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An analytical solution of macrodispersivity for adsorbing solute transport in unsaturated soils

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Abstract. An analytical solution of macrodispersivity was derived for the adsorbing solute transport in physically and chemically heterogeneous unsaturated soils under the condition of gravity-dominated flow. The unsaturated hydraulic conductivity and water content were treated as spatial random functions. The chemical adsorption was described by a linear equilibrium isotherm, and the adsorption coefficient was represented as a spatial random function with specified correlation structures. The closed-form expression for macrodispersivity was expressed as a function of the hydraulic and adsorbing statistical properties of the unsaturated soil. For a short solute travel distance the macrodispersivity linearly increased with the increase of the solute plume travel distance. The macrodispersivity approached an asymptotic value when the center of the solute plume moved a long distance. The general solution quantified the effects of various factors, such as variabilities of the water content and unsaturated hydraulic conductivity, mean water content, and the retardation factor, on the macrodispersivity.

1. Introduction

Experimental evidence and theoretical results suggest that solute spreading in the natural field is governed by the spatial variability of soil properties. Due to the spatial variability, the dispersivity measured at the laboratory scale cannot be used for the prediction of solute distributions at the field scale, which is of most interest for environmental applications. Stochastic models have been developed to represent the transport phenomenon of nonreactive solute at the large scale [e.g., *Dagan*, 1982; *Gelhar and Axness*, 1983]. Those theoretical studies reveal that the average solute concentration can be described by the convection-dispersion equation with an apparent dispersion coefficient that relates to the spatial variability of the saturated hydraulic conductivity field. Under steady state water flow and an uniform hydraulic gradient, *Dagan* [1984] obtains a closed-form expression of the dispersion coefficient in saturated soils. The longitudinal dispersion coefficient tends to a constant and the transverse dispersion coefficient tends to zero when the solute plume travels tens of the correlation scale of log-transformed saturated hydraulic conductivity. Field experiments for solute transport in the saturated soil showed a good agreement between solute spreading and spatial moments with theoretical analyses [*Freyberg*, 1986].

Many contaminants commonly encountered in the groundwater system undergo interactions with porous media. The solute transport processes become much more complicated when the solute moves through a heterogeneous medium with spatial variability of chemical properties [*Roberts et al.*, 1986]. Analytical solutions of reactive solute transport in saturated media demonstrate that the field dispersion coefficient relates to the retardation factor and first-order decay coefficient, and the retardation factor has a large impact on the longitudinal dispersion [*Kabala and Sposito*, 1991; *Bellin et al.*, 1993].

Groundwater contamination may result from surface contaminant spills or agricultural practices. Before contaminants reach the groundwater table, they move through and react with the unsaturated soil. Therefore quantitative description of chemical transport in the unsaturated zone is important for the management of potential hazardous chemicals in the ecosystem. Water flow is much more intricate in the unsaturated zone than in the saturated zone. Besides the high heterogeneity of the unsaturated soil, soil hydraulic functions, such as the unsaturated conductivity and the soil water capacity, depend on both soil properties and the soil water content or pressure head. *Russo* [1993] analyzes solute dispersion in heterogeneous unsaturated soils by using a general Lagrangian formulation related the stochastic theory of *Yeh et al.* [1985] for steady water flow. Because of the complexity of solute transport under unsaturated flow conditions, it is difficult to obtain a closed-form expression of the macrodispersivity. To our knowledge, little work has been done on solute transport adsorption in physically and chemically heterogeneous unsaturated soils.

In this paper we address the problem of combined effects of adsorbing solute transport in unsaturated heterogeneous soil. Under the gravity-dominated unsaturated flow, a closed-form solution of macrodispersivity was derived and expressed as a function of statistical properties of the unsaturated soil and chemical heterogeneities. The effects of various factors on the macrodispersivity were discussed based on the solution.

2. Theory

By using the general Lagrangian formulation and neglecting the pore scale dispersion, statistical properties of the solute particle velocity are related to the first- and second-order moments by [*Dagan*, 1984]

$$d\langle X\rangle/dt = \langle U\rangle \tag{1}$$

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$$\frac{1}{2}\frac{dM_{ij}}{dt} = \int_0^t C_{ij}(\langle U\rangle t')\,dt' \qquad (2)$$

Here $\langle X\rangle$ is the expected value of the particle position, M_{ij} is the component of the second-order spatial moments of the solute body, $\langle U\rangle$ is the average velocity of a solute particle, $C_{ij}(\mathbf{r}) = \langle U_i'(\mathbf{x})U_j'(\mathbf{x} - \mathbf{r})\rangle$ is the component of the cross covariance of solute velocities U_i and U_j. $U_i'(\mathbf{x}) = U_i(\mathbf{x}) - \langle U_i(\mathbf{x})\rangle$ is the perturbation of $U_i(\mathbf{x})$ from its mean $\langle U_i(\mathbf{x})\rangle$, and $\mathbf{r}$ is the separation vector. The macrodispersion coefficient D_{ij} can be related to the second-order moment by [*Aris*, 1956]

$$D_{ij} = \frac{1}{2}\frac{dM_{ij}}{dt} \qquad (3)$$

For the unsaturated soil, the soil water flux is expressed as

$$q_i = K(\psi)\frac{\partial(\psi + x_1)}{\partial x_i} \qquad (4)$$

where $K(\psi)$ is the unsaturated hydraulic conductivity, ψ is the suction head, and x_1 is the vertical coordinate, positive downward. When the chemical reaction with soil is a linear equilibrium type, the adsorbed concentration C_s is related to the soil water concentration C by

$$C_s(\mathbf{x}, t) = \frac{\rho K_d(\mathbf{x})}{\theta} C(\mathbf{x}, t) \qquad (5)$$

where ρ is the soil bulk density, $K_d(\mathbf{x})$ is the adsorption or distribution coefficient, and θ is the volumetric water content. By defining the retardation factor as

$$R = 1 - \rho K_d(\mathbf{x})/\theta \qquad (6)$$

the solute velocity $U = (U_1, U_2, U_3)$ is given by

$$U_i = q_i/y \qquad y = \theta R \qquad i = 1, 2, 3 \qquad (7)$$

The transport process of a linear equilibrium adsorption solute can be described by a convection-dispersion equation with the velocity U.

By expressing ψ in terms of its mean and perturbation, i.e.,

$$\psi = H + h \qquad \langle h\rangle = 0 \qquad (8)$$

the soil water flux can be written as

$$q_i = K(\psi)\left[\frac{\partial(H + x_1)}{\partial x_i} + \frac{\partial h}{\partial x_i}\right] = K(\psi)\left[J_i + \frac{\partial h}{\partial x_i}\right] \qquad (9)$$

where $J_i = \partial(H + x_1)/\partial x_i$ is the mean hydraulic gradient in the direction x_i. For the sake of simplicity it is assumed that the mean hydraulic gradient exists only in the vertical direction, i.e., $J_i = (J, 0, 0)$.

Under the condition of gravity-dominated flow, the mean hydraulic gradient in (9) tends to 1, and the variance tends to 0. This condition is supported by numerical and analytical results. In a numerical analysis of unsaturated gravity-dominated flow, *Russo* [1991] finds that the mean hydraulic gradient J is 1 and the variance σ_J^2 is 0.001. From a stochastic analysis of water flow in unsaturated soils, *Yeh et al.* [1985] obtain $\sigma_J^2 = 0.04\text{–}0.2\sigma_f^2 J$ for most soils. Here σ_f^2 is the variance of log-transformed saturated hydraulic conductivity. Taking $\sigma_f^2 = 0.3$ and $J = 1$, we have $\sigma_J^2 = 0.001\text{–}0.06$. Therefore (9) can be simplified to

$$q_i = K(\psi)J_i = (q, 0, 0) \qquad (10)$$

where $q = K(\psi)$ is the soil water flux in the vertical direction.

$K(\psi)$, $\theta(\psi)$, $K_d(\mathbf{x})$, and R are expressed in terms of their mean values and perturbations, i.e.,

$$\begin{aligned} K(\psi) &= \langle K\rangle + K' & \langle K'\rangle &= 0 \\ \theta(\psi) &= \langle\theta\rangle + \theta' & \langle\theta'\rangle &= 0 \\ K_d(X) &= \langle K_d\rangle + K_d' & \langle K_d'\rangle &= 0 \end{aligned} \qquad (11)$$

$$y = \langle y\rangle + y' \qquad \langle y\rangle = \langle\theta\rangle + \rho\langle K_d\rangle \qquad y' = \theta' + \rho K_d'$$

Similarly, the soil water flux can be written as

$$q = \langle q\rangle + q' \qquad \langle q\rangle = \langle K\rangle \qquad q' = K' \qquad (12)$$

From (7), (11), and (12) the solute velocity can be described by

$$U = \frac{\langle q\rangle + q'}{\langle y\rangle + y'} = (\langle q\rangle + q')\left(\frac{1}{\langle y\rangle} - \frac{y'}{\langle y\rangle^2} + \frac{y'^2}{\langle y\rangle^3} - \frac{y'^3}{\langle y\rangle^4} + \cdots\right) \qquad (13)$$

Neglecting the perturbation terms higher than first order, we have

$$\langle U\rangle = \langle q\rangle/\langle y\rangle \qquad (14)$$

Subtracting (14) from (13) and neglecting perturbation terms higher than first order, we have the perturbation of the solute velocity

$$U' = \frac{\langle q\rangle}{\langle y\rangle}\left(\frac{q'}{\langle q\rangle} - \frac{y'}{\langle y\rangle}\right) \qquad (15)$$

The covariance function of the solute velocity is determined from (15) as

$$\begin{aligned} C_{UU}(\mathbf{r}) &= \langle U'(\mathbf{x})U'(\mathbf{x} + \mathbf{r})\rangle \\ &= \frac{\langle q\rangle^2}{\langle y\rangle^2}\left[\frac{C_{qq}(\mathbf{r})}{\langle q\rangle^2} - \frac{C_{yq}(\mathbf{r}) + C_{yq}(-\mathbf{r})}{\langle q\rangle\langle y\rangle} + \frac{C_{yy}(\mathbf{r})}{\langle y\rangle^2}\right] \end{aligned} \qquad (16)$$

By using (11) and (12), the covariance and cross covariance of q and y in (16) are calculated by

$$C_{qq}(\mathbf{r}) = C_{KK}(\mathbf{r}) \qquad (17)$$

$$C_{yq}(\mathbf{r}) = C_{\theta K}(\mathbf{r}) + \rho C_{K_dK}(\mathbf{r}) \qquad (18)$$

$$C_{yy}(\mathbf{r}) = C_{\theta\theta}(\mathbf{r}) + \rho[C_{\theta K_d}(\mathbf{r}) + C_{\theta K_d}(-\mathbf{r})] + \rho^2 C_{K_dK_d}(\mathbf{r}) \qquad (19)$$

It is assumed that the unsaturated hydraulic conductivity $K(\mathbf{x}, H)$ can be described by [*Gardner*, 1958]

$$K(\mathbf{x}, H) = K_s(\mathbf{x})\exp[-\alpha(\mathbf{x})H] \qquad (20)$$

where $K_s(\mathbf{x})$ is the saturated hydraulic conductivity, α is the soil parameter related to the soil pore size distribution, and H is the mean suction head. The analyses of *Freeze* [1975] and *Sudicky* [1986] suggest that the distribution of the saturated conductivity be lognormal for most soils. It is assumed that the parameter α is a normal distribution. Both $\ln K_s$ and α are regarded as realizations of stationary second-order spatial random functions (SRFs) with anisotropic covariance functions of the form

$$C_{\eta\eta}(\mathbf{r}) = \sigma_\eta^2\exp\left\{-\left[\left(\frac{r_1}{\lambda_{\eta 1}}\right)^2 + \left(\frac{r_2}{\lambda_{\eta 2}}\right)^2 + \left(\frac{r_3}{\lambda_{\eta 3}}\right)^2\right]^{1/2}\right\} \qquad (21)$$

where η indicates ln (K_s) or α; σ_η^2 is the variance of η; r_1, r_2, and r_3 are the components of the separation vector **r**; and $\lambda_{\eta 1}$, $\lambda_{\eta 2}$, and $\lambda_{\eta 3}$ are the correlation lengths of η in the x_1, x_2, and x_3 directions; respectively. *Russo and Bouton* [1992] indicate that the correlation between ln K_s and α is weak and they can be considered as the uncorrelated SRFs. Corresponding to the model of the unsaturated hydraulic conductivity (equation (20)), the water content is expressed as [*Russo*, 1988]

$$\theta(\mathbf{x}, H) = \theta_r + (\theta_s - \theta_r)\{\exp\left[-\tfrac{1}{2}\alpha(\mathbf{x})H\right] \cdot \left[1 + \tfrac{1}{2}\alpha(\mathbf{x})H\right]\}^{2/m+2} \tag{22}$$

where θ_s and θ_r are the saturated and residual water contents, respectively, m is a parameter. Expressing ln K_s and α by the mean values and fluctuations, i.e.,

$$\begin{aligned} \ln(K_s) &= F + f \qquad \langle f \rangle = 0 \\ \alpha &= A + a \qquad \langle a \rangle = 0 \end{aligned} \tag{23}$$

we have

$$\ln\left[K(\mathbf{x}, H)\right] = \ln\left[K_s\right] - \alpha H = p = \langle p \rangle + p' \tag{24}$$

$$\langle p \rangle = F - AH \qquad p' = f - aH \qquad \langle p' \rangle = 0$$

The unsaturated hydraulic conductivity is expressed as

$$K(\mathbf{x}, H) = \exp\left[p(\mathbf{x}, H)\right] = K^G \exp\left[p'(\mathbf{x}, H)\right] \tag{25}$$

$$K^G = e^{\langle p \rangle} = K_s^G e^{-AH} \qquad K_s^G = e^F$$

Here, $p = \ln(K)$ is also a normal SRF because it is the sum of two normal SRFs.

Studies of solute transport in the laboratory and field [*Roberts et al.*, 1986] indicate that the reaction of solute with soil, such as adsorption, is a spatial variable. Therefore the spatial distribution of the adsorption coefficient is considered to be a SRF. Plausible variability of adsorption is assumed to be either correlated or uncorrelated with the log-transformed saturated hydraulic conductivity [*Destouni and Cvetkovic*, 1991; *Bellin et al.*, 1993; *Bosma et al.*, 1993]. If there is no correlation between the adsorption coefficient and the saturated hydraulic conductivity, the heterogeneity of the adsorption coefficient can be described as

$$K_d(\mathbf{x}) = K_d^G \exp\left[N_d(\mathbf{x})\right] \tag{26}$$

where K_d^G is the geometric mean of $K_d(\mathbf{x})$ and $N_d(\mathbf{x})$ is a normal SRF with a mean 0 and variance σ_d^2. The correlation function of $N_d(\mathbf{x})$ is described by an exponential form similar to (21). A perfect correlation between ln K_d and ln K_s is given by

$$K_d(\mathbf{x}) = K_d^G \exp\left[\beta f(\mathbf{x})\right] \tag{27}$$

For the positive (or negative) correlation between ln K_d and ln K_s, β is greater (or less) than 0.

Substituting $\alpha = A + a$ into (22) and retaining the first-order term of a, the water content can be expressed as a lognormal SRF

$$\theta = \theta_r + (\theta_s - \theta_r)e^{E + Ba} \tag{28}$$

where

$$E = \frac{2}{m+2}\left[-\frac{1}{2}AH + \ln\left(1 + \frac{1}{2}AH\right) - \frac{1}{2}\left(\frac{H\sigma_a}{2 + AH}\right)^2\right]$$

$$B = \frac{-AH^2}{(m+2)(AH+2)} \tag{29}$$

If $X(\mathbf{s})$ and $Y(\mathbf{s})$ are normal stationary SRFs, the cross-covariance function of $\xi = \exp\left[X(\mathbf{s})\right]$ and $\eta = \exp\left[bY(\mathbf{s})\right]$ is [*Christakos*, 1992]

$$C_{\xi\eta}(\mathbf{r}) = \exp\left[\langle X \rangle + b\langle Y \rangle + \tfrac{1}{2}(\sigma_X^2 + b^2\sigma_Y^2)\right] \cdot \{\exp\left[bC_{XY}(\mathbf{r})\right] - 1\} \tag{30}$$

where b is a constant, $\langle X \rangle$ and $\langle Y \rangle$ are the mean values, σ_X^2 and σ_Y^2 are the variances, and C_{XY} is the cross covariance of $X(\mathbf{s})$ and $Y(\mathbf{s})$. From (24) and in the case of noncorrelation between ln K_s and α, the covariance of $p = \ln K(\mathbf{x}, H)$ can be written in the form

$$C_{pp}(\mathbf{r}) = C_{ff}(\mathbf{r}) + H^2C_{aa}(\mathbf{r}) \tag{31}$$

By using (30), the covariance of water flux q is determined from (17), (24), (25), and (31) as

$$C_{qq}(\mathbf{r}) = (K^G)^2 \exp\left[\sigma_f^2 + H^2\sigma_a^2\right] \cdot \{\exp\left[C_{ff}(\mathbf{r}) - H^2C_{aa}(\mathbf{r})\right] - 1\} \tag{32}$$

The covariance of water content and the cross covariance of water content with unsaturated hydraulic conductivity are obtained from (24), (28), and (30); i.e.,

$$C_{\theta\theta}(\mathbf{r}) = (\theta_s - \theta_r)^2 \exp(2E + B^2\sigma_a^2) \cdot \{\exp\left[B^2C_{aa}(\mathbf{r})\right] - 1\} \tag{33}$$

$$C_{\theta K}(\mathbf{r}) = (\theta_s - \theta_r)\langle K \rangle \exp\left(E + \tfrac{1}{2}B^2\sigma_a^2\right) \cdot \{\exp\left[-BHC_{aa}(\mathbf{r})\right] - 1\} \tag{34}$$

For the perfect correlation between ln K_d and ln K_s, from (24), (27), and (30) we have

$$C_{K_dK}(\mathbf{r}) = K_d^GK^G \exp\left[\tfrac{1}{2}(\beta^2\sigma_f^2 + \sigma_f^2 + H^2\sigma_a^2)\right] \cdot \{\exp\left[\beta C_{ff}(\mathbf{r})\right] - 1\} \tag{35}$$

$$C_{K_dK_d}(\mathbf{r}) = (K_d^G)^2 \exp\left[\beta^2\sigma_f^2\right]\{\exp\left[\beta^2C_{ff}(\mathbf{r})\right] - 1\} \tag{36}$$

If ln K_d is not correlated with ln K_s, the covariance and cross-covariance functions are calculated from (24), (26), and (30) as

$$C_{K_dK}(\mathbf{r}) = 0 \tag{37}$$

$$C_{K_dK_d}(\mathbf{r}) = (K_d^G)^2 \exp\left[\sigma_d^2\right]\{\exp\left[C_{dd}(\mathbf{r})\right] - 1\} \tag{38}$$

where σ_d^2 and C_{dd} are the variance and covariance of the perturbation of ln K_d. The longitudinal macrodispersivity may be defined as $A_{zz} = D_{zz}/\langle U \rangle$. Then from (2) and (3) we obtain

$$A_{zz} = \frac{1}{\langle U \rangle}\int_0^t C_{UU}(\langle U \rangle t')\,dt' = \frac{1}{\langle U \rangle^2}\int_0^{z_c} C_{UU}(\xi)\,d\xi \tag{39}$$

where $z_c = \langle U \rangle t$ is the mean travel distance of the solute plume. By substituting (16) into (39) and assuming no correlation between θ and K_d, the macrodispersivity A_{zz} is then described by

$$A_{zz} = A_{z1} + A_{z2} + A_{z3} \tag{40}$$

where

$$\begin{aligned} A_{z1} = & \int_0^{z_c} \{\exp [C_{ff}(\xi) + H^2 C_{aa}(\xi)] - 1\}\, d\xi \\ & - \int_0^{z} \frac{1}{\langle q\rangle\langle v\rangle} [C_{\theta K}(\xi) + C_{\theta K}(-\xi)]\, d\xi \\ & + \int_0^{z} \frac{C_{\theta\theta}(\xi)}{\langle v\rangle^2}\, d\xi \end{aligned} \tag{41}$$

$$\langle q\rangle = \langle K\rangle = K^G \exp [\tfrac{1}{2}(\sigma_f^2 + H^2\sigma_a^2)]$$

For perfect correlation between ln K_d and ln K_s, A_{z2} and A_{z3} have the forms of

$$A_{z2} = -\int_0^{z} 2\left(1 - \frac{1}{\langle R\rangle}\right)\{\exp [\beta C_{ff}(\xi)] - 1\}\, d\xi \tag{42}$$

$$A_{z3} = \int_0^{z} \left(1 - \frac{1}{\langle R\rangle}\right)^2 \{\exp [\beta^2 C_{ff}(\xi)] - 1\}\, d\xi \tag{43}$$

where $\langle R\rangle = 1 - \rho\langle K_d\rangle/\langle\theta\rangle$, and $\langle K_d\rangle = K_d^G \exp (\beta^2\sigma_f^2/2)$. For noncorrelation between ln K_d and ln K_s, we have

$$A_{z2} = 0 \tag{44}$$

$$A_{z3} = \int_0^{z} \left(1 - \frac{1}{\langle R\rangle}\right)^2 \{\exp [C_{dd}(\xi)] - 1\}\, d\xi \tag{45}$$

where $\langle K_d\rangle = K_d^G \exp (\sigma_d^2/2)$.

In (40) the macrodispersivity A_{zz} is expressed as the linear combination of three parts, A_{z1}, A_{z2}, and A_{z3}. A_{z1} consists of three terms shown in (41), which represent the contributions to A_{z1} from the covariance of unsaturated hydraulic conductivity, the cross covariance of water content with unsaturated hydraulic conductivity, and the covariance of soil water content. A_{z2} relates to the cross covariance of retardation factor and unsaturated hydraulic conductivity, and A_{z3} relates to the covariance of retardation factor. For passive solute, A_{z2} and A_{z3} vanish. Because adsorption coefficient may be positively or negatively correlated with the soil saturated hydraulic conductivity, A_{z2} can be a positive or a negative contribution to A_{zz}. Therefore the correlation structure between ln K_d and ln K_s significantly affects the magnitude of macrodispersivity.

By substituting (31), (33), and (34) into (41), the following closed-form expression of A_{z1} is obtained (see appendix):

$$\begin{aligned} A_{z1} = \lambda_f \Bigg\{ & \sum_{n=1}^{\infty} \sum_{k=0}^{n} \frac{C_n^k \sigma_f^{2(n-k)} H^{2k} \sigma_a^{2k}}{[n - k(\rho - 1)]n!} \\ & - \sum_{n=1}^{\infty} \sum_{k=0}^{n} \frac{C_n^k \sigma_f^{2(n-k)} H^{2k} \sigma_a^{2k}}{[n + k(\rho - 1)]n!} \exp \left[-[n + k(\rho - 1)] \frac{z_c}{\lambda_f}\right]\Bigg\} \\ & + \frac{1}{\langle R\rangle^2} \left(\frac{\theta_s - \theta_r}{\langle\theta\rangle}\right)^2 \exp (2E + B^2\sigma_a^2) \frac{\lambda_f}{\rho} \\ & \cdot \left[\sum_{n=1}^{\infty} \frac{(B^2\sigma_a^2)^n}{nn!} - \sum_{n=1}^{\infty} \frac{(B^2\sigma_a^2)^n}{nn!} \exp \left(-n\rho \frac{z_c}{\lambda_f}\right)\right] \\ & - \frac{2}{\langle R\rangle} \left(\frac{\theta_s - \theta_r}{\langle\theta\rangle}\right) \exp \left(E + \frac{1}{2} B^2\sigma_a^2\right) \frac{\lambda_f}{\rho} \\ & \cdot \left[\sum_{n=1}^{\infty} \frac{(-BH\sigma_a^2)^n}{nn!} - \sum_{n=1}^{\infty} \frac{(-BH\sigma_a^2)^n}{nn!} \exp \left(-n\rho \frac{z_c}{\lambda_f}\right)\right] \end{aligned} \tag{46}$$

where C_n^k is the binomial coefficient and $\rho = \lambda_f/\lambda_a$.

Under the condition of perfect correlation between ln K_d and ln K_s, A_{z2} and A_{z3} have the forms of

$$A_{z2} = -2\left(1 - \frac{1}{\langle R\rangle}\right)\left[\sum_{n=1}^{\infty} \frac{(\beta\sigma_f^2)^n}{nn!} - \sum_{n=1}^{\infty} \frac{(\beta\sigma_f^2)^n}{nn!} \exp \left(-n \frac{z_c}{\lambda_f}\right)\right]\lambda_f \tag{47}$$

$$A_{z3} = \left(1 - \frac{1}{\langle R\rangle}\right)^2\left[\sum_{n=1}^{\infty} \frac{(\beta^2\sigma_f^2)^n}{nn!} - \sum_{n=1}^{\infty} \frac{(\beta^2\sigma_f^2)^n}{nn!} \exp \left(-n \frac{z_c}{\lambda_f}\right)\right]\lambda_f \tag{48}$$

For the noncorrelation between ln K_d and ln K_s, A_{z2} and A_{z3} can be simplified to

$$A_{z2} = 0 \tag{49}$$

$$A_{z3} = \left(1 - \frac{1}{\langle R\rangle}\right)^2 \lambda_d\left[\sum_{n=1}^{\infty} \frac{(\sigma_d^2)^n}{nn!} - \sum_{n=1}^{\infty} \frac{(\sigma_d^2)^n}{nn!} \exp \left[-\frac{z_c}{\lambda_d} n\right]\right] \tag{50}$$

When $z_c/\lambda_f \ll 1$, the macrodispersivities are given by

$$\begin{aligned} A_{zz} = \Bigg\{ & \frac{1}{\langle R\rangle^2} \left(\frac{\theta_s - \theta_r}{\langle\theta\rangle}\right)^2 \exp (2E + B^2\sigma_a^2)[\exp (B^2\sigma_a^2) - 1] \\ & - \frac{2}{\langle R\rangle} \frac{\theta_s - \theta_r}{\langle\theta\rangle} \exp (E + \tfrac{1}{2}B^2\sigma_a^2)[\exp (-BH\sigma_a^2) - 1] \\ & + [\exp (\sigma_f^2 + H^2\sigma_a^2) - 1] - 2\left(1 - \frac{1}{\langle R\rangle}\right) \\ & \cdot [\exp (\beta\sigma_f^2) - 1] + \left(1 - \frac{1}{\langle R\rangle}\right)^2 [\exp (\beta^2\sigma_f^2) - 1]\Bigg\} z_c \end{aligned} \tag{51}$$

$$\begin{aligned} A_{zz} = \Bigg\{ & \frac{1}{\langle R\rangle^2} \left(\frac{\theta_s - \theta_r}{\langle\theta\rangle}\right)^2 \exp (2E + B^2\sigma_a^2)[\exp (B^2\sigma_a^2) - 1] \\ & - \frac{2}{\langle R\rangle} \frac{\theta_s - \theta_r}{\langle\theta\rangle} \exp (E + \tfrac{1}{2}B^2\sigma_a^2)[\exp (-BH\sigma_a^2) - 1] \\ & + [\exp (\sigma_f^2 + H^2\sigma_a^2) - 1] + \left(1 - \frac{1}{\langle R\rangle}\right)^2 \\ & \cdot [\exp (\sigma_d^2) - 1]\Bigg\} z_c \end{aligned} \tag{52}$$

for the perfect correlation and noncorrelation between ln K_d and ln K_s, respectively. Equations (51) and (52) indicate that the macrodispersivities are linear functions of the solute travel distance z_c. The difference of the macrodispersivities between negative and positive correlations can be evaluated by

$$A_{zz}^{\mathrm{Neg}} - A_{zz}^{\mathrm{Pos}} = 4\left(1 - \frac{1}{\langle R\rangle}\right) \sinh\left(|\beta|\sigma_f^2\right) z_c \qquad (53)$$

where A_{zz}^{Neg} and A_{zz}^{Pos} are the macrodispersivities for negative and positive correlations between $\ln K_d$ and $\ln K_s$, respectively, and $\sinh(x)$ is the hyperbolic sine function.

For the case of $z_c/\lambda_f \gg 1$ and perfect correlation between $\ln K_s$ and $\ln K_d$, the macrodispersivity tends to a constant

$$\begin{aligned} A_{zz} = \Bigg\{ & \frac{1}{\rho\langle R\rangle^2}\left(\frac{\theta_s - \theta_r}{\langle\theta\rangle}\right)^2 \exp\left(2E + B^2\sigma_a^2\right)[Ei(B^2\sigma_a^2) - C \\ & - \ln(B^2\sigma_a^2)] - \frac{2}{\rho\langle R\rangle}\frac{\theta_s - \theta_r}{\langle\theta\rangle}\exp\left(E + \tfrac{1}{2}B^2\sigma_a^2\right) \\ & \cdot [Ei(-BH\sigma_a^2) - C - \ln(|BH|\sigma_a^2)] \\ & + \sum_{n=1}^{\infty}\sum_{k=0}^{n}\frac{C_n^k\sigma_f^{2(n-k)}H^{2k}\sigma_a^{2k}}{[n + k(\rho - 1)]n!} - 2\left(1 - \frac{1}{\langle R\rangle}\right) \\ & \cdot [Ei(\beta\sigma_f^2) - C - \ln(|\beta|\sigma_f^2)] + \left(1 - \frac{1}{\langle R\rangle}\right)^2 \\ & \cdot [Ei(\beta^2\sigma_f^2) - C - \ln(|\beta|\sigma_f^2)]\Bigg\}\lambda_f \end{aligned} \qquad (54)$$

Here $Ei(x)$ is the exponential integration, and $C = 0.577 \cdots$ is Euler's constant. The difference of the macrodispersivity between negative and positive correlations is

$$A_{zz}^{\mathrm{Neg}} - A_{zz}^{\mathrm{Pos}} = 2\left(1 - \frac{1}{\langle R\rangle}\right)[Ei(\beta\sigma_f^2) - Ei(-\beta\sigma_f^2)]\lambda_f \qquad (55)$$

3. Discussion

The main purpose of this study was to relate the longitudinal macrodispersivity to the statistical parameters of the unsaturated soil and chemical heterogeneity properties under the condition of gravity-dominated unsaturated flow. The general results of this study are illustrated in (46) to (50). Some results based on the analytical solutions are discussed as follows.

3.1. Asymptotic Behavior of Macrodispersivity

For short solute travel time, the macrodispersivity was proportional to the solute travel distance as indicated in (51) and (52). This short time characteristic of the macrodispersivity of adsorbing solute transport in the unsaturated soil was similar to that in the saturated soil studied by *Bellin et al.* [1993]. For the comparison of the present solution with Bellin et al.'s solution for the saturated situation, letting $H = 0$ and $\beta = \pm 1$ in (51), we obtained

$$\begin{aligned} A_{zz} = \Bigg\{ & e^{\sigma_f^2} - 1 - 2\left(1 - \frac{1}{\langle R\rangle}\right)\left(e^{\pm\sigma_f^2} - 1\right) \\ & + \left(1 - \frac{1}{\langle R\rangle}\right)^2\left(e^{\sigma_f^2} - 1\right)\Bigg\} z_c \end{aligned} \qquad (56)$$

Bekelin et al.'s [1993] solution for short time is

$$\begin{aligned} A_{zz} = \Bigg\{ & \frac{8}{15}\sigma_f^2 \pm \frac{-4}{3}\left(1 - \frac{1}{\langle R\rangle}\right)\sigma_f^2 \\ & + \left(1 - \frac{1}{\langle R\rangle}\right)^2\left(e^{\sigma_f^2} - 1\right)\Bigg\} z_c \end{aligned} \qquad (57)$$

The macrodispersivity evaluated from (56) was slightly larger than that from (57) for the short travel time. This difference was stemmed from the assumption of neglecting the perturbation of the hydraulic gradient during the derivation of (51).

When $z_c/\lambda_f \gg 1$, the macrodispersivity was expressed by (54), a linear function of the correlation length of $\ln K_s$. Here, A_{zz} depended on the statistical parameters of the soil, the adsorption parameters of the solute, and the soil saturation. As a special case of the saturated situation, i.e., $H = 0$, the first and second terms on the right-hand side of (54) vanished, and the general solution was reduced to

$$\begin{aligned} A_{zz} = \Bigg\{ & \left(\sigma_f^2 + \frac{\sigma_f^4}{4} + \frac{\sigma_f^6}{18} + \cdots\right) - 2\left(1 - \frac{1}{\langle R\rangle}\right) \\ & \cdot\left(\beta\sigma_f^2 + \frac{\beta^2\sigma_f^4}{4} + \frac{\beta^3\sigma_f^6}{18} + \cdots\right) \\ & + \left(1 - \frac{1}{\langle R\rangle}\right)^2\left(Ei(\sigma_f^2) - C - \ln\sigma_f^2\right)\Bigg\}\lambda_f \end{aligned} \qquad (58)$$

By neglecting the high-order terms of σ_f^2 and taking $\beta = \pm 1$, (58) is the same as *Bellin et al.*'s [1993] solution

$$\begin{aligned} A_{zz} = \Bigg\{ & \sigma_f^2 \pm 2\left(1 - \frac{1}{\langle R\rangle}\right)\sigma_f^2 \\ & + \left(1 - \frac{1}{\langle R\rangle}\right)^2\left(Ei(\sigma_f^2) - C - \ln\sigma_f^2\right)\Bigg\}\lambda_f \end{aligned} \qquad (59)$$

For nonreactive solute, $R = 1$, (58) is reduced to

$$A_{zz} = \left(\sigma_f^2 + \frac{\sigma_f^4}{4} + \frac{\sigma_f^6}{18} + \cdots\right)\lambda_f \qquad (60)$$

which has the same form as *Dagan*'s [1984] solution when neglecting the high order terms of σ_f^2. In Figure 1, the current solutions are compared with *Bellin et al.*'s [1993] solution for adsorbing solute and the *Dagan*'s [1984] solution for nonadsorbing solute in saturated soils. The agreement of our results with those of Dagan and Bellin et al. was very good when our solutions were simplified to the saturated situation.

3.2. Effects of σ_f^2, σ_a^2, $\langle\theta\rangle$, and Water Content Variability on Macrodispersivity

The coefficient of variation of the unsaturated hydraulic conductivity, CV_K, could be determined from (24) and (32) as

$$\mathrm{CV}_K = [\exp(\sigma_f^2 + H^2\sigma_a^2) - 1]^{1/2} \qquad (61)$$

The variability of unsaturated soil was related to $(\sigma_f^2 + H^2\sigma_a^2)$, which displayed combined effects of the soil variabilities and hydraulic properties. The effect of variability of α on the unsaturated soil variability was related to soil water content. The macrodispersivity A_{zz} versus the scaled solute travel distance, z_c/λ_f, is plotted in Figure 2 for different values of σ_f^2 and $\mathrm{CV}_a = \sigma_a/A$. It is shown that A_{zz} increases with the increasing σ_f^2 and CV_a because the variability of the unsaturated hydraulic conductivity increases with the increases of σ_f^2 and CV_a.

Figure 3 shows the effect of water content variability on the

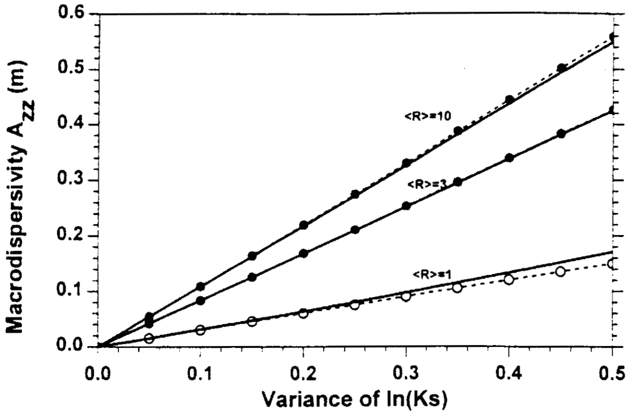

Figure 1. Macrodispersivities calculated by the current solution (solid lines) for different retardation factors and by the solutions of *Dagan* [1984] (open circles) and *Bellin et al.* [1993] (solid circles) for saturated water flow.

longitudinal macrodispersivity for different mean values of water content. The effect of water content variability on A_{zz} increased with decreasing mean water content. This was physically meaningful because the variabilities of water content and soil water velocity increased with the decrease of water content. The effect of water content variability on longitudinal macrodispersivity was due to the cross covariance of water content with unsaturated hydraulic conductivity and the covariance of water content in (41). The calculated results showed that the cross covariance of water content with the unsaturated hydraulic conductivity was much larger than the covariance of water content. Furthermore, the correlation of water content with the unsaturated hydraulic conductivity was positive, and consequently $C_{\theta K}(\mathbf{r})$ was larger than zero. Therefore macrodispersivity was smaller for the case of considering the water content variability than for the case of neglecting it because $C_{\theta K}(\mathbf{r})$ was a negative contribution to the macrodispersivity.

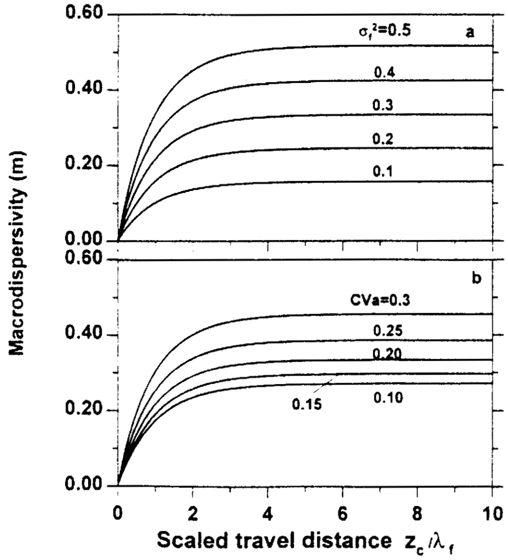

Figure 2. Macrodispersivities versus the scaled solute travel distance for (a) different values of σ_f^2, and (b) different values of CV_a, for $\langle R \rangle = 3.0$, $\langle \theta \rangle = 0.3$, $\lambda_f = \lambda_a = 0.3$ m, and $\beta = -1$.

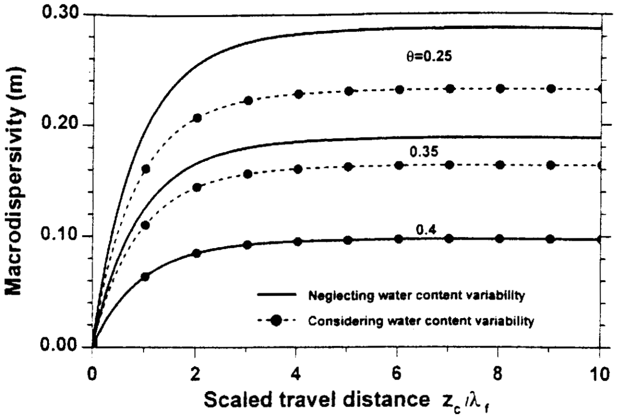

Figure 3. Macrodispersivities versus the scaled solute travel distance with and without considering the water content variability, for $\langle R \rangle = 1$, $\sigma_f^2 = 0.3$, $\mathrm{CV}_a = 0.2$, $\lambda_f = \lambda_a = 0.3$ m, and $\beta = -1$.

For soils with low water content, neglecting the water content variability would result in a large error in the evaluation of macrodispersivity.

The dependence of A_{zz} on the water content is shown in Figure 4. The macrodispersivity increased with decreasing water content. For comparison, the analytical expression of A_{zz} for steady, saturated water flow and adsorbing solute derived by *Bellin et al.* [1993] is also depicted in Figure 4. When water content tends to saturation, macrodispersivity calculated by (46)–(48) has a reasonable agreement with that of *Bellin et al.* [1993].

3.3. Effect of Retardation Factor and Correlation Structure on Macrodispersivity

For small and large solute travel distances, the differences of macrodispersivity between negative and positive correlations between ln K_d and ln K_s were given by (53) and (55), respectively. The differences did not depend on the soil saturation, which was the direct results of assuming K_d to depend on K_s only and not to depend on the water content. Because sinh (x) in (53) was an increasing function and $Ei(x) > Ei(-x)$ in (55)

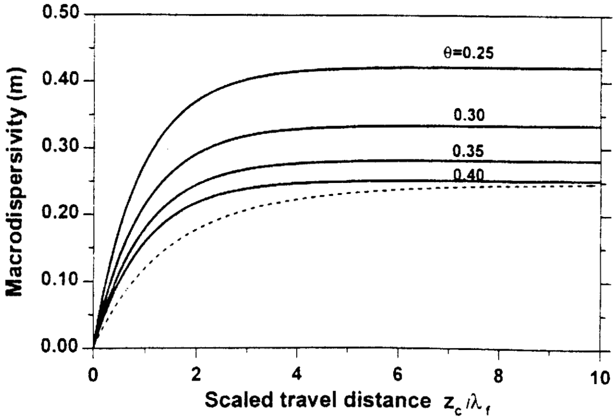

Figure 4. Macrodispersivities versus the scaled solute travel distance for different water contents, for $\langle R \rangle = 3$, $\sigma_f^2 = 0.3$, $\mathrm{CV}_a = 0.2$, $\lambda_f = \lambda_a = 0.3$ m, and $\beta = -1$. The dashed line represents the solution of *Bellin et al.* [1993] for saturated water flow.

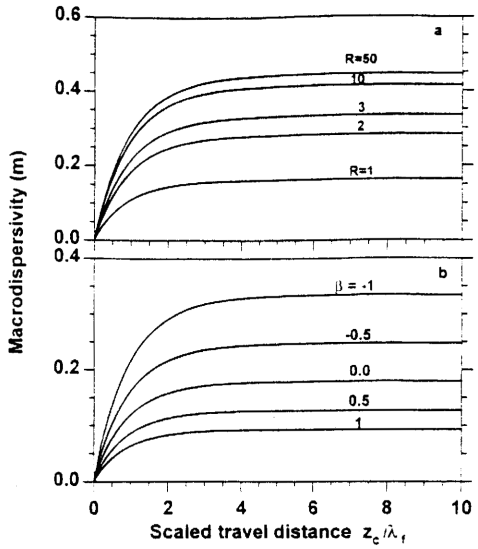

Figure 5. Macrodispersivities versus the scaled solute travel distance for (a) different retardation factors and (b) different correlation structures, for $\langle\theta\rangle = 0.3$, $\sigma_f^2 = 0.3$, $CV_a = 0.2$, and $\lambda_f = \lambda_a = 0.3$ m.

when $x > 0$. A_{zz}^{neg} was always larger than A_{zz}^{pos}. Physically, in the case of negative correlation between ln K_d and ln K_s, solute spreading was enhanced compared with the positively correlated situation.

The macrodispersivity versus the scaled solute travel distance for different values of $\langle R\rangle$ and β is shown in Figures 5a and 5b, respectively. The macrodispersivity was enhanced by the chemical heterogeneity. Even with the variability of adsorption coefficient kept as a constant, macrodispersivity increased with increasing mean retardation factor. This result is shown clearly by (48) and (50), in which A_{z3} is proportional to $(1 - 1/\langle R\rangle)^2$. It is worth notice that A_{zz} was much sensitive to small retardation factors.

The macrodispersivity was smaller for the positive correlated case than for the negative case (Figure 5b). The absolute value of β, which expressed the change rate of ln K_d with the change of f, played a very important role in the determination of macrodispersivity. It is obvious in (46)–(48) that A_{z1} and A_{z3} are not affected by the correlation structures between ln K_d and ln K_s. The foremost impact of the correlation structure on the behavior of macrodispersivity was caused by the interaction between the perturbations of water flux and retardation factor, which was expressed by A_{z2}. A_{z2} was less than zero for positive correlation, and greater than zero for negative correlation. The larger the absolute value of β was, the larger the absolute value of A_{z2}.

4. Conclusions

An analytical solution of macrodispersivity was derived for adsorbing solute transport in heterogeneous unsaturated soils under assumptions of gravity-dominated flow and negligible local dispersion. The unsaturated hydraulic conductivity and the water content were treated as spatial random functions. The chemical heterogeneity was represented by an adsorption coefficient which was assumed as a spatial random function with specified correlation structures. The perfect correlation and noncorrelation of the adsorption coefficient with the saturated hydraulic conductivity were considered.

The closed-form expression of the macrodispersivity was expressed as a function of the hydraulic and adsorbing statistical properties of the unsaturated soil. The general solution can be simplified to special cases, such as to the saturated soil and the nonadsorbing solute. The current solutions had an excellent agreement with the available solutions of *Dagan* [1984] and *Bellin et al.* [1993] for the special cases. For the short solute travel distance, the macrodispersivity linearly increased with the increase of the solute travel distance. The macrodispersivity tended to a constant when the center of the solute plume moved a couple of tenths of a correlation length of the saturated hydraulic conductivity. The macrodispersivity increased with decreasing water content and increasing variances of ln K_s and α. Neglecting the variability of water content would overestimate the macrodispersivity, especially for low water content. The correlation structure between adsorption coefficient and saturated hydraulic conductivity had significant impacts on macrodispersivity. Negative correlation between ln K_d and ln K_s enhanced the solute spreading compared with the positive correlation and noncorrelation. The macrodispersivity increased with increasing retardation factor.

Appendix

A general form of the integration in (41) is

$$I = \int_0^{z_c} \left\{ \exp\left[\sigma_f^2 \exp\left(-\frac{r}{\lambda_f}\right) + H^2\sigma_a^2 \exp\left(-\frac{r}{\lambda_a}\right)\right] - 1 \right\} dr \tag{A1}$$

By setting $\xi = \exp(-r/\lambda_f)$, $\rho = \lambda_f/\lambda_a$, and expanding the resulting integrand into an exponential series, (A1) becomes

$$I = \lambda_f \int_{e^{-z_c/\lambda_f}}^{1} \frac{1}{\xi} \sum_{n=1}^{\infty} \frac{(\sigma_f^2\xi + H^2\sigma_a^2\xi^\rho)^n}{n!} \, d\xi \tag{A2}$$

Using the binomial expansion in (A2), we have

$$I = \lambda_f \int_{e^{-z_c/\lambda_f}}^{1} \left\{ \sum_{n=1}^{\infty} \sum_{k=0}^{n} \frac{1}{n!} C_n^k \sigma_f^{2(n-k)} (H\sigma_a)^{2k} \xi^{n+k(\rho-1)-1} \right\} d\xi \tag{A3}$$

where C_n^k is the binomial coefficient. Because $n + k(\rho - 1) - 1 \neq -1$, integrating term by term in (A3) leads to

$$I = \lambda_f \sum_{n=1}^{\infty} \sum_{k=0}^{n} \frac{C_n^k \sigma_f^{2(n-k)} (H\sigma_a)^{2k}}{[n + k(\rho - 1)]n!} \cdot \left\{ 1 - \exp\left(-[n + k(\rho - 1)] \frac{z_c}{\lambda_f} \right) \right\} \tag{A4}$$

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