

On Mass Response Functions

ANDREA RINALDO

Dipartimento di Ingegneria, Università di Trento, Trento, Italy

ALESSANDRO MARANI

Dipartimento di Scienze Ambientali, Università di Venezia, Venezia, Italy

ALBERTO BELLIN

Dipartimento di Ingegneria, Università di Trento, Trento, Italy

Field transport of reactive solute species is investigated through a class of stochastic models, here termed mass response functions (MRFs), which incorporate simplified concepts of chemical/physical nonequilibrium kinetics in the formulation of transport by travel time distributions. MRFs are probability density functions (pdfs) associated with solute particles' travel time within transport volumes. The theory hinges on recent advances in modeling transport of solutes in groundwater and in basin scale transport volumes and links the approaches of surface hydrologists with recent subsurface transport models. The relationship between MRFs and the theory of solute transport by continuous motions is investigated. It is found that MRFs extend the basic formulation of transport of inert solutes to a particular case of sorption process. The relationship between MRFs and the basic differential convection-dispersion equation incorporating linear sorption is also investigated. It is found here that not only are transfer functions of solutes consistent with any mechanistic three-dimensional (3-D) model of convection dispersion, but also that they are, under limit conditions, the product of the travel time distribution of the carrier flow with a bounded continuous function. The latter is the solution to an initial value problem which results from solving the general 3-D differential equations of convection dispersion with sorption under some simplifying assumptions, and formally coincides with the resident concentration included (as an assumption) in the original MRF formulation. Travel time distributions and MRFs underlain by statistical constraints rather than by dynamical models are proposed. Non-Gaussian distributions are studied by statistical-mechanical tools and are found to represent the norm, rather than the exception, in this formulation of transport of reactive solutes. The concepts are applied to a field study and are shown to yield reliable models of solute migration in nonpoint pollution problems.

1. INTRODUCTION

In the wake of recent results [Jury *et al.*, 1986; Sposito *et al.*, 1986; Rinaldo and Marani, 1987; Dagan and Nguyen, 1989], it has become apparent that transfer function models (TFM) based on travel time distributions of solute migration may represent a promising way of expressing results from large-scale transport experiments or calculations.

In this paper the models of field solute transport through unsaturated soils proposed by Jury [1982] and Jury *et al.* [1986] and mass response functions (MRFs) for basin scale analysis developed for contaminant responses to rainfall pulses [Rinaldo and Marani, 1987; Rinaldo and Gambolati, 1988] are reexamined as predictive tools for solute migration in various phases of the hydrological cycle.

The class of models investigated here is related to mass balances interpreted in the context of probability theory [Rinaldo and Marani, 1987], and to the theory of diffusion by continuous motions [Taylor, 1921; Dagan, 1987], and is consistent with any mechanistic transport model with convection, dispersion, and linear sorption [Sposito *et al.*, 1986]. A comparison of travel time and concentration approaches (the latter being the usual solution to a boundary value problem in terms of concentration as a function of

space and time) to characterize transport by groundwater has recently been proposed [Dagan and Nguyen, 1989]. Most notably, a discussion of the relative merits of the two approaches pointed out a potential of travel time approaches for applications in that they (1) are robust in characterizing the transport process; (2) appeal to physical intuition and are of general nature; and (3) blend in a unique curve all sources of uncertainty in transport characterization.

The integral relations and the initial value problem [Rinaldo and Marani, 1987] describing both the carrier flow and the solute flux at the outlet control section of the transport volume are

$$Q(t) = \int_0^t f(t-t')i(t') dt' \quad (1)$$

$$Q_{\text{out}}(t) = \int_0^t G(t-t', t')i(t') dt' \quad (2)$$

$$G(t-t', t') = C'(t-t', t')f(t-t') \quad (3)$$

$$t = \tau + t' > 0 \quad \partial C'(\tau, t')/\partial \tau = h(t)\{C_E(t) - C'(\tau, t')\} \quad (4)$$

$$C'(0, t') = C_0(t')$$

where $Q(t)(L^3/T)$ is the carrier outflow rate; $Q_{\text{out}}(t) (M/T)$ is the flow rate of solute which represents all modes of loss

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Paper number 89WR00336.
0043-1397/89/89WR-00336\$05.00

from the soil transport volume through the control boundaries or through physical, chemical, or biological transformations; $G(t - t', t') = C'(t - t', t') f(t - t')$ (M/TL^3) is defined as the (instantaneous unit) mass response function, or the probability density functions (pdf) of solute lifetime in the transport volume, conditional on the occurrence of the carrier inflow $i(t')$; $i(t')$ (L^3/T) is the carrier flow input time distribution (recall that in the work by Jury *et al.*, [1986] $i(\cdot)$ was taken as the fractional rate of solute mass into the transport volume); $f(t - t')$ is the pdf of residence time of the carrier in the transport volume, i.e., the travel time distribution to the control surface; $t(T)$ is the current time; $t'(T)$ is the time of injection of an input rate of solute $C'(0, t')i(t')$; $\tau = t - t'(T)$ is the contact time between fixed and mobile phases, i.e., the travel time in the transport volume; $C'(t - t', t')$ is a resident concentration solution to (4). It may be thought of as the concentration attached to the indivisible particles whose collection forms the solute body or plume; $h(t)(T^{-1})$ is the overall mass transfer coefficient qualifying the speed of production/removal processes; $C_E(t)(M/L^3)$ is the equilibrium concentration in the mobile phase; $C_0(t')(M/L^3)$ is the assigned concentration of the input rate of solute. Equations (1) and (2) postulate the existence of a control section, where one observes the flux of water and solutes, acting as a trapping boundary. We believe that this is appropriate for basin-scale distances where the use of (1) (denoted as the instantaneous unit hydrograph approach in the literature of surface hydrology) is commonplace.

In this model, termed MRF because it links the theory of hydrologic response behind (1) (the instantaneous response function $f(\cdot)$ of runoff) and the TFM of reactive solute transport [Jury *et al.*, 1986], the time evolution of C' is controlled by the contact time $t - t'$ between fixed and mobile phases, and is conditional on the time of occurrence t' of the particle injection. In this model solutes enter or leave the transport volume because of sorption processes between fixed and mobile phases.

An important feature of the proposed approaches is the consistency of statistical schemes with the basic mass balance equation for a species in solution. Sposito *et al.* [1986] have already addressed this issue for the general one-dimensional (1-D) case and have concluded that TFM in the form (2) (where the kernel takes on the general form $G(t - t'|t')$ regardless of the link with $f(t - t')$) are consistent with "any mechanistic model of solute movement." Nevertheless, Sposito *et al.*'s [1986] 1-D deterministic model, termed two-component convection-dispersion equation (CDE), is restricted to one dimensional solute movement, steady water flow and linear sorption processes.

The issue of theoretical validation is crucial to the actual reexamination of MRFs. The interest in validation was originated because some objections were raised on applying the concept of transfer function models to field transport (G. Dagan, personal communication 1988), because it implied that prediction had to be anticipated by a large-scale transport experiment. Needless to say, this fact seemed to drastically reduce the usefulness of the approach. The challenge this theory must face as a predictive tool is to provide estimates of solute flow rates at monitoring sites on the basis of relatively easy measurements (e.g., hydraulic properties, geometry, sample measurements of concentration) of present conditions. This can only be done if the relation between the synthetic stochastic models and the underlying

mechanics of convection, dispersion, and production/removal processes is clearly established. In a foundational paper Sposito *et al.* [1986] proposed a rationalization of TFM of transport of reactive solutes in 1-D porous media which clarified the connection between TFM and 1-D two-component transport dynamics. This connection was further clarified by the recent analysis of the formulation of passive solute transport by travel time distributions [Dagan and Nguyen, 1989]. In the present paper the approach is extended to arbitrary 3-D transport volumes, and proof is given to the conditions which lead to the validity of the formulation (1), and (2) and of the reaction kinetics (4) assumed as model equation in the original paper [Rinaldo and Marani, 1987].

The contributions in this paper are (1) connecting MRFs with the stochastic theory of transport by continuous motions and its formulation by travel time distributions. It is shown that the approaches developed by surface hydrologists and recent subsurface transport models (in the latter both concentration and travel time approaches are included) can be related to MRFs under certain simplifying assumptions; (2) the proposal of MRFs which are not underlain directly by dynamical models, but rather by some statistical constraints. A section on derivations of solute lifetime distributions through statistical-mechanical arguments is developed, which narrows down on particular means of obtaining solutions to large-scale transport problems without actually solving the basic differential equations and (3) applying the concepts to a field study.

A discussion of the relative merits and the field of application for the model, set in the closure of the paper, emphasizes the potential of the MRF approach for modeling of water resources.

2. FORMULATION OF TRANSPORT BY SOLUTE LIFETIME DISTRIBUTIONS

To reexamine the assumptions built in the MRF approach, we consider a transport volume V_s as in Figure 1. A trapping surface S , which is crossed by all trajectories ensuing at a , belonging to the inlet section of solute, is selected as control surface. We assume that the choice of S does not preclude the treatment of time-varying velocities. Both convection and dispersion processes are assumed to result in an overall forward motion of the particle which, after the first arrival at S , cannot return upstream to cross S besides the first time (the absorbing barrier hypothesis in, for example, Cox and Miller [1965, p. 211]). This implies that (1) the time of crossing is defined in a unique manner and (2) the probability of a particle ensuing at a of ever reaching S is unity.

A solute body of concentration C_0 is introduced at time t_0 in a volume V_0 . The ambient concentration is $C = 0$. The initial solute body or the plume is regarded as a collection of indivisible particles which move in space due to diffusion and convection by fluid, and subject to sorption processes. Let the initial mass of the particle be $\Delta m_0 = n da C_0$, where n is an effective porosity of the porous medium, $n da$ is the volume element of the initial solute body V_0 (let $da = d^3a$ be the volume element), and C_0 is the initial concentration.

Here, unlike diffusion by continuous movements, the mass attached to each particle is not constant. This assumption, consistent with the basic assumption in the MRF

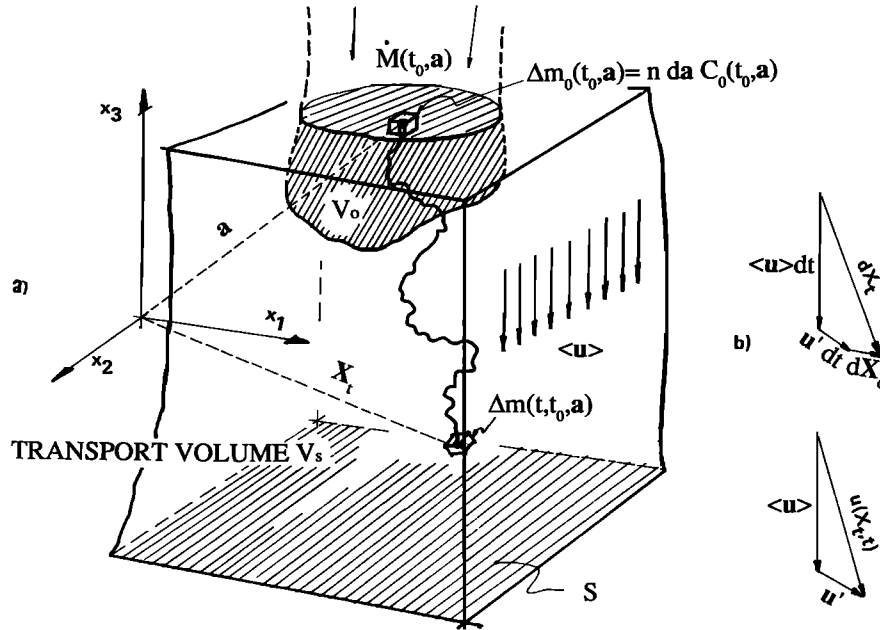


Fig. 1. (a) Schematic representation of the transport volume V_s with indication of the initial solute body and the total displacement of a particle. The control surface S is also indicated. (b) The decomposition of the total displacement into convection by the mean velocity, convection by velocity fluctuation and a "Brownian motion"-type component.

approach, postulates that the mass associated with the particle does not depend on the particle's position in space. Rather the mass is assumed to depend on the time $(t - t_0)$ spent within the transport volume, because production/removal processes affect Δm . We assume that the mass transfer by this process is characterized deterministically. The characterization of the particle's mass at time $t > t_0$ is therefore $\Delta m(t, t_0, \mathbf{a})$.

It is assumed [Dagan, 1987, p. 188] that the effective porosity n is constant owing to the little change experienced by n in comparison to that of conductivity in natural media. The trajectory of the particle is given by

$$\mathbf{x} = \mathbf{X}_t(t; t_0, \mathbf{a}) \quad (5)$$

where \mathbf{x} is a Cartesian coordinate vector, and $\mathbf{X}_t(t; t_0, \mathbf{a})$ a vectorial function, $\mathbf{x} = \mathbf{a}$ is the initial position of the particle at $t = t_0$, or $\mathbf{X}_t(t_0; t_0, \mathbf{a}) = \mathbf{a}$. \mathbf{X}_t decomposes generally as (Figure 1b).

$$\mathbf{X}_t(t; t_0, \mathbf{a}) = \mathbf{X} + \mathbf{X}_d \quad (6)$$

where \mathbf{X} and \mathbf{X}_d are defined by a suitable stochastic differential equation. Usually, [Dagan, 1984, 1987] \mathbf{X}_d is assumed as a "random walk" associated with pore scale dispersion; \mathbf{X} is also a random function because velocity in natural formations is not known with certainty because of the irregular spatial variability of the formation properties. Hence $\mathbf{X}_t(t; t_0, \mathbf{a})$ is expressed in statistical terms by its pdf $f(\mathbf{X}_t)$; i.e., $f d\mathbf{X}_t$ is the probability that a particle, at $\mathbf{x} = \mathbf{a}$ for $t = t_0$, is found at time t in the volume $d\mathbf{X}_t$ surrounding \mathbf{X}_t . The concentration distribution ΔC associated with the particle is then

$$n \Delta C(\mathbf{x}, t, t_0, \mathbf{a}) = \Delta m(t, t_0, \mathbf{a}) \delta(\mathbf{x} - \mathbf{X}_t) \quad (7)$$

where $\delta(\mathbf{x} - \mathbf{X}_t)$ is the Dirac distribution [Taylor, 1921; Dagan, 1987]. Ensemble averaging yields the basic relationship between the resident concentration and the displacement pdf

$$\begin{aligned} \langle \Delta C(\mathbf{x}, t, t_0, \mathbf{a}) \rangle &= \int \Delta C(\mathbf{x}, t, t_0, \mathbf{a}) f(\mathbf{X}_t) d\mathbf{X}_t \\ &= \Delta m(t, t_0, \mathbf{a}) f(\mathbf{x}, t, t_0, \mathbf{a}) / n \end{aligned} \quad (8)$$

Equation (8) extends the basic result [Dagan, 1987, equation (3.3)] in that the particle's mass is allowed to change in time. It is expedient to rewrite (8) as

$$\langle \Delta C(\mathbf{x}, t, t_0, \mathbf{a}) \rangle = \Delta m_0 \quad s(t, t_0, \mathbf{a}) f(\mathbf{x}, t, t_0, \mathbf{a}) / n \quad (9)$$

where $s(t, t_0, \mathbf{a}) = \Delta m(t, t_0, \mathbf{a}) / \Delta m_0(t_0, \mathbf{a})$ is a loss (gain) function of the particle as it travels through V_s , and $\Delta m_0(t_0, \mathbf{a}) = \Delta m(t_0, t_0, \mathbf{a})$ is the initial mass.

Due to the commutative properties of the integration and averaging operations, (8) is generalized for the cases of solute body of finite initial extent V_0 or for a plume injected through V_0 continuously. There, with $\Delta m_0 = n C_0(t_0, \mathbf{a}) \, da$, or $\Delta m_0 = \dot{M}(t_0, \mathbf{a}) \, da \, dt_0$ we get for a finite solute body or a plume

$$\langle C(\mathbf{x}, t, t_0) \rangle = \int_{V_0} C_0(t_0, \mathbf{a}) s(t, t_0, \mathbf{a}) f(\mathbf{x}, t, t_0, \mathbf{a}) \, da \quad (10)$$

$$\langle C(\mathbf{x}, t) \rangle = \int_0^t dt_0 \int_{V_0} \dot{M}(t_0, \mathbf{a}) s(t, t_0, \mathbf{a}) f(\mathbf{x}, t, t_0, \mathbf{a}) \, da \quad (11)$$

where C_0 is the initial concentration in V_0 and \dot{M} is the rate of solute input per unit time.

Let T be the travel time of a solute particle from the inlet to S . T is characterized by a cumulative probability distribution function $P(T < t | \mathbf{a}, t_0) = F(t; \mathbf{a}, t_0)$, which is the probability that a particle originating at $\mathbf{x} = \mathbf{a}$ and $t = t_0$ had crossed S at t .

Since $|\mathbf{X}_t|$ for transport by convection at any scale grows monotonously, we have [Cox and Miller, 1965, p. 221; Dagan and Nguyen, 1989]

$$F(t; \mathbf{a}, t_0) = 1 - \int_{V_s} f(\mathbf{x}, t, t_0, \mathbf{a}) d\mathbf{x} \quad (12)$$

where integration is over the domain V_s covered from trajectories from \mathbf{a} to S , and $d\mathbf{x} = d^3x$. Substitution of (8) into (12) yields

$$\begin{aligned} F(t; \mathbf{a}, t_0) &= \int_{V_s} \langle \Delta C(\mathbf{x}, t, t_0, \mathbf{a}) \rangle n / \Delta m(t, t_0, \mathbf{a}) d\mathbf{x} \\ &= \langle \Delta m_S \rangle / \Delta m \end{aligned} \quad (13)$$

where $\langle \Delta m_S \rangle$ is the expected value of the concentration integrated over V_s . If ergodicity applies, i.e., $\langle \Delta C \rangle$ is the actual concentration distribution for a large number of particles, $\langle \Delta m_S \rangle$ simply represents the mass of solute which has not been transported beyond S at time t . In contrast, Δm is the total mass changing due to sorption as if S did not exist. The pdf of travel time $f(t)$ from \mathbf{a} to the control surface S is obtained by differentiation as

$$f(t) = f(t; t_0, \mathbf{a}) = dF/dt = d(\langle \Delta m_S \rangle / \Delta m) dt \quad (14)$$

which, in the case of constant Δm and for ergodic conditions, is the solute flux through S divided by the total mass, which is also the initial mass. Here $f(t; t_0, \mathbf{a})$, which we term solute lifetime distribution, is the solute flux divided by the total mass at time t .

It is interesting to note that both (1) and (2) derive from (14) under some simplifying assumptions. To prove this assertion, we now consider that a particle is representative of a volume of water, i.e., $\Delta m_w = \rho d\mathbf{a}$, ρ being the density of water. In this case Δm_w does not depend on time, i.e., $s = 1$ in (10). Let $M_w(t)$ be the labeled volume of water stored in V_s at time t after a pulse $M_w dt_0 d\mathbf{a}$ of labeled particles. By the same procedure as from (9) to (11) (recall that in the case at hand M_w is a rate of volume injected per unit time which does not depend on t ; here $t_0 = 0$ for clarity) one obtains

$$\begin{aligned} \langle M_w(t) \rangle &= \int_{V_s} d\mathbf{x} n \langle \Delta C_w(\mathbf{x}, t) \rangle \\ &= \int_{V_s} d\mathbf{x} \int_0^t dt_0 \int_{V_0} d\mathbf{a} M_w(t_0, \mathbf{a}) f(\mathbf{x}, t, t_0, \mathbf{a}) \end{aligned} \quad (15)$$

Here we have introduced the somewhat unusual concept of concentration of water particles $\langle \Delta C_w(\mathbf{x}, t) \rangle$, a model already used in the literature of surface hydrology [Gupta et al., 1980]. In the case that the time and the space distributions are independent we have $M_w(t_0, \mathbf{a}) = i(t_0) l(\mathbf{a})$. If stationarity is assumed to prevail we have

$$F(t; \mathbf{a}, t_0) = F(t - t_0; \mathbf{a}) = 1 - \int_{V_s} f(\mathbf{x}, t - t_0, \mathbf{a}) d\mathbf{x} \quad (16)$$

and integration over the initial position yields

$$F(t - t_0) = \int_{V_0} d\mathbf{a} l(\mathbf{a}) \left[1 - \int_{V_s} d\mathbf{x} f(\mathbf{x}, t - t_0, \mathbf{a}) \right] \quad (17)$$

The model of hydrologic response assumed in (1) was based on uniform spatial distribution of input, i.e., $G(\mathbf{a}) = 1/V_0$. Substitution of (15) into (13) yields the final result, upon differentiation,

$$d\langle M_w(t) \rangle / dt = i(t) - \int_0^t dt_0 i(t_0) f(t - t_0) \quad (18)$$

because $F(0) = 0$. Equation (18) is the continuity equation adopted in the original MRF approach [Rinaldo and Marani, 1987, equation (10)]. The second term at right-hand side is the outflowing flux at the control section, i.e., discharge $Q(t)$. It follows from (12) that the mass flux at S in response to $i(t) = \delta(t)$, δ being Dirac's delta "function," is the pdf of travel time to S . Hence (1) derives directly from the theory of transport by continuous motions.

Interestingly, the result that the flux in response to an instantaneous unit impulse uniformly distributed is the pdf of the travel time distribution was derived independently in the literature in the case of the probabilistic theory of hydrologic response [Lienhard, 1964; Rodriguez-Iturbe and Valdes, 1979; Gupta et al., 1980] and in the formulation of transport of passive solutes by travel time distributions [Dagan, 1987; Dagan and Nguyen, 1989]. The different derivations and the independent reasoning shed light on several aspects of modern hydrology. Among the cross-fertilizations induced by the analogy, we may recall the handy means for computing $f(t)$ given in the papers on hydrologic response. On the other hand, in the context of the theory of transport in groundwater, Dagan [1982, 1984, 1986, 1987] argued that the statistical model, when ergodicity is not assumed, reduces to a mathematical vehicle to compute essentially deterministic quantities. This shows that implicit in the theory of hydrologic response is ergodicity. This means that in any realization $\langle \Delta m_s \rangle \sim \Delta m_s$, or the same mass of solute (or water) crosses S at time t . In this case the probability F rather than a measure of uncertainty represents deterministically the relative mass of solute which has left the transport volume through the control surface.

Let us now turn to the derivation of (2). The particle's mass Δm depends on time and on the initial position as in (7). The function M in (11), under the assumptions leading to the preceding result (18), is $M(t_0, \mathbf{a}) = i(t_0) l(\mathbf{a}) C_0(t_0, \mathbf{a})$. The MRF approach assumes that the initial concentration of the particles is independent of the position \mathbf{a} , and therefore $C_0(t_0, \mathbf{a}) \sim C_0(t_0)$. By the same token, $s(t, t_0, \mathbf{a}) = s(t - t_0, t_0)$. If $M(t)$ is the labeled solute mass stored in the control volume, after injection of $M(t_0, \mathbf{a}) dt_0 d\mathbf{a}$ labeled particles, we have from (11) and (17), with the above M ,

$$\begin{aligned} \langle M(t) \rangle &= \int_{V_s} d\mathbf{x} n \langle \Delta C(\mathbf{x}, t) \rangle \\ &= \int_0^t dt_0 i(t_0) C_0(t_0) s(t - t_0, t_0) \\ &\quad \cdot \int_{V_0} d\mathbf{a} l(\mathbf{a}) \int_{V_s} d\mathbf{x} f(\mathbf{x}, t - t_0, \mathbf{a}) \\ &= \int_0^t dt_0 i(t_0) C_0(t_0) s(t - t_0, t_0) [1 - F(t - t_0)] \end{aligned} \quad (19)$$

Differentiation yields the final result

$$\begin{aligned} d\langle M(t) \rangle / dt &= i(t) C_0(t) - \int_0^t dt_0 i(t_0) C_0(t_0) s(t - t_0, t_0) \\ &= (a) \quad \quad \quad - (b) \end{aligned}$$

$$- \int_0^t dt_0 i(t_0) F(t - t_0) C_0(t_0) \{ds(t - t_0, t_0)/dt\} \quad (20)$$

- (c)

Equation (20) is the probabilistic mass balance employed in the original MRF formulation [Rinaldo and Marani, 1987, equation (12)]. The physical meaning of (20) is that the rate of change of mass in the transport volume is (a) the input mass flux, minus (b) the mass flux at the control section minus (c) the rate of mass exchange due to sorption phenomena. Equation (2) is then derived from (20) by singling out the (b) term and denoting it by Q_{out} , i.e.,

$$Q_{out}(t) = \int_0^t dt_0 i(t_0) C'(t - t_0, t_0) f(t - t_0) \quad (21)$$

(where $C'(t - t_0, t_0) = C_0(t_0)s(t - t_0, t_0)$) which is the basic result in the original formulation [Rinaldo and Marani, 1987, equation (15)] connecting the travel time $f(t - t_0)$ and solute lifetime distributions $G(t - t_0, t_0) = C'(t - t_0, t_0)f(t - t_0)$.

The important implications of ergodicity of concentration upon travel time distributions have been discussed by Dagan [1984, 1986, 1987] and Dagan and Nguyen [1989]. Here such implications on solute lifetimes go unchanged because the dynamics of sorption processes is assumed deterministic.

A final note is related to the nature of the Lagrangean pdf $f(\mathbf{X}_t)$, which characterizes the dynamics of the system. In the important case of Gaussian $f(\mathbf{X}_t)$, f is completely characterized by the ensemble mean $\langle \mathbf{X}_t \rangle$, and the covariance matrix \mathbf{R} of \mathbf{X}_t about its ensemble mean $\langle \mathbf{X}_t \rangle$ ($\mathbf{R}_{ij} = \langle X'_i(t; a, t_0) X'_j(t; a, t_0) \rangle$, $X'_j = X_j - \langle X_j \rangle$, $i, j = 1, m$) and has the form of the multivariate normal pdf (22)

$$f(\mathbf{X}_t, t; t_0, \mathbf{a}) = (1/(2\pi)^{m/2} |\mathbf{R}|^{1/2}) \cdot \exp \left(-(1/2)(\mathbf{X}_t - \langle \mathbf{X}_t \rangle)^T \mathbf{R}^{-1} (\mathbf{X}_t - \langle \mathbf{X}_t \rangle) \right) \quad (22)$$

where $|\mathbf{R}|$ is the determinant of the covariance matrix, m is the number of space dimensions, and \mathbf{T} denotes transpose. In this case f satisfies the transport equation [Dagan, 1987]

$$\partial f / \partial t + d\langle X_j \rangle / dt \partial f / \partial X_j = (1/2) d\mathbf{R}_{ji} / dt \partial^2 f / \partial X_j \partial X_i \quad (23)$$

where the summation convention has been adopted. Substitution of (8) in (23) yields

$$\partial \langle \Delta C \rangle / \partial t + d\langle X_j \rangle / dt \partial \langle \Delta C \rangle / \partial x_j = (1/2) d\mathbf{R}_{ji} / dt \partial^2 \langle \Delta C \rangle / \partial x_j \partial x_i + \langle \langle \Delta C \rangle / \Delta m \rangle \partial \Delta m / \partial t \quad (24)$$

The last term in (24) represents the rate of mass exchanged by sorption. A two-component convection-dispersion equation (CDE) [e.g., van Genuchten, 1981] is therefore a model consistent with the assumptions built in the extension of the Lagrangean model leading to (1) and (2).

The crux of the matter at this point is the choice of kinetics for Δm , which affects both the formulation of transport by lifetime distributions via the term ds/dt in (20), and the two-component model equation (24) which needs be coupled by a local mass balance for the evaluation of the term $\partial \Delta m / \partial t$. In the approach by Rinaldo and Marani [1987] the chemical/physical nonequilibrium model was assumed as the reversible first-order initial value problem (4) thought of as representative of a large-scale model of the interactions between fixed and mobile phases. The question on whether

such model is consistent with (24) is therefore addressed the next section of this paper.

3. SOLUTE LIFETIME DISTRIBUTIONS AND THE TWO-COMPONENT CONVECTION-DISPERSION EQUATION

Written in a form that is convenient for mathematical analysis, the model two component CDE (suggested by e.g., Sposito et al. [1986]) is as follows:

$$BR \partial C_1(x, t) / \partial t + (1 - B)R \partial C_2(x, t) / \partial t = (1/P) \partial^2 C_1 / \partial x^2 - U \partial C_1 / \partial x \quad t > 0 \quad x \in V_s \quad (25a)$$

$$(1 - B)R \partial C_2 / \partial t = W[C_1(x, t) - C_2(x, t)] \quad (25b)$$

where C_i , $i = 1, 2$, are resident concentrations in mobile and fixed phases, respectively; U is a constant velocity; x and t are dimensionless space and time variables; V_s the domain of the transport volume; B , R , P , and W are adjustable parameters which can be interpreted physically [Sposito et al., 1986, Table 1] according to different mechanisms incorporated in the model. Phase 2 is fixed, and no diffusion occurs therein. It receives a mass flow $W[C_1 - C_2]$ (MT^{-1}), at given temperature and instantaneous mixing is assumed. Equation (25b) is related to chemical or physical nonequilibrium models (for a recent review, see Lassey [1988]), where (25a) expresses local mass conservation in the combined phase system.

It is stressed at this point that the formalism in the present discussion will be simplified in order to avoid beclouding the central idea with unnecessary details.

Equation (25) assume one-dimensional flow and solute transport, as well as constant convection. It can be extended to 3-D control volumes (let $\mathbf{x} = (x, y, z)$ be the Cartesian coordinate vector) as

$$BR \partial C_1(\mathbf{x}, t) / \partial t + (1 - B)R \partial C_2(\mathbf{x}, t) / \partial t = \nabla \cdot [\mathbf{D} \cdot \nabla C_1(\mathbf{x}, t)] - \mathbf{u}(\mathbf{x}, t) \cdot \nabla C_1(\mathbf{x}, t) \quad (26)$$

where \mathbf{D} is the dispersion tensor; $\mathbf{u}(\mathbf{x}, t)$ is the convection field; and ∇ is the gradient operator. Combining the 3-D form of (25b) with (26) one gets

$$(H - \partial / \partial t) C_1(\mathbf{x}, t) = W(C_1(\mathbf{x}, t) - C_2(\mathbf{x}, t)) \quad (27)$$

where H is a differential operator $= [\nabla \cdot (\mathbf{D} \cdot \nabla) - \mathbf{u} \cdot \nabla] / BR$; $W = W / (1 - B)R$. In fact, (27) is an integro-differential equation because (25b) has a general analytical solution in the form

$$C_2(\mathbf{x}, t) = e^{-Wt} \left(W \int_0^t e^{W\xi} C_1(\mathbf{x}, \xi) d\xi + C_2(\mathbf{x}, 0) \right) \quad (28)$$

Consider a general boundary value problem [Bartels and Churchill, 1942]

$$\partial C_1(\mathbf{x}, t) / \partial t = H\{C_1\} + F(\mathbf{x}, t) \quad t > 0 \quad x \in V_s \quad (29a)$$

$$\lambda\{C_1(\mathbf{x}_0, t)\} = c_0 C_1 + \sum_{i=1,3} c_i \partial C_1(\mathbf{x}_0, t) / \partial x_i \quad (29b)$$

$$t > 0 \quad \mathbf{x}_0 \in \partial V_s$$

$$C_1(\mathbf{x}, 0) = I_1(\mathbf{x}) \quad C_2(\mathbf{x}, 0) = I_2(\mathbf{x}) \quad \mathbf{x} \in V_s \quad (29c)$$

where F is the source term, g is (the surface condition at the boundary ∂V_s , and I is the initial condition) are prescribed functions.

It has been recently inferred [Sposito *et al.*, 1986] that such boundary conditions hold for resident concentrations (in the sense defined by Parker and van Genuchten [1984]) and that the solution for the 1-D case can be written in the form of (2), where $G(t - t'|t')$ equals the solution of (27) for the case of instantaneous source condition [Bartels and Churchill, 1942]. This result was proposed as a consequence of Duhamel's theorem: it had also been noted [Sposito *et al.*, 1986] that because of the linearity in the concentration variables, $G(t - t'|t') = G(t - t')$.

Our aim is somewhat different. It has been argued [Rinaldo and Marani, 1987] that the MRF $G(t - t_0|t_0)$ in (2) could be obtained as the product of the travel time distribution $f(t - t_0)$ in (1) and a bounded continuous function $C(t - t_0, t_0)$ derived by a suitable initial value problem tailored to nonequilibrium kinetics.

Let us focus our attention on (27) with no reaction term ($W = 0$), as seen in the context of stochastic modeling of groundwater transport. The corresponding solution for continuous injection at a rate g in (29b) is

$$C_1(\mathbf{x}, t) = \int_0^t g(\tau) \omega[\mathbf{x} - \mathbf{X}_t(t - \tau), t - \tau] d\tau \quad (30)$$

where \mathbf{X}_t is the Lagrangian coordinate of the convected particle; $\omega(\mathbf{x}, t)$ is the Gaussian distribution [Dagan, 1982, p. 837] as f in (22).

Let us return to the solution of (26) and (27). To reobtain (30) as an eigenfunction expansion, which is suitable to extension to the inhomogeneous case, let us consider the formal solution to the homogeneous equation (i.e., for $W = 0$)

$$HG = \partial G / \partial t \quad (31)$$

subject to the given boundary and initial conditions. In general, we can write, for Hermitian H , with uniform convergence

$$G(\mathbf{x}, t) = \sum_m A_m(t) \phi_m(\mathbf{x}) \quad (32)$$

where

$$H\phi_m = \lambda_m \phi_m \quad (33)$$

where λ_m are eigenvalues and ϕ_m are the corresponding orthonormal eigenfunctions. The nature of these eigenvalues is known from Sturm-Liouville theory [e.g., Churchill and Brown, 1973, p. 66], as in this case the $\{\lambda_m\}$ constitute a sequence of nonpositive numbers, with $\lambda_m \rightarrow -\infty$ as $m \rightarrow \infty$.

The solution for the homogeneous case (31) for the propagation of the initial condition $I_1(\mathbf{x}')$ is obtained by standard Green's function techniques as

$$G(\mathbf{x}, t) = \int d\mathbf{x}' \left\{ \sum_m \phi_m(\mathbf{x}') \phi_m(\mathbf{x}) \exp(\lambda_m t) \right\} I_1(\mathbf{x}') \quad (34)$$

In the general case in which an initial condition $I_1(\mathbf{x}')$ is propagated and a forcing term $i(\tau)$ at the boundary \mathbf{x}_0 is active, we have

$$G^*(\mathbf{x}, t) = \int d\mathbf{x}' \int_0^t d\tau i(\tau) \cdot \left\{ \sum_m \phi_m(\mathbf{x}') \phi_m(\mathbf{x}) \exp(\lambda_m(t - \tau)) \right\} I_1(\mathbf{x}') \quad (35)$$

For simplicity of notation, in the sequel only the propagation of the initial condition will be considered, i.e., $i(t) = \delta(t)$, such that the homogeneous solution $G^*(\mathbf{x}, t) = G(\mathbf{x}, t)$ in (34). We also assume, for simplicity of notation, that the initial distributions I_1 and I_2 of concentration in phase 1 and 2 are uniformly distributed in space.

It can be shown by direct contour integration in the case $I_1(\mathbf{x}') = \delta(\mathbf{x}' - \mathbf{x}_0)$, that the infinite sum of eigenfunctions in (34) converges to $\omega[\mathbf{x} - \mathbf{X}_t(t - \tau, \mathbf{x}_0), t - \tau]$ in (30) and that the solutions (34) and (30) are equivalent [Morse and Feshbach, 1953, p. 413].

The solution of the inhomogeneous boundary value problem (27), obtained by Green's function techniques (having noted that the Green's function of the inhomogeneous equation can be recovered from that of the homogeneous counterpart) is

$$C_1(\mathbf{x}, t) = W \int d\mathbf{x}' \int_0^t d\tau \cdot \left\{ \sum_m \phi_m(\mathbf{x}') \phi_m(\mathbf{x}) \exp((\lambda_m - W)(t - \tau)) \right\} C_2(\mathbf{x}', \tau) \quad (36)$$

We now turn to the assumptions (3). If the concentration in the fixed phase is proportional to the instantaneous fraction of mass sorbed, it is (recall that (36) is the solution to an instantaneous pulse at $t_0 = 0$) $C_2(\mathbf{x}', \tau) = C_2(\mathbf{x}', \tau, 0)$, in which we emphasize the conditionality of the concentration in phase 2 on the instantaneous fraction of solute mass sorbed. If furthermore we can assume that such instantaneous fraction of mass sorbed is independent of spatial location, it is

$$C_2(\mathbf{x}', \tau, 0) \sim C_2(\tau, 0) \quad (37)$$

We note that although the conditions leading to the validity of (34) are still awaiting a general definition, (37) is consistent with the postulates of our extension (8) of transport by continuous motions. Equation (37) therefore reduces to

$$C_1(\mathbf{x}, t) = W \int d\mathbf{x}' \int_0^t d\tau \cdot \left\{ \sum_m \phi_m(\mathbf{x}') \phi_m(\mathbf{x}) \exp((\lambda_m - W)(t - \tau)) \right\} C_2(\tau, 0) \\ = \int d\mathbf{x}' \sum_m \phi_m(\mathbf{x}') \phi_m(\mathbf{x}) \exp(\lambda_m t) W \exp(-Wt) \cdot \int_0^t d\tau \exp((\lambda_m - W)\tau) C_2(\tau, 0) \quad (38)$$

The term $\int d\mathbf{x}' \sum_m \phi_m(\mathbf{x}') \phi_m(\mathbf{x}) \exp(\lambda_m t)$ is the propagator of the initial condition, or the Green's function G in (34) of the complete convection-dispersion equation with $W = 0$, i.e., without source/sink or reaction term. This is [Cox and Miller, 1965, p. 221; Feller, 1971, p. 477; Dagan and Nguyen, 1989; Moore and Clarke, 1983] the travel time pdf to the control section S of the transport volume V_s as in (12) provided a uniform input is propagated as the initial condition. The solution to a Dirac delta "function" input at $\mathbf{x} = \mathbf{a}$, $t = 0$, gives the impulse response function, equivalent to a

pf, i.e., $\Delta m_0 = 1$ in (9). At the trapping surface S (Figure 1) of the transport volume, the functions

$$\begin{aligned} F(t) &= P(T > t) = \int_{V_s} d\mathbf{x} \langle G(\mathbf{x}, t) \rangle \\ &= \int_{V_s} d\mathbf{x} \int d\mathbf{x}' \sum_m \phi_m(\mathbf{x}') \phi_m(\mathbf{x}) \exp(\lambda_m t) \quad (39) \\ f(t) &= dF/dt \quad (40) \end{aligned}$$

are equivalent to (11) and (12) in that (34) is interpreted as solution for the ensemble mean concentration. These functions are well known in first-passage time problems occurring in statistics, where f is the pdf of the first passage T for a Wiener process starting at \mathbf{a} to reach an absorbing barrier at S . The exit boundary surface need therefore to be constructed in a suitable manner so that a Brownian trajectory in 3-D has to hit the control section S . This fact is somewhat implicit in the choice of an appropriate transport volume [Rinaldo and Marani, 1987, p. 2108].

At this point we further assume $\lambda_m \ll W$ in the Volterra integral (38), for $m < M$, M being a large enough cutoff number independent of \mathbf{x} and t . This is tantamount to assuming that the time scale of production/removal processes is larger than travel time in the transport volume. In this case the characteristic number M , [Rinaldo and Marani, 1987] is $\sim O(1)$, thereby implying that the characteristic time scales of transport and of sorption kinetics at most be comparable.

The solution for the general case (36) can therefore be written as (let $M(t)$ be the mass stored in the transport volume in the case of reactive tracer as in (19)):

$$\begin{aligned} \langle M(t) \rangle &= \int_{V_s} d\mathbf{x} \langle C_1(\mathbf{x}, t) \rangle = F(t)W \\ &\cdot \exp(-Wt) \int_0^t d\tau \exp(W\tau) C_2(\tau, 0) \quad (41) \end{aligned}$$

To stress the analogies with (19) and (20), we introduce a function $C_r(t, 0)$ defined by

$$C_r(t, 0) = W \exp(-Wt) \int_0^t d\tau \exp(W\tau) C_2(\tau, 0) \quad (42)$$

which has the dimensions of a concentration. This function is solution to the differential equation

$$\begin{aligned} \partial C_r(t, 0)/\partial t &= W[C_2(t + 0, 0) - C_r(t, 0)] \quad (43) \\ C_r(0, 0) &= 0 \end{aligned}$$

The analogy with (2) and (20) is complete. It follows from the original MRF approach [Rinaldo and Marani, 1987, (5)] that $h = W/(1 - B)R$ and $C_E(t) = C_2(t, 0)$ in (4); $t = \tau$ because here $t' = 0$. The function $C_r(\tau, t')$ in (3) and (4) and in the following developments is a resident concentration in the Lagrangean form derived by Rinaldo and Marani [1987] as an assumption. Equation (43) can therefore be employed in (20) to incorporate the dynamics of sorption processes into the formulation of transport by lifetime distributions. It follows therefore from (2), (20), and (37) that for instantaneous unit pulse at $t_0 = 0$, we have

$$Q_{\text{out}}(t) = G(t|0) = f(t)C(t, 0) \quad (44)$$

$$\partial C(t, 0)/\partial t = W[C_2(t + 0, 0) - C(t, 0)] \quad (45)$$

which is the solution of (2) with $i(t) = \delta(t)$. In general, for the i th impulse $i(t) = \delta(t - t')$ at time $t = t'$, the corresponding MRF

$$G(t - t'|t') = f(t - t')C(t - t') \quad (46)$$

as in (2) and (3).

4. MRF'S AND MOST PROBABLE DISTRIBUTIONS

The conceptual strategy suggested by (1), (2), and (3) implies the decoupled determination of travel time and lifetime distributions. The effects of convection/dispersion and sorption are, in this model, computed independently and then coupled by the Volterra integral equation (2) because the underlying mechanical model implies that solute particles move along with the carrier flow with the same velocity and interact with the surrounding media regardless of the particles' position. We might therefore speculate that as long as we are interested in the macroscopic distribution of residence times at some exit surface S of a large control volume, there is a way to derive the MRF without explicitly mentioning the underlying transport model. This can be achieved by maximum probability (or Boltzmann's) methods [e.g., Huang, 1963].

To build solute travel time distributions, it is observed that after instantaneous input of a large number N of particles over the area which corresponds to the entrance surface of the control volume, the proportion of particles arriving at the outlet surface S (Figure 1) equals the pdf of the travel time. This nonnegative variable is denoted by t and the number of arrivals at the outlet during the interval (t_{i-1}, t_i) will be designated by N_i . Let $t' < t_1 < \dots < t_i < t$ be a partition of t into subintervals of length Δt , where t' is the arbitrary origin taken as zero at no loss of generality. To consistency with (2) and (4), the N_i arrivals in Δt about t_i (over the i th subinterval) are associated with particles labeled with the same mass $\Delta m(t_i; 0, \mathbf{a})$ because mass transfer is assumed to depend only on the contact time t_i via (4).

Let $q_1(t), \dots, q_N(t)$ denote the positions of the particles such that $q_i(t)$ is in the control volume V_s for each $i = 1, \dots, N$. These coordinates $(q_1(0), \dots, q_N(0))$ are assumed independent and identically distributed (uniform) over the inlet surface of coordinates $\mathbf{x} = \mathbf{a}$ (Figure 1) at the injection. The time partition related to arrival counting induces a partition of V_s defined by a volume c_i subregion of V_s such that the time to the outlet of a particle in it is in $(t_i - \Delta t, t_i)$; in other words, the number of arrivals N_i counts the number of particles whose position coordinate $q_i(t)$ belongs to c_i . Clearly, $N_1 + N_2 + \dots = N$, where N_i are random but N is fixed.

The problem is now reduced to a traditional occupancy problem in probability. The joint density of N_1, \dots, N_m , where m is any large cutoff number, is a multinomial [Huang, 1963, p. 80; Feller, 1971]

$$P(N_1 = n_1, \dots, N_m = n_m) = N! \prod_i (p_i)^{n_i} / n_i! \quad (47)$$

$$i = 1, \dots, m$$

where $p_i = |c_i|/|V|$; $| \cdot |$ denotes the "volume" of the bracketed region [Lienhard, 1964; Lienhard and Meyer,

1967; Gupta and Waymire, 1983; Rinaldo and Marani, 1987]. This position can be described heuristically as follows. Physically, p_i is a probability and P is the number of ways in which the set of distinguishable objects (N_1, N_2, \dots, N_m) can be selected from N objects if there are p_i distinguishable ways of placing N_i objects in the i th partition. If the various cells constitute a subdivision of a large region Λ into smaller regions $\Lambda_1, \dots, \Lambda_m$ and if spatial homogeneity holds (i.e., the uniform measure applies), then it is natural to estimate the probability p_i by means of

$$p_i = |\Lambda_i|/|\Lambda| \quad i = 1, \dots, m \quad (48)$$

where the angle brackets denote Lebesgue measure.

The travel time distribution is characterized [Huang, 1961, p. 80, Lienhard, 1964] by maximum joint probability, subject to a fundamental couple of side conditions. One condition is the constraint of conservation

$$\sum_i N_i = N \quad i = 1, m \quad (49)$$

The other constraint applies to the time moments of the residence time distribution. This is, indeed, consistent with the physical significance of flux concentration implicit in (1) and (2): it has been observed, in fact, [Kreft and Zuber, 1978, 1986; Sposito and Barry, 1987] that if measured concentrations are the target of a mathematical description, physical significance can be attached only to time moments, because their spatial moments in general would have no physical meaning. Clearly,

$$E\tau^\beta = \lim_{\Delta t \rightarrow 0} \sum m b_i - 4q_{k=1,\infty} t_k^\beta P(t_{k-1} < \tau < t_k) \quad (50)$$

(where $P(t_{k-1} < \tau < t_k)$ is the probability associated to a discrete pdf of travel times) and, identifying P with N/N , one may estimate $E\tau^\beta$ in terms of $\sum_i N_i t_i^\beta$ for each $\beta > 0$. Hence a second constraint

$$\sum_i (N_i/N) t_i^\beta = K_\beta \quad K_\beta > 0 \quad i = 1, m \quad (51)$$

applies, where K_β equals $E\tau^\beta$. Since N_i and t_i are both positive in response to a pulse at $t' = 0$, this is generally valid.

Let N_i be those values of n_i maximizing $P(N_1 = N_1, \dots, N_m = N_m)$. Passing on to the logarithms, differentiating, setting the constraints by Lagrange multiplication and applying Stirling's formula we obtain

$$N_i = p_i \exp(-A - B t_i^\beta) \quad (52)$$

$$N/N = (p_i \exp(-B t_i^\beta)) \left\{ \sum_j p_j \exp(-B t_j^\beta) \right\}^{-1} \quad (53)$$

$i, j = 1, m$

The explicit form of (53) depends on the choice of dynamics implicit in the definition of p_i . If we assume [Lienhard and Meyer, 1967; Rinaldo and Marani, 1987] that

$$p_i = \gamma t_i^{\alpha-1} \quad \alpha > 1 \quad (54)$$

it follows that

$$N/N = (\gamma t_i^{\alpha-1} \exp(-B t_i^\beta)) \left\{ \sum_j \gamma t_j^{\alpha-1} \exp(-B t_j^\beta) \right\}^{-1} \quad (55)$$

$j = 1, \dots, m \quad m \rightarrow \infty$

The summations in the bracketed coefficient can be replaced with definite integrals, as Δt is taken to be small. Elimination of $N/\gamma \exp(-A)$ from the two constraints gives $B = \alpha/\beta K_\beta$. Hence letting $\Delta t \rightarrow 0$, and applying the mean value theorem, we obtain

$$f(t) = (\beta(\beta K_\beta/\alpha)^{-\alpha/\beta} \Gamma(\alpha/\beta)) t^{\alpha-1} \exp(-\alpha t^\beta/\beta K_\beta) \quad (56)$$

and by (3)

$$G(t, 0) = C'(t, 0) f(t) \quad (57)$$

Equation (57) for constant concentration ($C'(t, 0) = C_0$ (i.e., the inert tracer) is a generalized gamma distribution. Among its features [Lienhard and Meyer, 1967; Rinaldo and Marani, 1987], it has been observed that it reduces to standard gamma ($\beta = 1$), exponential ($\alpha = \beta = 1$), Maxwell ($\beta = 2$, $\alpha = 3$), or Weibull ($\alpha = \beta$) distributions.

The important result in (56) and (57) is that the existence of analytical forms for MRFs can be discussed. In particular we are interested in the possible occurrence of non-gaussian distributions for $f(t)$ because (recall equations (22) to (24)) they have important bearing on the usual study of transport phenomena. We examine here the lognormal and the inverse gaussian distributions to emphasize the generality of the tools and to suggest new inroads to the problem.

A lognormal distribution for MRFs is realistic only if (1) convection is steady and uniform, such that $Q_{out}(t)$ in (2) can be replaced, up to scaling, by the flux concentration $C(t)$ (see equation (69)) below; also compare with Jury *et al.* [1986, equation 17]; (2) the travel time distribution is normally distributed as

$$f(t) dt = \Omega \exp(-t^2/2\Theta^2) \quad (58)$$

where Ω and Θ are parameters of the distribution; (3) we let C to depend only on contact time, represented here by the travel time. Hence the derived distribution $g(C')$ is computed by $g(C'(t)) dC = f(t) dt$ [Rinaldo and Marani, 1987, equation (43)]; we then transform dt , dimensionless with h , according to (4) as

$$dt = dC'/(C' - C_E) \quad (59)$$

to obtain

$$G(t, 0) = g(C') = \exp\{-(\log(C' - C_E) - \Omega)^2/2\Theta^2\} \div \{\Theta(C' - C_E)(2\pi)^{1/2}\} \quad (60)$$

which is a lognormal distribution; (4) no removal/production process affects significantly the fraction of mass sorbed in the time scale of travel; hence C_E in (59) is constant and (5) an instantaneous pulse of solutes is employed. Otherwise, the dt/dC' relation would have to embed the convolutive effects of variable surface conditions which upset the lognormal character.

It is also important to note that the asymptotic Gaussian behavior for the dispersion processes on large time and spatial scale can be studied in this framework. In fact, if a diffusive regime is ever reached, at large times the ratio of

the time variance σ_t^2 and the spatial variance σ_x^2/U , where U is a scale of velocity [Taylor, 1921], must approach a constant value regardless of the initial condition affecting σ_t^2 [Tsai and Holly, 1978; Fischer et al., 1979]. Let us assume in (51)

$$\sum_i (N_i/N)(t_i - \mu)^2 = \sigma_x^2/U^2 \quad (61)$$

where μ is the average residence time thought of as the ratio of the spatial scale L and the scale of velocity U .

Under the assumptions that again no sorption process is significant ($C'(t, 0) = C'(0, 0)$) and that the path probability p_i in (54) tends to unity, one obtains, in analogy with the steps from (47) to (56):

$$G(t, 0) = C'(0, 0)U \exp(-U^2(t - \mu)^2/2\sigma_x^2/\sigma_x(2\pi)^{1/2}) \quad (62)$$

To obtain (67), one must introduce the approximation, valid as the traveled length L is large,

$$\text{ERF}(L\sqrt{B/U}) \rightarrow 1 \quad \gamma(3/2, L^2/U^2) \rightarrow 0 \quad (63)$$

in the limit as $\mu = L/U$ grows large, with $\Gamma(3/2) = \sqrt{\pi}/2$. ERF () and $\gamma(x, y)$ are respectively the error function and the incomplete gamma function of argument x, y . If we specialize (63) to a 1-D diffusion problem at constant convection, it reduces to $\sigma_x^2 = 2Dt$. Hence (63) reduces to the solution of traditional first-passage time problems in statistics or to particular cases of the solution of the convection-dispersion equation [Dagan, 1982].

5. DISCUSSION

The validity of the formulation (1) to (3) to characterize transport to a trapping boundary has been shown to be fully justified in the limiting case of short travel time with respect to sorption time. This is due to the assumption that solute particles move along trajectories with the same velocity of the carrier flow, and that they exchange mass with the surrounding environment irrespectively of the particles' position in space. A natural question therefore arises on whether the other asymptotic limit, that of large transport time compared to sorption time (which is more typical of subsurface flow), can be represented by a MRF model. Upon rescaling time by the retardation factor [e.g., Freeze and Cherry, 1979] an equivalence can be established, by the same approach leading to (8), between the expected value of concentration of a retarded tracer and a new pdf of trajectories. The latter is defined by the underlying probability model of movement of conservative solute particles with retarded velocity. The corresponding MRF model is therefore (1) with travel time characterized by retarded mean and same variance with respect of the travel time distribution of the carrier flow.

In the cases in which neither asymptotic limit is reached, the observation of Sposito et al. [1986] still stands, since a kernel $G(t - t', t')$ in (2) is generally consistent with any mechanistic model of two-component convection/dispersion, although no hint on his form can be derived a priori. The key factor in (1) to (3) for field application is decoupling, or the appearance of the travel time distribution $f(\cdot)$ of the carrier flow (i.e., the hydrologic response) in the transfer function $G(t - t', t')$. In this case f can be evaluated independently as inert solutes and carrier flow would hold the same travel time distribution.

Another key aspect is related to the definition of the absorbing barrier, i.e., the observation site S , which should not preclude the treatment of time-varying velocities or yield the sampling of a portion of the plume. This barrier S defines the accessible environment and is easily identified in the context of surface hydrology as the closure of the catchment where runoff is observed. The only 3-D example to date in the literature of subsurface transport [Dagan and Nguyen, 1989] defines S as a vertical plane normal to the direction of the flow at a distance from the source (a volume of leachate discharge) into a shallow unconfined aquifer).

By the above speculations derives that the field for application of the model (1)–(4) is therefore that of (1) large injection scale of solutes, in which the source of solutes is distributed in a nonpoint manner, because it is assumed the irrelevance of spatial location for the deduction of local concentrations. Travel (contact) time then controls mass transfer between fixed and mobile phases. We speculate that this may be the case when production/removal processes occur due to predominantly vertical movement through soil; (2) small travel time to a drainage system, as compared to sorption time. Although this largely depends on the solute and on the chemical, physical or biological process, we argue that efficient drainage systems serve to exit rapidly excess water warranting conditions for the possible validity of (3).

MRFs models are therefore suitable to predict transport phenomena of nonpoint nature where the process of loss/gain of solutes occurs in a confined zone (e.g., the topsoil about the root zone of crops subject to fertilization) where substantially vertical flow occurs. The related transport volume is therefore the topsoil, which is identified as a "sorption" or "generation" state [Rinaldo and Marani, 1987, equations (38) and (39)], whereas due to the brevity of residence time in subsurface flow and in the drainage system the other "routing" or "mixing" media are not affected by significant loss/gain processes. As in our initial formulation, therefore basin scale transport of solutes residual of agricultural activities represent an example of relevant environmental problem in which MRFs can be conveniently applied.

To strengthen our confidence in the soundness of the approach for nonpoint pollution processes, the above concepts have been applied to a field study. The validation proposed here is based on an inverse procedure of deconvolution of travel and loss/gain function in comparison with experiments in which water and solute inputs and outputs had been measured. The experimental study dealt with river quality related to extensive data gathered in the small (8.4 km²) Japanese catchment of the upper Ai river [Takeuchi et al., 1984], for basinwide solute NO₃-N circulation. The study, which presented no modeling effort, focused on the experimental determination of the concentration of solute NO₃-N in all components of the hydrological cycle (rain, surface, subsurface waters). Its findings clearly indicated that the high content of NO₃-N load to river water during floods was not brought in by rain or surface runoff, but by the discharge once in contact with the topsoil which turned out to be the sole significant source of solute NO₃-N supply.

The model (1) of the hydrologic response is tailored to a geomorphological scheme based on the information available in the paper. The geomorphological states are forested overland areas (O1), drained by a steep channel (C1) which flows into a larger, milder stream (C2). Flatter agricultural areas (O2)

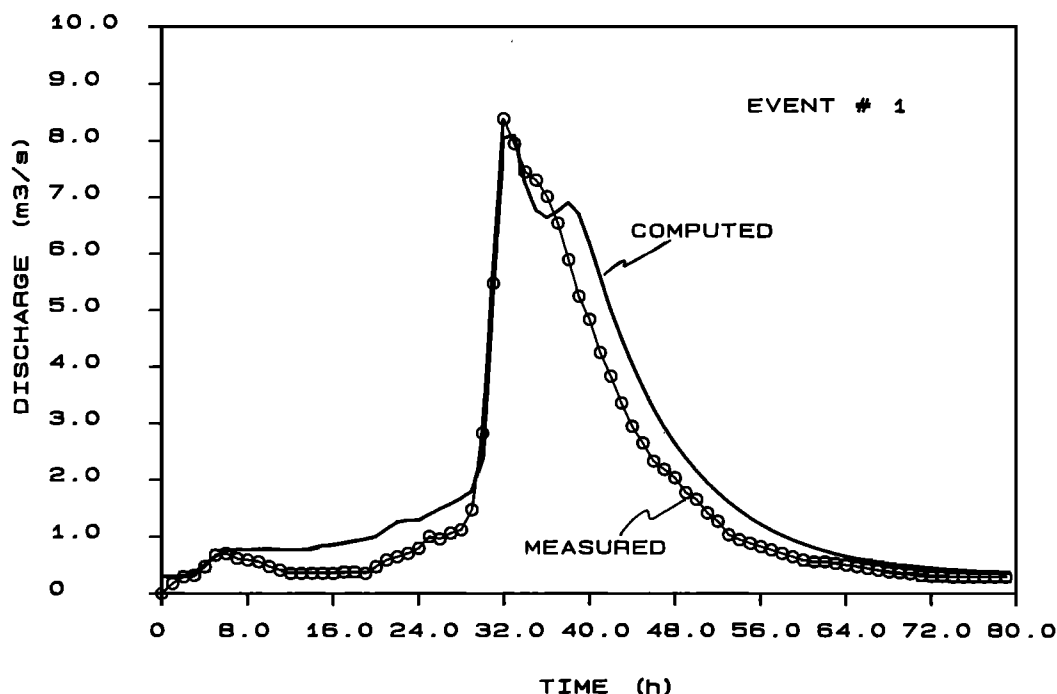


Fig. 2. Computed (solid curve) and measured (O) [Takeuchi et al., 1984, Figure 11] water discharges for event 1.

drain directly into the channel C2. The transitions are $O1 \rightarrow C1 \rightarrow C2$ and $O2 \rightarrow C2$. Surface and subsurface runoff components are accounted for in the model by separating the net inflow rates $i(t)$ into two components, namely, $i_s(t)$ and $i_p(t)$ [Rinaldo et al., 1988]. Let $f_{O1}(t)$, $f_{C1}(t)$, \dots , be the pdf's of statistically independent residence time in the basin states (a superscript s or p eventually denotes surface or subsurface detention); $p(1)$, $p(2)$ the proportion of area draining into the overland states $O1$ and $O2$ (recall that in general $p(i)$ is a path probability [Rodríguez-Iturbe and Valdes, 1979; Gupta et al., 1980; Gupta and Waymire, 1983]); the asterisk denotes the convolution operator. The model equation (1) of water discharge at the control section becomes

$$Q(t) = \int_0^t i_s(x) u_s(t-x) dx + \int_0^t i_p(x) u_p(t-x) dx \quad (64)$$

$$u_i(t) = p(1) f_{O1}^i f_{C1} f_{C2}(t) + p(2) f_{O2}^i f_{C2}(t) \quad (65)$$

$$i = s, p$$

The model of the hydrologic response (65) specializes the classic form of the geomorphologic unit hydrograph proposed by Gupta et al. [1980] to the simplified transition probabilities $p(1) = A_{O1}/A = 0.86$, $p(2) = A_{O2}/A = 0.14$, where A_{O1} is the area of the overland state 1, A_{O2} is the area of overland state 2, and A is the total area of the catchment. Overland states are identified with forested and agricultural/urban areas the dimensions of which are given [Takeuchi et al., 1984].

The MRF model of $\text{NO}_3\text{-N}$ flux at the control section is then by (2) and (3) given by

$$Q_{\text{out}}(t) = \int_0^t dx i_s(x) G_s(t-x|x) + \int_0^t dx i_p(x) G_p(t-x|x) \quad (66)$$

$$G_s(t|t') = \{p(1)[C_s(t, t') f_{O1}^s(t)] f_{C1} + p(2) \cdot [C_s(t, t') f_{O2}^s(t)] f_{C2}(t) \quad (67)$$

$$G_p(t|t') = \{p(1)[C_p(t, t') f_{O1}^p(t)] f_{C1} + p(2) \cdot [C_p(t, t') f_{O2}^p(t)] f_{C2}(t) \quad (68)$$

The concentration at the control section (the quantity observed in the field) is then defined as the ratio of solute and water fluxes as

$$C(t) = Q_{\text{out}}(t)/Q(t) \quad (69)$$

The complete description of the MRF needs only specification of the resident concentrations $C_i(t, t')$, $i = s, p$ through integration of (4). The application of a second-order accurate scheme and the assumption $C_E(t) = C_E(0) + M_s(t)/K_D$, where K_D is a distribution coefficient of the sorbed mass, and $M_s(t)$ is the instantaneous fraction of solute mass sorbed, yields

$$C'(i, j) = C'(i-1, j) \exp(-h\Delta t) + [1 - \exp(-h\Delta t)] \cdot [2C_E(0) + (M_s(i+j) + M_s(i+j-1))/K_D]/2 \quad (70)$$

where $C'(i, j) = C'(i\Delta t, j\Delta t)$ define a concentration matrix; Δt is the partition of time for the discrete solution. The implicitness of (70) derives from the dependence of M_s on the actual concentrations C' and on the travel time pdfs f . An efficient computational procedure has been employed to solve (70) [Rinaldo et al., 1988]. The choice of pdf's for the residence time distribution has been made as one-parameter exponentials

$$f_{\Sigma}(t) = \exp(-t/\tau_{\Sigma})/\tau_{\Sigma} \quad \Sigma = O1^s, O1^p, O2^s, O2^p, C1, C2 \quad (71)$$

because the geomorphological insight is rather superficial for the catchment at hand. The numerical convolutions are then

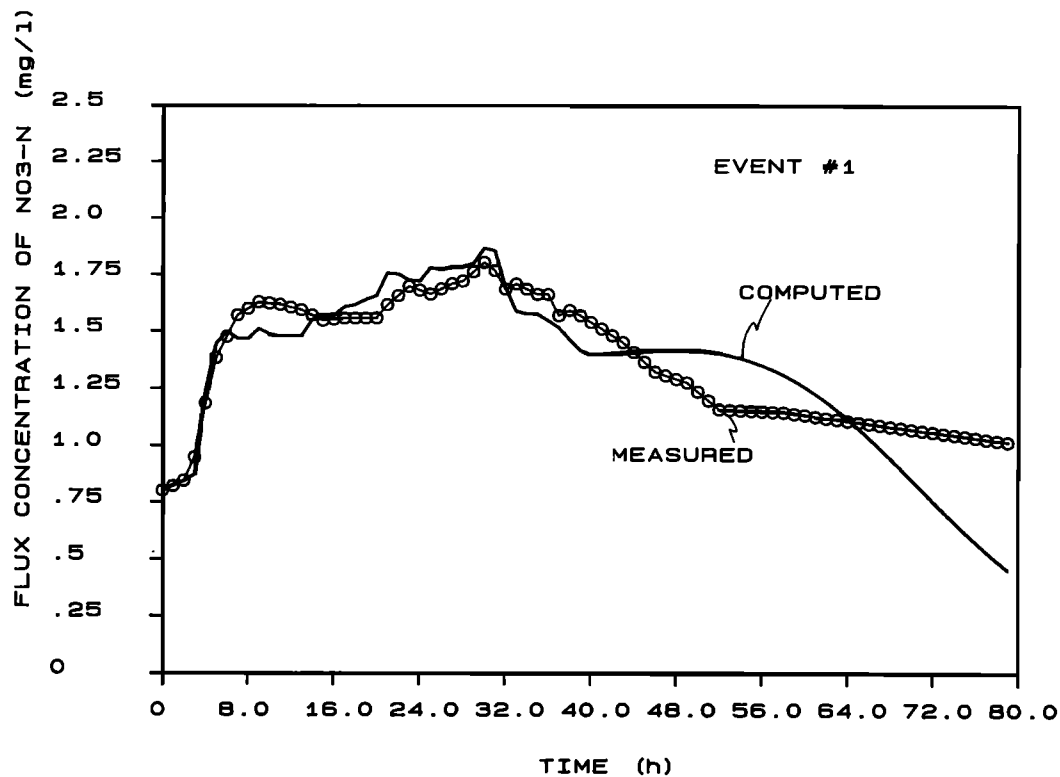


Fig. 3. Computed (solid curve) and measured (O) [Takeuchi et al., 1984, Figure 11] flux concentrations of solute $\text{NO}_3\text{-N}$ at the control section for event 1.

evaluated analytically (for complete expression of general n -fold convolution, see, for example, Gupta et al., [1980, equations (17)–(19)]. The parameters τ_z of the distributions are evaluated by least square error minimization via a standard routine. The test event is the distribution of measured discharges and solute flux concentrations for the event 1 [Takeuchi et al., 1984, Figure 8f].

The fitted discharges for the calibration event are reported in Figure 2. The parameters obtained by least square minimization are as follows: $\tau_{O1} = 0.9$ hour; $\tau_{O1}^p = 8.5$ hours; $\tau_{O2} = 1.1$ hours; $\tau_{O2}^p = 9.4$ hours; $\tau_{C1} = 0.5$ hour; and $\tau_{C2} = 0.8$ hour. The calibration of the parameters of the nonequilibrium model has been performed comparing (69) with the concentration measured at the control section of the Ai

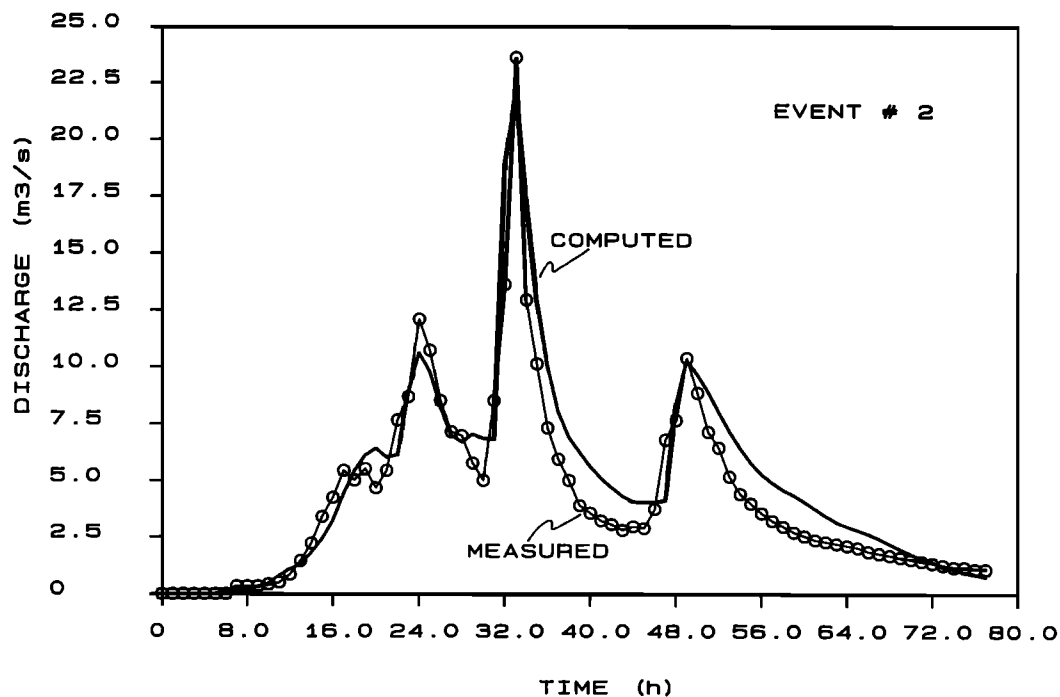


Fig. 4. Computed (solid curve) and measured (O) [Takeuchi et al., 1984, Figure 10] water discharges for event 2.

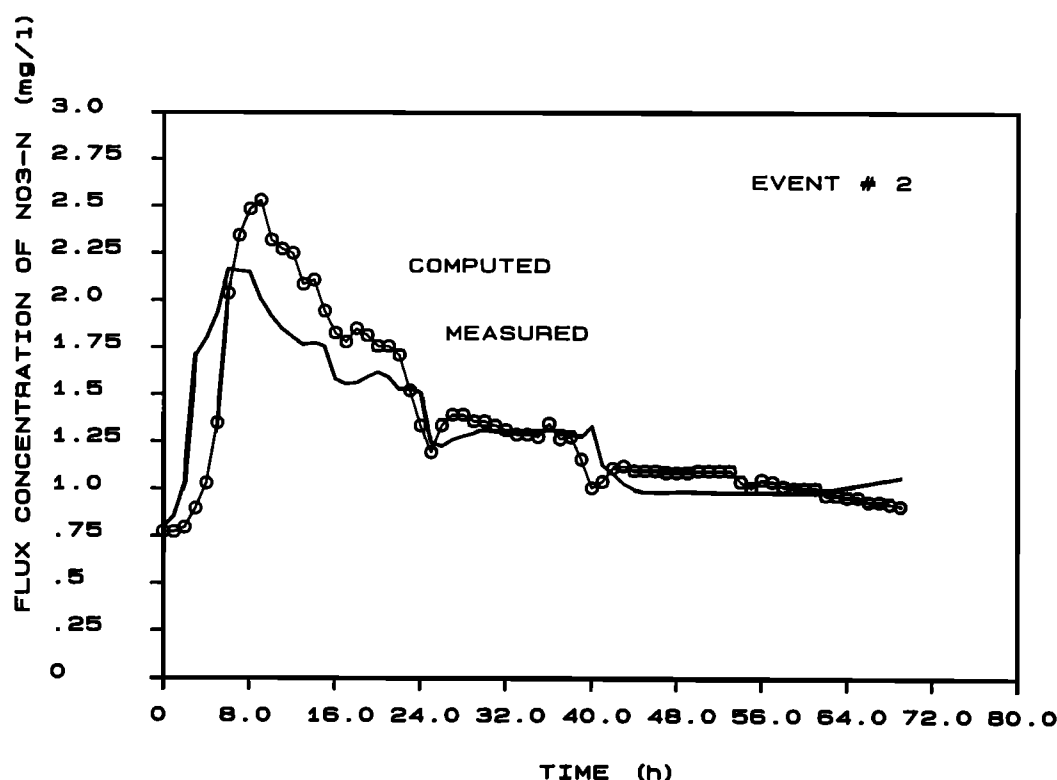


Fig. 5. Computed (solid curve) and measured (O) [Takeuchi *et al.*, 1984, Figure 10] flux concentrations of solute $\text{NO}_3\text{-N}$ at the control section for event 2.

river. The calibrated curve of computed flux concentration (equation (25)) is plotted in Figure 3. The parameters are as follows for the surface layer s , $h = 2.7$ hours; $K_D = 0.1$; $C_E(0) = 13.2$ mg/L; for the subsurface layer p , h is fixed at the same value of the surface state; $K_D = 0.11$; $C_E(0) = 11.7$ mg/L. It is assumed that the concentration of solutes in rainwater is negligible ($C'(0, 0) = 0$ mg/L).

The reliability of the model has been tested by predicting the behavior of another gauged event on the basis of the parameters calibrated by the first curve. The measured values [Takeuchi *et al.*, 1984, Figure 8e] refer to a hydrologic event characterized by very intense rainfall. Water discharges are predicted as in Figure 4. The agreement of computed and measured discharges is good, underlining the reliability of the hydrologic model in the case of intense storms. Measured and predicted flux concentrations according to our prediction are shown in Figure 5. The prediction is deemed satisfactory because the error between instantaneous values of predicted and measured concentrations is less than 20%. However, the predicted mass released is 30% less than that measured because a defect in the computed concentration appeared at the time of maximum discharge. We observe, in particular, that the dilution of recharge in the concentrations are estimated qualitatively in a correct framework and that the excess of dilution that occasionally occurs in the calculated concentrations may be due to a corresponding error in the prediction of the flow component. Improving the parameter estimation technique may overcome such shortcomings, but still a predictive character of the MRF model is, in the writers' opinion, warranted.

Figures 6 and 7 show the prediction of another event [Takeuchi *et al.*, 1984] characterized by short and intense precipitation yielding a small fraction of net rainfall. Al-

though water discharges are predicted satisfactorily from the engineering viewpoint, it is apparent that the estimated fraction of flow through the two possible routes is partly misestimated. In fact, the total water volume is quite correct, but the predicted concentrations (Figure 7) suffer from an insufficient prediction of the runoff components which is probably due to the calibration of the rainfall model performed on an intense storm event. Interestingly, in this case the total mass released is predicted quite correctly. The need for reliable hydrological models to characterize well solute transport over basin scales is nevertheless quite clear. It is also clear, in the writers' opinion, that the correct prediction of the order of magnitude of flux concentrations in a case significantly different from that of calibration underscores the robustness of the approach.

It is therefore the writers' opinion that notwithstanding the need for further clarification of a number of issues (e.g., the interval of confidence expected for predictions; the impact of uncertainty upon parameter estimation), MRFs provide some new theoretical insight and tools for practical applications in the study of water resources.

6. CONCLUSIONS

In the present paper the relation between concentration and travel time distribution approaches with models of MRF has been discussed in the context of transport theory in heterogeneous large-scale media. Following are the major conclusions of the paper.

1. The MRF theory was first examined in connection with the underlying dynamical models of solute transport through heterogeneous media. MRFs were proved to extend the basic formulation of transport by continuous motions to a particular case of removal/production processes. It was

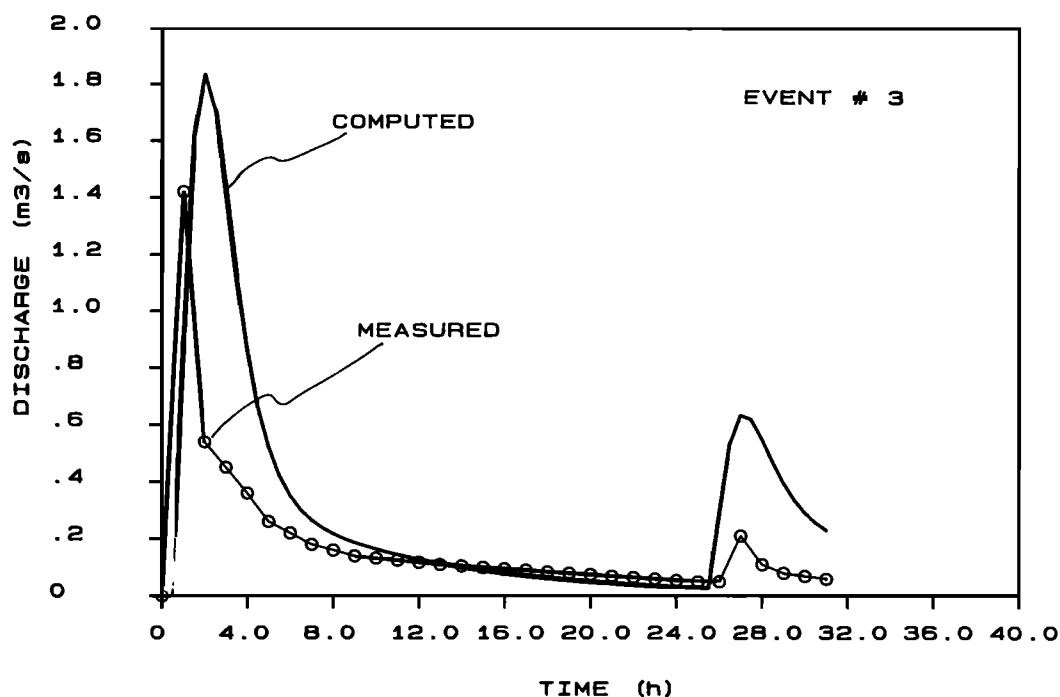


Fig. 6. The same as Figure 4 for event 3 [Takeuchi *et al.*, 1984].

also inferred that the MRF formalism is consistent with (and, under limit assumptions, can be derived from) the general 3-D differential mass balance equations for a two-component system. It is concluded that solute lifetime distributions can be thought of as the product of travel time distributions and a suitable resident concentration if the equilibrium concen-

tration for the mobile phase (solute in the transport volume) depends weakly on spatial location. This implies that solute transfer between mobile and fixed phases is controlled by the contact time (i.e., the travel time distribution).

2. MRFs were defined as an extension of travel time distributions to incorporate simplified concepts of produc-

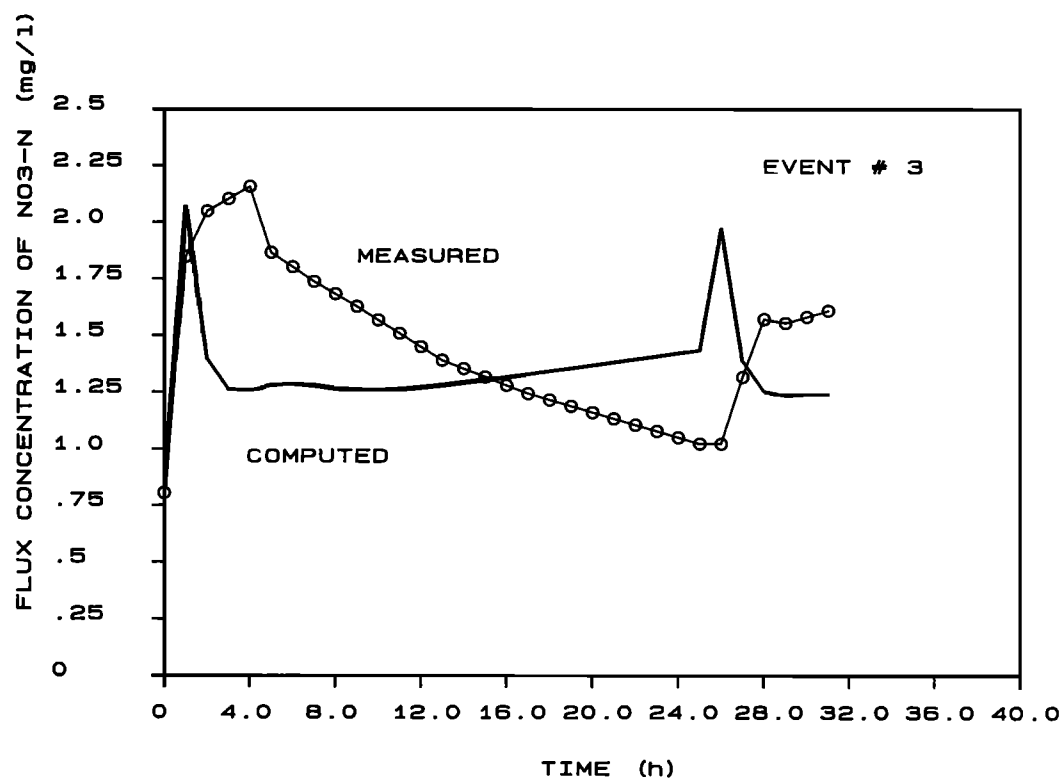


Fig. 7. The same as Figure 5 for event [Takeuchi *et al.*, 1984].

tion/removal of solutes. The form of MRFs employed as an assumption by the original formulation, was derived through a formal solution to the general 3-D equations of two-component convection-dispersion in the limit case of short travel time compared to loss/gain (sorption) time. A validation was given in such a limit case to the use of MRFs as the product of travel time distributions and of a bounded continuous function associated with an initial value problem for a resident concentration. Computations of transport of reactive solutes can therefore be performed by evaluating independently the effects of convection/dispersion and those of sorption, which are then coupled by a Volterra-type integral equation. In the other limit case, of large travel time with respect to sorption time, MRF degenerate into travel time distributions with retarded mean and same variance. In the case of comparable time scales of transport and loss/gain, the effect of the travel time pdf on the MRF cannot be clearly distinguished although it was ascertained that a TFM model is generally consistent with any dynamical model.

3. Evaluation of travel times was performed through maximum probability algorithms aiming at the features of large-scale transport dynamics. It was concluded that quite possibly a general solute lifetime distribution does not exist in analytic form (e.g., the lognormal, the inverse ERF) whenever the time scale of sorption kinetics is comparable with that of transport and/or the input rate of solute mass cannot be modeled accurately by a Dirac-delta function. It was also concluded that non-Gaussian distributions of travel time (and of the parent lifetime distributions) represent the norm, rather than an exception, in this representation of transport.

4. The application of MRF concepts to a field study revealed reliability and robustness for application to non-point pollution problems.

5. Questions remain open on (1) the effect of uncertainty on parameter estimation; (2) the effects of variable rates of reaction experienced by a traveling particle depending on its position; and (3) the effects of the possible correlation of the parameters of sorption processes with the conductivity of the medium. On this issues research is in progress in the search of a more general characterization of transport by pdfs.

Acknowledgments. This research is supported by funds granted by Ente di Sviluppo Agricolo del Veneto through its project Razionalizzazione del Consumo dei Fertilizzanti in Agricoltura, by the Consiglio Nazionale delle Ricerche, Gruppo per la Prevenzione delle Catastrofi Idrogeologiche (linea 4, M. Civita head); and the Italian Ministry for Public Education (fondi 40%; project Fenomeni di Trasporto di Inquinanti nel Ciclo Idrologico). The authors are grateful to G. Gambolati of the University of Padua, S. P. Neuman, University of Arizona, and D. Hernandez, formerly at the Milan Polytechnic, for having commented on a draft of this paper. The authors are deeply indebted to G. Dagan, of the Tel Aviv University, for the valuable suggestions and the enlightening conversations on this issue. The authors would also like to thank two anonymous reviewers for their careful reading of the paper and their constructive comments.

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- A. Bellin and A. Rinaldo, Dipartimento di Ingegneria, Università di Trento, Mesiano di Povo, I-38050 Trento, Italy.
- A. Marani, Dipartimento di Scienze Ambientali, Università di Venezia, S. Marta, I-30124 Venezia, Italy.

(Received May 6, 1988;
revised January 31, 1989;
accepted February 8, 1989.)