Transport of Kinetically Sorbing Solutes in Heterogeneous Sediments with Multimodal Conductivity and Hierarchical Organization Across Scales

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Introduction

Solute transport in the subsurface is controlled by geologic heterogeneity across scales. In reactive transport characterized by low Damkohler numbers, it is also controlled by the rate of kinetic mass transfer. A theory for the influence of sedimentary texture on the transport of kinetically sorbing solutes in heterogeneous porous formations is derived using the Lagrangian-based stochastic methodology. The resulting model represents the hierarchical organization of sedimentary textures and associated modes of log conductivity (K) for reactive hydrofacies through a hierarchical Markov Chain. The model characterizes kinetic sorption using a spatially uniform linear reversible rate expression. Our main interest is to investigate the relative effects of sorption kinetics and dispersion. Our analysis is focused on model parameters defined at each hierarchical level (scale) including the integral scales of K spatial correlation, the anisotropy ratios (ratio of the vertical conductivity integral scales to the horizontal counterpart), the indicator correlation scales, and the contrast in mean K between facies defined at different scales. Anisotropy ratios have negligible effect upon the longitudinal dispersion of sorbing solutes. Dispersion depends mostly on indicator correlation scales, integral scales, and the contrast of the mean conductivity between units at different scales. It is most sensitive to the contrast in mean K.

Transport of Kinetically Sorbing Solutes

The governing equations for transport of kinetically sorbing solutes are represented as follows (Quinodoz and Valocchi, 1993):

$$\frac{\partial c}{\partial t} + U.\nabla c = \frac{\partial s}{\partial t}$$

$$\frac{\partial s}{\partial t} = k_f c - k_r s = k_r (K_d c - s)$$

where c and s are the solute concentrations in liquid (mobile) and solid (immobile) phases, respectively, U is the pore water velocity, k_f and k_r are the forward and backward rate coefficients and $K_d = k_f / k_r$ is the partition coefficient.

Solving the governing equations using Lagrangian-based theory will lead to the following longitudinal dispersivity for plume spreading undergoing kinetic reactions(Massabo et al., 2008):

$$\alpha_{11}(t) = \frac{1}{2}\frac{1}{|U|}\frac{dX_{ij}}{dt} = \alpha^{(1)}{}_{11}(t) + \alpha^{(2)}{}_{11}(t)$$

$$\alpha^{(1)}{}_{11}(t) = \frac{\alpha_{11}{}^{(nr)}(\mu_{tm})}{R_s(t)} \quad , \quad \alpha^{(2)}{}_{11}(t) = \frac{K_d}{\mathrm{R}^3{}_d}\frac{U_i}{k_r}\frac{U_j}{|U|}F(k_r, t, K_d)$$

$$F(k_r, t, K_d) = \frac{1}{2}(1+K_d e^{-k_r R_d t})^{-3}\{2(1-K_d e^{-k_r R_d t})^3 e^{-k_r R_d t} K_d (1-K_d)(k_r R_d t)^2 (1+\frac{1-K_d}{e^{k_r R_d t}}) - e^{-k_r R_d t}(1-(k_r R_d t)^2 K_d)$$
$$+ 2K_d{}^2 \frac{1-k_r R_d t}{e^{k_r R_d t}}(e^{-k_r R_d t}K_d - 3) + \frac{1+\Upsilon}{e^{k_r R_d t}}[6 e^{-k_r R_d t} K_d - (1+k_r R_d t)]\}$$

where $\alpha_{11}{}^{(1)}$ returns the combined effects of the reaction kinetics and formation heterogeneity (dispersion -kinetic term), and $\alpha_{11}{}^{(2)}$ is just the contribution from the reaction kinetics (kinetics only term). The $\alpha_{11}{}^{(nr)}$ is the dispersivity tensor of a nonreactive solute and R_s is the time-dependent retardation factor:

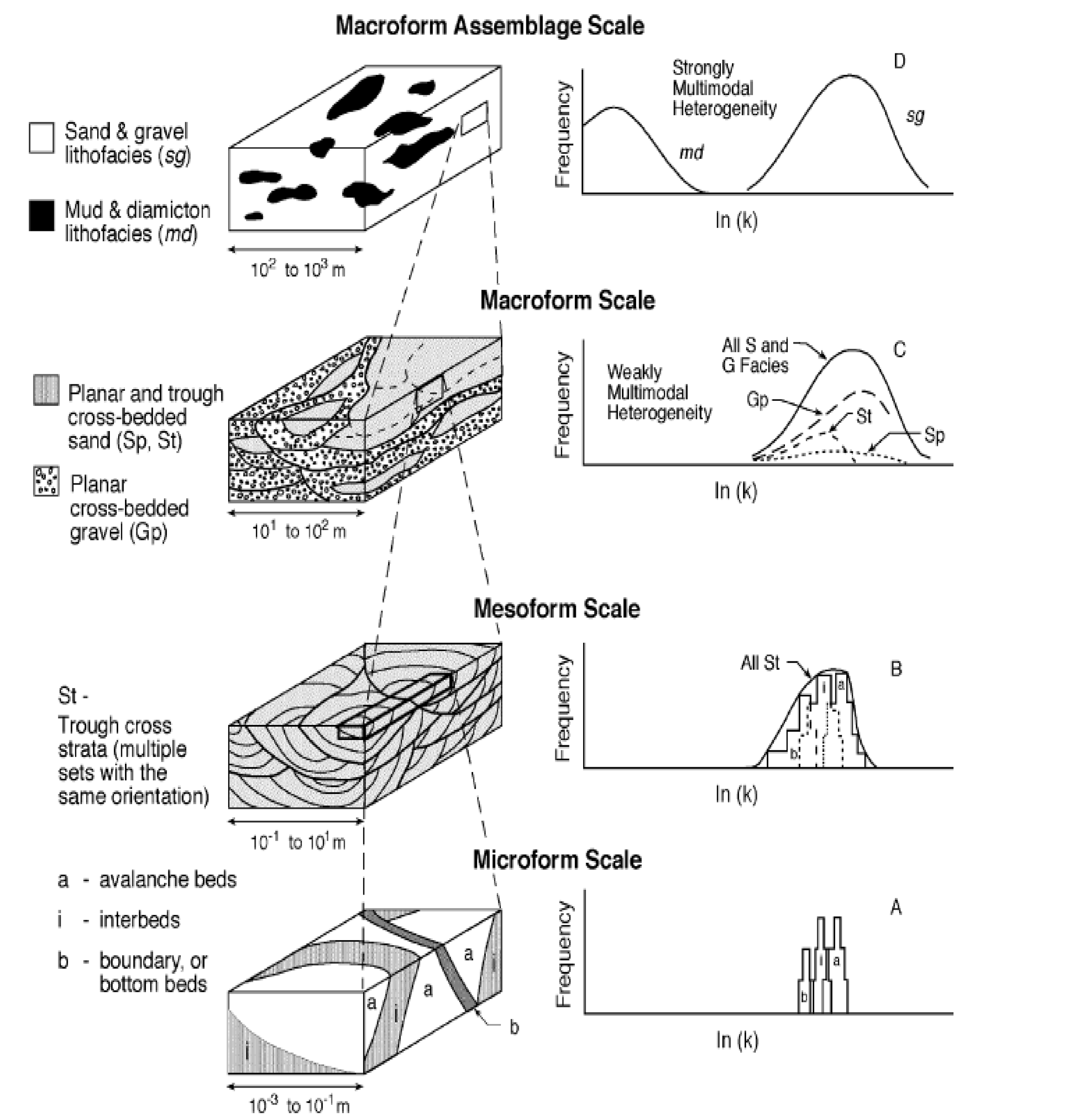
$$R_s(t) = R_d (1+K_d e^{-k_r R_d t})^2 [1 + K_d e^{-k_r R_d t} R_d [3 + (1-K_d)k_r t] + K^3{}_d e^{-2k_r R_d t}]^{-1}$$

$$R_d = 1 + K_d$$

Hierarchical Sedimentary Architecture

Sedimentary deposits can be conceptualized as an aggregation of stratal units. These units can be defined at different spatial scales within a hierarchical framework, i.e., the larger-scale unit types are made up of smaller-scale unit types which, in turn, are made up of still smaller unit types, and so on. The spatial correlation of K can be strongly related to this hierarchical stratal architecture.

Figure 1. Conceptual framework of heterogeneous sediment with multimodal conductivity and hierarchical organization across scales.(A) Microform scale, (B) Mesoform scale variance increases relative to microforms as larger volume is sampled,(C) Macroform scale. (D) Macroform scale (from Dai et al., 2004).



The hierarchy of sedimentary units and subpopulations for $Y=ln(K)$ can be represented with combined continuous indicator spatial variables. The anisotropic covariance model for $Y=ln(K)$ and its global integral scale are:

$$C_Y(\tilde{h}) = \sum_{o=1}^{N}\sum_{k=1}^{N_o} p^2{}_{ok}\sigma^2{}_{ok} e^{(\frac{-\tilde{h}}{\lambda_{ok}})} + \sum_{o=1}^{N}\sum_{k=1}^{N_o} p_{ok}(1-p_{ok})\sigma^2{}_{ok} e^{(\frac{-\tilde{h}}{\frac{\lambda_{ok}\lambda_I}{(\lambda_{ok}+\lambda_I)}})} + \frac{1}{2}\sum_{o=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N_o}\sum_{i=1}^{N_j}(m_{ok}-m_{ji})^2 p_{ok} p_{ji} e^{(\frac{-\tilde{h}}{\lambda_I})}$$

$$\lambda_Y = \frac{\sum_{o=1}^{N}\sum_{k=1}^{N_o} p^2{}_{ok}\sigma^2{}_{ok}\lambda_{ok} + \sum_{o=1}^{N}\sum_{k=1}^{N_o} p_{ok}(1-p_{ok})\sigma^2{}_{ok}\frac{\lambda_{ok}\lambda_I}{(\lambda_{ok}+\lambda_I)} + \frac{1}{2}\sum_{o=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N_o}\sum_{i=1}^{N_j}(m_{ok}-m_{ji})^2 p_{ok} p_{ji}\lambda_I}{\sum_{o=1}^{N}\sum_{k=1}^{N_o} p^2{}_{ok}\sigma^2{}_{ok} + \frac{1}{2}\sum_{o=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N_o}\sum_{i=1}^{N_j} p_{ok} p_{ji}(m_{ok}-m_{ji})^2}$$

The dispersivity tensor of a nonreactive solute with multimodal conductivity and hierarchical organization across scales is given by:

Table 1. Coefficients of ζ and η used in the calculation of dispersivity tensor

μ	1	2	3
$\zeta_{\mu ok}$	λ_{ok}	$\lambda_{ok}\lambda_I/(\lambda_{ok}+\lambda_I)$	λ_I
$\eta_{\mu ok}$	$\sigma^2{}_{ok} p^2{}_{ok}$	$\sigma^2{}_{ok} p_{ok}(1-p_{ok})$	$\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N_j} p_{ok} p_{ji}(m_{ok}-m_{ji})^2$

$$\alpha^{(nr)}{}_{11}(t) = \sum_{\mu=1}^{3}\sum_{o=1}^{N}\sum_{k=1}^{N_o}\xi_{\mu ok}\,\eta_{\mu ok}\{1-e^{(-\tau_{\mu k})} - \varepsilon\int_0^\infty (2RJ_1(R\tau_{\mu ok})\frac{2(1+R^2)^{\frac{3}{2}} - \varepsilon R(3+3R^2-\varepsilon^2R^2)}{(1+R^2-\varepsilon^2R^2)^2(1+R^2)^{\frac{3}{2}}} + F(R))\,dR\}$$

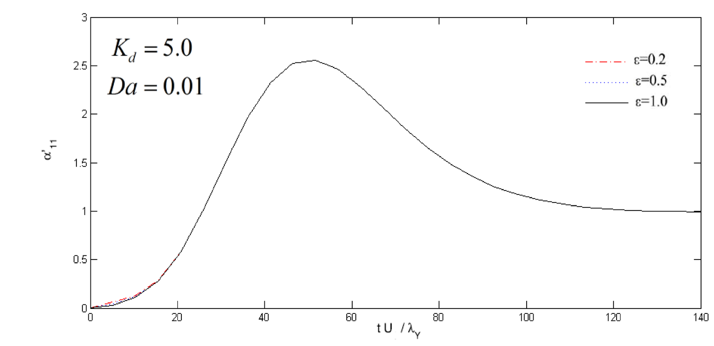
Numerical Example

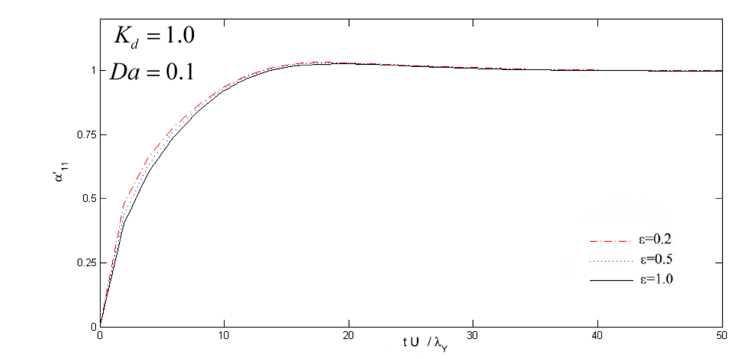
The impact of different parameters including, anisotropy ratio, indicator scale, integral scales, and mean conductivity upon overall spreading of the kinetically sorbing solutes was investigated. Our main interest was to investigate the relative effect of sorption kinetics and dispersion. Therefore, in our analysis we set the Damkohler number to 0.1 so that the advection timescale is smaller than the timescale of reaction.

Table 2. The parameters used for computing the longitudinal dispersivity

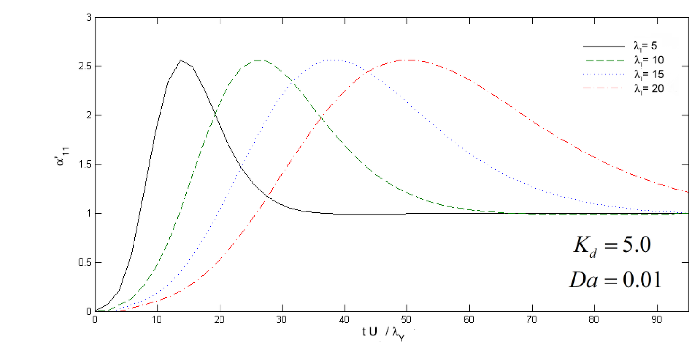
Mesoform (o)	Microform (k)	p_{ok}	K_{Gok} (m/d)	m_{ok}	λ_{ok} (m)	$\sigma^2{}_{ok}$	λ_I (m)
1	1	0.2	0.1	-2.303	3	0.1	10
2	1	0.5	0.5	-0.693	5	0.2	10
	2	0.3	1.0	0	3	0.3	10

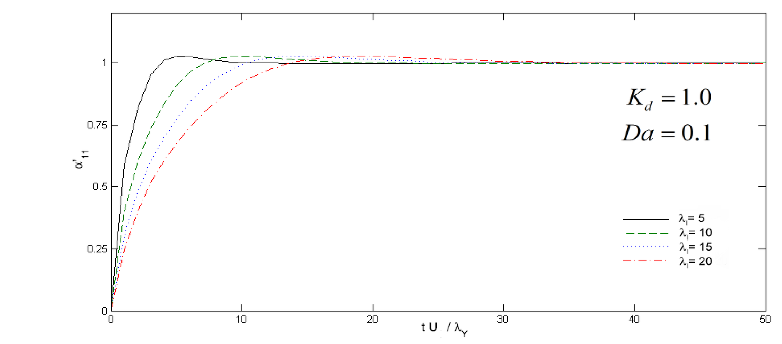
1. The influence of anisotropy ratio:



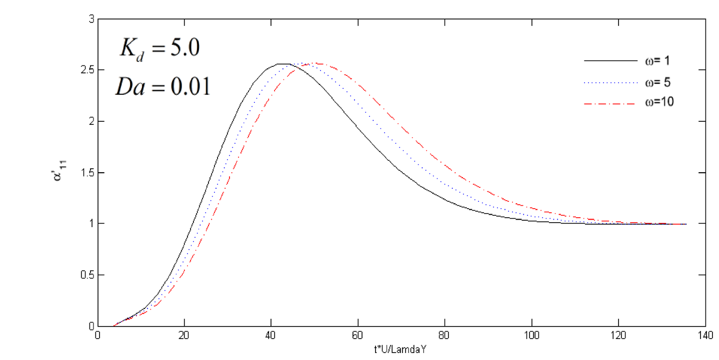


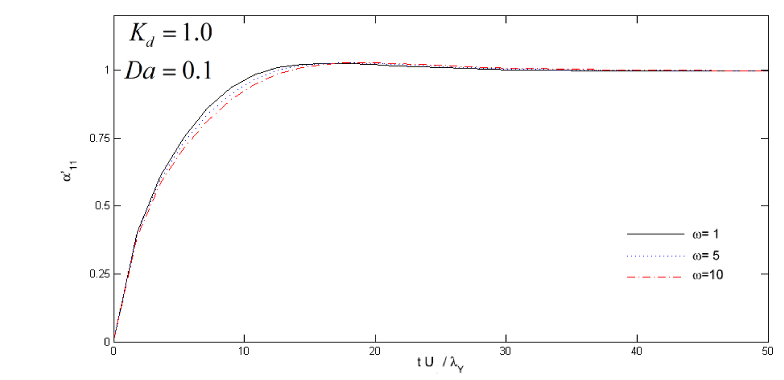
2. The influence of indicator scale:



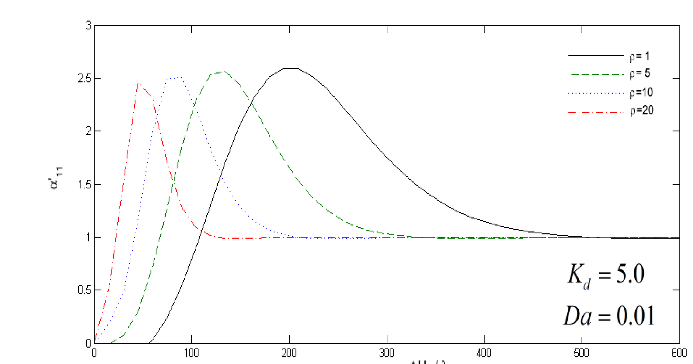


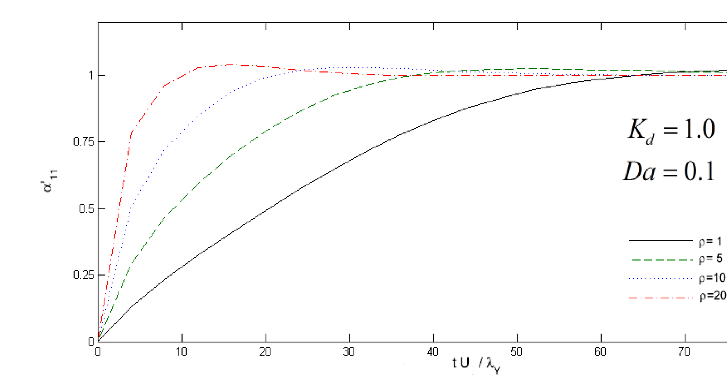
3. The influence of integral scale





4. The influence of mean conductivity





Conclusion

Anisotropy ratio has a negligible effect upon the longitudinal dispersivity coefficients of sorbing solutes under low Damkohler numbers (kinetic control). The values of dispersion coefficients vary with the changes of indicator correlation scale, integral scale, and the contrast of the mean log conductivity between different units. Among the parameters examined, the dispersivity coefficient is most sensitive to contrast in mean conductivity. Note that for a large value of K_d there is a unusual behavior in dispersivity of sorbing solute with an early peak that can be larger than its asymptotic value. This effect is related to the existence of a double peak in the mobile phase concentration distribution. The first peak is caused by the portion of mass that has not been adsorbed and travel with mean flow velocity. The second peak corresponds to the particles that have adsorbed and desorbed back into the mobile phase.

References

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