Effect of Sorption Processes on Pump-and-Treat Remediation Practices Under Heterogeneous Conditions

M. Riva, A. Guadagnini and X. Sanchez-Vila

Abstract We analyze the impact of physical and chemical heterogeneity on solute travel time to a pumping well. Environmental applications related to our work include risk evaluation of a pump-and-treat aquifer remediation practice. We consider a non-conservative solute undergoing reversible linear instantaneous equilibrium sorption. Both the distribution coefficient, K_d, and the transmissivity field, T, are considered spatially variable, and are modeled as partially correlated spatial random functions. Groundwater flow and solute transport are then solved within the context of a Monte Carlo framework. Transport of the reactive solute is analyzed within a Lagrangian framework, upon neglecting the influence of local-scale dispersion. From a suite of scenarios, simple expressions of the first two statistical moments of particles travel time to the pumping well are derived as a function of: (i) physical and chemical degree of heterogeneity of the system, and (ii) level of correlation between physical and chemical properties. A key result is that the effects of the chemical and physical heterogeneities on the mean travel time can be decoupled. On the contrary, their relative role in governing travel time variance is more complex, and a separation of the two effects is not observed.

1 Introduction

A most typical aquifer remediation scheme is that of extracting the pollutants dissolved in groundwater through pumping. If the relative impact of the natural background flow is negligible, a fully convergent quasi-radial flow develops. Relevant aspects related to this remediation method include the estimation of the time required to reduce resident concentrations below a given threshold. For this purpose, a key concept is the evaluation of residence time, defined as the time that a particle injected in the system takes to reach the location of the pumping well. Demarcation of drinking well protection regions is also based on this concept.

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A key issue in the analysis of this problem is the geochemical behavior of pollutants, since several processes lead effectively to an increase in solutes residence time. In particular we are interested in sorptive pollutants, and more specifically, in the impact of heterogeneity of the parameters describing sorption upon residence times. These parameters can be conveniently described by random fields, whose statistics are usually inferred from experimental data. This renders the corresponding flow and transport equations stochastic. As a consequence, solute particles residence time becomes a random variable.

The methodologies most commonly adopted to analyze the stochastic nature of solute residence times within extraction well fields are based either on numerical Monte Carlo simulations (either unconditional or conditional on a variety of information) or on the solution of approximate equations satisfied by the moments of travel times. The Monte Carlo method offers the appealing and convenient feature of allowing deriving information on the complete probability distribution of a given variable, as well as analyzing the response of the system in terms of specific target values of interest. Some target values include the time of first arrival and peak and late arrival times of contaminants to a pumping well.

General aspects for the evaluation of travel time moments of sorptive solutes under non-uniform flow conditions were presented by Cvetkovic et al. (1998) in an unconditional frame and by Sanchez-Vila and Rubin (2003) in a conditional framework.

The work presented here is an extension of Riva et al. (1999, 2006), who presented numerical (Monte Carlo-based) and analytical (based on recursive approximations of moment equations) results rendering the mean and variance of the residence time of a conservative solute in a two-dimensional field under convergent flow conditions. With the same flow configuration, we explore the low-order statistical moments of the residence time of reactive solute particles travelling in a physically and geochemically heterogeneous field. We consider that the solute undergoes reversible linear instantaneous equilibrium sorption, with spatially variable retardation factor, $R(\boldsymbol{x})$. This equilibrium model is based on the assumption that the typical time scale of the chemical reactions is small when compared to the typical time scales of advective-dispersive transport processes. This situation is frequently met in the presence of pumping well fields used in the context of remediation of contaminated aquifers (Valocchi, 1986).

2 Problem Statement

We consider incompressible steady state convergent flow created by a well located at the center of a circular randomly heterogeneous porous domain of radial extent L. The well pumps at a constant deterministic rate, Q. Hydraulic head, H_L, is deterministically prescribed along the outer circular boundary (Fig. 1). Here the quantities of interest are the ensemble mean and variance of the travel time of non-conservative solute particles released at time $t_0 = 0$ at a fixed point of polar coordinates $\mathbf{r}_0 \equiv (r_0, \theta_0)$, assuming the well located at $r = 0$. The location of the injection point is envisioned as a length characterizing the maximum extent of the initial polluted region.

Disregarding the effect of local dispersion, the residence time of a reactive solute particle is given by

$$t = \int_{r_0}^{0} R\left(\mathbf{r}\right) \frac{dr}{V_r\left(r, \varphi\left(r, \mathbf{r_0}\right)\right)} \tag{1}$$

Here, V_r is the radial component of the seepage velocity [LT^{-1}] evaluated along the trajectory, $\varphi\left(r, \mathbf{r}_0\right)$, of a particle which originates from $\mathbf{r}_0$ (see Figure 1), and R is the retardation factor [−], given by

$$R = 1 + \frac{\rho_b K_d}{n}, \tag{2}$$

where K_d is the distribution coefficient [$\mathrm{L}^3\mathrm{M}^{-1}$], and n and ρ_b respectively are advective porosity [−] and the bulk density [ML^{-3}] of the solid matrix.

Assuming that transmissivity, T, and K_d are Spatial Random Functions, the residence time becomes a random variable. There are experimental evidences of a certain degree of correlation between T and K_d (Roberts et al., 1986; Robin et al., 1991; Allen-King et al., 1998, 2002). The assumption of an imperfect correlation between these two variables relies on the observation that, while T depends, for a given fluid, only on the characteristics of the solid matrix of the medium, which are in turn related to grain size and orientation, K_d is also a function of the type of contaminant and of the chemical properties of the medium (including pH and organic content). We adopt the following model, postulated by Robin et al. (1991) to describe the relationship between T and K_d:

$$Z = lnK_d = lnK_{dG} + \beta Y' + W. \tag{3}$$

Here, $Y' = Y - \langle Y \rangle$, $\langle \cdot \rangle$ indicates ensemble averaging, $Y = ln\,T$, K_{dG} is the geometric mean of K_d and β is a dimensionless coefficient reflecting the degree of linear correlation between the two variables (Y and Z). The actual value of β

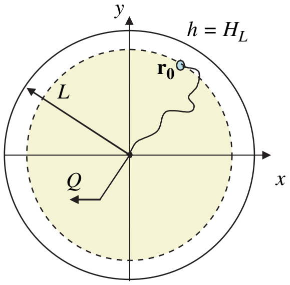

Fig. 1 Sketch of the computational domain

depends on the measurement scale, the solute and the medium mineralogy. It can be either negative (Robin et al., 1991) or positive (Mackay et al., 1986; Allen-King et al., 1998). The quantity W is modeled as a Gaussian process independent of Y and accounts for imperfect correlation between Z and Y. In this sense W includes the effects of factors which are independent from grain size distribution. It also comprises measurement uncertainties.

Without any loss of generality, we model Y and W as statistically independent stationary random fields, with zero mean, variance σ_Y^2 and σ_W^2, respectively, and spherical isotropic covariance structures

$$C_i(h) = \sigma_i^2 \begin{cases} 1 - 1.5\left(\frac{h}{\lambda_i}\right) + 0.5\left(\frac{h}{\lambda_i}\right)^3 & h \le \lambda_i \\ 0 & h > \lambda_i \end{cases} \qquad i = Y,\ W, \tag{4}$$

where λ_Y and λ_W are the corresponding correlation scales. On these premises, the autocovariance of Z is provided by the following expression:

$$C_Z(h) = \beta^2 C_Y(h) + C_W(h). \tag{5}$$

Our analysis considers the impact on the statistics of particles travel times of the following quantities: (a) degree of correlation between T and K_d; (b) the degree of heterogeneity of the aquifer; and (c) the values of integral distances I_Y and I_W.

3 Numerical Simulations

Numerical Monte Carlo simulation of flow and particle movement are performed within a square domain of 100 × 100 elements of uniform size ($\Delta x = \Delta y = \delta = 0.2$). A pumping well discharging at a constant rate $Q = 100$ is located at the central node ($x_w = 10$; $y_w = 10$). A circular boundary of radius $\mathrm{L} = 50\delta$ was defined around the well by designating all external cells as inactive. Head was prescribed in the outer boundary. The following parameters where fixed during the simulations: $n = 0.3$; $\rho_b = 1.6$; $K_{dG} = 0.28$; and $\sigma_Y^2 = 1.0$. All the above quantities are defined in consistent units.

Flow is solved by Galerkin finite elements using bilinear shape functions. Solute movement in each realization is modeled by Particle Tracking, upon injecting a particle at distance $|\mathbf{r}_0| = 9.0$ from the well. Advection is modeled by using a maximum displacement equal to δ / 1000 between two subsequent time steps. This value was chosen empirically by adjusting it until an acceptable compromise between simulation time and numerical accuracy in the reproduction of the particle trajectory was obtained. We note that, in the absence of dispersion, the trajectory of a reactive contaminant coincides with that of a conservative solute (the retardation factor affects only residence times, not trajectories). Tracking was stopped when the particle reached one of the cells sharing the well node. The remaining travel time was then computed analytically by means of the solution for homogenous media, $t' = \pi n r^2/Q$, r being the remaining distance to the well.

The combined impact of physical and chemical heterogeneity of the aquifer is studied by means of unconditional Monte Carlo simulations for a number of scenarios. We set $\sigma_Y^2 = 1$ and $\lambda_Y = 2.67$, and adopt various values of β ($\beta = -1.0, -0.5, 0.0, 0.5, 1.0$), λ_w ($\lambda_w = 0, \lambda_Y, 10\,\lambda_Y$) and σ_W^2. The 39 unconditional scenarios explored are detailed in Table 1. The values of σ_W^2 were chosen so as to obtain variances of Z, σ_z^2, equal to 0.5, 1.25, 2. With these combinations of parameters, the mean retardation factors range between 2.9 and 5.1 depending on the simulations considered. These values are typical of organic contaminants (where $R \approx (2 \ldots 10)$). Additional runs were performed with $\sigma_Y^2 = \sigma_W^2 = 1$, $I_Y = 10.0$ and two values of λ_w ($\lambda_w = \lambda_Y$, 0.1 λ_Y) and with $\sigma_Y^2 = 0.5, 1.5$ (by keeping $I_Y = I_w = 1.0$).

The unconditional realizations of the independent random variables Y and W were obtained using the Gaussian sequential co-simulator code GCOSIM3D (Gómez-Hernández and Journel, 1993). Each realization constitutes, then, a sample from a multivariate Gaussian, statistically homogeneous field, with ensemble mean $\langle Y \rangle = 0$, $\langle W \rangle = 0$, given variances, and isotropic spherical covariance functions given by (4). The random realizations of Z are obtained from (3).

From preliminary runs, the number of Monte Carlo simulations needed to obtain stable values of the travel time moments increases with (1) the order of the statistical moment considered, (2) increasing σ_Z^2 and I_Z, and (3) decreasing β. We observe that negative values of β have a negative impact on the rate of stability of mean and variance of particles travel time for a given σ_Z^2/σ_Y^2 ratio. This behavior can be explained since the $\beta < 0$ regions imply that large T values are associated with small retardation factors, thus, originating small local residence times for a particle. Contrariwise, low transmissivity regions, associated with large R values, imply large particle residence times. As a consequence, the variance of residence times

Table 1 Main controlling parameters adopted in the Monte Carlo simulations

$I_Y = 1.0; \sigma_Y^2 = 1.0$

Run No.	I_W/I_Y	β	σ_W^2	Run No.	I_W/I_Y	β	σ_W^2	Run No.	I_W/I_Y	β	σ_W^2
1		−1	0.25	14		−1	0.25	27		−1	0.25
2			1	15			1	28			1
3		−0.5	0.25	16		−0.5	0.25	29		−0.5	0.25
4			1	17			1	30			1
5			1.75	18			1.75	31			1.75
6	0	0.0	0.5	19	1	0.0	0.5	32	10	0.0	0.5
7			1.25	20			1.25	33			1.25
8			2	21			2	34			2
9		0.5	0.25	22		0.5	0.25	35		0.5	0.25
10			1	23			1	36			1
11			1.75	24			1.75	37			1.75
12		1	0.25	25		1	0.25	38		1	0.25
13			1	26			1	39			1

increases when $\beta < 0$, and a large number of Monte Carlo iterations is needed to attain stability. The opposite behavior is observed for positive β values. We found that convergence is obtained with 5000 Monte Carlo iterations for each unconditional case, with the only exception of the scenario characterized by $\sigma_z^2 = 2.0$ and $I_W/I_Y = 10$, where stability is not reached after 10000 simulations.

4 Dimensional Analysis

Results from Monte Carlo simulations were treated in the framework of dimensional analysis. In this context, the (random) residence time of a non-conservative solute particle can be expressed by the following functional format

$$t = f(Q, L, r_0, H_L, T, K_d, \beta, n, \rho_b). \tag{6}$$

Here, the two random fields T and K_d are fully defined in terms of their geometric mean, variance, shape of covariance function, correlation scale and, eventually, measured values at conditioning points. In the absence of conditioning, the functional form rendering the *i-th* order statistical moment of travel time, $\mathrm{E}^i[t]$, becomes,

$$E^i\,[t] = f(Q, L, r_0, H_L, n, \rho_b, T_G, \sigma_Y^2, \lambda_Y, \alpha_Y, K_{dG}, \sigma_Z^2, \lambda_Z, \alpha_Z, \beta). \tag{7}$$

Here α_j (with $j = Y, Z$) is a dimensionless coefficient which accounts for the model adopted for the auto-correlation function, and $T_G = \exp(\langle Y \rangle)$.

We start by noting that the deterministic hydraulic head H_L at the boundary does not affect the contaminant travel time. We then select L, K_{dG} and Q as fundamental quantities and rewrite Eq. (7) in dimensionless format as

$$E^i\left[t\frac{Q}{L^2}\right] = f\left[\frac{r_0}{L}, n, \rho_b K_{dG}, \frac{T_G L}{Q}, \frac{\lambda_Y}{L}, \frac{\lambda_Z}{\lambda_Y}, \sigma_Y^2, \sigma_Z^2, \alpha_Y, \alpha_Z, \beta\right]. \tag{8}$$

In this study we do not explore the dependence of travel time moments on the injection location and consider fixed values for T_G, n and ρ_b. Furthermore, as already indicated, we adopt a spherical covariance function for Y. This implies that we are concerned with the following functional dependences:

$$E^i\left[t\frac{Q}{L^2}\right] = E^i\,[\bar{t}] = f\left[\frac{\lambda_Z}{\lambda_Y}, \frac{\lambda_Y}{L}, \sigma_Z^2, \sigma_Y^2, \alpha_Z, \beta\right]. \tag{9}$$

5 Mean Travel Time

Figure 2 depicts the dependence of mean dimensionless travel time, $\langle \bar{t} \rangle$, on β and σ_Z^2 for $I_W/I_Y = 0$, $I_Y = 1.0$ and $\sigma_Y^2 = 1.0$. The mean value for a conservative solute, $\langle t_{NR} \rangle$, and that corresponding to a solute subject to a constant retardation factor, with $K_d = K_{dG}$ (that is $\langle t_{HR}\rangle = R_{HR} \quad \langle t_{NR}\rangle$, where $R_{HR} = 1 + \rho_b K_{dG}/n$), in a randomly heterogeneous Y field with the same values of I_Y and σ_Y^2, are also reported for comparison.

We note that (i) when Z is heterogeneous the mean residence time is always larger than that obtained when the reactive process is modeled by means of a constant $K_d = K_{dG}$; (ii) $\langle \bar{t}\rangle$ shows a supra-linear increase with the degree of chemical heterogeneity, as expressed by σ_z^2; and (iii) $\langle \bar{t}\rangle$ decreases as β increases, and this effect is more visible for large σ_z^2 values. The latter observation arises from the fact that regions with low transmissivity and large retardation factors (this combination occurs for negative β) dominate the mean residence time. Additional scenarios (not reported) show a negligible effect of I_W/I_Y in mean travel time.

On the basis of the complete set of Monte Carlo-based results displayed in Fig. 3, we propose the following empirical expression, in terms of dimensionless groups, relating the difference between $\langle \bar{t}\rangle$ and $\langle \bar{t}_{HR}\rangle$:

$$\langle \bar{t}\rangle - \langle \bar{t}_{HR}\rangle = \sigma_Z\left[\sigma_Z^2 - \beta\right]. \tag{10}$$

The key result encapsulated in Fig. 3 is that the effects of the geological and chemical heterogeneity on the mean residence time can be separated in the range of parameters studied. While $\langle t_{HR}\rangle$ depends on geological heterogeneity (i.e., σ_Y^2 and L/I_Y) and can be interpreted, for instance, by the analytical solution of Riva et al. (2006), the quantity $\langle \bar{t}\rangle - \langle t_{HR}\rangle$ depends on the degree of geochemical heterogeneity and it appears to be practically insensitive to variations in I_W/I_Y, σ_Y^2 and L/I_Y.

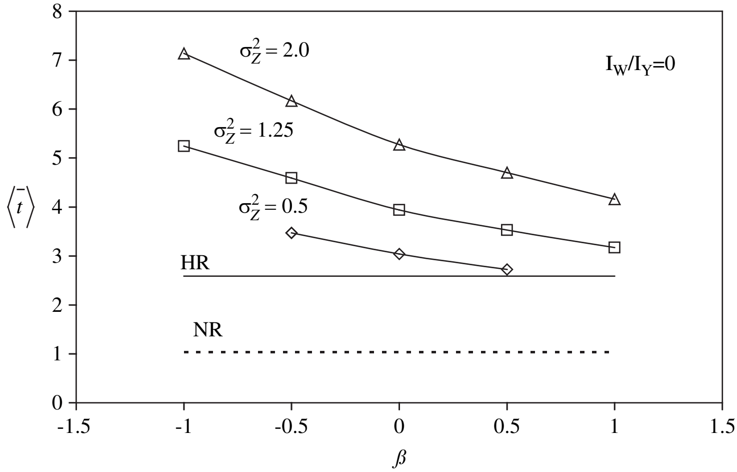

Fig. 2 Dependence of mean dimensionless travel time, $\langle \bar{t}\rangle$, on β and σ_Z^2 for $I_W/I_Y = 0$. The values corresponding to a conservative contaminant (dotted line, labeled NR) and that obtained for constant retardation factor, with $K_d = K_{dG}$, in a randomly heterogeneous Y field (continuous line, labeled HR) are also reported

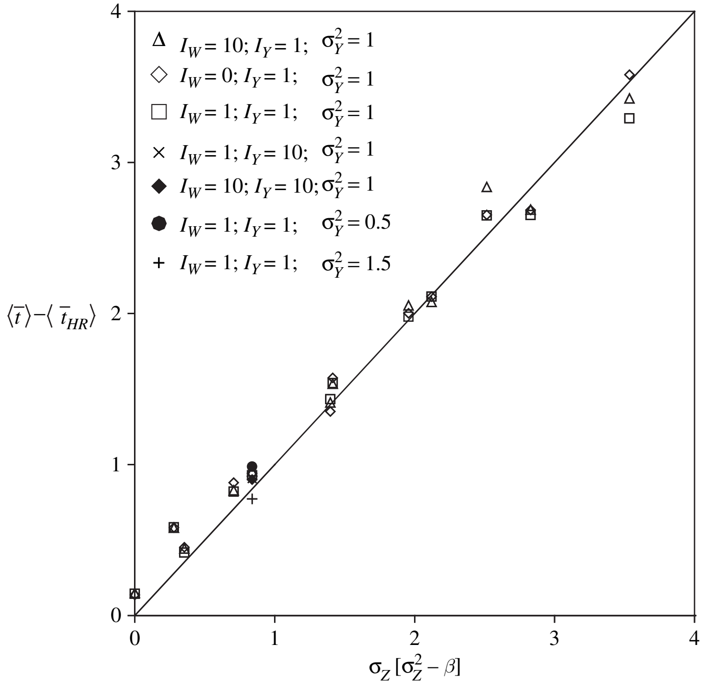

Fig. 3 Mean travel time as a function of $\sigma_z\ [\sigma_z^2 - \beta]$. The mean values for different scenarios and the 1:1 line are displayed

6 Variance of Travel Time

Figure 4 depicts the variance of the dimensionless log-travel time, $\sigma^2_{ln\bar{t}}$, as a function of β and σ_z^2 for $I_W/I_Y = 0$, 1.0. We present the logarithm of travel time since the travel time distribution in radial flows is more closely related to a log-Normal than to a Normal distribution. The result corresponding to conservative solute (equal to that corresponding to any constant retardation factor) is also displayed.

We note that the variance of log-travel time decreases as β increases. This is consistent with previous observations about the interplay between physical and chemical heterogeneity of the system, as expressed by β. This decreasing in variance is causing the decrease in mean travel time with β, since the travel time distribution is positively skewed. We also note that for positive β values, modeling the subsurface as a chemically homogeneous system can lead to significant overestimation of the uncertainty associated with the process.

The variance of the logarithm of travel time increases with σ_Z^2 and is also strongly affected by the ratio I_W/I_Y. As opposed to what is observed for mean travel time, the variance significantly increases with I_W/I_Y. This observation is consistent with the fact that increasing I_W/I_Y leads to fields with larger spatial persistence of chemical properties. This implies a large variability in probability space. The rate of increase of $\sigma^2_{ln\bar{t}}$ with I_W/I_Y is amplified for large σ_Z^2 values.

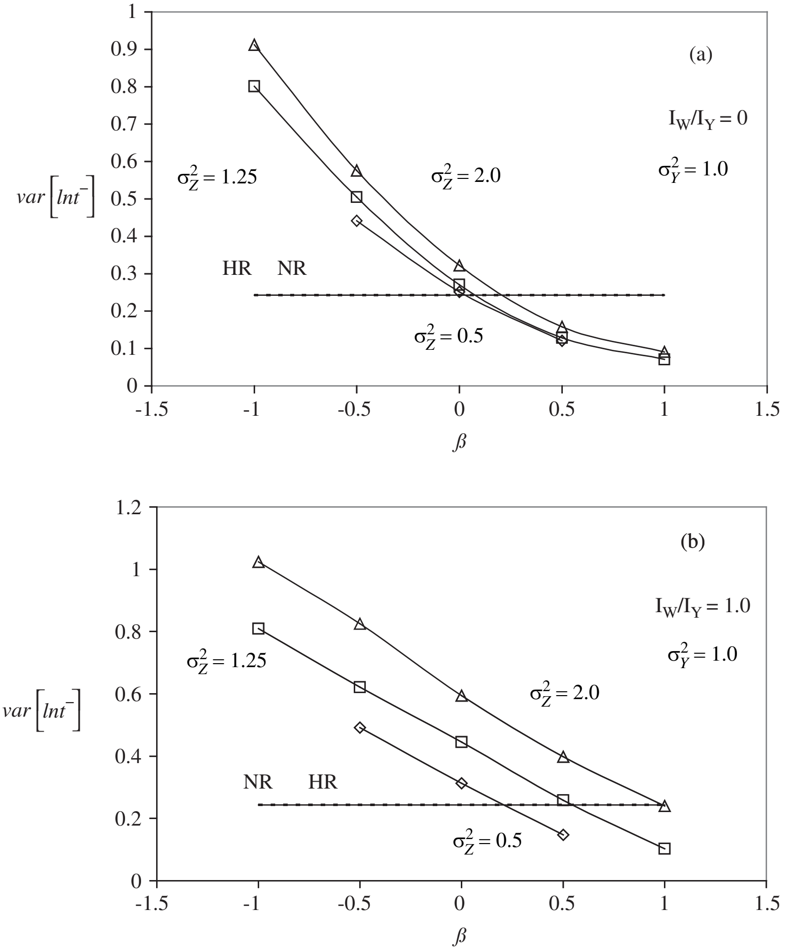

Fig. 4 Variance of natural logarithm of normalized travel time as a function of β and σ_Z^2, with $\sigma_Y^2 = 1$, $I_Y = 1$ and (a) $I_W/I_Y = 0$; (b) $I_W/I_Y = 1$. The values corresponding to a conservative contaminant (dotted line, labeled NR) and that obtained for constant retardation factor, with $K_d = K_{dG}$, in a randomly heterogeneous Y field (continuous line, labeled HR) are also reported

On the basis of the complete set of Monte Carlo simulations we propose the following empirical expression, relating the difference between the variance of the travel times obtained in a geochemically heterogeneous system, $\sigma^2_{ln\bar{t}}$, and that typical of a chemically homogeneous (with $K_d = K_{dG}$) but geologically heterogeneous system, $\sigma^2_{ln\bar{t},\,NR}$, to the dimensionless groups appearing in (9):

$$\sigma^2_{ln\bar{t}} - \sigma^2_{ln\bar{t},\,NR} = \beta\sigma_z^{2\varepsilon} + \alpha\,\sigma_z^2\left(1 - \upsilon\beta\right) - \upsilon\,\beta\sigma^2_{ln\bar{t},\,NR}. \qquad (11)$$

Here α, ν, and ε are positive coefficients, which depend only on I_W/I_Y:

$$\alpha = 0.2\, e^{-2\frac{I_W}{I_Y}} - 0.4\, e^{-\frac{I_W}{I_Y}} + 0.3; \qquad 0.1 \le \alpha \le 0.3 \tag{12}$$

$$\upsilon = -e^{-2\frac{I_W}{I_Y}} + 2.9\, e^{-\frac{I_W}{I_Y}} + 2.4; \qquad 2.4 \le \nu \le 4.3 \tag{13}$$

$$\varepsilon = -1.7\, e^{-2\frac{I_W}{I_Y}} + 1.7\, e^{-\frac{I_W}{I_Y}} + 0.3; \qquad 0.3 \le \varepsilon \le 0.7 \tag{14}$$

The values for $\sigma^2_{ln\bar{t},\,NR}$ can be obtained, for instance, by the Monte Carlo-based results of Riva et al. (1999) or by the analytical solution of Riva et al. (2006). The expressions (12)–(14) were derived on the basis of the tests reported in Table 1 (with fixed $I_Y = 1$ and $\sigma_Y^2 = 1$). The synthesis of the results corresponding to all the scenarios analyzed is reported in Fig. 5.

In order to analyze the robustness and reliability of Eq. (11)–(14) for varying degrees of geological heterogeneity of the system, we also juxtaposed to the results of Fig. 5 the outcome of the tests performed by increasing I_Y to 10 (while keeping unit variance of Y) and setting $\sigma_Y^2 = 0.5, 1.5$, while keeping $I_Y = 1$.

The points corresponding to the scenario characterized by $\sigma_z^2 = 2.0$ and $I_W/I_Y = 10$ are not presented, since we did not obtain stable results after 10000

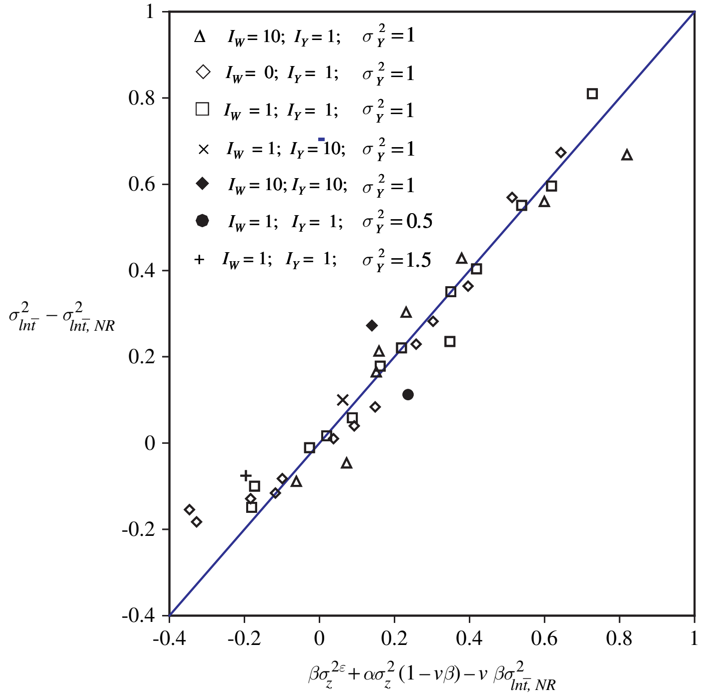

Fig. 5 Variance of log-travel time as a function of the empirical expression provided in (11) with the coefficients obtained from (12) to (14). The values obtained for the different scenarios analyzed through Monte Carlo simulations are presented to show the goodness of the fit

simulations. With reference to the structure of the relationship provided by (11), the following observations can be made:

1. under chemically homogeneous conditions ($\sigma_z^2 = 0$ and $\beta = 0$), the trivial solution $\sigma_{ln\bar{\tau}}^2 = \sigma_{ln\bar{\tau},\,NR}^2$ can be retrieved;
2. $\sigma_{ln\bar{\tau}}^2$ display a (generally) nonlinear dependence on σ_z^2;
3. when $\beta = 0$ (i.e., chemical and physical heterogeneities lack correlation) the difference $\sigma_{ln\bar{\tau}}^2 - \sigma_{ln\bar{\tau},\,NR}^2$ increases linearly with the degree of chemical heterogeneity (σ_z^2) and it is not influenced significantly by the physical heterogeneity;
4. when $\beta < 0$ the effect of the physical heterogeneity is amplified (see the last term appearing in (11)) and $\sigma_{ln\bar{\tau}}^2$ increases; the opposite holds for $\beta > 0$;
5. the degree of chemical heterogeneity, i.e., σ_z^2, causes the difference $\sigma_{ln\bar{\tau}}^2 - \sigma_{ln\bar{\tau},\,NR}^2$ to increase if $\beta \sigma_z^{\varepsilon} > \alpha\,(\upsilon\beta - 1)$.

7 Conclusions

The residence time of reactive solute particles displaced in a convergent flow which takes place in a geochemically heterogeneous aquifer is analyzed in the context of a numerical unconditional Monte Carlo framework. In our approach we disregard the effects of local scale diffusion and dispersion processes and model randomness of solute particle trajectories as a process which depends solely on the random physical heterogeneity of the system. On the basis of several synthetic scenarios accounting for the influence of variations in the statistical parameters characterizing $Y = lnT$ and $Z = lnK_d$ (variance, covariance, integral scale and degree of correlation) we derive simple empirical expressions of the first two statistical moments of the travel time of contaminant particles. These expressions relate ensemble mean and variance of particles residence time to (*i*) the physical and chemical degree of heterogeneity of the system, and (*ii*) the level of correlation between physical and chemical properties. A key result is that the effects of the chemical and physical heterogeneities on the mean travel time can be clearly separated. On the other hand, a clear separation of these same two effects on the residence time variance could not be identified. The results of the study are relevant in the context of *a priori* analyses of the efficiency of a pump and treat method in that they are conducive to an estimate of the residual contaminant mass in the groundwater after a given operational time. More generally, they are aimed at supporting the evaluation of the time required for groundwater remediation actions and at providing a measure of the associated risk.

On these basis, the empirical expressions which are derived can be used (in principle) only within the range of parameters examined, for convergent flow conditions and for linear instantaneous reversible sorption. Furthermore, our results do not incorporate the effect of conditioning on different types of information. As such, they can be useful in providing preliminary analyses of the risk involved in pump-and-treat scenarios. More sophisticated design protocols capable of assimilating different types of data, information and/or geochemical processes are then required in the final design stage of the remediation practice.

References

Allen-King RM, Halket RM, Gaylord DR, Robin MJL (1998) Characterizing the heterogeneity and correlation of perchloroethene sorption and hydraulic conductivity using a facies-based approach, Water Resour Res, 34 (3): 385–396

Allen-King RM, Grathwohl P, Ball WP (2002) New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks, Adv Water Resour, 25: 985–1016

Cvetkovic V, Dagan G, Cheng H (1998) Contaminant transport in aquifers with spatially variable hydraulic and sorption parameters, Proceedings Royal Soc. London A, 454: 2173–2207

Gómez-Hernández JJ, Journel AG (1993) Joint sequential simulation of multi-Gaussian field. In: Geostatitics Troia'92, vol 1. pp 85–94

Mackay, DM, Freyberg DL, Roberts PV, Cherry JA (1986) A natural gradient experiment on solute transport in a sand aquifer 1. Approach and overview of plume movement, Water Resources Research, 22 (13): 2017–2029

Riva M, Guadagnini A, Ballio F (1999) Time related capture zones for radial flow in two-dimensional randomly heterogeneous media, Stoch. Environ. Res. Risk Assess. 13 (3): 217–230

Riva M, Sánchez-Vila X, Guadagnini A, De Simoni M, Willmann M (2006) Travel time and trajectory moments of conservative solutes in two-dimensional convergent flows, J. Contam. Hydrol., 82: 23–43

Roberts PV, Goltz MN, Mackay DM (1986) A natural gradient experiment on solute transport in a sand aquifer 3. Retardation estimates and mass balances for organic solutes, Water Resour Res, 22 (13): 2047–2058

Robin MJL, Sudicky EA, Gillham RW, Kachanoski RG (1991) Spatial Variability of Strontium Distribution Coefficients and Their Correlation With Hydraulic Conductivity in the Canadian Forces Base Borden Aquifer, Water Resour Res, 27 (10): 2619–2632

Sanchez-Vila X, Rubin Y (2003) Travel time moments for sorbing solutes in heterogeneous domains under nonuniform flow conditions, Water Resour Res, 39(4): 1086, doi: 10.1029/2002WR001399

Valocchi J (1986) Effect of radial flow on deviation from local equilibrium during sorbing solute transport through homogeneous soils, Water Resour Res, 22 (12): 1693–1701