Effects of Local Transverse Dispersion on Macro-scale Coefficients of Decaying Solute Transport in a Stratified Formation

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Abstract
Estimating the values of dispersion and biochemical reaction rates of heterogeneous aquifers is critical to predicting the temporal evolution and fate of reactive solutes. While previous studies have investigated field-scale heterogeneity of transport and biochemical properties of porous media, effects of local dispersion have not been well understood. In this paper, longitudinal macro-dispersivity, effective decay rate, and effective solute velocity are derived for a stratified aquifer, and the effects of local dispersion, especially the local transverse dispersion, are studied. It is shown that the inclusion of local transverse dispersion leads to enlarged effective decay rate, and that ignoring it may significantly underestimate the effective rate. The Damkohler ($Da$) number and the coefficient of variation (CV) of decay rate have slight influence to macro-coefficients under very small $Pe$ number (with large local transverse dispersion). However, $Da$ number has growing effect on the asymptotic effective decay rate with the decrease in $Pe$ number, and results in constant asymptotic values regardless of $Da$ number under the condition with very large $Pe$ number. Larger CV of decay rate leads to smaller effective decay rate and effective velocity, and longitudinal macro-coefficient. The longitudinal macro-dispersivity is found to depend on the correlation between the hydraulic conductivity and the decay rate if the local longitudinal dispersion is spatially variable.

Keywords Groundwater · Dispersion · Heterogeneous formations · Decay rate

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1 Introduction

Transport and transformation of contaminants in porous media depend on the heterogeneity of physical and biochemical properties. The properties cannot be characterized in a deterministic manner, and are always treated as random variables. Hydrogeologists have used stochastic methods to study the effects of heterogeneity on subsurface flow and solute transport (Gelhar et al. 1992; Dagan 1989; Rajaram 2016; Fiori et al. 2016, 2017; Zech et al. 2015). Many theoretical analyses have been done to elucidate the effect of physical heterogeneities (variability of hydraulic conductivity) upon conservative solute transport (e.g., Gelhar et al. 1979; Matheron and De Marsily 1980; Pickens and Grisak 1981; Güven et al. 1984; Oktay et al. 1984; Güven and Molz 1986; Gelhar 1993; Chaudhuri and Sekhar 2005; Dong et al. 2018). Besides these theoretical studies, numerical simulation has been another important way of investigating macro-dispersion (e.g., Bakshevskaia and Pozdniakov 2016; Meyer 2018). Moreover, a lot of experiments on macro-dispersion at field scale or laboratory scale have also been conducted (e.g., Sudicky 1986; Zheng et al. 2011; Sharifi Haddad et al. 2015; Kretz et al. 2003; Bouchelaghem and Almosni 2003; Straface and De Biase 2013; Cupola et al. 2015). Characteristics of macro-dispersion have been extensively analyzed in above-mentioned works.

In addition to the study of heterogeneity of physical properties (e.g., hydraulic conductivity), heterogeneity of biochemical properties (e.g., decay rate, retardation factor and attachment coefficient) has also been investigated (e.g., Chrysikopoulos et al. 1990, 1992a, b; Katzourakis and Chrysikopoulos 2018). Dagan (1989) analyzed the center of mass displacement of a solute under spatially variable decay rate and retardation factor. Kabala and Sposito (1991) presented a theoretical analysis of field-scale coefficients of dispersion, retardation, and first-order decay. While their results were in the form of integrals of cross-correlation spectra, they illustrated that these field-scale coefficients were time dependent with random local-scale parameters. Miralles-Wilhelm and Gelhar (1996) analyzed the transient transport of decaying solute by using spectral perturbation approach. Their work focused on the case of an imperfectly stratified aquifer, and the local-scale dispersion was neglected. Chang and Urroz (1999) investigated the same problem as Miralles-Wilhelm and Gelhar (1996) in the statistically anisotropic and isotropic, heterogeneous porous medium. Due to generally large Peclet number in many aquifers, the local dispersion was usually ignored in most of previous theoretical analyses for the convenience of deriving analytical equations. Along with analytical analysis, there are numerous numerical efforts to study the effects of physical and chemical heterogeneity on reaction rate in the porous medium (e.g., Cunningham and Fadel 2007; Atchley et al. 2014; Dentz et al. 2011; Sanz-Prat et al. 2015, 2016; Loschko et al. 2018). In these mentioned works, the local dispersion is commonly treated as constant or not considered. However, the importance of local dispersion, especially local transverse dispersion, to reactive solute transport has been found in previous studies. For example, Oya and Valocchi (1998) studied transport and biodegradation of solutes in a stratified aquifer with vertical stratification of pore-scale water velocity and retardation factor. Their results demonstrated that local transverse dispersion was a critical process that controls the asymptotic transport and biodegradation properties. Janssen et al. (2006) modeled an adsorbing contaminant undergoing nonlinear biodegradation in heterogeneous aquifers. They found that solute mixing caused by pore-scale dispersion was essential for the bio-reaction process. Meanwhile, many studies have revealed that local transverse dispersion is one of the essential mechanisms for the transverse mixing of multi-component reactive species (e.g., Wright et al. 2017; Loschko et al. 2016; Cirpka 2015; Anna et al. 2013).
As local dispersion represents the pore-scale heterogeneity and controls the concentration gradient in the pore space where reactions take place, it may play an important role in reactive solute transport (Alhashmi et al. 2016). This paper contributes to discussing the role of local transverse dispersion in controlling field-scale characteristics of decaying solute transport through a stratified formation. By introducing a stratified formation, physical and biochemical properties vary only in the vertical direction. The simplification may help gain insights on complicated behavior of reactive solute transport. Many theoretical analyses of solute transport have been conducted under this simplified condition (e.g., Gelhar et al. 1979; Matheron and De Marsily 1980; Oya and Valocchi 1998; Fiori and Dagan 2002; Fernàndez-Garcia et al. 2008). These works have shown that the simplified stratified formation allowed exploring critical building blocks of transport processes that can be recognized in more complex systems. In this paper, the analytical expressions of field-scale longitudinal macro-dispersion, effective decay rate, and effective velocity of a decaying solute (first-order decay) in perfectly stratified formations are derived by using the spectral perturbation approaches (Gelhar 1987; Miralles-Wilhelm and Gelhar 1996). We note that the perturbation approach is only valid for small or moderate heterogeneity. A particular focus of this study is to investigate the effects of local dispersion, especially local transverse dispersion, on these effective transport and transformation coefficients. It is expected that this study can broaden the understanding on the complex interaction between convection, dispersion, and reaction.

The rest of the paper is organized as follows: Sect. 2 recapitulates the derivation of effective parameters. Results of effective parameters under different Peclet numbers are illustrated in Sect. 3, and discussions on the results are presented. New findings different with previous studies are underlined. Finally, Sect. 4 concludes the paper.

2 Methodology

Local transverse dispersion takes into account the effects of variable velocity at the pore scale and is an upscaled quantity at the Darcy scale. It is a critical mixing process for contaminant biodegradation despite dominating role of the spatially varying advection at the field scale. The setup of the stratified medium is depicted in Fig. 1. Heterogeneities are attributed to the spatial variability of hydraulic conductivity and decay rate. The hydraulic conductivity and decay rate only vary in vertical direction $z$, namely the correlation scale of hydraulic conductivity and decay rate in the $x$-direction is infinite, while the correlation scale in the $z$-direction is limited. The domain is considered as infinite so that solute transport is not influenced by the presence of boundaries. Three transport regimes, depending on travel time, were discussed by Dagan (1989): (i) for $t D_T / l^2 \ll 1$, where $D_T$ stands for the transverse pore-scale dispersion coefficient and $l$ for vertical integral scale, (ii) for $t D_T / l^2 \gg 1$ but $t D_T / L^2 \ll 1$, where $L$ is the formation thickness, and (iii) $t D_T / L^2 \gg 1$. Due to the assumed unbounded formation, we focus on the second regime.
2.1 Governing Equations

2.1.1 Steady Flow Field

The groundwater flow in a stratified aquifer is assumed to be in the steady state and unidirectional along the layers. The groundwater velocity is determined by the Darcy’s law:

\[ U(z) = \frac{K(z)J}{n} \]  

(1)

where \( K \) is the hydraulic conductivity, \( J \) is the constant negative hydraulic gradient in \( x \)-direction, and \( n \) is the constant porosity.

2.1.2 Solute Transport

The solute is injected across the layers over a line whose extent is large compared to the integral scale of the layers’ conductivity. By using the ergodicity assumption, it is assumed that expectation of the concentration is equal to the space average of concentration across the layers.

In the stratified formation, mass transport of a contaminant with the first-order decay is described by:

\[ \frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = \frac{\partial}{\partial x} \left( D_L \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial z} \left( D_T \frac{\partial C}{\partial z} \right) - \mu C \]  

(2)
where \( C \) is the concentration of contaminant; \( D_L \) and \( D_T \) are the local longitudinal and transverse dispersion coefficients, respectively; \( \mu \) is the first-order decay rate. It should be noted that the local transverse dispersion in our two-dimensional case is the transverse vertical dispersion in a three-dimensional formation.

### 2.2 Random Fields

Physical heterogeneity in the subsurface material is represented by a spatially variable hydraulic conductivity field. The variation of groundwater velocity is related to hydraulic conductivity through Eq. (1). Biochemical heterogeneity is represented by spatially variable decay rate in this study. The temporal and spatial distribution of contaminant concentration is controlled by spatially variable hydraulic conductivity and decay rate through Eq. (2). So, the solute concentration \( C \) and the groundwater velocity \( U \) are random fields.

#### 2.2.1 Physical Heterogeneities

The hydraulic conductivity \( K \) is decomposed into a mean \( \bar{K} \) and a small perturbation \( k \) as:

\[
K = \bar{K} + k
\]

The perturbation is assumed to be a statistically homogeneous random field with the spectrum (Gelhar et al. 1979):

\[
S_{kk}(r) = \frac{8\sigma_k^2 l^5 r^4}{3\pi(1 + l^2 r^2)^3}
\]

where \( l \) is the correlation length in \( z \)-direction, \( \sigma_k^2 \) is the variance of the \( K \) field, and \( r \) is the wave number of spectral space. The effects of the chosen spectrum of Eq. (4) have been studied by Matheron and De Marsily (1980). The influence of the auto-covariance structure of hydraulic conductivity on macro-dispersion can be found in the work of Hsu (2003).

Similarly, the groundwater velocity is decomposed as:

\[
U = \bar{U} + U'
\]

\[
U' = \frac{\bar{U}}{\bar{K}} k
\]

The perturbation of the groundwater velocity \( U' \) is related to the perturbation of hydraulic conductivity \( k \) through the Darcy’s law. The local longitudinal and transverse dispersion coefficient can be written as:

\[
D_L = a_L U
\]

\[
D_T = a_T U
\]

where \( a_L \) is the average local longitudinal dispersivity and \( a_T \) is the average local transverse dispersivity. Due to velocity fluctuations, local dispersion coefficients are also random fields, and their decompositions are as follows:

\[
D_L = \bar{D}_L + D'_L
\]

\[
D_T = \bar{D}_T + D'_T
\]
The perturbation of longitudinal dispersion coefficient $D'_L$ can be related to the perturbation of hydraulic conductivity $k$ through relationship (Gelhar et al. 1979):

$$D'_L = \frac{3D_L}{2K}k$$  \hspace{1cm} (8)

2.2.2 Biochemical Heterogeneities

The degradation rate for a contaminant in an aquifer may also vary spatially (Allen-King et al. 2006; Atchley et al. 2014). This can be caused by the spatial variability in the activity of bacteria responsible for solute decay (e.g., Fennell et al. 2001; Hoelen et al. 2006; Caprio et al. 2014) or by the spatial variability in environmental factors (e.g., temperature, PH, and oxygen level; e.g., Kristensen et al. 1992; Tomaszewski et al. 2017). It is commonly hypothesized that there is a certain relationship between the spatially varying hydraulic conductivity and a spatially varying degradation rate (e.g., Miralles-Wilhelm and Gelhar 1996; Cunningham and Fadel 2007; Atchley et al. 2014). A simple linear relationship is assumed here (Miralles-Wilhelm and Gelhar 1996)

$$\mu = b + \alpha K + \delta$$  \hspace{1cm} (9)

where $b$ and $\alpha$ are intercept and slope of the linear correlation between $\mu$ and $K$, respectively; $\delta$ is a random residual with zero mean to account for a possibly imperfect correlation. It is noted that the linear relationship of Eq. (9) is a simplification without experimental validation. Then, the perturbation relationship between hydraulic conductivity and decay rate is:

$$\bar{\mu} = b + \alpha \bar{K}$$

$$\mu' = \alpha k + \delta$$  \hspace{1cm} (10)

2.2.3 Transport Variable

The concentration $C$ is controlled by the above-mentioned heterogeneous parameters through Eq. (2), and can be decomposed into a mean and a perturbation as:

$$C(x, z, t) = \bar{C}(x, t) + C'(x, z, t)$$  \hspace{1cm} (11)

Note that the mean concentration is considered to be independent of $z$ in a stratified formation (Gelhar et al. 1979; Oktay et al. 1984).

2.3 Development of Cross-correlation Terms

Decomposing the random fields in Eq. (2) into means and small perturbations, taking expectation of the equation and retaining terms to second order in perturbations yield the mean transport equation:

$$\frac{\partial \bar{C}}{\partial t} + \bar{U} \frac{\partial \bar{C}}{\partial x} + \frac{\partial}{\partial x} \left( U' C' \right) = \bar{D}_L \frac{\partial^2 \bar{C}}{\partial x^2} + \frac{\partial^2}{\partial x^2} \left( \bar{D}' L C' \right) + \frac{\partial^2}{\partial z^2} D'_T C' - \bar{\mu} \bar{C} - \mu' C'$$  \hspace{1cm} (12)

In comparison with the work of Miralles-Wilhelm and Gelhar (1996), Eq. (12) has two additional terms, $E$ and $F$, due to the consideration of the local dispersion. For a statistically homogeneous field, term $F$ is zero. The field-scale effects are produced by the cross-correlation terms involved in the mean transport equation (e.g. Gelhar and Axness....
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The main work is to calculate the cross-correlation terms of D, E, and G. A moving coordinate system that follows the mean advective movement of the plume in space is introduced for the convenience of derivation (Gelhar and Axness 1983; Chang and Urroz 1999):

\begin{align}
\zeta_1 &= x - \bar{U}t \\
\zeta_2 &= z
\end{align}

By applying the coordinate changes, Eq. (12) becomes

\begin{equation}
\frac{\partial \bar{C}}{\partial t} + \frac{\partial}{\partial \zeta_1} U' \bar{C}' = \bar{D}_L \frac{\partial^2 \bar{C}}{\partial \zeta_1^2} + \bar{D}_L' \frac{\partial^2 \bar{C}'}{\partial \zeta_1^2} - \bar{\mu} \bar{C} - \bar{\mu}' \bar{C}'
\end{equation}

By subtracting this mean transport equation from Eq. (2) in the new coordinate system, the following first-order approximation of the transport equation for the concentration perturbation \( \bar{C}' \) is obtained:

\begin{equation}
\frac{\partial \bar{C}'}{\partial t} + U' \frac{\partial}{\partial \zeta_1} \bar{C}' = \bar{D}_L \frac{\partial^2 \bar{C}'}{\partial \zeta_1^2} - \bar{\mu} \bar{C}' - \bar{\mu}' \bar{C}'
\end{equation}

The spatial variation of local dispersion introduces three additional perturbation terms, \( M, N, \) and \( O \). Terms \( M \) and \( O \) are, respectively, related to mean transverse local dispersion and longitudinal local dispersion. Term \( N \) is for perturbation of longitudinal local dispersion. A perturbation term for local transverse dispersion is not presented due to the assumption that the mean concentration is considered to be independent of \( z \). The regular spectral approach is employed to solve the differential equation of the concentration perturbation Eq. (15).

The perturbed quantities are assumed to be locally stationary in space (their covariance function would depend only on the separation vector between the locations) and represented by (Lumley and Panofsky 1964):

\begin{align}
C' &= \int_{-\infty}^{\infty} \exp(irz)dZ_C(r, t) \\
&= \int_{-\infty}^{\infty} \exp(i r \zeta_2)dZ_C(r, t) \\
Y' &= \int_{-\infty}^{\infty} \exp(irz)dZ_Y(r) \\
&= \int_{-\infty}^{\infty} \exp(i r \zeta_2)dZ_Y(r)
\end{align}

where \( Y \) represents any time-independent random fields in Eq. (2). After substituting these representations into Eq. (15), the perturbation equation can be rewritten in spectral space as:

\begin{equation}
\frac{\partial dZ_C}{\partial t} + (\bar{D}_T r^2 + \bar{\mu}) dZ_C - \bar{D}_L \frac{\partial^2 dZ_C}{\partial \zeta_1^2} = G_2 dZ_D + G_1 dZ_U - \tilde{C} dZ_{\mu}
\end{equation}

with

\begin{equation}
G_1 = -\frac{\partial \bar{C}}{\partial \zeta_1} \quad G_2 = \frac{\partial^2 \bar{C}}{\partial \zeta_1^2}
\end{equation}

Due to the consideration of decay process, direct applicability of previous approximations (Gelhar and Axness 1983; Gelhar 1987) to solve the perturbation transport equation is excluded. To obtain a solution of Eq. (18), the time-scaling approach, which has been proven
useful in analyzing the problem of transport and decay in the heterogeneous aquifer (Miralles-Wilhelm and Gelhar 1996, 2000), is used here. The approach considers decay as the only cause of concentration perturbations variation in time, and introduces a new frame of reference that “follow” the plume in time. Then, the temporal changing of the concentration perturbations, mean concentration gradient, and mean concentration caused by the decay process is removed. These variables are scaled in time by solving following intermediate simplified equation (Miralles-Wilhelm and Gelhar 1996):

\[
\frac{\partial dZ_C}{\partial t} = -\mu_e dZ_C
\]  

(20)

The equation introduces the effective decay rate \( \mu_e \), which is defined as the effective value of plume decay rate at field scale. Due to the heterogeneities of decay rate, the effective decay rate \( \mu_e \) can be different from the mean decay rate. Equation (20) assumes that the concentration perturbations are attenuated at the rate of \( \mu_e \).

The solution of Eq. (20) leads to the following time-scaling expression (Miralles-Wilhelm and Gelhar 1996):

\[
dZ_C = dZ_\tilde{C} \exp \left( -\int_0^t \mu_e dt' \right)
\]  

(21)

where \( dZ_\tilde{C} \) is the spectral amplitudes for conservative quantity. Equation (18) can now be written in terms of \( dZ_\tilde{C} \),

\[
\frac{\partial dZ_\tilde{C}}{\partial t} + (\bar{D}_r r^2 + \bar{\mu} - \mu_e) dZ_\tilde{C} - \bar{D}_L \frac{\partial^2 dZ_\tilde{C}}{\partial \xi_1^2} = (G_2 dZ_{DL} + G_1 dZ_U - \bar{C} dZ_\mu) \exp \left( \int_0^t \mu_e dt' \right)
\]  

(22)

By using the method presented in Gelhar et al. (1979), the solution of the above equation is approximated by:

\[
dZ_\tilde{C} = \frac{1 - e^{\beta t}}{\beta} (G_2 dZ_{DL} + G_1 dZ_U - \bar{C} dZ_\mu) \exp \left( \int_0^t \mu_e dt' \right)
\]  

(23)

with

\[
\beta(r) = \bar{D}_r r^2 + \bar{\mu} - \mu_e
\]  

(24)

It should be noted that the mean longitudinal dispersion coefficient is neglected in the above-approximated solution and that the mean transverse dispersion is contained in \( \beta \). Then, the solution is written as:

\[
dZ_C = \frac{1 - e^{-\beta t}}{\beta} (G_2 dZ_{DL} + G_1 dZ_U - \bar{C} dZ_\mu)
\]  

(25)

Note that the perturbation term \( H \) of longitudinal dispersion coefficient is retained in the above concentration perturbation equation.

By using the spectral representation theorem (Lumley and Panofsky 1964), the cross-correlation terms that appear in Eq. (14) can be written as (detailed derivation is given in “Appendix”):

\[
\overline{U'C'} = G_2 I_1 + G_1 I_2 - \bar{C} I_3
\]  

(26)

\[
\overline{D_{L'C'}} = G_2 I_4 + G_1 I_1 - \bar{C} I_5
\]  

(27)

\[
\overline{\mu'C'} = G_2 I_5 + G_1 I_3 - \bar{C} I_6
\]  

(28)
The integral terms are as follows:

\[ I_1(t) = \int_{-\infty}^{\infty} \frac{1 - e^{-\beta t}}{\beta} S_{U D_L} dr \]
\[ = \frac{4 \bar{D}_L l^2 \sigma_k^2}{\pi a_T K^2} S \]  
\[ (29) \]

\[ I_2(t) = \int_{-\infty}^{\infty} \frac{1 - e^{-\beta t}}{\beta} S_{U U} dr \]
\[ = \frac{8 \bar{U} l^2 \sigma_k^2}{3 \pi a_T K^2} S \]  
\[ (30) \]

\[ I_3(t) = \int_{-\infty}^{\infty} \frac{1 - e^{-\beta t}}{\beta} S_{U \mu} dr \]
\[ = \frac{8 \alpha l^2 \sigma_k^2}{3 \pi a_T K} S \]  
\[ (31) \]

\[ I_4(t) = \int_{-\infty}^{\infty} \frac{1 - e^{-\beta t}}{\beta} S_{D_L D_L} dr \]
\[ = \frac{6 \bar{D}_L^2 l^2 \sigma_k^2}{\pi D_T K^2} S \]  
\[ (32) \]

\[ I_5(t) = \int_{-\infty}^{\infty} \frac{1 - e^{-\beta t}}{\beta} S_{D_L \mu} dr \]
\[ = \frac{4 \alpha \bar{D}_L l^2 \sigma_k^2}{\pi D_T K} S \]  
\[ (33) \]

\[ I_6(t) = \int_{-\infty}^{\infty} \frac{1 - e^{-\beta t}}{\beta} S_{\mu \mu} dr \]
\[ = \frac{8 l^2 \sigma_k^2}{3 \pi D_T} \]  
\[ (34) \]

with

\[ S = \int_{-\infty}^{\infty} \frac{\lambda^4 (1 - \exp[-(\lambda^2 + \chi) a_T T])}{(\lambda^2 + \chi)(1 + \lambda^2)^3} d\lambda \]  
\[ (35) \]

\[ \chi = \frac{\bar{\mu} - \mu e I^2}{D_T} \]
\[ \lambda = l r \quad T = \frac{\bar{U} t}{l} \]  
\[ (36) \]

**2.4 Macro-scale Coefficients**

After substituting Eqs. (26–28) into Eq. (14), the macro-scale coefficients of reaction, advection, and dispersion form following mean equation

\[ \frac{\partial \bar{C}}{\partial t} - 2I_3 \frac{\partial \bar{C}}{\partial \xi_1} + (2I_5 - I_2 - \bar{D}_L) \frac{\partial^2 \bar{C}}{\partial \xi_1^2} + 2I_1 \frac{\partial^3 \bar{C}}{\partial \xi_1^3} - I_4 \frac{\partial^4 \bar{C}}{\partial \xi_1^4} = -(\bar{\mu} - I_6) \bar{C} \]  
\[ (37) \]

where the effects of high-order derivative terms \( P \) and \( Q \) are not investigated in the analysis below.
The mean equation is rewritten by using the original coordinate system,

\[
\frac{\partial \bar{C}}{\partial t} + (\bar{U} - 2I_3) \frac{\partial \bar{C}}{\partial x} - (I_2 - 2I_5 + \bar{D}_L) \frac{\partial^2 \bar{C}}{\partial x^2} = - (\mu - I_6) \bar{C}
\]  

(38)

The zero-order spatial derivatives of concentration in Eq. (38) are grouped together, and then, the effective decay rate can be given as:

\[
\mu_e = \bar{\mu} - I_6 = \bar{\mu} - \frac{8l^2\sigma^2}{3\pi D_T} S
\]

(39)

Variable \(\chi(t)\) results from Eq. (39) and definition Eq. (36) as:

\[
\chi = \frac{8l^4\sigma^2}{3\pi D_T^2} S
\]

(40)

From definition Eq. (36), we get for the effective decay rate:

\[
\mu_e = \bar{\mu} - \frac{\bar{D}_T \chi(t)}{l^2}
\]

(41)

Note that the time-dependent effective decay rate coefficient is the effective value of plume decay rate with respect to the displacement of a solute plume. The first-order spatial derivatives of concentration in Eq. (38) are grouped together to define the effective velocity which is the field-scale velocity of the mean plume. The effective velocity is given by:

\[
U_e = \bar{U} - 2I_3 = \bar{U} - \frac{16\alpha l^2\sigma^2}{3\pi a_T K} S
\]

(42)

The second-order spatial derivatives of concentrations in Eq. (38) are grouped together to obtain the longitudinal field-scale dispersion coefficient. The longitudinal macro-dispersion coefficient is given by:

\[
D_e = I_2 - 2I_5 + \bar{D}_L = (\bar{U} - 3\alpha a_L K) \frac{8l^2\sigma^2}{3\pi a_T K} S + \bar{D}_L
\]

(43)

And the longitudinal macro-dispersivity \(A_e\) is given by (Gelhar et al. 1979; Gelhar and Axness 1983):

\[
A_e = \frac{I_2 + \bar{D}_L - 2I_5}{U} = \left(1 - \frac{3\alpha a_L K}{U}\right) \frac{8l^2\sigma^2}{3\pi a_T K} S + a_L
\]

(44)

Comparing with the analytical solution in Miralles-Wilhelm and Gelhar (1996), our derivation includes the local transverse dispersion. Particularly, the longitudinal macro-dispersivity of the reactive solute is also influenced by the \(\mu - K\) correlation, which has not been investigated in previous studies. The effects of the local transverse dispersion on effective advection, dispersion, and reaction are discussed in the following section.

### 3 Results and Discussion

The macro-scale coefficients are quantitatively evaluated as functions of the following dimensionless parameters:

- \(\frac{\bar{U}l}{T}\): dimensionless time;
\( \bar{\mu}_l \) : the Damkohler number that describes the ratio of reaction rate to convection rate;
\( \frac{l}{\sigma_T^2} \) : the Peclet number that describes the ratio of convection rate to local transverse dispersion rate;
\( \sigma_n / \bar{\mu} \) : the coefficient of variation of the decay rate;
\( \frac{\sigma^2}{\sigma_k^2} \) : the square of the correlation coefficient between decay rate and hydraulic conductivity.

The effect of the mean decay rate, the variability of the decay rate, and the degree of correlation between the decay rate and hydraulic conductivity under different Peclet numbers are investigated. A value of \( \frac{\sigma^2}{K^2} = 0.25 \) suggested by Gelhar et al. (1979) is used.

### 3.1 Effective Decay Rate

Figures 2 and 3, respectively, present the temporal variation of effective decay rate with respect to \( Da \) (Damkohler number) and CV (the coefficient of variation of decay rate) under different \( Pe \) (Peclet number) conditions. The figures stem from Eq. (41) which was evaluated based on expression (36) and the numerically evaluated integral (35). It is seen from both figures that the effective decay rate decreases from the mean decay rate over time and reaches an asymptotic value. This has been reported in Miralles-Wilhelm and Gelhar (1996) and Chang and Urroz (1999) and is analogous to the dissolution rate which is found to diminish with increasing time or distance (Hunt et al. 2015). A recent pore-scale study illustrated a similar result that heterogeneity (spatial heterogeneous reaction rate in their work) can lead to macroscopic rates of biochemical reaction smaller than those of homogeneous cases (Yan et al. 2017). It is shown in Figs. 2 and 3 that the asymptotic value of effective decay rate increases with decreasing Peclet number (increasing local transverse dispersion), which implies that the enhanced local transverse dispersion enlarges effective decay rate. This phenomenon is comprehensible, since stronger local transverse dispersion relative to convection facilitates the transverse mixing and has an accelerating impact on the biochemical reaction of contaminant plumes (Cirpka et al. 1999, 2011; Cirpka 2015; Chiogna et al. 2011).

Figure 2 further demonstrates that the increase in \( Da \) number reduces the asymptotic effective decay rate. Under the condition of \( Pe = 1 \), the impact of different \( Da \) numbers is negligible during the whole travel time, and the effective decay rate is close to the spatially averaged decay rate. This implies that the spatially averaged decay rate may be used as the substitute of the effective decay rate if \( Pe \) is rather small, regardless of the \( Da \) number. However, small \( Pe \) number (for example, 1) is rare in reality (Delgado 2007; Rahman et al. 2005). The effect of different \( Da \) numbers on asymptotic effective decay rate is prominent when the \( Pe \) number becomes large (for example, 100). As the \( Pe \) number further increases to infinity (indicating local transverse dispersion is negligible), the effective decay rates under different \( Da \) numbers approach to the same asymptotic value. Namely, the effect of \( Da \) number on the asymptotic effective decay rate will ultimately disappear if local transverse dispersion is negligible. This implies that the effects of different \( Da \) numbers can be neglected in the estimation of effective decay rate in a stratified aquifer when the local transverse dispersion is negligible.

In Fig. 3, increasing the CV of the decay rate results in decreasing effective reaction rate relative to the mean value. It is found that the asymptotic values of effective decay rate for different CV values become closer with decreasing \( Pe \) number (increasing local transverse dispersion) in Fig. 3. Namely, the decrease in \( Pe \) number (indicating the increase in local
transverse dispersion) alleviates the effect of the spatial variability of decay rate. For example, when Pe number is 1, the effective decay rates all approach to the mean value, regardless of the CV of decay rate. This finding is relevant for estimating effective decay rate: Neglecting local transverse dispersion may magnify the effect of spatial variability of the decay rate, because local transverse dispersion can smooth the effect of decay variability. Furthermore, it is seen in Fig. 2 that the effective decay rates for small Da (for example, Da = 0.01) under different Pe numbers all stay close to the mean values at the early time and their differences become dramatically large at the late time. The same results can be seen from the transient development of effective decay rates for CV = 0.75 under different Pe numbers in Fig. 3. This means that the effect of local transverse dispersion on effective decay rate is weak at the early time and becomes apparent with time. A similar result was obtained by Fernández-Garcia et al. (2008). However, in their study, the impact of transverse dispersion was evaluated with numerical simulation. This finding has important practical implication in estimating effective decay rate: Without considering local transverse dispersion, the deviation of estimated effective decay rate may continue to increase with travel time.
3.2 Longitudinal Macro-dispersivity

In Fig. 4a, b [stemming from Eq. (44)], the transient development of longitudinal macro-dispersivity of reactive solute under different Da and CV numbers is presented. The effective dispersivity of conservative solute derived by Gelhar et al. (1979) is also plotted for comparison. It is seen that increasing Da and CV numbers leads to decreasing longitudinal macro-dispersivity. The asymptotic longitudinal macro-dispersivity of reactive solute is smaller than that of conservative solute, and depends on Da numbers and CV of the decay rate. A new finding, which is indicated by Eq. (43), is that the longitudinal macro-dispersivity is further influenced by the correlation $\mu - K$. The effects of the positive ($\alpha > 0$) and negative ($\alpha < 0$) correlation $\mu - K$ are plotted in Fig. 4c, d [stemming from Eq. (44)].

When positive correlation is considered, the longitudinal macro-dispersivity decreases with stronger correlation. When the correlation is negative, the influence is reversed. Through Monte Carlo simulations, Cunningham and Fadel (2007) showed that contaminant plume behaviors depend on the correlation between hydraulic conductivity and decay rate constant.
Fig. 4 Transient development of longitudinal macro-dispersivity: a as a function of $Da$; b as a function of CV of decay rate; c as a function of the degree of positive correlation $\mu - K$; d as a function of the degree of negative correlation $\mu - K$. The longitudinal macro-dispersivity is normalized by the asymptotic value of effective dispersivity $A_\infty$ in Gelhar et al. (1979) for convenience of comparison.

Atchley et al. (2014) demonstrated that reactive plume development also relies on the correlation between the reactive surface area and hydraulic heterogeneity. Although the effect of the correlation $\mu - K$ is relatively small in our results when the local longitudinal dispersion is small, it illustrates that similar to the effective decay rate, longitudinal macro-dispersivity is actually influenced by the correlation $\mu - K$.

The effects of $Da$ number and CV of decay rate on longitudinal macro-dispersivity under different $Pe$ numbers are shown in Figs. 5 and 6 [stemming from Eq. (44)], respectively. As indicated in Gelhar et al. (1979) and Matheron and De Marsily (1980), longitudinal macro-dispersivity can be dramatically changed by the transverse local dispersion in stratified formations. In Fig. 5, longitudinal macro-dispersivities for $Da = 0.01$ under different $Pe$ numbers ($Pe = 100$, $Pe = 1000$, $Pe = \infty$) nearly keep unchanged in the early time and become different in the late time, which demonstrates that the effects of local transverse dispersion on longitudinal macro-dispersivity gradually manifest with travel time. Figure 5 further shows that the differences of macro-dispersivities under different $Da$ numbers increase with the increase in $Pe$ number. This means that macro-dispersivity is subject to heavy influence of $Da$ number when $Pe$ is very large (indicating negligible transverse dis-
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Fig. 5 Transient development of longitudinal macro-dispersivity as a function of $Da$ and $Pe$ for $CV = 0.5$, $l/\sigma_T = 100$ and $\frac{a^2 \sigma_k^2}{\sigma_{\mu}^2} = 0.5$

dispersion). With decreased $Pe$ numbers (larger local transverse dispersion), the impact of $Da$ number becomes weaker. The magnitudes of macro-dispersivities under different $Da$ numbers are almost unchanged when $Pe$ number is very small ($Pe = 1$). Namely, increasing local transverse dispersion weakens the effect of $Da$ number on longitudinal macro-dispersivity. The effects of $CV$ on longitudinal macro-dispersivity under different $Pe$ numbers are alike. Therefore, large local transverse dispersion can reduce the impact of spatial variation of decay rate on longitudinal macro-dispersivity, as shown in Fig. 6. In short, the local transverse dispersion smooths the effects of $Da$ and $CV$ on longitudinal macro-dispersivity. This finding implies that neglecting local transverse dispersion may also magnify the effects of $Da$ and $CV$ on macro-dispersivity.

3.3 Effective Velocity

Figure 7 [stemming from Eq. (42)] shows the effects of $Da$ number on the effective velocity under different $Pe$ numbers. When $Pe$ is 1, the effective velocities under different $Da$ numbers approach to mean velocity during the whole travel time and the impact of $Da$ numbers is small. The effect of different $Da$ numbers on asymptotic effective velocity is prominent
when the $Pe$ number becomes large (for example, 100). As the $Pe$ number further increases to infinity (indicating local transverse dispersion is negligible), the effective velocity under different $Da$ numbers approaches to the same asymptotic value again. This implies that the effect of $Da$ number can be neglected for the estimation of effective velocity in a stratified aquifer when local transverse dispersion is negligible. The effects of CV of decay rate on effective velocity under different $Pe$ numbers are alike, and figures are not presented. Figure 8 [stemming from Eq. (42)] shows the effects of the degree of the correlation $\mu - K$ on the effective velocity. When there is no correlation between hydraulic conductivity and decay rate ($\alpha = 0$), the effective velocity is equal to mean velocity regardless of the $Pe$ number. Otherwise, a larger correlation results in larger reduction of effective velocity from the spatial average velocity. This becomes more obvious for very large $Pe$ number. With the decreased $Pe$ number (indicating increased transverse dispersion), such reduction from the average value decreases. That is to say, increasing local transverse dispersion can also weaken the effects of the correlation $\mu - K$ on effective velocity. Only the results under positive correlation ($\alpha > 0$) are presented. An exact opposite phenomenon can be found under a negative correlation, which is not shown in the context.
4 Conclusions

By considering heterogeneity of hydraulic conductivity, local dispersion, and decay rate, this study developed analytical expressions for effective field-scale contaminant transport and reaction parameters in a stratified aquifer. The effects of spatial variability of these parameters on the field-scale behavior of reactive solute plume were analyzed with respect to the effective decay rate, the longitudinal macro-dispersivity, and the effective velocity. While previous studies have studied the effective parameters under infinite $Pe$ number and ignored the influence of local transverse dispersion, our results comprehensively revealed the effects of local transverse dispersion upon the effective parameters in a stratified aquifer under various conditions. Besides the simplified stratified formation, the involved simplifications are summarized here:

1. Linear relationship [Eq. (9)] between decay rate and hydraulic conductivity
2. Simplified form of Eq. (20) for time scaling
3. Neglecting higher-order terms during the solution of Eq. (22)
Neglecting higher-order terms P and Q in Eq. (37).

The following conclusions are made:

(1) Larger average local transverse dispersion (decreasing Pe number) leads to larger effective decay rate, which approaches to the spatial mean of decay rate. The factors discussed (Da number and the CV of decay rate) impose slight effect on the asymptotic effective decay rate under very small Pe number. Larger CV of decay rate leads to smaller effective decay rate relative to the mean value, and the influence is strongest with very large Pe number (negligible transverse dispersion). The asymptotic effective decay rate relative to mean value also depends on the relative strength of reaction and convection (Da number). However, such effect will disappear when local transverse dispersion is negligible (very large Pe). These findings imply that when we estimate effective decay rate at field scale, neglecting local transverse dispersion may magnify the influence of the discussed factors and underestimate the effective decay rate. The deviation in the estimate of effective decay rate may continue to increase with travel time if local transverse dispersion is ignored.
(2) The effects of $Da$ number and the CV of decay rate on the longitudinal macro-dispersivity are more prominent under decreasing local transverse dispersion, and have weak influence on the longitudinal macro-dispersivity under very small $Pe$ condition (very large local transverse dispersion). Another interesting finding is that the longitudinal macro-dispersivity is dependent on the correlation $\mu - K$ by introducing spatially variable longitudinal local dispersion. The effect of correlation $\mu - K$ on longitudinal macro-dispersivity is controlled by the magnitude of longitudinal local dispersion. These findings show that ignoring local transverse dispersion may enlarge the effect of the mentioned factors and overestimate the longitudinal macro-dispersivity.

(3) Similarly, the effective velocities under different $Da$ numbers or CV approach to the mean velocity when the transverse dispersion is rather large (i.e., $Pe = 1$). The asymptotic effective velocity relative to mean velocity is less sensitive to $Da$ number and the CV of decay rate with decreasing local transverse dispersion.

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A Calculation of Integral Expressions

The cross-correlation integral expressions $I_1$, $I_2$, $I_3$, $I_4$, $I_5$, and $I_6$ are related to the general integral expression:

$$I(t) = \int_{-\infty}^{\infty} \frac{1 - \beta t}{\beta} S_{kk} dr$$ \hspace{1cm} (A.1)

Replacing the expression for $\beta(r)$ in Eq. (24) and the spectrum for hydraulic conductivity perturbation from Eq. (4), Eq. (A.1) takes the following form:

$$I(t) = \int_{-\infty}^{\infty} \frac{1 - e^{-(D_T r^2 + \bar{\mu} - \mu_e)t}}{D_T r^2 + \bar{\mu} - \mu_e} \frac{8\sigma_1^2 l^6 r^4}{3\pi (1 + l^2 r^2)^3} dr$$ \hspace{1cm} (A.2)

Introducing the change of variable Eq. (36) and Eq. (A.2) simplifies to:

$$I(t) = \frac{8l^2 \sigma_k^2}{3\pi D_T} \int_{-\infty}^{\infty} \frac{1 - \exp[-(\lambda^2 + \chi)^{\frac{2\pi}{T} t}]}{\lambda^2 + \chi} \frac{\lambda^4}{(1 + \lambda^2)^3} d\lambda$$ \hspace{1cm} (A.3)

The integral can be numerically evaluated.

The results presented in Eqs. (29–34) are arrived by recognizing that for the stratified formations, the spectra for the cross-correlation can be related to $S_{kk}$ based on Eqs. (4), (8) and (10):

$$S_{U_D_L} = \frac{3\tilde{D}_L \tilde{U}}{2K^2} S_{kk} \quad S_{U_U} = \frac{\tilde{U}^2}{K^2} S_{kk} \quad S_{U_{\mu}} = \frac{\alpha \tilde{U}}{K} S_{kk} \quad (A.4)$$

$$S_{D_L_D_L} = \frac{9\tilde{D}_L^2}{4K^2} S_{kk} \quad S_{D_L_{\mu}} = \frac{3\alpha \tilde{D}_L}{2K} S_{kk} \quad S_{\mu_{\mu}} = \alpha^2 S_{kk} + S_\delta \quad (A.5)$$

The partial correlation residual $\delta$ is assumed to be a statistically homogeneous random field (Miralles-Wilhelm and Gelhar 1996).
References


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