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On the distribution of multicomponent mixtures over generalized exposure time in subsurface flow and reactive transport: Foundations, and formulations for groundwater age, chemical heterogeneity, and biodegradation

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Abstract. The fate of materials undergoing transport and reactions in natural porous media sometimes depends on the time of exposure of the conveyed material to other materials present in the system. The distribution of groundwater age, the effects of mineral chemical heterogeneity on reactive solute transport, and the occurrence of lag in reaction systems are some areas of hydrogeology that involve exposure time in an important way. A general balance equation for accounting for such effects is provided through an extended transport operator that incorporates generalized exposure time as an additional independent coordinate. Evolution of material distributions over exposure time appears within this transport operator as a convective process that represents space- and time-dependent generalized exposure of material constituents undergoing physical transport and nonequilibrium chemical and microbiological mass transformations. The general equation is derived from basic mass balance arguments by treating the constituents as a mixture of overlapping continua and developing evolution equations for the mixture material densities in the new dimensions of space, time, and exposure time. Example applications of the approach to each of the three examples above are described.

1. Introduction

The fate of materials undergoing transport in porous media sometimes depends on the time of exposure of the conveyed material to other materials present in the system. Such dependency appears in diverse ways, three of which are introduced here as example phenomena that will be analyzed in this article. In the case where the conveyed material is the water itself and the other material is the aquifer solid phase, the exposure time is the groundwater age [e.g., *Goode*, 1996; *Varni and Carrera*, 1998]. This quantity is important in recharge source identification and residence-time determination. If the conveyed material is a dissolved or suspended constituent that reacts with another (mobile or immobile) component, the exposure time is the reaction time. This quantity is important in subsurface reactive transport in general and in assessing the effects of chemical (solid phase) heterogeneity in particular [e.g., *Espinoza and Valocchi*, 1997]. In the case where the conveyed material is a microorganism and the other material is a dissolved substrate that induces a metabolic response in the microbe, the exposure time is the time during which degradation and microbial growth is possible. This quantity is important not only for determining reaction time as in the previous example but also as it is necessary for keeping track of the time lag in metabolic activity induction, that is, metabolic lag. Metabolic lag can significantly affect degradation rates especially in high-Peclet flows [*Wood et al.*, 1995; *Murphy et al.*, 1997].

Outside of these examples is a general need for more robust methods for scaling subsurface reactive transport processes that involve material distributions as opposed to concentrations. To the author's knowledge, there is no general modeling approach to flow and transport processes that depend on material exposure time in ways that are meaningful to the fate (e.g., reactions) and transport of constituents. The purpose of this article is to provide a theoretical basis for generating governing differential equations that can quantitatively account for fate and transport of material mixtures that are distributions over exposure time. We first derive the fundamental generalized balance equation for materials that undergo motion in spatial, temporal, and exposure-time coordinates, and then we apply the balance equation thus obtained to generate governing equations for each of the three examples noted above.

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2. Derivation of Balance Equations

2.1. Exposure Time as an Independent Dimension Over Which Density May be Distributed

Exposure time is defined here as an independent dimension over which individual constituent (water, solutes, suspended colloids) elemental masses are distributed, just as they are distributed over a spatial dimension. Thus we define the space over which such distributions evolve as the $N + 1$ dimensional space constructed by augmenting the N physical dimensions with one real dimension representing generalized exposure time. This dimension is a continuous measure orthogonal to the remaining coordinates. If we express the physical space as $\mathbf{x}'$, then we define the augmented space $\mathbf{x}$ as follows in the case of $N = 3$:

$$\mathbf{x} = (\mathbf{x}', x_4) = (x_1, x_2, x_3, x_4)$$

We will rely heavily on this notation throughout the remainder of the article, without necessarily implying $N = 3$. Then the dimensions of the evolution of the distribution is constructed as the $R^{N+1} \times R^1$ space

$$(\mathbf{x}, t)$$

and a point in the physical distance and time dimensions only lies in the $R^N \times R^1$ space

$$(\mathbf{x}', t)$$

Volumetric mass density of a mixture constituent (water, solute, colloid) is conventionally expressed as a distribution over the usual physical dimensions as $\rho(\mathbf{x}', t)$. Here we further organize the volumetric mass density of a constituent into a distribution over physical space, generalized exposure time, and time, expressed as

$$\rho(\mathbf{x}, t) = \rho(\mathbf{x}', x_{N+1}, t)$$

and formulate an evolution equation for the distribution of volumetric mass density over the augmented space $(\mathbf{x}, t)$. We use elementary mixture theory of continuum mechanics [e.g., *Allen et al.*, 1988] for the formulation, here including general kinetics of nonequilibrium mass transformations, and where the densities are distributed over the $(\mathbf{x}, t)$ space as opposed to the simply physical $(\mathbf{x}', t)$ space. In addition, we require the formulation to be conservative (including all significant interacting species) so that we may make global mass balance statements for the system considered as a mixture.

2.2. Mass Density as a Differentiable Property in the Augmented (x, t) Space

Like conventional densities in $(\mathbf{x}', t)$ space, quantities such as mass density are treated as macroscopic continua in the $(\mathbf{x}, t)$ space by defining them as volume averages over a domain-invariant representative elementary volume (REV′ [e.g., *Bear*, 1972; *Lichtner*, 1996]). This application of the classical continuum hypothesis allows expression of mass balance identities for constituents of systems which are truly discontinuous at the microscale, such as water-solid mixtures of natural porous media, via partial differential equations involving continuous and differentiable approximate constituent densities. For extending the definition of density to the augmented $(\mathbf{x}, t)$ space it is necessary to extend a continuum hypothesis in this space. Unlike the $\mathbf{x}'$ dimensions, which, in reality, support distributions over discontinuous multiple phases (e.g., solid, water), the x_{N+1} dimension represents a natural as well as mathematical continuum, and so extending the averaging volume REV′ in the $\mathbf{x}'$ space to an extended averaging volume REV in the $\mathbf{x}$ space is not necessary. However, we still require continuity and differentiability of densities over the x_{N+1} dimension, in order to treat the $(\mathbf{x}, t)$ space mass densities as continua. It is not difficult to come up with empirical distributions of masses that challenge this assumption, for example, the initial distribution of groundwater age may be assumed Dirac. We circumvent this difficulty by introducing an Eulerian mass predensity m^α at the microscale, defined as an average over molecular scales, that takes account of uncertainty not only in the physical position of molecule i in $\mathbf{x}'$ coordinates [cf. *Cushman*, 1997], but also in its position in the exposure-time coordinate x_{N+1}. That is, the microscale density of constituent α ($\alpha = 1, \ldots, N_c$ = the number of constituents in the mixture) in the aqueous phase is defined as the sum of all molecular occurrences in a volume $d\mathbf{x}$ (greater than the molecular scale but below the microscale); uncertainty in the point-wise position in the augmented $\mathbf{x}$ space is incorporated by representing this molecular occurrence as a Gaussian distribution of the molecular mass:

$$m^\alpha(\mathbf{x}, t) \equiv \sum_{i=1}^{M} m_i^\alpha \int_{R^{N+1}} \delta(\mathbf{x} - \mathbf{x}^\alpha(\mathbf{X}_i^\alpha, t) - \mathbf{z}) g_1(\mathbf{z})\, dU(\mathbf{z})$$

$$= \sum_{i=1}^{M} m_i^\alpha g_1(\mathbf{x} - \mathbf{x}^\alpha(\mathbf{X}_i^\alpha, t)) \tag{1}$$

where m_i^α is the mass of molecule i of constituent α appearing in the volume represented as $d\mathbf{x}$, g_1 is the Gaussian distribution of unit weight, M is the number of molecules in $d\mathbf{x}$, dU tiles $d\mathbf{x}$, and where $\mathbf{x}^\alpha(\mathbf{X}_i^\alpha, t)$ is the actual coordinate of the molecule $\mathbf{X}_i^\alpha$ according to the motion equation for the center of mass of the molecule (or miniscule). With appropriate parameterization of the Gaussian per molecular characteristics of constituent α, the microscale density m_i^α is smooth in all N + 1 coordinates, although very steep near molecules. Further smoothing constructions may be introduced at larger intermediate scales by reapplication of (1) for index i corresponding to miniscules, for example, sets of molecules grouped by proximity to a local exposure time. This provides a smooth material density in the aqueous phase; physical discontinuities associated with the aqueous-solid phase interface in the $\mathbf{x}'$ space will now be dealt with via conventional volume averaging.

Mixtures of water and certain other dissolved or suspended constituents occurring in a porous medium, where the constituents may interact chemically or biologically, may now be defined in our extended space. Define for each constituent the macroscopic volumetric mass density in the $(\mathbf{x}, t)$ space as an integral over a representative elementary volume in the $(\mathbf{x}', t)$ space:

$$\rho^\alpha(\mathbf{x}, t) \equiv \frac{1}{|\mathrm{REV}'(\mathbf{x}')|} \int_{\mathrm{REV}'(\mathbf{x}')} \chi^w(\mathbf{x}' - \mathbf{y}') m^\alpha(\mathbf{x} - \{\mathbf{y}', 0\})\, d\mathbf{y}' \tag{2}$$

where χ^w is the indicator function equal to unity for $\mathbf{x}' - \mathbf{y}'$ within the aqueous phase and zero within the solid phase, and m^α is the previously defined microscopically variable constituent mass density within the aqueous phase at $\{\mathbf{x}' - \mathbf{y}', x_{N+1}\}$. The local vector $\mathbf{y}'$ spans the volume $\mathrm{REV}'(\mathbf{x}')$. Our use of the discontinuous indicator function here is but one arbitrary choice of observation-weight function; regardless of the continuity of the weight function, ρ^α will be smooth because m^α is smooth [*Cushman*, 1997].

2.3. Kinematics and Mass Balance in the Augmented (x, t) Space

As in analogy to conventional densities, $\rho^\alpha(\mathbf{x}, t)$ is here an approximate (smoothed) mass density that gives at time t the local $\mathbf{x}'$-volume-averaged mass of constituent α per unit volume of (porous media × exposure time) in dimensions $\mathbf{x} = \{x_1, \ldots, x_N, x_{N+1}\}$. With this representation in hand we may proceed with the conventional derivation of mass balance relations in the augmented $(\mathbf{x}, t)$ space via the mechanics of mixtures. Each constituent α is assumed to behave as a continuous material, and the constituent mixture forms overlapping continua of conserved matter. Then we may label miniscule material points of the body of component α distributed in N physical dimensions with the variable $\mathbf{X}^\alpha = (X_1^\alpha, \ldots, X_N^\alpha,$

X^α_{N+1}), assigned as the coordinates in **x** space in some reference configuration of the body. Note that the reference configuration allows cases where X^α_{N+1} is the same for all material points. Motion of the material point labeled $\mathbf{X}^\alpha$ is described formally by the mapping from $\mathbf{X}^\alpha$ and t to the coordinate position **x**, expressed as the function $\mathbf{x}^\alpha(\mathbf{X}^\alpha, t)$. We may define the Lagrangean velocity as the time rate of change of the spatial position of these material particles in the $N + 1$-dimensional **x** space as

$$\mathbf{V}^\alpha(\mathbf{X}^\alpha, t) = \frac{\partial}{\partial t}\mathbf{x}^\alpha(\mathbf{X}^\alpha, t) \tag{3}$$

Now $\mathbf{V}^\alpha$ is the usual Lagrangean velocity vector in N dimensions augmented here with the $N + 1^{\text{th}}$ component of velocity associated with displacements along the generalized exposure-time dimension. The Eulerian velocity is then defined in the usual way per constituent α as

$$\mathbf{v}^\alpha(\mathbf{x}^\alpha, t) = \mathbf{V}^\alpha(\mathbf{X}^\alpha(\mathbf{x}^\alpha, t), t) \tag{4}$$

and $\mathbf{v}^\alpha$ is likewise an $N + 1$-dimensional vector with the first N components corresponding to physical transport velocities and with the $N + 1^{\text{th}}$ component associated with Eulerian transport rate along the generalized exposure-time axis. Formally,

$$v^\alpha_{N+1} = v^\alpha_{N+1}(\mathbf{x}, t) = \frac{\partial}{\partial t}\mathbf{x}^\alpha({\chi^\alpha_{N+1}}^{-1}(\mathbf{x}, t), t)\bigg|_{\mathbf{x}^\alpha} \tag{5}$$

where ${\chi^\alpha_{N+1}}^{-1}(\mathbf{x}, t)$ is the $N + 1^{\text{th}}$ component of the inverse of the motion equation (compare the appendix), giving the material particle label of the $N + 1^{\text{th}}$ dimension X^α_{N+1} corresponding to the reference configuration in the exposure-time dimension, as a function of the material particle position **x** at time t. This definition indicates that the velocity is that of the particle labeled $\mathbf{X}^\alpha$ at the instant it occurs at **x**, and we use this to define the rate at which exposure time increases per unit time as a function of **x** and t.

Three other important properties include the overall mass density

$$\rho \equiv \sum_\alpha \rho^\alpha, \tag{6}$$

the barycentric, or constituent mass-averaged velocity

$$\mathbf{v} \equiv \frac{1}{\rho}\sum_\alpha \rho^\alpha \mathbf{v}^\alpha, \tag{7}$$

and the local mixing velocity

$$\mathbf{u}^\alpha \equiv \mathbf{v}^\alpha - \mathbf{v}. \tag{8}$$

Mixture constituents are identified by the superscript α (= $1, \ldots, N_c$), allowing for both mobile constituents, and immobile constituents that may be associated with the solid or biophase if such phases can be treated as fully and immediately permeable and volumeless. A more rigorous foundation would accommodate multiple (macroscopic) phases in the index α. For simplicity of the development and with our focus on the aqueous phase and the dissolved or suspended components within it, we restrict ourselves to a single phase, with the corresponding mass densities defined as overlapping continua via the REV′ average in (2). With this restriction we exclude the occurrence of discontinuous surfaces within any material body making up the mixture, and so we may express the global mass balance for the mixture appearing in the volume $V(t)$ as

$$\sum_\alpha \left(\frac{d}{dt}\int_{V^\alpha(t)} \rho^\alpha\, d\mathbf{x}\right) = 0, \tag{9}$$

where $V^\alpha(t)$ is an arbitrary but continuous subdomain of the $N + 1$-dimensional space and where the differentiation is total because the argument is exclusively a function of time. From this global mass balance statement (9) we derive the local balance equations in the $(\mathbf{x}, t)$ space in fashion exactly analogous to the classical way in the $(\mathbf{x}', t)$ space (Appendix):

$$\frac{\partial}{\partial t}\rho^\alpha + \nabla'\cdot(\mathbf{v}'\rho^\alpha) - \nabla'\cdot(\mathbf{D}'\cdot\nabla'\rho^\alpha) + \frac{\partial}{\partial x_{N+1}}(v^\alpha_{N+1}\rho^\alpha) = e^\alpha \tag{10}$$

The reactions term e^α in (10) represents the material mass density rate of transformation due to a number N_r of reactions, and is the α^{th} term of the vector formed as the inner product of the (N_r by N_c) reactions stoichiometry matrix **S**, transposed and the (N_r by 1) reaction rate vector χ. More detail on the reactions formulation is given by, for example, *Lichtner* [1996]; here χ expresses reaction rates that are exclusively kinetically controlled and written in terms of mass densities as opposed to solute concentrations. That is,

$$\frac{d\rho^\alpha}{dt}\bigg|_{RXN} = \sum_{l=1}^{N_r} S^{\alpha,l}\chi^l.$$

We now differentiate aqueous-volumetric mass concentrations from the bulk phase mass density by introducing the porosity as the aqueous volume fraction of the $\mathbf{x}'$ space (porosity more rigorously arises as a volume fraction when macroscopic multiple phases are accounted).

$$c^\alpha(\mathbf{x}, t) \equiv \rho^\alpha(\mathbf{x}, t)/\theta(\mathbf{x}', t) \tag{11}$$

For simplicity, we will usually assume porosity to be constant of both $\mathbf{x}'$ and t. Note that in general the reactions terms that appear in e^α originally as functions of the densities ρ^β (where β indexes the N_c constituents as does α) are now in terms of the product θc^α. Only when the porosity is constant or the reactions in the transformation of constituent α are first order can the whole system be put in terms of c^α. In any case, however, we may consistently define a new reactions term $r^\alpha \equiv \theta^{-1}e^\alpha$ and recast (10) as

$$\frac{\partial}{\partial t}c^\alpha + \nabla'\cdot(\mathbf{v}'c^\alpha) - \nabla'\cdot(\mathbf{D}'\cdot\nabla'c^\alpha) + \frac{\partial}{\partial x_{N+1}}(v^\alpha_{N+1}c^\alpha) = r^\alpha \tag{12}$$

Equation (12) can be recognized as the usual convection dispersion equation with reaction term and with a new term reflecting possibly nonuniform and transient constituent displacement in the x_{N+1} dimension, that is, generalized exposure time. The exposure-time velocity v^α_{N+1} is the rate of change of a material point location on the exposure-time axis x_{N+1} per unit time defined by (5). This velocity may be a constant; in the groundwater age problem it is unity (and we use equation (10) in general). It may be expressed as a function of $\mathbf{x}'$ only, reflecting exposure of a solute to some reactive mineral as in the presence of chemical heterogeneity. It may also arise as a function of $\mathbf{x}'$ and t, as when the exposure time is coupled to the presence of another aqueous species as in a multicomponent reactive transport system (e.g., biodegradation). Finally, the exposure-time velocity may be in general dependent on the entire space $(\mathbf{x}, t)$ including the exposure-time coordinate x_{N+1}; however, for utilitarian reasons we will usually assume this is not the case. It is important to note also that the reactions term is specifiable as a general function of both the concentrations c^α and of the spatial coordinate $\mathbf{x}'$ and of time t, and now also of the exposure-time coordinate. This affords the use of equations of the form of (12) when the system involves distributions that matter to the reactions. Examples include distributions of microbes over contiguous time of attachment to solid surfaces, which may dictate detachment kinetics [*Ginn et al.*, 1998], or distributions over molecular weight of components of natural organic matter which may induce hysteresis in sorption [*Van der Weerd et al.*, 1998].

Equation (10) or in simpler form (12) is the primary result of this article. It arises from extending the classical derivation of local mass balance for transport in porous media into the new space $(\mathbf{x}, t)$, under the usual continuum-mechanical assumptions of continuity of the material in the new space, impenetrability of a material with itself (allowing for overlapping continua of the mixture as a whole), and the existence of an REV in $\mathbf{x}'$ for averaging that is invariant in the new space. The resulting balance law may be viewed as an evolution equation for a distribution (as opposed to a mass concentration in a spatial volume) undergoing fate and transport in porous media. Other examples of distributional evolution equations have been derived as particle-population balance laws [*Randolph*, 1964; *Hulbert and Katz*, 1964] that are extensions of the Danckwertz-Zweiterling treatment of segregation in reactors [e.g., *Danckwertz*, 1953] to transient conditions [*Chen*, 1971]. Such applications in chemical engineering typically involve reactions within purely aqueous-phase mixtures that take place within reactors so that the spatial dependencies (e.g., the transport operator) are eliminated by integration [e.g., *Chen*, 1971]. Here the distribution evolution equation represents the time-dependent and nonuniform transport in the spatial dimensions of heterogeneous porous media and the dimension of exposure time, and includes multicomponent reactions involving both aqueous and solid phases occurring in hydrogeological systems.

More attention needs to be paid to conditions for differentiability in the exposure-time dimension x_{N+1}, which has been assumed almost everywhere through the construction of the predensity in (1) that is smoothed on the molecular scale. For instance bio-colloidal suspensions involve material mass grouped into literal microcorpuscles each with well-defined histories, thus requiring a larger-scale smoothing hypothesis. The sharpness of the distribution over exposure time may be ameliorated when solute-flux averaging [e.g., *Dagan*, 1989; *Jury and Roth*, 1990] is applied to solutes governed by (12). Solute-flux averaging via the probabilistic approach describes concentrations on the supra-REV scale, and thus may smooth various potentially sharp exposure-time distributions into an exposure-time distribution characterizing solutes arriving at a water table or other large-scale control plane. Such averaging is beyond the present scope: here mixtures exhibit distributions over exposure time that are pointwise defined at the REV scale.

We may treat the new first-order term in the transport equation in analogy to a physical convective process, grouping this term with the physical convection term $\nabla' \cdot (\mathbf{v}'c^\alpha)$ in the definition of the secondary characteristics of the transport in the new space. That is, we may express the first-order terms of (12) taken together as $\nabla \cdot (\mathbf{v}c^\alpha)$, where $\mathbf{v} = \{\mathbf{v}', v^\alpha_{N+1}\}$, and determine from this $N + 1$-component velocity field the characteristic paths along which boundary information may propagate into the domain, just as is done for physical velocity fields in the $(\mathbf{x}', t)$ space. The field $\mathbf{v}$ has the important property that for $v^\alpha_{N+1} = v^\alpha_{N+1}(\mathbf{x}, t) = v^\alpha_{N+1}(\mathbf{x}', t)$; that is, when the exposure-time velocity does not depend on x_{N+1}, the divergence of the $N + 1$-dimensional velocity field is given by the divergence of the N-dimensional physical velocity field. Therefore motion which is isochoric ($\nabla \cdot \mathbf{v}' = 0$) in $\mathbf{x}'$ is in this case isochoric in $\mathbf{x}$ as well. Note also that this velocity field combines barycentric components that are constituent-invariant, with the $N + 1^{\text{th}}$ component that is constituent particular, and so in the general case the characteristics for convective transport are constituent-dependent. A practical sidelight of this formulation is that one may augment $\mathbf{D}'$ with another dimension (add a column and a row) of artificial dispersion coefficients involving the x_{N+1} direction (these dispersion coefficients may be zero) and express (12) in exact analogy to a convection-dispersion equation, for example,

$$\frac{\partial}{\partial t} c^\alpha + \nabla \cdot (\mathbf{v}c^\alpha) - \nabla \cdot (\mathbf{D} \cdot \nabla c^\alpha) = r^\alpha \tag{13}$$

which for specified $\mathbf{v}$ and $N < 3$ may be solved using conventional solute transport codes for $N + 1$ spatial dimensions. The complexity introduced by the additional dimension is in the form of constituent-dependent convections in the new dimension, which, depending on the nature of the problem, may involve sharply changing exposure-time velocities. This might be more efficiently approached numerically via Lagrangian (e.g., particle tracking, streamtube) extensions of transport solvers into the exposure-time dimension, as opposed to via Eulerian discretization schemes, especially for $N = 2$ or 3.

In the general formulation and in the examples below, there is no diffusion/dispersion in the exposure-time dimension. This may arise in other formulations by at least two means. First, if a material exhibits particle-scale heterogeneity in its intrinsic exposure-time velocity, then convective displacement in the exposure-time dimension may exhibit multiple individual velocities distributed about a mean, yielding a dispersive-like transport superposed on the mean exposure-time displacement. Such an instance which is akin to kinematic dispersion in porous media is suggested in example 3 below. Second, if material can communicate information (here, exposure time) amongst its spatially neighboring particles, then material may "diffuse" in the exposure-time dimension. Tracking such diffusions would require constitutive theories (analogous to Fick's law) for expressing the resulting diffusive flux. A starting point for developing such constitutive laws is via the definition of the material-diffusive velocity in equation (A10) of the appendix.

Boundary and initial condition information in a given application are to be handled by extending the specification of solute concentrations along the space (initial conditions) and time (boundary conditions) axes, to include their distributions along the exposure-time axis as well. Since the effect of the extension on the original differential equation of transport is to add convection in the $N + 1^{\text{th}}$ dimension, it is required that the boundary and initial condition specification provide solution data for all of the characteristics (trajectories) in the augmented $N + 1$-dimensional $\mathbf{x}$ space. Because the exposure-time velocities can vary per component, the characteristics in the augmented space may also; however, projections of these characteristics onto the N-dimensional $\mathbf{x}'$ space yields the (unique) original characteristics in the exclusively spatial coordinates. One must also remember that the dependence of transport on x_{N+1} is not of course associated with a physical departure of the characteristics, and when accounting processes such as reactions that depend on material overlap, one must typically project material densities onto the $(\mathbf{x}', t)$ space. Such projections are defined $c^{\alpha^T}(\mathbf{x}', t) \equiv \int_{-\infty}^{\infty} c^{\alpha}(\mathbf{x}, t)\, dx_{N+1}$. This will be illustrated in the third of the following three examples.

It is important to note that because the material concentrations c^{α} are now distributed over an additional dimension, their gradients in the N true spatial dimensions are not the same as the gradients of the projections of the concentrations in those dimensions. That is, in general $[\nabla' c^{\alpha^T}(\mathbf{x}', t)]_i \neq [\nabla c^{\alpha}(\mathbf{x}, t)]_i$ for $i = 1, \ldots, N$. Consequently, the convective and dispersive fluxes in the (real) spatial dimensions actually change upon the introduction of the new exposure-time dimension. For illustration, consider the conventional convective-diffusive transport of a square pulse of material in a uniform one-dimensional flow field, which at some time t exhibits the classical profile along the spatial coordinate x_1 as shown in Figure 1a. The center of mass of the profile is at some spatial coordinate $x_1' = vt$. Now suppose that the exposure time of the material is considered and that the first half of the influent pulse has exposure time x_2' and the second half has exposure time x_2''. For simplicity, suppose further that the exposure time velocity is zero everywhere. The distribution of mass then occurs over both the x_1 (physical) and x_2 (exposure time) axes as illustrated in Figure 1b. At time t, material with exposure time equal to x_2' will appear as the (lighter gray) half pulse at coordinate $x_2 = x_2'$, and material with exposure time equal to x_2'' will appear as the (darker gray) half pulse at coordinate $x_2 = x_2''$ as depicted in Figure 1b. (We assume some appropriately smoothed Dirac-type densities at the two locations in x_2, as discussed in the derivation section.) Because of the accounting of the distribution over the exposure-time axis, the densities in the model correspond to those depicted in Figure 1b and exhibit the gradients shown there as well. Consequently, spatial diffusive/dispersive fluxes will occur at spatial location x_1', leading to a mixing of material from the two different exposure times in the neighborhood of the spatial location x_1. Thus the projection of the physically observable material densities onto the space axis x_1 will exhibit overlap of materials with different exposure times as shown in Figure 1c, and the measureable composition of the profile will appear as shown in Figure 1d. There, the profile appears as conventionally depicted in Figure 1a, but now the gradation in grayscale shows the corresponding mixing in exposure times of the diffusing materials. This mixing occurs in real systems, but is not accounted in the conventional (purely spatial-temporal) model which does not distinguish mass distribution over the exposure-time axis and so does not account for density gradients that appear when such distinctions are maintained. However, one must take care that the constitutive theory used to specify the diffusive/dispersive flux honors the physics of the true mixture, which may depend on how different exposure times affect the behavior of different materials.

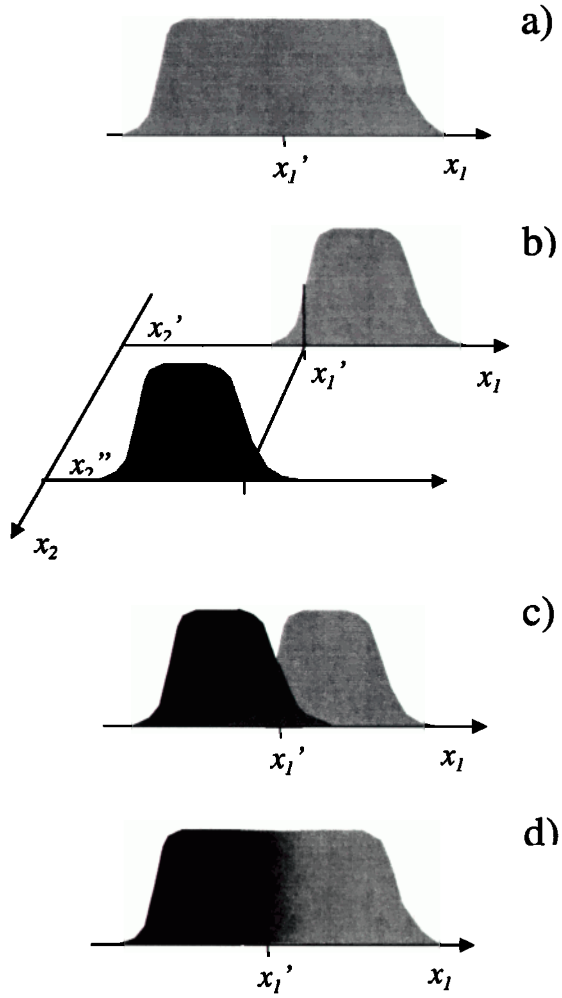

Figure 1. (a) Profile of conventional solute pulse undergoing convective-dispersive transport in one spatial dimension, x_1; (b) pulse of Figure 1a expressed as two component halves, each with distinct exposure time measured on the x_2 axis; (c) projection (superposition) of the two half pulses of Figure 1b onto the x_1 axis; (d) observed pulse profile exhibiting gradation in (mixed) exposure time.

3. Example Applications

We apply the general balance equation established above to develop particular evolution equations for materials undergoing transport and/or reaction processes where exposure time is important. These examples, already noted, include the evolution of the distribution of groundwater age, aqueous-solid phase reaction in the presence of a large-scale heterogeneity in mineralogy, and aerobic biodegradation of a solute by microorganisms that exhibit metabolic lag.

3.1. Example 1: A Governing Equation for the Distribution of Groundwater Age

The need for improved quantitative methods for simulating measureable groundwater ages as opposed to purely kinematic age (mixing ignored) is comprehensively discussed by *Campana* [1987] and by *Varni and Carrera* [1998]. The latter authors extend the work of *Goode* [1996], where the governing equation for the mean groundwater age is provided, to develop an equation for a particular groundwater age (via recharge time

τ). The authors use this basis to devise a set of recursive moment equations which can be solved sequentially to determine the moments of groundwater age. However, as also pointed out by *Campana* [1987], use of age moments may not adequately describe the important age densities represented in a given sample because the shape of the underlying distribution is generally not known. *Campana* [1987] utilizes the same particle-population notions embraced here to develop a discrete-state compartment model that is restricted to steady state conditions and to highly simplified "mixing-cell" representations of the aquifer. The present article generalizes these previous studies by providing a single equation for the entire distribution of groundwater age in a general framework for simulating flow in multidimensional heterogeneous porous media under transient conditions.

Equation (10) describes the evolution of in particular the $\alpha = w$ [bulk-volumetric water mass density] constituent and may be exploited to generate equations governing not only the mean and other moments of groundwater age but in fact the complete distribution of groundwater age at a point $(\mathbf{x}', t)$. We define groundwater age as the (exposure) time that a continuum particle of water spends in the ground. The rate of increase of exposure time per unit time while in the ground is then clearly unity, and so we take $v_{N+1}^w = 1$ everywhere in the flow domain. We suppose that aging of water during its traversal of other parts of the ground that are not part of the simulated flow domain is accounted through specification of boundary and initial conditions in $(\mathbf{x}, t)$ where as previously defined for N physical dimensions, $\mathbf{x} = (\mathbf{x}', x_{N+1}) = (x_1, \cdots, x_N, x_{N+1})$ and x_{N+1} is the dimension of generalized exposure time, or in this case, age. Suppose that a solution to the physical flow problem provides the physical velocity field which is steady, $\mathbf{v}'(\mathbf{x}')$. Then the governing equation for the distribution of groundwater over the physical coordinates $\mathbf{x}'$ within domain Ω and the age dimension x_{N+1} is given immediately by (10):

$$\frac{\partial}{\partial t}\rho^w + \nabla'\cdot(\mathbf{v}'\rho^w) - \nabla'\cdot(\mathbf{D}'\cdot\nabla'\rho^w) + \frac{\partial}{\partial x_{N+1}}(\rho^w) = e^w \tag{14}$$

with appropriate boundary conditions ρ^w or $\nabla\rho^w \cdot \mathbf{n}$ for all time at $\mathbf{x} = \mathbf{x}_0$ (including dimension x_{N+1}) in $\partial\Omega$ and initial concentrations ρ^w everywhere in $\mathbf{x}$ at some t^0. In (14), e^w is the source of water at physical location $\mathbf{x}'$ with age specified as x_{N+1}, and the second-order term represents self-diffusion of water densities in the physical $\mathbf{x}'$ coordinates and allows mixing of waters of various x_{N+1}. In the steady state case, (14) becomes

$$\frac{\partial\rho^w}{\partial x_{N+1}} + \nabla'\cdot(\mathbf{v}'\rho^w) - \nabla'\cdot(\mathbf{D}'\cdot\nabla'\rho^w) = e^w \tag{15}$$

which is of the form of the conventional transient convection-dispersion transport equation with reaction term e^w. Given boundary condition data ρ^w or $\nabla\rho^w \cdot \mathbf{n}$ for all exposure times x_{N+1} at $\mathbf{x}' = \mathbf{x}_0'$ (not including dimension x_{N+1}) in $\partial\Omega'$ and initial concentrations ρ^w everywhere in $\mathbf{x}'$ at some x_{N+1}^0, equation (15) may be solved for the complete distribution of groundwater age at any point in physical space $\mathbf{x}'$ coordinates at steady state conditions.

We may analyze (14) further to determine particular evolution equations for various moments of the distribution of groundwater age. Integrating (14) over x_{N+1} gives the equation for the zeroth moment of age, for example, the water balance equation:

$$\frac{\partial}{\partial t}\rho^{w^T} + \nabla'\cdot(\mathbf{v}'\rho^{w^T}) - \nabla'\cdot(\mathbf{D}'\cdot\nabla'\rho^{w^T}) = e^{w^T} \tag{16}$$

(Under the integration the last term on the left-hand side of (14) vanishes everywhere in Ω except at the boundaries, which are carried by the boundary conditions, because the aging velocity is everywhere positive.) Ignoring the self-diffusion which mixes waters, that in (16) are indistinguishable (formally, the local mixing velocity defined in (8) is zero in (16)), and using the definition of porosity given by (11) for the bulk-volumetric water density

$$\rho^w(\mathbf{x}, t) \equiv \theta(\mathbf{x}', t)c^w(\mathbf{x}, t) \tag{17}$$

with (here a small departure from the superscript T notation for consistency) ρ representing the total aqueous-volume water density; that is,

$$\rho^{w^T}(\mathbf{x}', t) = \theta(\mathbf{x}', t)\int_0^\infty c^w\, dx_{N+1} \equiv \theta(\mathbf{x}', t)\rho(\mathbf{x}', t), \tag{18}$$

yields from (16)

$$\frac{\partial\theta\rho}{\partial t} + \nabla'\cdot(\mathbf{q}'\rho) = e^{w^T} \tag{19}$$

where $\mathbf{q}' \equiv \mathbf{v}'\theta$. For incompressible flow and steady porosity or water content we obtain the usual equation for steady flow with source term

$$\nabla'\cdot\mathbf{q}' = e^{w^T} \tag{20}$$

Similarly, we may obtain the first moment equation from (14) by multiplying (14) by age x_{N+1} and integrating over age x_{N+1}, obtaining

$$\frac{\partial}{\partial t}\theta\bar{a} + \nabla'\cdot(q'\bar{a}) - \nabla'\cdot(\mathbf{D}'\cdot\nabla'[\theta\bar{a}]) + \theta\int_0^\infty x_{N+1}\frac{\partial c^w}{\partial x_{N+1}}\, dx_{N+1} = \int_0^\infty x_{N+1}e^w\, dx_{N+1} \tag{21}$$

where we have again used (17) to define porosity, as above $\mathbf{q}' \equiv \mathbf{v}'\theta$, and where we define $\bar{a}(\mathbf{x}', t) \equiv \int_0^\infty x_{N+1}c^w(\mathbf{x}, t)\, dx_{N+1}$. The integral on the left-hand side of (21) reduces via integration by parts as follows

$$\int_0^\infty x_{N+1}\frac{\partial c^w}{\partial x_{N+1}}\, dx_{N+1} = -\int_0^\infty c^w\, dx_{N+1} + x_{N+1}c^w]_0^\infty$$

$$= -\rho(\mathbf{x}', t) + 0 = -\rho(\mathbf{x}', t)$$

and so we obtain

$$\frac{\partial}{\partial t}\theta\bar{a} + \nabla'\cdot(q'\bar{a}) - \nabla'\cdot(\mathbf{D}'\cdot\nabla'[\theta\bar{a}]) - \theta\rho = F \tag{22}$$

where $F \equiv \int_0^\infty x_{N+1}e^w\, dx_{N+1}$. For constant and steady porosity θ and total aqueous-volume water density ρ, we may normalize by these quantities to obtain

$$\frac{\partial A}{\partial t} + \nabla' \cdot (\mathbf{v}'A) - \nabla' \cdot (\mathbf{D}' \cdot \nabla' A) - 1 = [\theta\rho]^{-1}F \tag{23}$$

where

$$A \equiv \frac{\bar{a}}{\rho} = \frac{\int_0^\infty x_{N+1}c^w \, dx_{N+1}}{\int_0^\infty c^w \, dx_{N+1}} \tag{24}$$

is the normalized mean groundwater age, that is, the first moment of the c^w distribution over x_{N+1}. The same form of (23), but with different underlying definitions, appears in the work of *Goode* [1996], and in the work of *Varni and Carrera* [1998], and the steady state version appears in the work of *Spaulding* [1958]. Equations (19) and (23) are the governing equations for the evolution of the zeroth and first moments of the age distribution, respectively. The equation governing the evolution of the complete age distribution, (14), is to the author's knowledge novel.

3.2. Example 2: A Governing Equation for the Distribution of Reaction Times

Chemical heterogeneity in solid-phase mineralogic properties is a potentially significant factor in the fate and transport of solutes that interact with the solid-phase through sorption, surface complexation, or other mass transfer processes. In some geologies the spatial variability of the mineralogic control on reactions may be characterized as a binary deterministic space function. For example, *Sturgeon et al.* [1998] describe the occurrence of mineralogic (ferric- and manganese-oxyhydroxide) heterogeneities and their spatial correlation to different lithofacies in a glacio-fluvial depositional aquifer. In this case we may define an approximate macroscale deterministic function of space, η, that indicates the presence or absence of a mineral, as follows:

$$\eta(\mathbf{x}') \approx \begin{cases} 1 & \text{reactive mineral appears at } \mathbf{x}' \\ 0 & \text{otherwise} \end{cases} \tag{25}$$

In a more careful description, η will arise as an REV$'$-averaged mineral indicator function that will be more smooth. For this example we will assume that the mineral heterogeneity appears only at scales that are very large with respect to the REV$'$ averaging volume, so that the macroscale η may be approximated as an indicator function.

One may conceptualize more general continuous function representations of the mineralogy that reflect the density of reactive material or the number of reactive (e.g., sorption) sites per local macroscopic volume. In the latter case such a function might take the form

$$\zeta(\mathbf{x}') \equiv \frac{1}{|\mathrm{REV}'(\mathbf{x}')|} \int_{\mathrm{REV}'(\mathbf{x}')} [1 - \chi^w(\mathbf{x}' - \mathbf{y}')] n^\alpha(\mathbf{x}' - \mathbf{y}') \, d\mathbf{y}' \tag{26}$$

where χ^w is the indicator of the aqueous phase introduced previously, n^α is the microscale number density of sorption sites per solid volume, and then ζ is the macroscale bulk-volumetric density of sorption sites that ranges continuously from zero to some maximum. We will return to this form at the end of the example.

It is often useful to know the length of time that a given solute is exposed to such reactive zones during transport because in the case of nonequilibrium reactions, it is the time of exposure (i.e., exposure times) rather than the spatial extents of the reactive zones that can be used to quantify the amount of mass transformation due to the reaction. This fact is the basis for the upscaling of transport with kinetically controlled reactions by reformulation of transport in terms of travel time [e.g., *Lassey*, 1988; *Simmons et al.*, 1995; *Dagan and Cvetkovic*, 1996], but these approaches require the transport to be purely convective and (more to the point) that the immobile phase reactivity be uniformly distributed or in some cases [e.g., *Simmons et al.*, 1995] specified via a joint solute flux distribution with travel time. In the absence of this information these methods are generally inapplicable in the presence of either significant chemical heterogeneity or significant diffusive/dispersive fluxes or, as is generally the case in natural porous media, both.

Thus we are faced with the same question as in the groundwater age problem above; that is, how do material age distributions evolve via convective/dispersive transport, but now only certain parts of the aquifer (those where reactive immobile phase exists) count. In the general case of multidimensional convective-dispersive transport with significant pore-scale mixing in nonuniform velocity fields, solutes at any given point in $\mathbf{x}'$ and t will exhibit a distribution of exposure times to such immobile reactive zones, or more simply, reaction times. With conventional models it is only possible to determine the effects of such reaction times by actually solving the complete reactive transport model itself. With equation (13) it is possible to determine the approximate distribution of reaction times by solving (13) in $N + 1$ dimensions for a passive surrogate tracer under the same physical transport and boundary/initial condition specification, for example, with the reactions term set equal to zero, and with the reactions-time velocity v^α_{N+1} set equal to $\eta(\mathbf{x}')$

$$\frac{\partial}{\partial t} c^\alpha + \nabla \cdot (\mathbf{v}c^\alpha) - \nabla \cdot (\mathbf{D} \cdot \nabla c^\alpha) = 0 \tag{27}$$

where $\mathbf{v} = \{\mathbf{v}', \eta(\mathbf{x}')\}$ and where $\mathbf{D}$ is as defined in (13). Since (27) is in the form of a conventional convection-dispersion equation in $N + 1$ dimensions, it may be solved using commonly available techniques for $N < 3$ dimensions. Note that the distribution of surrogate solute over the reaction-time coordinate at $\mathbf{x}'$, t will not reflect exactly the distribution of the reacting solute due to the solute removal due to the reaction kinetics itself, and the utility of this approach in determining reaction-time distributions will depend on the scale of the chemical heterogeneity, the form of the transformation kinetics, and the Peclet number for the transport, in general. Plate 1 shows an example where the trajectory of vertical piston flow of a solute infiltrating through a mineralogically heterogeneous solid phase is expressed as a trajectory in the augmented vertical-space and exposure-time dimensions. The distribution of cumulative reaction time experienced by solutes undergoing vertical transport in unsaturated media may in principle be addressed in this fashion, either with or without the solute-flux averaging inherent in available streamtube models.

In the case where it is useful to monitor the distribution of exposures to total reactive mineral density, or to sorption site number density, one may adopt a continuous rather than indicator measure of the exposure speed, such as $v^\alpha_{N+1} = \zeta(\mathbf{x}')$

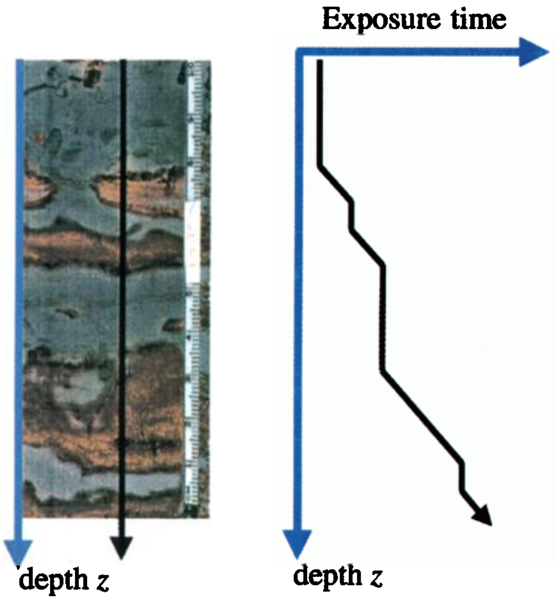

Plate 1. Simplified, purely convective steady vertical flow (piston flow) is depicted by the arrow tracing solute trajectory through a chemically heterogeneous (colored areas represent high iron- or manganese-oxide content) section. The change in the reaction-time coordinate of a solute parcel is illustrated by the trajectory (on the right) in the plane constructed of the vertical spatial axis and the exposure-time axis, where reaction time is only accrued during transport through the metal-oxide zones shown in the plate.

as defined in (26). In this way the exposure speed can be made to vary proportionally to the density of reactive surfaces. Application of (27) in a Monte Carlo sense, as well as stochastic analysis [e.g., *Espinoza and Valocchi*, 1997], may be useful when statistical descriptions of the $\zeta(\mathbf{x}')$ or to $\eta(\mathbf{x}')$ fields are available.

3.3. Example 3: Governing Equations for Biodegradation With Metabolic Lag

Another example where the distribution of exposure time of one material to another dissolved material is important appears in the in situ aerobic biodegradation of a convecting solute contaminant by native microbes that partition between solid and aqueous phases in the subsurface. Suppose that a dissolved substrate (the electron donor), with concentration c^s, is degraded in the presence of dissolved oxygen, with concentration c^0 (the terminal electron acceptor for the degradation), by microorganisms that partition kinetically between the aqueous phase, m_m, and the solid phase, m_ι. The biochemistry underlying the canonical reaction system associated with these coupled processes is established in the bioremediation literature [see, e.g., *Murphy et al.*, 1997, and references therein] and will not be detailed here beyond a summary. The primary assumptions are the following: the rates of substrate transfer into cellular membranes are rapid relative to the rate of degradation, so that the degradation rate is governed by the rate of metabolic activity; the metabolic activity is limited by availability of oxygen and substrate according to dual-Monod kinetics; the aqueous and attached microbes are volumeless phases, fully penetrated by the aqueous media; microbial decay and microbial maintenance respiration are insignificant; the microbes partition between the aqueous and solid phases according to reversible first-order kinetics that is invariant with metabolic activity, and the degradation rate is the same for both phases. Finally, suppose that there is significant lag in the induction of metabolic activity.

Here we focus on the phenomenon of metabolic lag. The transition from oligotrophic to eutrophic conditions that arises when native, resting-state microbes encounter a moving plume of substrate contaminant is often associated with a time lag in the development of the microorganisms' capability to degrade the substrate. Lag occurs because the resting-state organism has not yet established the enzymatic structures necessary for the degradation. When the microbes occur as a permanently immobile phase in the porous matrix, it is possible to incorporate this lag in metabolic potential in the kinetics of degradation [e.g., *Wood et al.*, 1995]. This is accomplished by multiplying the overall rate of reaction by a factor, $\lambda(c'(\mathbf{x}', t))$, that is zero for oligotrophic ($c = 0$ for some time) conditions and rises to unity some lag time after the appearance of substrate above some threshold level ($c > c_{\text{critical}}$). The behavior of this functional is illustrated in Figure 2a for the local substrate concentration history depicted there. This Figure 2a shows a piecewise linear λ as in the work of *Wood et al.* [1995]; this particular form is an empiricism, and other approximate functions may be devised. The term λ is a functional dependent on the history of "local" (in $\mathbf{x}'$) concentrations of substrate and describes the metabolic state of the local microorganisms. This approach suffices when the microbes are immobile because in this case local has an unambiguous definition. Then it is possible to measure the time of exposure of an attached microbe to a dissolved and transported substrate and to define a useful λ.

However, in the presence of transport and nonequilibrium partitioning of microbes to and from the immobile phase, this approach is incapable of representing the effect of a lag in metabolic potential because the microbes at any point in space and time in general reflect a mixture of microbes from all points upstream and thus a distribution of metabolic potentials. That is, the microbes at $(\mathbf{x}', t)$ will be distributed over a generalized exposure-time (to substrate concentrations above the threshold) dimension. As prerequisites for the application of (12) to this phenomena, we define the exposure-time velocities for the mobile and immobile microbes, $v_{N+1}^{m_m}$ and $v_{N+1}^{m_\iota}$, and describe the metabolic potential function, $\lambda(x_{N+1})$, that we will use instead of the previously described functional.

The rate at which mobile and immobile microbes "move" along the exposure-time axis is defined as $v_{N+1}^{m_m}$ and $v_{N+1}^{m_\iota}$, respectively. There are a number of feasible definitions for these velocities, each of which infers its own constitutive assumptions regarding the microbiological processes. For instance, here we assume independence between a microbes' propensity for partitioning and its time of exposure to substrate (so that the partitioning kinetics are invariant with x_{N+1}^{α}), and between the microbes' phase and its exposure speed. Thus $v_{N+1}^{m_m} = v_{N+1}^{m_\iota}$ and depends only on the presence or absence of total local substrate, $c^{s^T}(\mathbf{x}', t) = \int_0^\infty c^s(\mathbf{x}, t)\, dx_{N+1}$ (this integral projects the total substrate concentration from $\mathbf{x}$ to $\mathbf{x}'$). Under these assumptions a natural choice is to take $v_{N+1}^{m_m}(\mathbf{x}', t) = v_{N+1}^{m_\iota}(\mathbf{x}', t) = 1$ for total local substrate concentrations $c^{s^T}(\mathbf{x}', t) > c^{s^T}_{\text{critical}}$, and 0 otherwise. That is, $v_{N+1}^{m_\iota}(\mathbf{x}', t) = v_{N+1}^{m_m}(\mathbf{x}', t) = H(c^{s^T}(\mathbf{x}', t) - c^{s}_{\text{critical}})$ where H is the Heaviside step function. A smoothed approximation of the Heaviside that may be useful in numerical solutions is

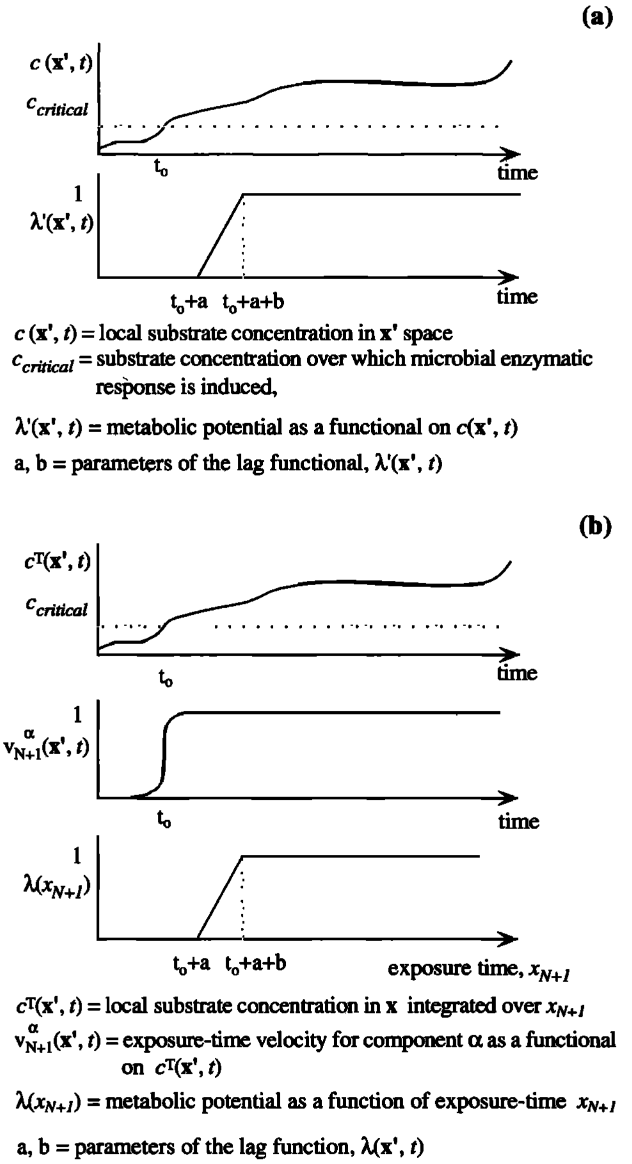

Figure 2. (a) Top figure shows an example history of local resident concentration of substrate at some point $\mathbf{x}'$ in the subsurface as a function of time; the bottom figure illustrates the value of the metabolic potential functional for attached (solid phase) microorganisms that are in a resting state at time prior to time t_0. The induction of an enzymatic response begins after lag time a since local substrate exceeds the threshold value c_{critical}, and the ramp-up period to full metabolic potential occurs over time lag b. (b) Top figure shows the same concentration history as depicted in Figure 2a, however now expressed as the projected total concentration integrated over the exposure-time dimension; the second figure shows the corresponding value of the exposure-time velocity v^{α}_{N+1} at that same $\mathbf{x}'$ as a function of time; the third figure shows the same response of the metabolic potential, but now expressed as a function of the independent exposure-time coordinate x_{N+1}.

$$H'(y) \equiv \frac{1}{2}\left[\frac{y}{|y| + \varepsilon} + 1\right]$$

where ε is a positive smoothing parameter.

For the immobile microbe density at the spatial point $\mathbf{x}'$ and generalized exposure time x_{N+1} and time t, the metabolic potential of these organisms is given immediately by the knowledge of how long they have been exposed to substrate; this in turn is given directly by the x_{N+1} coordinate of the density. Thus the metabolic potential of microbes at $\mathbf{x} = \{\mathbf{x}', x_{N+1}\}$ is given as a simple function (not functional) $\lambda(x_{N+1})$ as depicted in Figure 2b. This formulation also relies on the assumptions that exposure to substrate is cumulative, no matter how short the individual exposure events are, and that the microbes do not return to a resting state. The former is unrealistic but in steady flow with contiguous contaminant plumes should not incur significant error. These conditions are adopted for simplicity; more detailed definitions of the exposure-time velocities can be devised to handle more general cases.

With these preliminaries in hand we can proceed to apply (12) to write balance equations for this system. Taking $\nabla \cdot \mathbf{v}' = 0$, $v^{s}_{N+1} = v^{o_2}_{N+1} = 0$, $v^{m_m}_{N+1}$ and $v^{m_i}_{N+1}$ as defined above,

$$\frac{\partial}{\partial t} c^{s} + \mathbf{v}' \cdot \nabla' c^{s} - \nabla' \cdot \mathbf{D}' \cdot \nabla' c^{s} = r^{s}$$

$$\frac{\partial}{\partial t} c^{o_2} + \mathbf{v}' \cdot \nabla' c^{o_2} - \nabla' \cdot \mathbf{D}' \cdot \nabla' c^{o_2} = r^{o_2}$$

$$\frac{\partial c^{m_m}}{\partial t} + \mathbf{v}' \cdot \nabla' c^{m_m} - \nabla' \cdot \mathbf{D}' \cdot \nabla' c^{m_m} + H(c^{s^T} - c^{s}_{\text{critical}}) \frac{\partial c^{m_m}}{\partial x_{N+1}} = r^{m_m} \tag{28}$$

$$\frac{\partial c^{m_i}}{\partial t} + H(c^{s^T} - c^{s}_{\text{critical}}) \frac{\partial c^{m_i}}{\partial x_{N+1}} = r^{m_i}$$

In analogy to conventional dual-Monod kinetics for simplified aerobic biodegradation systems [e.g., *Murphy et al.*, 1997], the growth rate is limited by the total available mass concentrations of substrate, $c^{s^T}(\mathbf{x}', t) = \int_0^\infty c^{s}(\mathbf{x}, t)\, dx_{N+1}$, and of oxygen, $c^{o^T}(\mathbf{x}', t) = \int_0^\infty c^{o}(\mathbf{x}, t)\, dx_{N+1}$, via conventional dual-Monod kinetics with a first-order dependence on biomass, and a metabolic potential factor $\lambda(x_{N+1})$. Under these conditions the reaction system is written as follows:

(R1)

$$\frac{1}{Y} s + F \frac{1}{Y} O_2 \overset{\text{lag}}{\Rightarrow} m_m + CO_2^{*} \quad \text{biodegradation by aqueous } (m) \text{ microbes}$$

(R2)

$$\frac{1}{Y} s + F \frac{1}{Y} O_2 \overset{\text{lag}}{\Rightarrow} m_i + CO_2^{*} \quad \text{biodegradation by attached } (i) \text{ microbes}$$

(R3) $m_m \Leftrightarrow m_i$ phase partitioning by microbes

where the starred quantities are unaccounted decay products. The factors preceding the species are the stoichiometric coefficients. The overall rates of the reactions are given by

Reaction 1

$$r_1 = \mu c^{m_m}\left[\frac{c^{s^T}}{c^{s^T} + k_s}\right]\left[\frac{c^{o^T}}{c^{o^T} + k_o}\right]$$

Reaction 2

$$r_2 = \mu c^{m_i}\left[\frac{c^{s^T}}{c^{s^T}+k_s}\right]\left[\frac{c^{o^T}}{c^{o^T}+k_o}\right]$$

Reaction 3

$$r_3 = k_f c^{m_m} - k_r c^{m_i}$$

The specific growth rate μ and partitioning rate coefficients are in units of per time, whereas k_o and k_s which are half-saturation constants for the reaction-limiting Monod terms that appear in brackets are in the same units as c^{sT} and c^{oT}, respectively. The reaction rates for individual species are expressed by summing the overall rates of reactions participated in by an individual species, each weighted by the corresponding stoichiometric coefficient, following the convention that stoichiometric coefficients for reactants (species appearing on the left-hand side of the reaction) are negative. We obtain in this way r^α for each constituent and write the full system in detail as

$$\begin{aligned}
&\frac{\partial}{\partial t}c^s + \mathbf{v}'\cdot\nabla' c^s - \nabla'\cdot(\mathbf{D}'\cdot\nabla' c^s) = -\frac{\mu}{Y}\lambda(x_{N+1})(c^{m_m} + c^{m_i})\left[\frac{c^{s^T}}{c^{s^T}+k_s}\right]\left[\frac{c^{o_2^T}}{c^{o^T}+k_o}\right]\\
&\frac{\partial}{\partial t}c^o + \mathbf{v}'\cdot\nabla' c^o - \nabla'\cdot(\mathbf{D}'\cdot\nabla' c^o) = -F\frac{\mu}{Y}\lambda(x_{N+1})(c^{m_m} + c^{m_i})\left[\frac{c^{s^T}}{c^{s^T}+k_s}\right]\left[\frac{c^{o_2^T}}{c^{o^T}+k_o}\right]\\
&\frac{\partial c^{m_m}}{\partial t} + \mathbf{v}'\cdot\nabla' c^{m_m} - \nabla'\cdot(\mathbf{D}'\cdot\nabla' c^{m_m}) + H(c^{s^T}(\mathbf{x}',t) - c^s_{\text{critical}})\frac{\partial c^{m_m}}{\partial x_{N+1}} = \mu\lambda(x_{N+1})c^{m_m}\left[\frac{c^{s^T}}{c^{s^T}+k_s}\right]\left[\frac{c^{o^T}}{c^{o^T}+k_o}\right] - k_f c^{m_m} + k_r c^{m_i}\\
&\frac{\partial c^{m_i}}{\partial t} + H(c^{s^T}(\mathbf{x}',t) - c^s_{\text{critical}})\frac{\partial c^{m_i}}{\partial x_{N+1}} = \mu\lambda(x_{N+1})c^{m_i}\left[\frac{c^{s^T}}{c^{s^T}+k_s}\right]\cdot\left[\frac{c^{o^T}}{c^{o^T}+k_o}\right] + k_f c^{m_m} - k_r c^{m_i}
\end{aligned} \tag{29}$$

We do not require or observe the distribution of densities of substrate or oxygen over the x_{N+1} axis; we observe the total density projected into $(\mathbf{x}', t)$. To put our equations into terms of these measurable quantities, we integrate the first two with respect to x_{N+1}. We obtain

$$\begin{aligned}
&\frac{\partial c^{s^T}}{\partial t} + \mathbf{v}'\cdot\nabla' c^{s^T} - \nabla'\cdot(\mathbf{D}'\cdot\nabla' c^{s^T}) = -\int_0^\infty \lambda(x_{N+1})(c^{m_m} + c^{m_i})\,dx_{N+1}\frac{\mu}{Y}\left[\frac{c^{s^T}}{c^{s^T}+k_s}\right]\cdot\left[\frac{c^{o^T}}{c^{o^T}+k_o}\right]\\
&\frac{\partial c^{o^T}}{\partial t}c^{o^T} + \mathbf{v}'\cdot\nabla' c^{o^T} - \nabla'\cdot(\mathbf{D}'\cdot\nabla' c^{o^T}) = -\int_0^\infty \lambda(x_{N+1})(c^{m_m} + c^{m_i})\,dx_{N+1}F\frac{\mu}{Y}\left[\frac{c^{s^T}}{c^{s^T}+k_s}\right]\left[\frac{c^{o^T}}{c^{o^T}+k_o}\right]\\
&\frac{\partial c^{m_m}}{\partial t} + \mathbf{v}'\cdot\nabla' c^{m_m} - \nabla'\cdot(\mathbf{D}'\cdot\nabla' c^{m_m}) + H(c^{s^T}(\mathbf{x}',t) - c^s_{\text{critical}})\frac{\partial c^{m_m}}{\partial x_{N+1}} = \mu\lambda(x_{N+1})c^{m_m}\left[\frac{c^{s^T}}{c^{s^T}+k_s}\right]\left[\frac{c^{o^T}}{c^{o^T}+k_o}\right] - k_f c^{m_m} + k_r c^{m_i}\\
&\frac{\partial c^{m_i}}{\partial t} + H(c^{s^T}(\mathbf{x}',t) - c^s_{\text{critical}})\frac{\partial c^{m_i}}{\partial x_{N+1}} = \mu\lambda(x_{N+1})c^{m_i}\left[\frac{c^{s^T}}{c^{s^T}+k_s}\right]\cdot\left[\frac{c^{o^T}}{c^{o^T}+k_o}\right] + k_f c^{m_m} - k_r c^{m_i}
\end{aligned} \tag{30}$$

The complete system then consists of equation set (30) in the four variables c^{o^T}, c^{s^T}, c^{m_m}, c^{m_i}. These equations are in the form of (13) and can in principle be solved for $N < 3$ using solvers for convective-dispersive reactive transport with general reaction systems such as RAFT [*Chilakapati*, 1995]. This is accomplished by treating the concentrations as distributed in $N + 1$ "spatial" dimensions (one of which is actually exposure time), extending the boundary and initial condition information to include the exposure times of boundary concentrations and the exposure-times distributions of initially present species, respectively, and by augmenting the velocity vector with another component in the x_{N+1} dimension that is zero for substrate and oxygen and is given by the Heaviside functions appearing in (30) for mobile and immobile microbes, respectively.

In the special case that the lag function $\lambda(x_{N+1})$ is unity everywhere we should recover from (30) the conventional dual-Monod kinetics with convective-dispersive transport [e.g., *Murphy et al.*, 1997]. To show this, we first note that the integrals in the first two equations of (30) both become simply $(c^{m_m^T} + c^{m_i^T})$. Second, we integrate the last two equations of (30) using the fact that

$$\begin{aligned}
&\int_0^\infty H(c^{s^T}(\mathbf{x}',t) - c^s_{\text{critical}})\frac{\partial c^{m_m}}{\partial x_{N+1}}\,dx_{N+1} = H(c^{s^T}(\mathbf{x}',t) - c^s_{\text{critical}})\int_0^\infty \frac{\partial c^{m_m}}{\partial x_{N+1}}\,dx_{N+1} = H(c^{s^T}(\mathbf{x}',t) - c^s_{\text{critical}})\\
&\cdot[c^{m_m}(\mathbf{x}', x_{N+1} = \infty, t) - c^{m_m}(\mathbf{x}', x_{N+1} = 0, t)]\\
&= H(c^{s^T}(\mathbf{x}',t) - c^s_{\text{critical}})[0 - c^{m_m}(\mathbf{x}', x_{N+1} = 0, t)] = 0
\end{aligned} \tag{31}$$

(The last step follows by construction of the exposure-time velocity: whenever the second term in brackets is nonzero (indicating some microbial density at zero exposure time), some microbes must have zero exposure to the substrate, thus the exposure velocity term must be zero.) Then (30) reduces to the conventional simplified reactive transport model for aerobic biodegradation under the remaining microbiological assumptions [e.g., *Murphy et al.*, 1997]:

$$
\begin{aligned}
&\frac{\partial c^{s^T}}{\partial t} + \mathbf{v}' \cdot \nabla' c^{s^T} - \nabla' \cdot (\mathbf{D}' \cdot \nabla' c^{s^T}) = -\frac{\mu}{Y}\left[\frac{c^{s^T}}{c^{s^T} + k_s}\right] \\
&\qquad \cdot \left[\frac{c^{o^T}}{c^{o^T} + k_o}\right](c^{m_m^T} + c^{m_i^T}) \\
&\frac{\partial c^{o^T}}{\partial t} + \mathbf{v}' \cdot \nabla' c^{o^T} - \nabla' \cdot (\mathbf{D}' \cdot \nabla' c^{o_2^T}) = -F\frac{\mu}{Y}\left[\frac{c^{s^T}}{c^{s^T} + k_s}\right] \\
&\qquad \cdot \left[\frac{c^{o^T}}{c^{o^T} + k_o}\right](c^{m_m^T} + c^{m_i^T}) \\
&\frac{\partial c^{m_m^T}}{\partial t} + \mathbf{v}' \cdot \nabla' c^{m_m^T} - \nabla' \cdot (\mathbf{D}' \cdot \nabla' c^{m_m^T}) = \mu\left[\frac{c^{s^T}}{c^{s^T} + k_s}\right] \\
&\qquad \cdot \left[\frac{c^{o^T}}{c^{o^T} + k_o}\right]c^{m_m} - k_f c^{m_m^T} + k_r c^{m_i^T} \\
&\frac{\partial c^{m_i^T}}{\partial t} = \mu\left[\frac{c^{s^T}}{c^{s^T} + k_s}\right]\left[\frac{c^{o^T}}{c^{o^T} + k_o}\right]c^{m_i} + k_f c^{m_m^T} - k_r c^{m_i^T}
\end{aligned}
\tag{32}
$$

In (32) as in all the examples so far as well as in the general formulation, the transport in the exposure-time axis is purely convective. In the present example it may be possible to realize a diffusive transport in the exposure-time axis, as follows. If the microorganisms are subjected to microscale variations in induction concentrations (perhaps because of cell clumping) so that they are not all exposed at the same rate, or if the microorganisms themselves exhibit a physiological variation in the speed of their metabolic response, then the effective velocities of each microorganism in the exposure-time dimension will be distributed around some mean. In this case the transport in the exposure-time domain might take on a diffusive-convective form, with diffusions corresponding to different exposure rates of different microbes, about the mean rate.

4. Summary

A simple extension of conventional mass balance arguments is applied to develop a general local balance law (10) that provides evolution equations for mass density distributions over the augmented space $\mathbf{x} = \{\mathbf{x}', x_{N+1}\}$ and time. This is accomplished by smoothing distributions over the new independent coordinate x_{N+1} depicting exposure time and treating displacements along this axis as a generalized convective process. The method requires the specification of the exposure velocity governing transport rates along the exposure-time axis, and this specification enrolls constitutive theory describing the way the material under consideration cumulates exposure time, or age. This approach is somewhat simpler than the more rational incorporation of material properties in a thermodynamic sense as internal variables of material continua [e.g., *Coussy*, 1995], but the latter approach may provide a particular basis for the requisite constitutive theories in different applications, and so deserves further study.

The method is applied to generate governing differential equations for three disparate hydrogeological phenomena involving groundwater age, chemical heterogeneity, and bioremediation, respectively. The equations derived range from nonlinear integro-differential convection-dispersion reaction equations to facsimiles of the conventional local convection-dispersion equation, and each of the results derived are novel to the author's knowledge. In the bioremediation and groundwater age applications, the derived generalized equations are demonstrated to reduce to published conventional forms under the appropriate simplifying assumptions or exposure-time averaging operations (respectively).

Appendix

Here we extend the conventional mixture theory formulation of local mass balance for overlapping continua to densities occurring in the $\mathbf{x}$ space; the exposition is in close analogy to the elementary case dealing with densities in the physical $\mathbf{x}'$ dimensions with only a few minor variations. We begin from the global mass balance statement (9)

$$\sum_\alpha \left(\frac{d}{dt}\int_{V^\alpha(t)} \rho^\alpha \, d\mathbf{x}\right) = 0,$$

and first invert the motion equation $\mathbf{x}^\alpha(\mathbf{X}^\alpha, t)$ to determine the domain $V^\alpha(0)$ at $t = 0$, of the material coordinates that appear in $V^\alpha(t)$ at t; that is, $\mathbf{X}^\alpha = \chi^{\alpha^{-1}}(\mathbf{x}^\alpha, t)$ where χ^α is the mapping $\mathbf{x}^\alpha(\mathbf{X}^\alpha, t)$. Then a differential of Lagrangean coordinates $d\mathbf{x}^\alpha$ of a body material at time t is given by the weighed differential $d\mathbf{X}^\alpha$ of the body configuration $\mathbf{X}^\alpha$ at $t = 0$; that is, $d\mathbf{x}^\alpha = |\mathbf{J}^\alpha| d\mathbf{X}^\alpha$ maps continuous elements in $V^\alpha(t)$ to continuous elements in $V^\alpha(0)$. Thus we make the change of variables in (8) to obtain an integral over a body that is not a function of time,

$$\sum_\alpha \left(\frac{d}{dt}\int_{V^\alpha(0)} \rho^\alpha \left|J^\alpha\right| \, d\mathbf{X}^\alpha\right) = 0 \tag{A1}$$

Because the body domain $V(0)$ refers to the reference configuration where $\mathbf{X}^\alpha = \chi^{\alpha^{-1}}(\mathbf{x}^\alpha, 0) = \mathbf{x}^\alpha$ by construction of the reference configuration, we may integrate on $\mathbf{x}^\alpha$ as well.

$$\sum_\alpha \left(\frac{d}{dt}\int_{V^\alpha(0)} \rho^\alpha \left|J^\alpha\right| \, d\mathbf{x}^\alpha\right) = 0 \tag{A2}$$

Expanding the total derivative, and using the material derivative since the arguments now depend explicitly and in the case of mobile constituents implicitly on time,

$$\sum_\alpha \left(\int_{V^\alpha(0)} \left[\left|J^\alpha\right| \frac{D^\alpha}{Dt}\rho^\alpha + \rho^\alpha \frac{D^\alpha}{Dt}\left|J^\alpha\right|\right] d\mathbf{x}^\alpha\right) = 0 \tag{A3}$$

where the material derivative is

$$\frac{D^\alpha}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v}^\alpha \cdot \nabla$$

for mobile constituents and is

$$\frac{D^\alpha}{Dt} \equiv \frac{\partial}{\partial t}$$

for immobile components. Using the fact that [e.g., *Allen et al.*, 1988, p. 7]

$$\frac{D^\alpha}{Dt}|\mathbf{J}^\alpha| \equiv [\nabla \cdot \mathbf{v}^\alpha]|\mathbf{J}^\alpha|$$

and that this result holds for in general finite $N + 1$ dimensions (e.g., the same result is used for a molecular phase space in deriving Liouville's theorem of statistical mechanics [*Cushman*, 1997, pp. 58–61]), we obtain

$$\sum_\alpha \left(\int_{V^\alpha(0)} \left[\frac{D^\alpha}{Dt} \rho^\alpha + \rho^\alpha \nabla \cdot \mathbf{v}^\alpha \right] \left| J^\alpha \right| d\mathbf{x}^\alpha \right) = 0 \quad \text{(A4)}$$

Reversing the previous change of variables to integrate over $V^\alpha(t)$,

$$\sum_\alpha \left(\int_{V^\alpha(t)} \left[\frac{D^\alpha}{Dt} \rho^\alpha + \rho^\alpha \nabla \cdot \mathbf{v}^\alpha \right] d\mathbf{x}^\alpha \right) = 0 \quad \text{(A5)}$$

To (A5) we apply the duBois-Reymond lemma to localize the integrals simultaneously. This is possible basically because $V(t)$ is arbitrary and so (A5) can be stated for all small neighborhoods of the mixture domain, for allowable smallness, with the REV understood as the real lower cutoff in the $\mathbf{x}'$ subspace, and the domain of the Gaussian mollifying function g_1 as the real lower cutoff in the x_{N+1} dimension. Under these conditions and the existence of the REV$'$ as an $\mathbf{x}$-domain-invariant-averaging volume, we may localize (A5) to obtain

$$\sum_\alpha \left(\left[\frac{D^\alpha}{Dt} \rho^\alpha + \rho^\alpha \nabla \cdot \mathbf{v}^\alpha \right] \right) = 0. \quad \text{(A6)}$$

Assuming that no term in the summation is unbounded, we may disaggregate the zero into component-wise rates, each of which corresponds to an overall rate of mass transformation. This assumption amounts to treating all chemical or biotic transformation rates as finite. Equilibrium or relatively fast reactions violate this assumption but may be handled by first treating such reactions as instantaneous and using the resulting algebraic relations to reduce the system [e.g., *Chilakapati et al.*, 1998]. Again for the present illustration and without much loss of generality, we restrict ourselves to the entirely kinetic case. We may then write localized balance equations for each individual constituent as

$$\frac{D^\alpha}{Dt} \rho^\alpha + \rho^\alpha \nabla \cdot \mathbf{v}^\alpha = e^\alpha \qquad \text{for } \alpha = \{\text{constituents}\} \quad \text{(A7)}$$

where e^α is the overall rate of transformation of constituent α possibly due to multiple interactions and where now $\Sigma_\alpha e^\alpha = 0$. By the definition of the material derivative (for mobile species syntactically; for the immobile species simply take $\mathbf{v}^\alpha = 0$ in the following),

$$\frac{\partial}{\partial t} \rho^\alpha + \nabla \cdot (\mathbf{v}^\alpha \rho^\alpha) = e^\alpha \quad \text{(A8)}$$

We typically have in hand the barycentric (as opposed to component-wise) velocity in the first N (physical) dimensions, and we have the component-wise velocity in the $N + 1^{\text{th}}$ exposure-time dimension. Therefore we split the velocity into physical and exposure-time components so that $\mathbf{v}^\alpha = \{\mathbf{v}^{\alpha\prime}, v^\alpha_{N+1}\}$ and write (A8) as

$$\frac{\partial}{\partial t} \rho^\alpha + \nabla' \cdot (\mathbf{v}^{\alpha\prime} \rho^\alpha) + \frac{\partial}{\partial x_{N+1}} (v^\alpha_{N+1} \rho^\alpha) = e^\alpha \quad \text{(A9)}$$

where $\nabla' \equiv \{\partial/\partial x_i\}$ for $i = 1, \ldots, N$ physical coordinates. Now introducing the barycentric physical velocity via

$$\mathbf{v}^{\alpha\prime} = \mathbf{v}' + (\mathbf{v}^{\alpha\prime} - \mathbf{v}') \quad \text{(A10)}$$

we obtain

$$\frac{\partial}{\partial t} \rho^\alpha + \nabla' \cdot (\mathbf{v}' \rho^\alpha) + \nabla' \cdot (\mathbf{j}^{\alpha\prime}_D) + \frac{\partial}{\partial x_{N+1}} (v^\alpha_{N+1} \rho^\alpha) = e^\alpha \quad \text{(A11)}$$

where we have introduced the flux of mass due to the mixing velocity $(\mathbf{v}^{\alpha\prime} - \mathbf{v}')$, $\mathbf{j}^{\alpha}_D{}' = (\mathbf{v}^{\alpha\prime} - \mathbf{v}')\rho^\alpha$ that reflects the diffusive and pore-scale dispersive processes. We adopt the Fickian constitutive theory for diffusion and by analogy for dispersion as is conventionally done in order to express this flux as a potential in mass density; that is,

$$\mathbf{j}^{\alpha\prime}_D \equiv -\mathbf{D}' \cdot \nabla' \rho^\alpha \quad \text{(A12)}$$

where $\mathbf{D}$ is taken as the classical diffusion-dispersion tensor with components

$$(\mathbf{D})_{ij} = (d^m + \alpha_T \sqrt{v'_i v'_i}) \delta_{ij} + \frac{(\alpha_L - \alpha_T)}{\sqrt{v'_i v'_i}} v'_i v'_j \quad \text{(A13)}$$

and where $i = 1, \ldots, N$; $j = 1, \ldots, N$, d^m is the effective molecular diffusivity in porous medium (typically less than that for bulk fluids), $\sqrt{v'_i v'_i}$ is the magnitude of the pore water velocity, α_L is the longitudinal local dispersivity, α_T is the lateral local dispersivity, and δ_{ij} is the Kronecker delta. With (21) and (22) we arrive at the $N + 1$-dimensional analogy to the classical local mass balance expression for overlapping continua,

$$\frac{\partial}{\partial t} \rho^\alpha + \nabla' \cdot (\mathbf{v}' \rho^\alpha) + \nabla' \cdot (\mathbf{D}' \cdot \nabla' \rho^\alpha) + \frac{\partial}{\partial x_{N+1}} (v^\alpha_{N+1} \rho^\alpha) = e^\alpha. \quad \text{(A14)}$$

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