

## Reply

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We appreciate the comment by Zhang [this issue] and the opportunity to elaborate more on our solution for linearly equilibrium sorption solutes in physically and geochemically heterogeneous formations. In his comment, Zhang suggests eliminating some terms from (20) of our paper for the sake of consistency and proposes an alternative solution. Zhang considers the cases of perfect positive and negative correlation between the log conductivity  $Y$  and  $\ln K_d$ , where  $K_d$  is the partition coefficient, and he develops first-order solutions for the retarded velocity covariance function and for the second plume moments. Zhang's solution is obtained directly from (20) of the paper by Bellin *et al.* [1993] by replacing  $\langle R \rangle$ ,  $C_R$ ,  $C_{YR}$ , and  $\exp[\sigma_Y^2/2]$  with their first-order approximations. This simplification has a different impact on the second-order plume moments depending on the log conductivity variance  $\sigma_Y^2$  and the geometric mean of the retardation coefficient  $K_d^G$ . In the following we demonstrate that while for small values of  $K_d^G$  and  $\sigma_Y^2$  the two solutions are in good agreement, for large values of  $K_d^G$  and for formations moderately heterogeneous a not fully consistent yet, judicious retention of high-order terms enhances the agreement between our solution and nonlinear solutions obtained numerically.

Before describing the main differences between the two solutions we recall briefly the assumptions employed in the derivation of the second moment's tensor, which for a linearly equilibrium adsorbing solute, assumes the following expression:

$$X_{ij}^{\prime R} = 2 \int_0^{t'} (t' - \tau') v_{ij}^{\prime R}(\langle \mathbf{X}^R(\tau') \rangle) d\tau' \quad (1)$$

where  $t' = tU/(\langle R \rangle I_Y)$  is the dimensionless time,  $\langle \mathbf{X}^R \rangle$  is the particle mean trajectory, and  $v_{ij}^{\prime R}$  is the dimensionless retarded velocity covariance function. In addition,  $U$  is the mean velocity, and  $I_Y$  is the log conductivity integral scale.

The challenge in deriving  $v_{ij}^{\prime R}$  is to compute the fluctuation of the retarded velocity. Because of the stationarity of  $R$  and  $\mathbf{v}$  and by expanding the term  $1/R = 1/(\langle R \rangle + R')$  around  $\langle R \rangle$  and truncating at first order in  $R'$ , we obtain the following expression [Bellin *et al.*, 1993]:

$$v_i^{\prime R} = \frac{1}{\langle R \rangle} \left[ U \frac{R'}{\langle R \rangle} \delta_{1i} - v_i' \right] \quad (2)$$

where  $\delta_{1i}$  is the Kronecker delta. The fluctuations around the mean of the retardation coefficient are related to the fluctuations of the log conductivity through the following expression:

$$R' = K_d^G [e^{\pm Y} - e^{\sigma_Y^2/2}] \quad (3)$$

The double sign in (3) has been adopted to represent in the same expression the cases of perfect positive and negative correlation. Inspection of (2) reveals that  $v_i^{\prime R}$  depends on the order of magnitude of the fluctuations of the velocity and the retardation coefficient. After this preparatory step we consider the expression of the retarded velocity covariance function [Bellin *et al.*, 1993, equation (20)]:

$$v_{ij}^{\prime R}(\mathbf{r}) = \delta_{i1} \delta_{j1} \frac{U^2}{\langle R \rangle^2} \left[ \frac{C_R(\mathbf{r})}{\langle R \rangle^2} - 2 \frac{C_{YR}(\mathbf{r})}{\langle R \rangle} \mp \frac{K_d^G}{\langle R \rangle} e^{(\sigma_Y^2/2)} T_{j1}(\mathbf{r}) \right] + v_{ij}'(\mathbf{r}) \quad (4)$$

where the double sign of the third term represents the positive and negative cases, respectively. Since for  $i \neq 1$  or  $j \neq 1$ ,  $v_{ij}^{\prime R} = v_{ij}'$ , we limit our attention to  $v_{11}^{\prime R}$ . The presence of  $R'$  in (2) introduces three extra terms in  $v_{11}^{\prime R}$  which are not present in the case of a nonreactive solute. The first term is proportional to  $C_R$  and represents the spreading of a plume traveling in a homogeneous media with a spatially variable sorption reaction. In our solution this contribution, which depends only on the spatial variability of  $R$ , is evaluated without approximations. The order of magnitude of this contribution is

$$\frac{\sigma_R^2}{\langle R \rangle^2} = \frac{(K_d^G)^2 e^{\sigma_Y^2} (e^{\sigma_Y^2} - 1)}{(1 + K_d^G e^{\sigma_Y^2/2})^2} \quad (5)$$

In his solution, Zhang [this issue] approximates  $\sigma_R^2/\langle R \rangle^2$  as follows:

$$\frac{\sigma_R^2}{\langle R \rangle^2} = (K_d^G)^2 \sigma_Y^2 \quad (6)$$

The ratio  $\beta$  between these two expressions is

$$\beta = \frac{e^{\sigma_Y^2} (e^{\sigma_Y^2} - 1) (1 + K_d^G)^2}{\sigma_Y^2 [1 + K_d^G e^{(\sigma_Y^2/2)}]^2} \quad (7)$$

Figure 1, which shows  $\beta$  versus  $\sigma_Y^2$  for different  $K_d^G$  values, reveals that for constant  $K_d^G$ ,  $\beta$  increases with  $\sigma_Y^2$ , while for constant  $\sigma_Y^2$  it decreases as  $K_d^G$  increases. The differences are particularly evident for small  $K_d^G$  and large  $\sigma_Y^2$ . The ratio between the sum of the second and the third term of (4) and the sum of the corresponding terms in the solution by Zhang assumes the following form:

$$\gamma = \frac{K_d^G e^{\sigma_Y^2/2}}{\langle R \rangle Z_R} = \frac{e^{\sigma_Y^2/2} (1 + K_d^G)}{(1 + K_d^G e^{\sigma_Y^2/2})} \quad (8)$$

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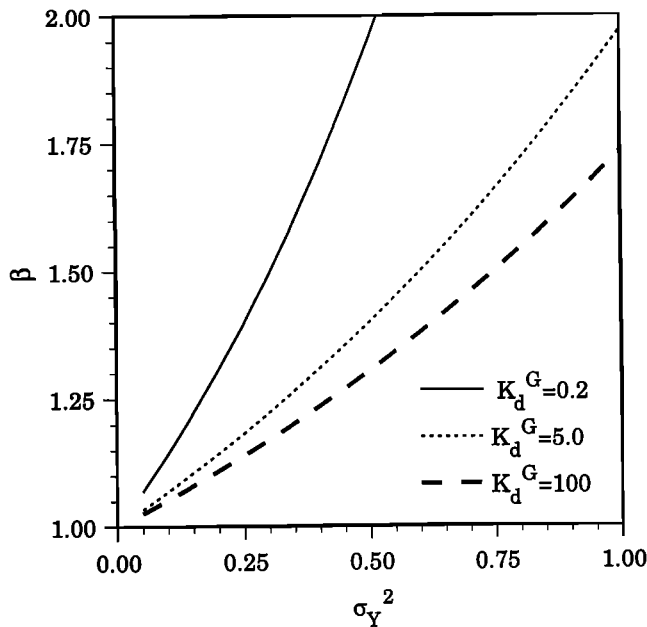


Figure 1. Function  $\beta$  versus  $\sigma_Y^2$  for different  $K_d^G$  values.

and it is shown in Figure 2. Figure 2 reveals that for a given  $K_d^G$ ,  $\gamma$  increases with  $\sigma_Y^2$ , while for a given  $\sigma_Y^2$  it decreases quickly as  $K_d^G$  increases. The behavior of  $\gamma$  is qualitatively similar to that of  $\beta$ . For  $\sigma_Y^2 \rightarrow 0$  both  $\beta$  and  $\gamma$  tend to 1. The reactive solutes detected in most cases of aquifer contamination are characterized by partitioning coefficients ranging from values smaller than 1 to 100 or more. In view of future applications it is interesting to evaluate the limits of  $\beta$  and  $\gamma$  for small and large  $K_d^G$ . For  $K_d^G \rightarrow 0$ ,  $\beta$  and  $\gamma$  assume the following expressions:

$$\beta = \frac{(e^{\sigma_Y^2} - 1)e^{\sigma_Y^2}}{\sigma_Y^2} \quad \gamma = e^{\sigma_Y^2/2} \quad (9)$$

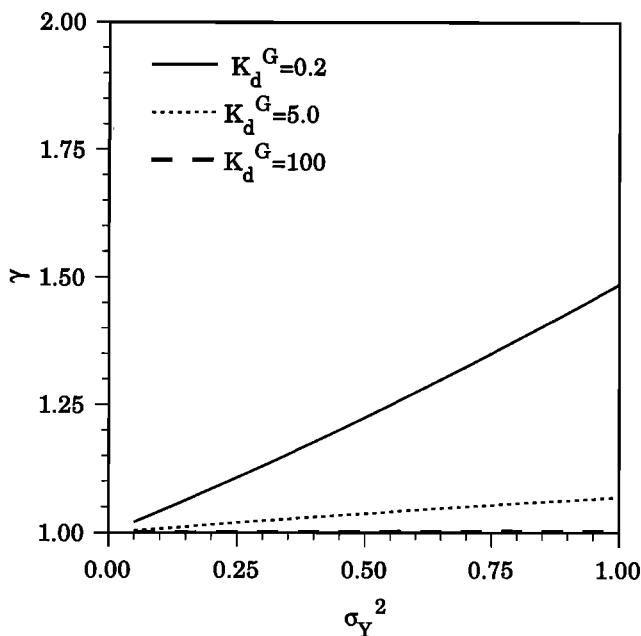


Figure 2. Function  $\gamma$  versus  $\sigma_Y^2$  for different  $K_d^G$ .

On the other hand, for  $K_d^G \rightarrow \infty$  we obtain

$$\beta = \frac{(e^{\sigma_Y^2} - 1)}{\sigma_Y^2} \quad \gamma = 1 \quad (10)$$

The above limits show that the differences between the two analytical solutions depend on  $K_d^G$ . In particular, we observe that for large  $K_d^G$  values the difference between the two solutions is mainly due to the first term of (4).

The second and the third terms on the right-hand side of (4) originate from the cross correlation between  $v'_1$  and  $R'$ :

$$\begin{aligned} \langle v'_1(\mathbf{x})R'(\mathbf{x} + \mathbf{r}) \rangle &= \langle [v'_1^{(1)}(\mathbf{x}) + v'_1^{(2)}(\mathbf{x}) + v'_1^{(3)}(\mathbf{x}) + \dots] \\ &\quad \cdot [R'^{(1)}(\mathbf{x} + \mathbf{r}) + R'^{(2)}(\mathbf{x} + \mathbf{r}) + R'^{(3)}(\mathbf{x} + \mathbf{r}) + \dots] \rangle \\ &= \left\langle v'_1^{(1)}(\mathbf{x}) \sum_{n=1}^{\infty} R'^{(n)}(\mathbf{x} + \mathbf{r}) \right\rangle \\ &\quad + \left\langle v'_1^{(2)}(\mathbf{x}) \sum_{n=1}^{\infty} R'^{(n)}(\mathbf{x} + \mathbf{r}) \right\rangle + \dots \\ &= \langle v'_1^{(1)}(\mathbf{x})R'^{(1)}(\mathbf{x} + \mathbf{r}) \rangle + \sum_{n=2}^{\infty} \langle v'_1^{(1)}R'^{(n)}(\mathbf{x} + \mathbf{r}) \rangle \\ &\quad + \text{higher-order terms} \end{aligned} \quad (11)$$

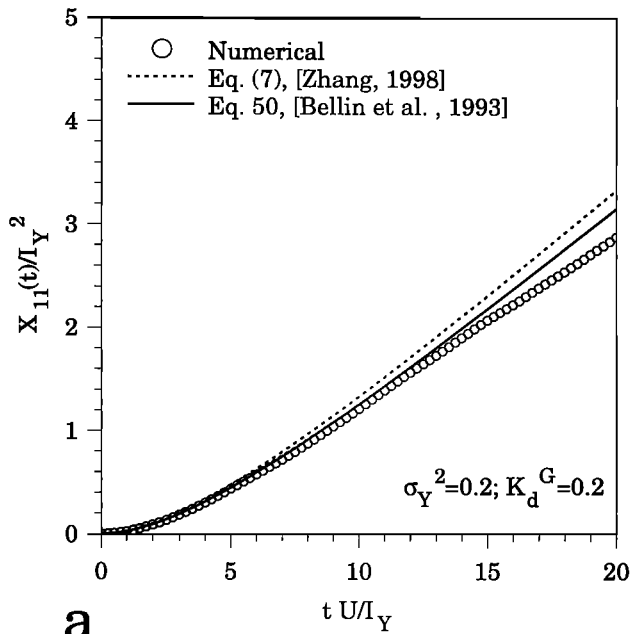
where the exponent  $n$  indicates the order of magnitude, that is,  $R'^{(n)}$  is the component of order  $\sigma_Y^n$ . Besides the approximation introduced by Zhang [this issue] in the evaluation of the first term in (4) the difference between the two solutions is related to the number of terms retained in (11). While Zhang retains only the first term on the right-hand side, we retained all the terms originating from the interaction between  $v'_1^{(1)}$  and  $R'^{(n)}$ , with  $n = 1, \dots, \infty$ .

An intrinsic hypothesis in our solutions is that products of order larger than  $n = 1$  in the expansion of  $v'_1$  are negligible. Numerical simulations by Bellin et al. [1992] and the analytical second-order solution by Hsu et al. [1996] demonstrated that terms of order higher than  $\sigma_Y^2$  are significant for the evaluation of  $v_{11}$  only at very small lags. Hence it may be reasonable to assume, pending further developments, that the longitudinal component of the cross-covariance function between  $v'_1$  and  $R'$  can be accurately represented by retaining only the term of order  $\sigma_Y$  in the expansion of  $v'_1$ . In the paper by Bosma et al. [1993] we compared our solutions with numerical simulations obtaining in all cases a good agreement between the two solutions. In light of the new results by Zhang [this issue] and to test further this hypothesis, we set up a series of numerical experiments using the methodology described by Bosma et al. [1993].

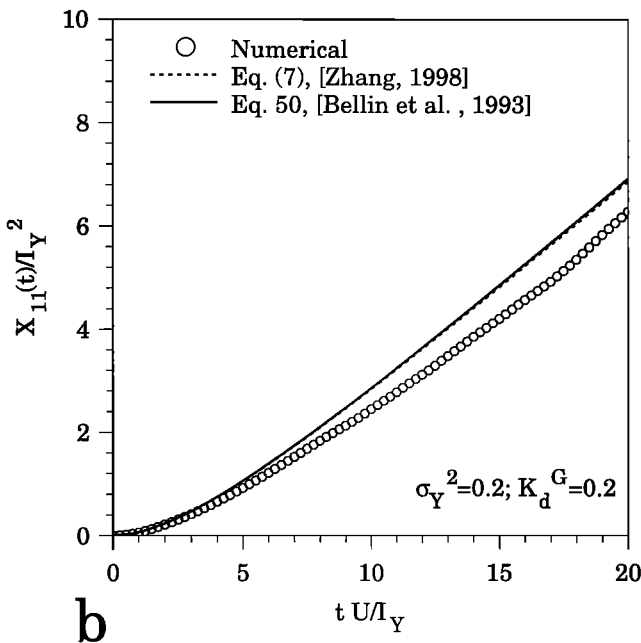
Figures 3a and 3b show the longitudinal second-order moments for perfect positive and negative correlation and for a two-dimensional isotropic formation with  $\sigma_Y^2 = 0.2$  and  $K_d^G = 0.2$ . For this set of parameters, which are the same as those used by Zhang [this issue] in his comment, the two solutions are in good agreement. However, our solution shows a better agreement with the numerical solution for the positive correlation case. This is more evident in Figures 4a and 4b which show  $X_{11}$  for  $\sigma_Y^2 = 1$  and  $K_d^G = 0.2$ . The combination of a moderately large log conductivity variance and a small value of  $K_d^G$ , which reduces considerably the amplitude of  $R'$ , makes

this example suitable to test our hypothesis. For the positive correlation case our solution is in good agreement with the fully nonlinear numerical solution, while Zhang's solution overestimates it appreciably, as can be expected from the linear solution.

Inspection of Figure 4a reveals that the second term and the following terms on the right-hand side of (11) are negative since  $X_{11}$  reduces progressively as new terms are added in the expansion. Notice also that the first term on the right-hand side of (11) is negative since it reduces  $X_{11}$  with respect to the nonreactive case. The analysis of the sign of the terms originating from the expansion of (11) confirms this finding. Since

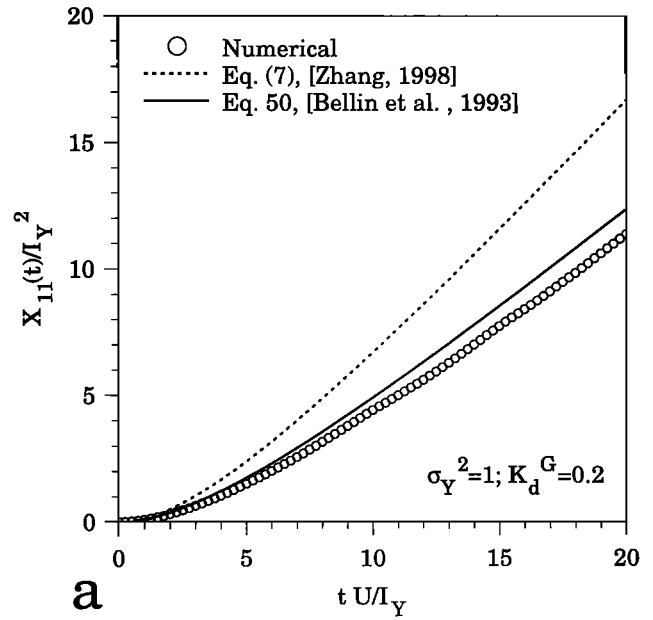


a

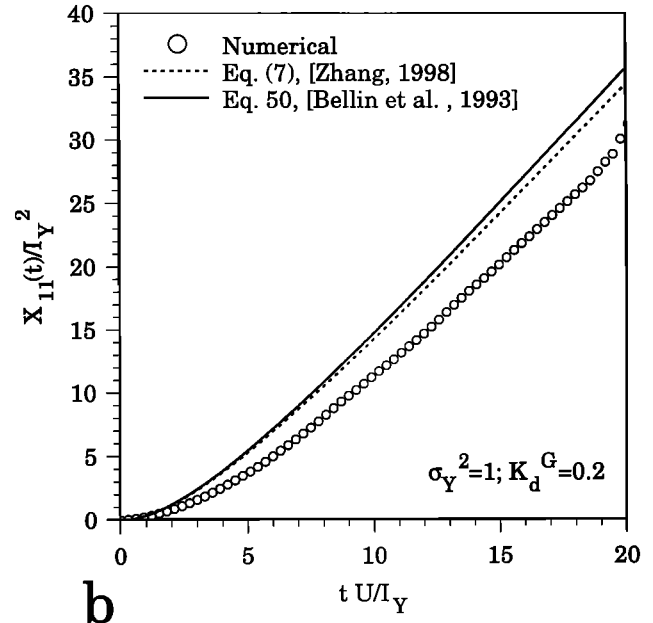


b

**Figure 3.** Second-order longitudinal plume moment for  $K_d^G = 0.2$  and  $\sigma_Y^2 = 0.2$ : (a) perfect positive correlation and (b) perfect negative correlation.



a

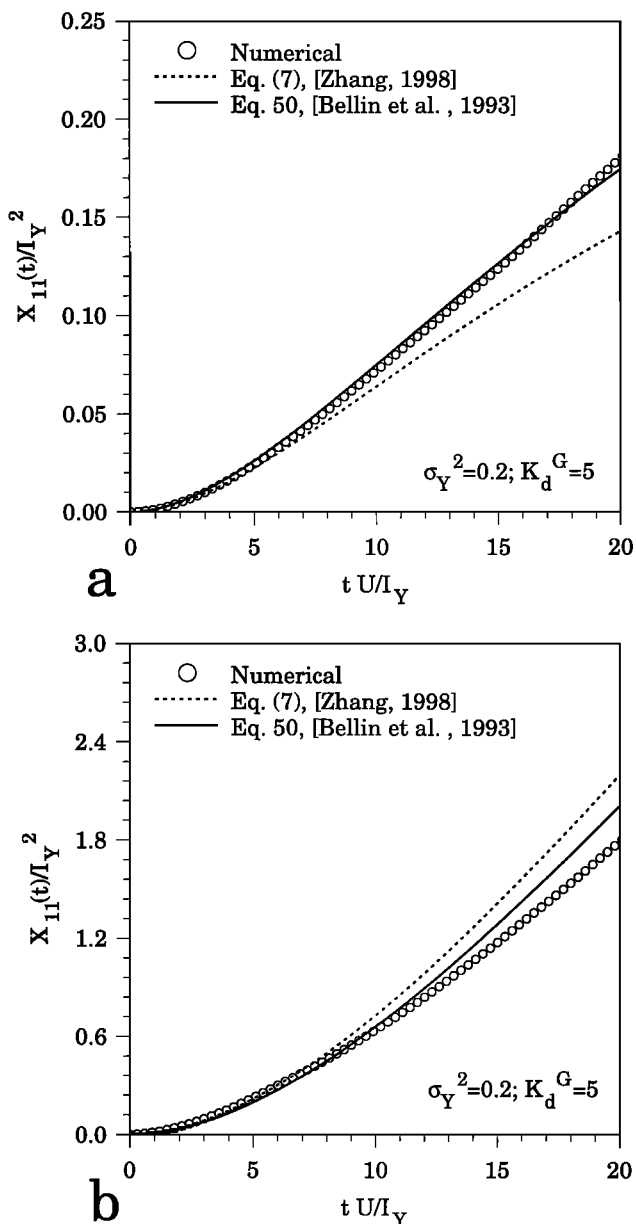


b

**Figure 4.** Second-order longitudinal plume moment for  $K_d^G = 0.2$  and  $\sigma_Y^2 = 1$ : (a) perfect positive correlation and (b) perfect negative correlation.

all the terms in (11) are negative one can conclude that a not fully consistent expansion of (11) improves the solution.

For the negative correlation case shown in Figures 4b and 3b the two analytical solutions are in good agreement. Figures 5a and 5b show the case in which geochemical heterogeneities overwhelm physical heterogeneities, and as a consequence, the fluctuations of  $R$  are much stronger than in the previous case. The parameters employed are  $K_d^G = 5$  and  $\sigma_Y^2 = 0.2$ . For the positive correlation case shown in Figure 5a the two solutions are in better agreement compared to the case shown in Figure 4a. The small value of  $\sigma_Y^2$  reduces the differences between the two solutions, and at the same time the linearization of  $\langle R \rangle$  in Zhang's [this issue] solution compensates partially for the re-



**Figure 5.** Second-order longitudinal plume moment for  $K_d^G = 5$  and  $\sigma_Y^2 = 0.2$ : (a) perfect positive correlation and (b) perfect negative correlation.

duced impact of the three terms in (4), resulting in an overall slight underestimation of  $X_{11}$ . Figure 5b shows the negative correlation case. In both the positive and negative cases our solution provides a very good match to the numerical results.

In summary, we demonstrated through considerations concerning the order of magnitude of the terms representing the interaction between physical and geochemical heterogeneities, by developing the complete solution for transport, and by linearization of the solution that our quasi-linear solutions for  $X_{11}$  represent closely the transport of linearly equilibrium adsorbing solutes in a wide range of value of heterogeneity parameters which goes beyond the range of values covered by linear theories. The two solutions are in good agreement when both  $\sigma_Y^2$  and  $K_d^G$  are small, that is, in the case analyzed by Zhang [this issue].

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