was limited to saturated condutions. However, validation under different matric heads may be done by another study. The referee further criticizes the value of 1.10 chosen for mean tourtuousity. This value was chosen based on the discussion by Radulovich et al. (1989). The literature was already cited in the manuscript. The referee suggests that sensitivity of chosen values may be tested. However, this may result in negligible difference in values of tau to be used in different columns. As it was already stated in the manuscript, the short columns were deliberately chosen to decrease the effect of uncontrolled variables such as tortuousity. The average value of pore water velocity for all the effective

capillaries in the column was calculated by Eq. (8). This equation takes geometric mean of corresponding capillary bundles calculated with the segments. The calculations showed that the equation is highly robust to number of segment chosen since it takes the geometric mean of segments, and around 20 segments was ideal. That is why use of 20 segments was suggested in the manuscript.

5. As also stated by the referee, Nielsen and Biggar observed that some of the water in the system was immobile/less mobile. Experimental setup used by Nielsen and Biggar (30 cm long columns unfiromly distributed soil agrregates) was highly proper to obtaine symmetrical BTCs. Even under those conditions, they observed that some water was not displaced during the test. This shows that column lengt may not be main suspect for presence of some immobile water in the system. Some other resons should be sought behind this phenomenon. Also, traditional mobile/immobile water concept used in multiple dominas (such as two region physical nonequlibrium model) is somehow vogue. Water deemed immobile in a relatively high mean flow rate, may be deemed mobile when the flow rate becomes lower in the same system. Therefore, the model used in this study assumes that some of the water in the system is completely immobile and it calculates size spectrum of pores (effective pores) in only the mobile regions. The model used in this study assumes that the amount of immobile water content never changes with changing mean pore water velocity in the system. The columns were saturated with 0.01 M KBr solution and then were leached with this solution extensively until steady state flow conditions were set to prevent a flow insatiability caused suddenly changed ionic strength. Therefore the referee's concerns of flow instability and density dependent flow may be needles. Also, the method used in this study, have been used by numerous of published studies.

6. Inspecting the pore size spectra graphs in Figs 1-4 (right graphs), shows that the location of pore spectra on the x-axes gradually shits left against decreased particle size. The ANOVA test conducted later on the request of Referee 1 showed that means of pore water velocity was significantly different ($P<0.05$) for different particle size treat-

ments. This showed that, referee's concern of that data are not reproducible due to high in treatment variability (significant error) is needles. In addition, inspecting the Figs. 1-4 (right figures) show that the location of pore size spectra on the x-axis gradually shifted to left against decreased particle size, also justifying that the model described well the relation between particle size and effective pore size. However, it was stated in the manuscripts that pore size spectra of replicates were highly dissimilar and it was attributed to the artifacts caused during packing as already stated above. These differences can be attributed the differences in the geometry of effective pores and lenses of more homogenous particle domains formed at packing.

7. The referee criticizes the P and r values, stating that these values would not be correct. The values were given in the Fig.5. I conducted a correlation analysis between measured and calculated values (by Minitab), which are graphed in the Fig.5, and I found those reported values of r and P. I am providing my measured and calculated values at the end of this letter (Table 1). Please run a correlation analysis and see the results. As it is well known, a correlation analysis measures the similarity between values of two variables. That is, it measures if high values of one variable match with high values of other variable (positive relation), or high values of one variable match low values of the other (negative relation). Also, the P value of correlation analysis depends on sample number as well as it depends on strength of relationship. The correlation analysis doesn't measure any global and local trend in the prediction. That is why a 1:1-line was used together with r and P of correlation test to judge both quantity and quality of prediction value of the model. I have already stated the weakness of the model in the manuscript, stating that it underestimated at high end of the data. This weakness may be investigated in another study. In modeling studies, contrary to mathematical equations, no prediction model is expected perfect, since always some uncertainty lies between predicted and measured values. For example, most widely used regression models have a systematic smoothing effect. Kriging technique used in many areas often results in local and global trends in predictions depending on the semivariograms and nature of the data used. I think that the model should be used with different data

sets to identify the possible reasons behind this weakness. However, such an effort requires several different studies conducted with different materials.

8. The manuscript was gone over for typographical error, grammar mistakes and wrong sentence structures. The corrections were made, accordingly.

9. The changes made in accordance with referee's suggestions are added to revised manuscript.

Table. 1. Data for measured and calculated values of pore water velocity (cm s-1) v-measured v-calculated

0.115 0.115

0.126 0.083

0.11 0.074

0.084 0.07

0.099 0.11

0.11 0.068

0.077 0.064

0.086 0.062

0.089 0.052

0018 0.01

0.01 0.013

0.015 0.006

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Please also note the supplement to this comment:
http://www.hydrol-earth-syst-sci-discuss.net/8/C5336/2011/hessd-8-C5336-2011-supplement.pdf

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