A New Modeling Tool to Estimate Cleanup Rates in Highly Heterogeneous Aquifers with Matrix Diffusion and Time-Dependent Source Mass Flux

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Background/Objectives

With the advent of high resolution site characterization (HRSC) tools, it is now known that most sites are highly heterogeneous with mobile contaminants moving along a preferential transport pathways particularly when the variance of hydraulic conductivity measurements is greater than one. In addition to heterogeneous advection, contaminants also diffuse into nearby low permeability silt and clay immobile zones with slow back-diffusion rates into the mobile zones. For plume transport in heterogeneous mobile and immobile zones, the standard ADE can fail to capture the frequently observed long tails of contaminant concentration versus time in monitor well data leading to significantly underestimated cleanup timeframes. Based on the success of the continuous time random walk (CTRW) modeling framework in capturing observed tailing in many field and laboratory studies, this paper presents an extended ADE model that simulates heterogeneous advection, sorption, matrix diffusion, and sequential first-order reactions of both parent (e.g. TCE) and its degradation products (e.g. cis 1,2 DCE and VC). New analytical solutions are presented that can simulate effects on downgradient plume concentrations as a result of changes in source mass flux over time from either natural source zone depletion (NSZD) or active source zone remediation.

Approach/Activities

Because of the inability to fully characterize the variability in subsurface permeability and diffusion coefficient values in highly heterogeneous mobile and immobile zones even with HSRC tools, both advection and matrix diffusion are represented stochastically using a generalized ADE. This new extension of the ADE uses probability density functions to represent contaminant transport in the mobile and immobile zones. The key parameter for the extended model is the power law exponent (β) of the travel time function, which is related to the variance of hydraulic conductivity data measurements Burnell et. al. (2018). As a case study example, this new CTRW modeling tool is then applied to estimate the cleanup timeframe of both parent (TCE) and its degradation products (cis 1,2 DCE and VC) based on the observed long tails of slow decreasing concentrations over time in monitor well data at the Harris CERCLA site in Palm Bay, FL.

Mathematical Model

$$\frac{\partial C_1(x,t)}{\partial t} = \int_0^t \frac{M_1(t-t')}{R_1} e^{-k_1(t-t')} \left(-v\frac{\partial C_1(x,t')}{\partial x} + D\frac{\partial^2 C_1(x,t')}{\partial x^2}\right) dt' - k_1 C_1(x,t)$$

$$\frac{\partial C_2(x,t)}{\partial t} = \int_0^t \frac{M_2(t-t')}{R_2} e^{-k_2(t-t')} \left(-v\frac{\partial C_2(x,t')}{\partial x} + D\frac{\partial^2 C_2(x,t')}{\partial x^2}\right) dt' + \frac{k_1 y_{21} R_1}{R_2} C_1(x,t) - k_2 C_2(x,t)$$

$$\frac{\partial C_3(x,t)}{\partial t} = \int_0^t \frac{M_3(t-t')}{R_3} e^{-k_3(t-t')} \left(-v\frac{\partial C_3(x,t')}{\partial x} + D\frac{\partial^2 C_3(x,t')}{\partial x^2}\right) dt' + \frac{k_2 y_{32} R_2}{R_3} C_2(x,t) - k_3 C_3(x,t)$$

The initial and boundary conditions are:

$$C_1(x,0) = C_2(x,0) = C_3(x,0) = 0$$

$$C_1(0,t) = e^{-\gamma t} \quad C_2(0,t) = C_3(0,t) = 0$$

$$C_1, C_2, C_3 \to 0 \quad as \quad x \to \infty$$

In these equations, C_1, C_2, and C_3 are the flux concentrations for three sequentially degrading dissolved species (e.g. TCE, cis 1,2 DCE, and VC), y_{ij} is the yield coefficient with i=1,2 and j=2,3, k_i and R_i are the degradation rate constant and average retardation factor, respectively, for species i, v is the transport velocity, and D is the hydrodynamic dispersion coefficient. As indicated in the initial condition, no mass is assumed to be present initially. For these boundary conditions, the parent (e.g. TCE) is assumed to be a decaying source. In addition, the concentrations are assumed to vanish at large distances from the source.

Analytical Solution

The general solution for transient plume transport in Laplace space is:

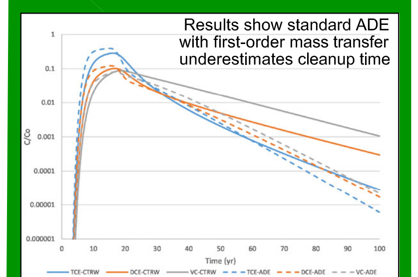
$$\tilde{C}_1(x,s) = \frac{C_{10} e^{r_1 x}}{s+\gamma}$$

$$\tilde{C}_2(x,s) = \frac{C_{10} k_1 y_{21} \tilde{M}_1 (s+k_1)(e^{r_2 x} - e^{r_1 x})}{(s+\gamma)\left[\left(k_1\frac{R_1}{R_2}+s\right)\tilde{M}_2(s+k_2) - \frac{R_2(k_2+s)}{R_1}\tilde{M}_1(s+k_1)\right]}$$

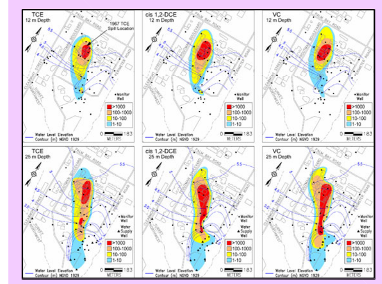
$$\tilde{C}_3(x,s) = \frac{C_{10} k_1 y_{21} k_2 y_{32} \tilde{M}_1' \tilde{M}_2' (e^{r_3 x} - e^{r_2 x})}{(s+\gamma)\left[\left(k_1\frac{R_1}{R_2}+s\right)\tilde{M}_2' - \left(k_2\frac{R_2}{R_3}+s\right)\tilde{M}_1'\right]\left[\left(k_2\frac{R_2}{R_3}+s\right)\tilde{M}_3' - (k_3+s)\tilde{M}_2'\right]} - \frac{C_{10} k_1 y_{21} k_2 y_{32} \tilde{M}_1' \tilde{M}_2' (e^{r_3 x} - e^{r_1 x})}{(s+\gamma)\left[\left(k_1\frac{R_1}{R_2}+s\right)\tilde{M}_2' - \left(k_2\frac{R_2}{R_3}+s\right)\tilde{M}_1'\right]\left[\left(k_1\frac{R_1}{R_2}+s\right)\tilde{M}_3' - (k_3+s)\tilde{M}_1'\right]}$$

where $r_i = \frac{1}{2D}\left(v - \sqrt{v^2 + 4DR_i\frac{(s+k_i)}{\tilde{M}_i(s+k_i)}}\right)$ and $\tilde{M}_i' = \frac{\tilde{M}_i(s+k_i)}{R_i}$. These Laplace domain solutions can be easily inverted numerically using the de Hoog (1982) algorithm to provide either flux concentration plume spatial profiles at various times or breakthrough concentration versus time curves at a given location.

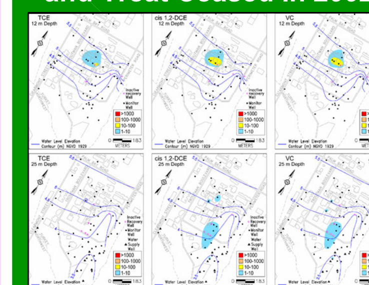
Comparison with Standard ADE and Matrix Diffusion

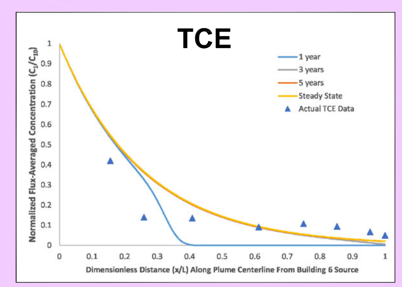


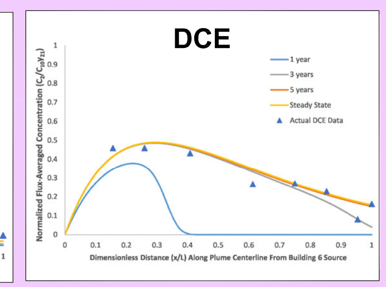
1984 Steady-state Plumes Before Remediation

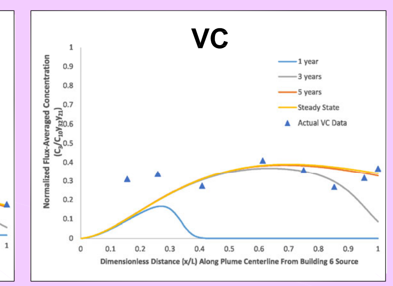


2018 Plumes After Pump and Treat Ceased in 2002

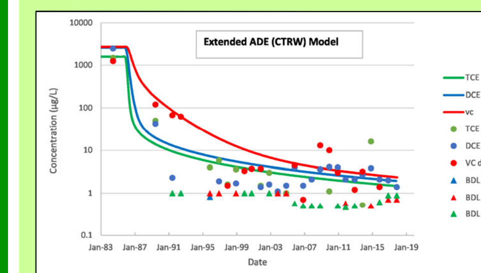








Application of Tool for MNA at CERCLA Site in FL



Long Tails at MW-35D not Captured Using Standard ADE with Matrix Diffusion

Results/Lessons Learned

Results of this study indicates that standard ADE models, which use first-order mass transfer for matrix diffusion, may under-predict both the cleanup rates and overall cleanup timeframe particularly when degradation rates are low. The extended ADE (CTRW) model in this study is a natural extension of the standard ADE and is parsimonious with only a few model parameters that can be measured in the field. Both mobile and immobile zone concentrations can be estimated for comparison with field data. This extended ADE model is easy to use and is applicable for adsorption-desorption, matrix diffusion, and mass destruction via first-order sequential first-order reactions. With the extension of this modeling framework for time-dependent source releases, this modeling tool is expected to be particularly useful for improving estimates of the MNA cleanup timeframes of large dilute plumes as part of long term site management.