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

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The mobility of reactive solutes in porous media is commonly quantified by implementing an effective retardation coefficient (R) in the advection-dispersion equation (ADE) to account for adsorption-desorption reactions. The ADE assumes dispersion in accordance with Fick's law; however, anomalous (i.e. non-Fickian) transport behavior can occur in systems where R is variable (*1-2*). 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 R arises from variability in the geochemical properties controlling sorption-desorption kinetics between the solute and mineral surfaces. While this has been examined in the context of a heterogeneous porous medium, 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.

Differences in the transport rates of NOM subcomponents through porous media occur due to heterogeneity in the geochemical properties of these components, which in turn is strongly correlated to their molecular weight (MW). Specifically, high-MW NOM fractions preferentially adsorb to mineral surfaces, and are less mobile than their hydrophilic, low-MW counterparts. The resulting 'adsorptive fractionation' can manifest itself in extended tailing of breakthrough curves (BTCs). Evidence of this phenomenon has been observed in laboratory column experiments and field tracer tests (*3-4*).

NOM solutions were passed through columns containing naturally Fe/Al oxide-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 BTCs displayed power-law tailing at late times, a behavior that cannot be captured by the ADE model. Furthermore, analysis of the MW distribution of NOM in the effluent solution over time by high-pressure size exclusion chromatography (HPSEC) revealed 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.

References

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