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How well are breakthrough-curve shape-measures determined by the available data?

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The shape of a non-reactive solute breakthrough curve (BTC) provides a means of inferring soil transport properties. It is, for instance, often stated that 'early tracer arrival' or 'pronounced tailing' suggest preferential flow. One example of a measure for the former is the arrival-time of the solute-peak relative to the mean arrival-time, an example of the latter is the skewness. However, the adequacy and robustness of such measures have rarely been investigated quantitatively. One reason for this may be the difficulty of extracting a transfer-function from the BTC. Instead, the convection-dispersion equation (CDE) or the mobile-immobile model (MIM) is most often fitted to the data. In principle, the CDE or MIM parameters may be used to reconstruct a transfer-function for the BTC from which shape-measures may be derived. The CDE (or MIM) acts then as a regularization constraint for the de-convolution of the BTC. Both transport models assume Gaussian solute transport, the CDE entirely, the MIM only in the mobile domain. As it is known that the prerequisites for Gaussian transport in undisturbed soils are a rare exception rather than the rule, these two models cannot be considered as optimal for the regularization of the BTC de-convolution. Instead, other functions may perform as well or even better, for example the log-normal or the Gamma function.
In this study, we applied 7 different de-convolution approaches to 121 BTCs sampled from the peer-reviewed literature. We investigated the sensitivity of 18 shape-measures to the choice of regularization method. The least sensitive shape-measures were the peak-concentration, the absolute first temporal moment, the normalized time-lag between the arrival of 5% and 85% tracer mass, the truncated standard deviation (truncation after 3 mean arrival-times), and the normalized arrival time of the first 5% of the tracer mass. In contrast, the standard deviation and skewness (or the 2nd and 3rd temporal moments) were more defined by the choice of regularization method than by the data, since they are strongly affected by later arrival times which are not often sampled. We conclude in accordance with preceding studies that the standard deviation and skewness are not suitable to characterize BTCs unless data for the very late arrival times are available and an optimal regularization approach can be identified. Robust shape-measures, such as the normalized arrival-time of the first 5% of the tracer, may be derived from CDE or MIM parameters and used for BTC classification, for example, with respect to the degree of preferential flow.