# MODELLING OF NON-FICKIAN TRANSPORT IN LABORATORY SAND COLUMNS: THE ROLE OF SOLUTE HETEROGENEITY

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Transport of reactive sorbing solutes through porous media is commonly quantified by implementing an effective retardation coefficient in the advection-dispersion equation (ADE), which describes dispersion in accordance with Fick's law. However, anomalous (non-Fickian) transport behavior can be observed in systems with heterogeneous retardation coefficients (Dentz & Castro, 2009). In such systems, the ADE is unable to reproduce the non-Fickian nature of plume shapes and breakthrough curves, motivating the development and application of alternative solute transport theories, such as the continuous time random walk (CTRW) or multi-rate mass transfer (MRMT).

Heterogeneity in retardation coefficients in practice arises from variability in the geochemical properties controlling sorption-desorption kinetics between the solute and mineral surfaces. These distributions have been described in the context of heterogeneity of the porous medium, but to date little attention has been given to the potential role of a geochemically heterogeneous solute. In this work, we consider a system in which anomalous transport arises during the passage of natural organic matter (NOM), a polydisperse mixture of compounds derived from the breakdown of plants and microorganisms in the environment, through homogeneous laboratory sand columns.

NOM solutions were passed through columns containing either hematite, corundum, or a naturally-coated quartz sand at a variety of pH and ionic strength conditions. Influent and effluent NOM concentration was measured as UV absorbance at 254 nm. The resulting breakthrough curves are non-Fickian, displaying power-law tailing at late times. Such curves cannot be predicted by the ADE model. Reactivity of NOM components is known to be related to their molecular weight (MW), which tends to be log-normally distributed in aquatic NOM isolates (Cabaniss et al., 2000). Low-MW compounds are more water-soluble, have a higher diffusion coefficient, and due to their smaller structure, are able to enter nanopores which exclude macromolecules. Conversely, high-MW components are hydrophobic, less mobile, and have a greater affinity for metal binding than their smaller counterparts.

By analyzing the transport of different NOM components in the effluent solution over time we see that there is a clear heterogeneity in the retardation of the different NOM components. Using the approaches of Dentz & Castro (2009) and Dentz & Bolster (2011) we can show that the effective upscaled transport can be modeled as a CTRW. To this end we demonstrate that the CTRW and MRMT models (which can be shown to be intricately related) can indeed faithfully capture the observed behavior.

From a practical perspective, our experiments demonstrate increased mobility of low-MW fractions of NOM relative to high-MW fractions, which – given the ability of NOM to bind to organic compounds, metals, and radionuclides – could have important implications for contaminant transport in groundwater systems.