



On the striking similarity between the moments of breakthrough curves for a heterogeneous medium and a homogeneous medium with a matrix diffusion term

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Abstract

A usual method to obtain aquifer parameters is to analyze the moments of the breakthrough curves (BTCs) in tracer tests. The parameters to be estimated in this analysis would depend on the conceptual model adopted. Intuitively, if different processes were considered, the shape of the BTCs should be quite different, and one would tend to think that the time and space evolution of the temporal moments should also be quite different. Contrarily, in this paper, we show that two very different conceptual models of solute transport lead to virtually identical moments of the BTC. The two models selected for this study are the classical advection–dispersion equation with a Fickian macrodispersive term and a homogeneous medium advection model with mass-transfer between mobile and immobile matrix phases, for three different models of matrix shape. In both models, the first three moments are linear with travel distance, while the fourth moment is a second order polynomial. This agreement allows us to choose parameters yielding the same moments in the two models. As we consider two fitting parameters, we select them to match the second and third moment. Match in the first moment is obtained from physical arguments. It turns out that the resulting leading term of the fourth moment is identical for both models. As a direct consequence of this work, it follows that for large travel distances it would not be possible to discriminate between conceptual models using data from a single BTC.

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1. Introduction

Solute transport in heterogeneous media has been the subject of a large amount of research in recent years, both theoretically and in real site applications. Theoretical analysis is generally carried out in

a geostatistical frame, where the variables that appear in the transport equation are treated as Spatial Random Functions (Matheron, 1971). This has led to much work oriented to study the behavior of hydraulic heads and/or concentrations and to find the values of effective and equivalent parameters for groundwater flow and solute transport. The working methodologies and the main results are summarized in the books by Dagan (1989), Gelhar (1993) and Zhang (2002) or Rubin (2003).

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One of the most prominent effects of heterogeneity is dispersion. Spatial variability of water velocity causes the solutes to disperse. In fact, one of the most significant findings of stochastic hydrogeology has been the derivation of the equation controlling transport at long distances from the equation controlling transport at the local scale and the assumption of heterogeneous velocity. The usual representation is the advection–dispersion equation (ADE) with a Fickian macrodispersion term

$$\varphi \frac{\partial \langle C \rangle}{\partial t} + \langle \mathbf{q} \rangle \nabla \langle C \rangle - \nabla (\mathbf{A} \langle \mathbf{q} \rangle \nabla \langle C \rangle) = 0, \quad (1)$$

where $\langle C \rangle$ is the expected value of the concentration of any given solute, φ is total porosity, $\langle \mathbf{q} \rangle$ is the expectation of Darcy's velocity, and \mathbf{A} is the macrodispersivity tensor. This last tensor accounts for molecular diffusion plus the effects of random departures of the local velocities from their mean value. A lot of work has been devoted in the stochastic hydrogeology literature to find the close form expression for this tensor. The pioneering work in this subject was that of Gelhar and Axness (1983), who derived the expression for the different components in \mathbf{A} , a_{ij} , under a number of simple geologic structures and flow conditions.

This Fickian representation of dispersion is not valid at intermediate distances. In fact, a vast amount of research has been devoted to explaining and representing the well-known scale-dependence of dispersivity. Dagan (1984), under the hypothesis of $\langle C \rangle$ Gaussian, derives a solution where the a_{ij} terms become functions of travel time (τ) from the source. In particular, the longitudinal dispersivity, a_{11} , is found to grow linearly for small and reaches an asymptote for large travel distances (Dagan, 1984). Similar results are obtained by Neuman et al. (1987) using a different approach. Dagan (1987, 1988); Neuman and Zhang (1990) derive the time dependent macrodispersivity tensor from particle displacement moments. Jaekel and Vereecken (1997) applied the renormalization group method to obtain also a scale dependent tensor, still local in space. Their findings were later validated numerically by Schwarze et al. (2001).

Due to the time dependence, different attempts have been made to find asymptotic values for macrodispersion in fields consisting of more than one scale (Zhan and Wheatcraft, 1996; McLaughlin and Ruan, 2001; Lunati

et al., 2002). Dagan and Neuman (1991) and a number of authors, thereafter (Cushman and Ginn, 1993; Kavvas and Karakas, 1996; Dentz et al., 2000) derive a different aspect for the equation, where the dispersive term is non-local in either space or time (and thus the macrodispersive term is non-Fickian). Several results are also available for transport in non-uniform flow incorporating conditional moments (Neuman, 1993; Butera and Tanda, 1999; Guadagnini and Neuman, 2001).

Unfortunately, the above non-local approaches are difficult to apply in real problems. Therefore, dispersion is still represented by means of a Fickian (macrodispersive) term in most cases. Problems caused by this choice are reviewed by Carrera (1993). Among them, we wish to stress here the inaccurate reproduction of both plumes and breakthrough curves (BTCs) (see also Kennedy and Lennox, 2001). Contrary to what Fickian dispersion predicts, actual plumes often display a highly asymmetric shape, with the maximum displaced towards the front. By the same token, Fickian models fitted to early time data rarely reproduce the long tails exhibited by late time breakthrough data. As an example, in Fig. 1, we show the calibration of a convergent flow tracer tests performed at El Cabril site in southern Spain (UPC-UPM, 1991) obtained by fitting early time data with the standard ADE. From the figure, late time data is poorly predicted and the total mass calibrated is lower than the actual input mass.

The two features commented (asymmetric spatial distributions and long tails) can be simulated by means of a term representing the exchange of solute between mobile and immobile regions. This type of formulation is often used to represent matrix diffusion in fractured media (Neretnieks, 1980; Barker and Foster, 1981); sorption (coupled or uncoupled to diffusion) into slowly moving portions of soils (Sposito et al., 1986; Shapiro, 2001; Wörman et al., 2003); non-instantaneous (kinetic) reversible mass transfer (Cunningham et al., 1997; Haggerty and Gorelick, 1998; McKenna et al., 2001); the effect of connectivity of highly conductive features (Zinn and Harvey, 2003); low permeability inclusions (Guswa and Freyberg, 2000); and other phenomena (Zimmerman et al., 2002; Carrera et al., 1998). We will call this term 'matrix diffusion' for shortness, because it can be viewed as representing a diffusive exchange between a flowing portion

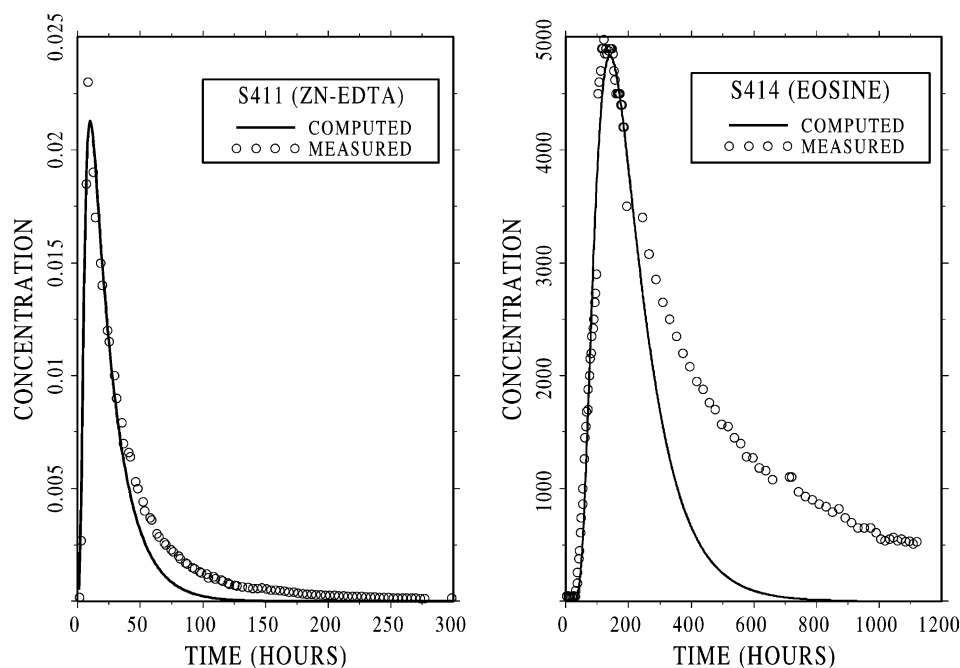


Fig. 1. Calibration of a convergent flow tracer test performed at El Cabril (Spain). Interpretation with the standard ADE after fitting early time data (adapted from UPC-UPM, 1991). Best fit is obtained with a reduced input mass.

and a non-flowing, or matrix, portion. Solute diffusing into the non-flowing portion is delayed, thus leading to asymmetric plumes, reduction in peak concentrations and long-tailed BTCs. In Fig. 2, we see the same BTC than in Fig. 1 now interpreted allowing linear exchange with an immobile water phase (UPC-UPM, 1991). In this case, the peak is again well characterized, but now tailing is well reproduced.

The results shown in Figs. 1 and 2 suggest that a matrix diffusion term could be used for representing dispersion more accurately than a Fickian term, thus providing a better reproduction of transport through heterogeneous media. In fact, Carrera et al. (1998) showed that the matrix diffusion term can be substituted by means of a convolution product resembling analogous terms used by Dagan and Neuman (1991) or by Berkowitz and Scher (1995). Also, Guswa and Freyberg (2002) show that a mass transfer term performed much better than a dispersive term in a bimodal aquifer where low permeability inclusions are found in a high conductive matrix.

The original motivation of our work was to seek a matrix diffusion representation of dispersion that is consistent with stochastic formulations of transport in

heterogeneous media. That is, we expected that by fitting macrodispersion with a matrix diffusion term, we could reproduce the time evolution of the dispersion coefficient that has been derived by stochastic methods. As it turns out, such a representation is not possible. We will see that the evolution of the BTC moments is not adequate. Still, this representation can be viewed as a convenient alternative to Fickian macrodispersion, that is, valid after ergodic conditions have been attained. One of the critical points is that the parameters included in the mass transfer term should have a physical meaning, and, therefore, should be related to actual parameters characterizing the heterogeneity of the medium.

The approach to reach such objective is as follows. First, we derive the moments of the expected BTC corresponding to a heterogeneous medium assuming that the ADE with a Fickian macrodispersive term holds. Second, we find the travel time moments for a homogeneous medium in which a matrix diffusion term was considered. The last point is to show how a proper identification of parameters leads to identical temporal moments up to fourth order in the case of large travel distances. Finally, we discuss the physical

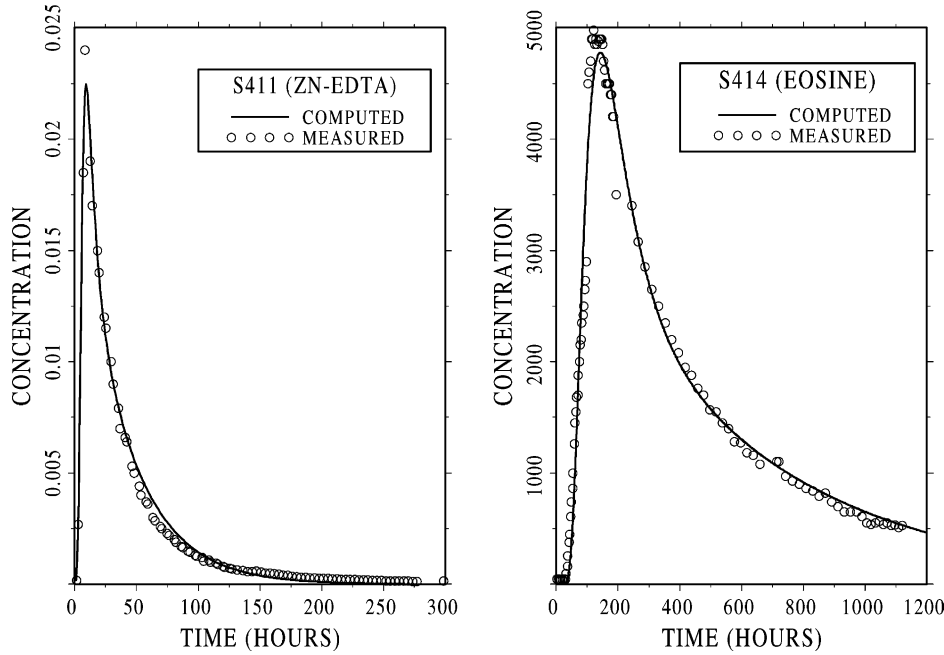


Fig. 2. Calibration of a convergent flow tracer test performed at El Cabril (Spain). Interpretation after allowing linear exchange with an immobile water phase (adapted from UPC-UPM, 1991).

meaning of the identified parameters as well as some implications and extensions of our work.

2. Temporal moments for the ADE with a Fickian macrodispersive term

Under mean uniform flow in the x -direction (without any loss of generality), and considering that for steady-state flow and long travel distances the transverse macrodispersivity is negligible with respect to the longitudinal one (Dagan, 1988), we can rewrite Eq. (1) as

$$\varphi \frac{\partial \langle C \rangle}{\partial t} + \langle q \rangle \frac{\partial \langle C \rangle}{\partial x} - a_{11} \langle q \rangle \frac{\partial^2 \langle C \rangle}{\partial x^2} = 0, \quad (2)$$

where a_{11} is (longitudinal) dispersivity and can be written in terms of the parameters that characterize the hydraulic conductivity Spatial Random Function. As an example, for isotropic media $a_{11} = \sigma_Y^2 I$ (Dagan, 1989), where σ_Y^2 is the variance of log-conductivity and I is the integral distance in the x -direction. We disregard local dispersion, because it is usually very small compared to the macrodispersive term. It

must be pointed that the two simplifications (namely, neglecting transverse dispersion and local dispersion) have been adopted without loss of generality. That is, they do not affect later results, as we will be interested in travel time towards a plane located perpendicular to the mean flow direction (Cvetkovic et al., 1992), which can be reduced to a single point along the flow direction under these two simplifications. Actually, Berglund and Fiori (1997) showed that pore-scale (local) dispersion affects transport primarily through transverse mixing.

We consider the case of an instantaneous point injection in an initially clean aquifer, which can be taken as a kernel for any other kind of injection in space and time. The goal is to get an expression for the temporal moments of the BTC at a point located at distance x . To this end, it is convenient to set the problem in the Laplace space

$$\varphi s \bar{C} + \langle q \rangle \frac{\partial \bar{C}}{\partial x} - a_{11} \langle q \rangle \frac{\partial^2 \bar{C}}{\partial x^2} = 0, \quad (3)$$

where s is the Laplace variable and \bar{C} is the Laplace transform of $\langle C \rangle$. The analytical solution for this

problem becomes:

$$\bar{C}(x, s) = \exp \left\{ \frac{x}{2a_{11}} \left(1 - \sqrt{1 + \frac{4\varphi a_{11}}{\langle q \rangle} s} \right) \right\}. \quad (4)$$

Inversion of Eq. (4), would yield the expected BTC. However, we are only interested in its moments, which are easier to find from the solution of C in Laplace space. The non-centered temporal moments, defined as

$$T_i(x) = \int_0^\infty t^i \langle C(x, t) \rangle dt / \int_0^\infty \langle C(x, t) \rangle dt,$$

can be obtained by taking the limits of sequential derivatives of Eq. (4) with respect to s (Aris, 1958):

$$T_i(x) = \lim_{s \rightarrow 0} \frac{(-1)^i}{\bar{C}(x, s)} \frac{d^i \bar{C}(x, s)}{ds^i}. \quad (5)$$

The central moments can be obtained from the non-centered ones as

$$\begin{aligned} \sigma_\tau^2(x) &= T_2(x) - T_1^2(x), \\ \Sigma_\tau(x) &= T_3(x) - 3T_2(x)T_1(x) + 2T_1^3(x), \\ M_{4,\tau}(x) &= T_4(x) - 4T_3(x)T_1(x) + 6T_2(x)T_1^2(x) - 3T_1^4(x), \end{aligned} \quad (6)$$

where σ_τ^2 , Σ_τ , and $M_{4,\tau}$ are the second (variance), third and fourth order central moments of the expected BTC, respectively.

A relative simple way to obtain the different $T_i(x)$ terms is to perform a McLaurin expansion of the function inside the exponential in Eq. (4), that is

$$\begin{aligned} \bar{C}(x, s) = \exp \left\{ -\frac{x}{\langle U \rangle} \left(s - \frac{a_{11}}{\langle U \rangle} s^2 + 2 \frac{a_{11}^2}{\langle U \rangle^2} s^3 \right. \right. \\ \left. \left. - 5 \frac{a_{11}^3}{\langle U \rangle^3} s^4 + O(s^5) \right) \right\}, \end{aligned} \quad (7)$$

with $\langle U \rangle = \langle q \rangle / \varphi$ meaning the expected value of the advective velocity. Sequential differentiation of Eq. (7) and substitution in Eqs. (5) and (6) leads to the temporal moments:

$$T_1(x) = \frac{x}{\langle U \rangle}, \quad (8a)$$

$$\sigma_\tau^2(x) = 2 \frac{a_{11}}{\langle U \rangle^2} x, \quad (8b)$$

$$\Sigma_\tau(x) = 12 \frac{a_{11}^2}{\langle U \rangle^3} x, \quad (8c)$$

$$M_{4,\tau}(x) = 12 \frac{a_{11}^2}{\langle U \rangle^4} x^2 + 120 \frac{a_{11}^3}{\langle U \rangle^4} x. \quad (8d)$$

As a result, the first three moments are linear with travel distance, while the fourth order moment is a second order polynomial. Notice that for large distances the leading term in the fourth order moment (8d) is the one in x^2 , but in general there will also be a contribution in x . We will come back to this point later.

3. Homogeneous media with a matrix diffusion term

Matrix diffusion is a transport mechanism by which solutes transfer from the water flowing portions of permeable media to the non-flowing portions (matrix) and vice versa. In any geological formation, the volume of voids (totally filled with water in the case of saturated flow) can be separated for modeling purposes into two zones. The first one includes the voids that can be reached by flowing water (mobile zone), while the second represents those that cannot (immobile zone). The solute can only enter this second zone by molecular diffusion. The term matrix diffusion refers to this exchange between mobile and immobile zones (Neretnieks, 1980). While most of the work in matrix diffusion is concentrated on low permeability fractured media (Rasmuson and Neretnieks, 1981; Rasmuson, 1984; Shapiro, 2001; Wörman et al., 2003), this process can also be encountered in granular materials (Wood et al., 1990; Cunningham et al., 1997) or clays (Carrera et al., 1990).

The effects of matrix diffusion are diverse. On one hand, a large volume of voids becomes accessible to the solute by diffusion. This causes an apparent retardation with respect to solutes that do not enter the matrix (Maloszewski and Zuber, 1985; Goltz and Roberts, 1987). An interesting example is that of Zuber et al. (2001), who presented a case in Poland where matrix diffusion causes a huge retardation (on the order of 50) that is assumed to be the cause of detected pollution still not affecting a phreatic aquifer. On the other hand, diffused solutes may take a long

time to come out of the matrix. This causes tailing in BTCs.

The objective of this section is to find the moments of BTC when we incorporate a term that accounts for diffusion into the matrix instead of the Fickian dispersion term of Eq. (2). Therefore, the processes considered are advection along x in the mobile zone, and mass transfer by diffusion between the mobile and the immobile zones. No retardation is considered in either zone, although it would be straight forwards to consider it in our derivation. Local dispersion is also neglected in order to make it comparable to the ADE case, but again it would be straightforward to incorporate it. The transport equation finally becomes (Carrera et al., 1998)

$$\varphi_f \frac{\partial C_f}{\partial t} + \sigma_{mx} \varphi'_m D_m \frac{\partial C_m}{\partial \eta} \bigg|_{\eta=\eta_{\max}} + q' \frac{\partial C_f}{\partial x} = 0, \quad (9)$$

where $C_f(x, t)$ is concentration in the flowing zone; $C_m(x, \eta, t)$ is concentration in the matrix; η is the distance from the inner point in the matrix towards the flowing zone; η_{\max} is the size of the matrix (therefore, $\eta = \eta_{\max}$ corresponds to the interface between the two zones); q' is Darcy's velocity; φ_f is the mobile zone porosity; φ'_m is matrix porosity (defined as volume of voids per unit volume of matrix); D_m is the molecular diffusion coefficient; σ_{mx} is the specific surface of the matrix (matrix surface area per unit volume of aquifer) evaluated at the interface. Different variations of Eq. (9) have been used by most authors (Rasmuson and Neretnieks, 1980, 1981; Grisak and Pickens, 1981; Barker, 1982, 1985; Moench, 1984; Sudicky and Frind, 1992; Maloszewski and Zuber, 1993; Novakowski and Lapcevic, 1994; Haggerty and Gorelick, 1995; Kennedy and Lennox, 1995; Wörman et al., 2003, among others).

Concentration in the matrix, C_m , is given by the diffusion equation (assuming no retardation)

$$\sigma_m(\eta) \frac{\partial C_m}{\partial t} = \frac{\partial}{\partial \eta} \left(D_m \sigma_m(\eta) \frac{\partial C_m}{\partial \eta} \right), \quad (10)$$

where $\sigma_m(\eta)$ is the specific diffusion surface at depth η , with $\sigma_m(\eta_{\max}) = \sigma_{mx}$. There is a direct relationship between the diffusion surface and the model selected for the geometry of the matrix. The three more typical geometries used for the matrix are that of slabs, cylinders, and spheres. In these three cases, $\sigma_m(\eta)$ is proportional to η^n , with $n = 0, 1$, and 2 , respectively.

Eq. (10) is solved subject to

$$C_m(x, r, t = 0) = 0, \quad (11a)$$

$$C_m(x, r = 1, t) = C_f(x, t) \quad \text{at } \Gamma_m, \quad (11b)$$

$$\frac{\partial C_m}{\partial r}(x, r = 0, t) = 0, \quad (11c)$$

where we have introduced a new notation $r = \eta/\eta_{\max}$; Eq. (11a) is the initial condition, which corresponds to initially clean matrix; Eq. (11b) expresses continuity of concentrations at Γ_m (or $r = 1$), which is the interface between the flowing and matrix zones (continuity of mass flux was implicitly imposed in the derivation of Eq. (9)). Finally, Eq. (11c) is the boundary condition at the innermost portion of the matrix, which depends on the geometry of matrix blocks. Thus, $r = 1$ corresponds to the half distance between fractures for a slab model, and is equal to the radius in spheres or cylinders.

Eq. (10) can be solved in Laplace space. After some minor manipulation Eq. (10) can be rewritten as

$$\frac{1}{r^n} \frac{\partial}{\partial r} \left(r^n \frac{\partial \bar{C}_m}{\partial r} \right) - g^2 \bar{C}_m = 0, \quad (12)$$

where $g = \sqrt{s/D'_m}$, s being Laplace variable and $D'_m = D_m/\eta_{\max}^2$. $\bar{C}_m(x, r, s)$ is the Laplace transform of the concentration in the matrix. The general solution to Eq. (12) subject to BC (Eqs. (11a) and (11c)) and boundness of the solution is given by Gradshteyn and Ryzhik (1980), section 8.49, and taking into account the relationships between Bessel Functions, $J_\nu(z)$, and Modified Bessel Functions, $I_\nu(z)$

$$\bar{C}_m(x, r, s) = r^\nu \frac{I_{-\nu}(gr)}{I_{-\nu}(g)} F(x, s), \quad (13)$$

with $\nu = (1 - n)/2$, and $I_{-\nu}(z)$ stands for Modified Bessel function of order $-\nu$. Applying BC (Eq. (11b)), it follows immediately that $F(x, s) = \bar{C}_f(x, s)$, where $\bar{C}_f(x, s)$ is the Laplace transform of the concentration in the mobile phase.

The next step is to go back to the transport Eq. (9) and get a similar expression for the Laplace transform of the concentration of the mobile phase, $\bar{C}_f(x, s)$. Assuming a pulse injection at point $x = 0$ (i.e. $C_f(x = 0, t) = \delta(t)$), and after some manipulation

the solution is

$$\overline{C_f}(x, s) = \exp\left(-\frac{s}{U'}x - (n+1)\frac{\varphi_m D'_m}{\varphi_f} \frac{x}{U'} g \frac{I_{1-\nu}(g)}{I_{-\nu}(g)}\right), \quad (14)$$

with $U' = q'/\varphi_f$ and $\varphi_m = \sigma_{mx} \varphi'_m \eta_{max}/(n+1)$ is the porosity of the matrix (defined as volume of voids per unit volume of aquifer; recall that φ'_m was expressed per unit volume of matrix).

From here, we can proceed to find the different moments of the BTC. Again a relatively simple way to obtain the different $T_i(x)$ terms is to perform a McLaurin expansion around $s=0$ of the exponent in Eq. (14), leading to:

$$\overline{C_f}(x, s) = \exp\left\{-\frac{x}{U'}\left(\left(1 + \frac{\varphi_m}{\varphi_f}\right)s - A \frac{\varphi_m}{\varphi_f} \frac{s^2}{D'_m} + B \frac{\varphi_m}{\varphi_f} \frac{s^3}{D'_m 2} - C \frac{\varphi_m}{\varphi_f} \frac{s^4}{D'_m 3} + O(s^5)\right)\right\}. \quad (15)$$

The values for A , B and C depend on the geometry model and can be found in Table 1.

From Eq. (5) and by successive derivation, we can obtain again the temporal moments. The final expressions are:

$$T_1(x) = \frac{x(\varphi_m + \varphi_f)}{q'}, \quad (16a)$$

$$\sigma_{\tau}^2(x) = E \frac{1}{D'_m} \frac{\varphi_m x}{q'}, \quad (16b)$$

$$\Sigma_{\tau}(x) = F \frac{1}{D'_{m^2}} \frac{\varphi_m x}{q'}, \quad (16c)$$

$$M_{4,\tau}(x) = G \frac{1}{D'_{m^2}} \left(\frac{\varphi_m}{\varphi_f}\right)^2 \left(\frac{x}{U'}\right)^2 + H \frac{1}{D'_{m^3}} \frac{\varphi_m}{q'} x. \quad (16d)$$

Table 1
Values for A , B , and C in Eq. (15) for different matrix shapes

Matrix shape	A	B	C
Slabs	1/3	2/15	17/315
Cylinders	1/8	1/48	11/3072
Spheres	1/15	2/315	1/1575

Table 2

Values for E , F , G , and H in Eqs. (16a)–(16d) for different matrix shapes

Matrix shape	E	F	G	H
Slabs	2/3	4/5	4/3	136/105
Cylinders	1/4	1/8	3/16	11/128
Spheres	2/15	4/105	4/75	8/525

The values for E , F , G and H depend again on the matrix geometry model and are displayed in Table 2 for the three most common ones. The compact expressions presented here would allow obtaining the temporal moments for other geometries in which n would be a fractional value.

From Eqs. (16a)–(16d), we see that the mean arrival time is identical to that of a single porosity media with the total porosity ($\varphi_m + \varphi_f$) of the double porosity media. This is independent of the value of the matrix diffusion coefficient, and of matrix block shape and size. This result was also obtained by Goltz and Roberts (1987), Harvey and Gorelick (1995) and Carrera et al. (1998).

Another interesting result is that the second and third order moments are linear with travel distance, while the fourth order moment is a second order polynomial with respect to x . Note that the same behavior was found for the ADE with a Fickian macrodispersive term (Eqs. (8a)–(8d)). This implies that the behavior of the double porosity transport equation is qualitatively similar to that of single porosity with a Fickian dispersion term, at least up to fourth order moments, despite the dissimilarities discussed in the introduction. While this is nice, it disproves the conjecture, mentioned in the introduction, that a matrix diffusion term might display scale dependent dispersion. This would have required the second order moment (Eq. (16b)) to incorporate a non-linear term with a behavior of order x^2 for short distances (in order to be comparable with the expression presented for example in Cvetkovic et al. (1996)). Still, the equivalence to Eq. (2) suggests that one may choose matrix diffusion parameters to yield the same moments as Fickian transport. This is discussed in Section 4.

4. Identification of terms

4.1. Identification of the travel time statistical moments

The objective of this section is to find a set of parameters that makes the first temporal moments identical in both formulations. In the process of fitting parameters, it is necessary to keep invariant some fundamental values. Specifically, we impose that water flux (Darcy velocity) and total porosity should be kept invariant. Therefore, porosity (φ) used in Eq. (2) should be equal to total porosity of the double porosity formulation ($\varphi_m + \varphi_f$), and both equal to the value measured by field or lab methods. Therefore:

$$\varphi = \varphi_m + \varphi_f. \quad (17)$$

Imposing now that Darcy's velocity be kept constant in both formulations:

$$\langle U \rangle \varphi = \langle q \rangle = q' = U' \varphi_f. \quad (18)$$

Substituting Eqs. (17) and (18) in the expressions for the first temporal moments Eqs. (8a) and (16a), it results immediately that they are equal. That is, ensuring that water flux and total porosity remain invariant leads naturally to the same value for the first temporal moment.

Now only two independent parameters remain to be identified, (φ_m and D'_m). To that end, we impose the exact identification of the second and third order moments; that is, Eqs. (8b), (8c) and (16b), (16c).

This process results in:

$$D'_m = \frac{F}{6E} \frac{\langle U \rangle}{a_{11}}, \quad (19a)$$

$$\varphi_m = \frac{F}{3E^2} \varphi_f. \quad (19b)$$

These expressions, as well as the resulting ones for φ_f and U' for the different matrix shape models, are presented in Table 3. Finally, for the fourth order moment is obtained by substituting the expressions for φ_m , φ_f and D'_m into Eq. (16d). This leads to:

$$M_{4,\tau}(x) = \frac{4G}{E^2} \frac{a_{11}^2}{\langle U \rangle^4} x^2 + \frac{72EH}{F^2} \frac{a_{11}^3}{\langle U \rangle^4} x. \quad (20)$$

Formally, Eq. (20) looks like Eq. (8d). Most importantly, for the three models, $4G/E^2$ equals 12. Therefore, the leading term is invariant (independent of matrix shape) and identical to the one for Fickian dispersion (Eq. (8b)). Only the coefficient in the linear term of the polynomial varies from model to model. Defining $J = 72EH/F^2$, the corresponding values for the three models can be seen in Table 3.

Comparing these last results with Eq. (8d), we see that the set of parameters that leads to identical first three temporal moments also leads to an exact identification of the leading term in the fourth order, while the linear term in Eq. (8d) is not well reproduced (giving values in the range (97,101), depending on the model considered when the coefficient for the ADE equation was 120). It should also be noticed that the J values are quite similar,

Table 3

Values for the different parameters that would lead to a total identification of the three first moments of the BTC plus the leading term of the fourth order

Matrix shape	φ_m	D'_m	φ_f	U'	J
Slabs	$\varphi_m = \frac{3}{5} \varphi_f$	$D'_m = \frac{1}{5} \frac{\langle U \rangle}{a_{11}}$	$\varphi_f = \frac{2}{5} \varphi$	$U' = \frac{5}{2} \langle U \rangle$	680/7
Cylinders	$\varphi_m = \frac{2}{3} \varphi_f$	$D'_m = \frac{1}{12} \frac{\langle U \rangle}{a_{11}}$	$\varphi_f = \frac{1}{3} \varphi$	$U' = 3 \langle U \rangle$	99
Spheres	$\varphi_m = \frac{5}{7} \varphi_f$	$D'_m = \frac{1}{21} \frac{\langle U \rangle}{a_{11}}$	$\varphi_f = \frac{2}{7} \varphi$	$U' = \frac{7}{2} \langle U \rangle$	504/5

so that any particular BTC that could be interpreted using any of the models, would allow using any other model for matrix diffusion with a different set of parameters. This is valid only for large travel distances, where the linear term is less relevant. Close to the inlet boundary the linear term is dominant, leading to the well known shape difference between the BTCs when a matrix diffusion or a macrodispersion term are considered.

4.2. Analysis and physical interpretation of the parameters

We discuss now some potential physical interpretation of the parameters obtained in the identification process. The equivalence in the Darcy velocity that comes for the expressions for mean travel time is important, as it means equivalence in flow rates. As part of the solute gets retarded in the matrix it is necessary to select an advective velocity, which is larger than the expected velocity in the heterogeneous case. In Table 3, we see the ratio of both velocities, which ranges between $[5/2, 7/2]$ depending of the model selected. As Darcy's velocity is constant, the only way to have this relationship is to consider a mobile porosity, which is a small fraction of the total one. The values range from $2/5$ to $2/7$. Therefore, the immobile porosity is slightly larger than the mobile one for all models in this type of identification.

On the other hand D'_m is a diffusion type parameter. It indicates the facility of the solute to move from the mobile to the immobile zone and vice versa. From Eq. (19a), it follows that D'_m becomes inversely proportional to a_{11} , and directly proportional to $\langle U \rangle$. Regarding the latter, the reason is that large $\langle U \rangle$ will not allow diffusion to act long enough; then, only a small quantity of solute will go into the immobile zone, and the variance would decrease. The proportionality between D'_m and $\langle U \rangle$ is of outmost importance. The main difference between dispersion and diffusion is precisely their dependence on velocity. Dispersion is caused by heterogeneous velocity and should be nearly invariant to changes in gradient. That is, if the regional gradient is multiplied by a factor of two, then all velocities should also be multiplied by that factor. The plume then will move twice as fast, but the dispersing paths will remain identical. As a result, the same plume shape will be reached, only

twice as fast. Because of this, matrix diffusion fittings of BTCs have sometimes been regarded as fitting tricks, leading to models without predicting capabilities. What our findings suggests is that prediction capabilities will be maintained provided that matrix diffusion is taken as proportional to water flux, at least the portion of matrix diffusion aimed at representing dispersion.

Examination of the second moment of the BTCs yields the explanation for the inverse relationship between D'_m and a_{11} . A large value of a_{11} leads to a larger variance of travel time. The effect is the opposite for D'_m , as a large value tends to homogenize the concentrations at the mobile phase and the matrix, leading to a behavior closer to instantaneous equilibrium and consequently a reduction in the variance of travel time.

Two final comments; when the identification process is performed, we see that we can fit the first three moments, but that the homogeneous media with matrix diffusion leads to smaller fourth order independently of the matrix particle model selected. In any case, the difference decreases with increasing travel distance, as the leading term coincides for all models.

Last, it could be possible to extend the methodology to higher order moments. The problem then would be the error associated to the evaluation of these terms. In general, the BTC has a considerable tailing. High order moments are then extremely uncertain.

5. Conclusions

The main conclusion from our work is that macrodispersion (or any kind of Fickian dispersion, for that matter) can be represented by means of a term that expresses exchange of solutes between mobile and immobile zones (MD). Using this term instead of the Fickian dispersion term of the conventional ADE allows reproducing the first three moments of the BTC and nearly so the fourth one.

Therefore, in principle, it would be possible to use indistinctly MD or ADE in order to represent macrodispersion in a given heterogeneous aquifer. One may even argue that the matrix-diffusion representation is more convenient than the Fickian

representation of dispersion. Actually, it displays the asymmetry expected in spatial distribution of concentrations, which a Fickian representation does not. Also, it allows restricting Fickian dispersion to the local one, thus avoiding the negative side effects of large dispersivities (such as upstream dispersion). However, the proposed representation of dispersion fails to match the time evolution of the second-order moment of travel time. Therefore, while it might be convenient as an alternative for the macrodispersive ADE, it cannot avoid the fact that the fitted parameters would also be time dependent, thus restricting their applicability to real cases, same as a single value of dispersion is not valid to fit solute transport at different scales.

From Eq. (19a), the diffusion coefficient obtained by representing dispersion with a matrix diffusion term depends on velocity. Since matrix diffusion is often used to fit BTCs displaying long tails, and tailing is likely to be caused by a combination of both true (velocity independent) diffusion and heterogeneity, the resulting model will not be able to predict dispersion at different flow rates unless the diffusion coefficient is modified accordingly. Therefore, one would need to perform tests with different flow rates so as to discriminate the dependence on velocity of the fitting parameter or, in other words, the contribution of true diffusion and heterogeneity to transport.

Our results can also be seen from another point of view. When interpreting BTCs from tracer tests, hydrogeologists face the problem of having to infer the processes that the solute has undergone. The possibility of fitting similar temporal moments with different conceptual models shows that the simple study of the curve would not allow the identification of processes. While, we have studied only two conceptual models (MD and ADE), we must keep in mind that a solute that undergoes mass-transfer rate-limited processes that are controlled by reactions kinetics would have a BTC practically indistinguishable from that of a solute undergoing first order matrix diffusion (Selroos and Cvetkovic, 1992; Haggerty and Gorelick, 1995). Therefore, it would be possible to obtain a third set of parameters that could also fit a particular BTC with the same quality of fitting.

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