

AN ELLAM APPROXIMATION FOR ADVECTIVE-DISPERSIVE TRANSPORT WITH NONLINEAR EQUILIBRIUM AND NONEQUILIBRIUM SORPTION

MATTHEW W. FARTHING¹, CHRISTOPHER E. KEES², THOMAS F. RUSSELL³, AND CASS T. MILLER¹

¹Center for the Integrated Study of the Environment, Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, North Carolina 27599-7431, USA

²Coastal and Hydraulics Laboratory, US Army Engineer Research and Development Center, Vicksburg, Mississippi 39180, USA

³Department of Mathematics, University of Colorado at Denver, P.O. Box 173364, Campus Box 170, Denver, CO 80217-3364, USA

ABSTRACT

We consider an Eulerian-Lagrangian localized adjoint method (ELLAM) applied to nonlinear model equations governing solute transport and sorption in porous media. Solute transport in the aqueous phase is modeled by standard advection and hydrodynamic dispersion, while two types of solid phase are distinguished — a fraction which achieves equilibrium with the aqueous phase quickly, and another which does not. The rapidly sorbing fraction is modeled using a local equilibrium assumption, while a first-order rate expression is used for the slowly sorbing fraction. The presence of both equilibrium and nonequilibrium sorption can be challenging for Eulerian-Lagrangian methods, since information may propagate along different characteristic directions in the space-time domain. Here, we present an implementation of a finite element ELLAM (FE-ELLAM) discretization in both fully coupled and operator-split frameworks for the reactive transport model. We then evaluate our method for test problems exhibiting a range of mass transfer behavior.

1. INTRODUCTION

For an array of transport problems, ELLAM discretizations have demonstrated the ability to resolve sharp fronts accurately, while conserving mass and incorporating boundary conditions in a systematic way [Russell and Celia, 2002]. In particular, ELLAMs have proven successful for practical multidimensional linear transport problems [Binning and Celia, 2002] and have been incorporated into production-level codes [Russell et al., 2003]. While formulations for multiphase flow and reactive transport problems have also appeared [Bell and Binning, 2004; Dahle et al., 1995; Våg et al., 1996], more work is warranted to develop ELLAMs for nonlinear systems [Russell and Celia, 2002]. Recently, an ELLAM approach performed well for a reactive transport problem with nonlinear, equilibrium sorption [Farthing et al., 2006]. Although equilibrium models are regularly used,

a more general formulation is appropriate in many cases [Barry *et al.*, 2002]. Accordingly, we seek to extend the approach in Farthing *et al.* [2006] to a system including both equilibrium and nonequilibrium sorption processes. The resulting model is applicable to a wider range of physical systems and is also useful from the perspective of developing Eulerian-Lagrangian methods, since solution information can propagate along different directions in the space-time domain.

2. FORMULATION

We begin with a common model for advective-dispersive transport in the presence of nonlinear sorption to a fixed solid phase. Two components of the solid phase are distinguished. One is assumed to achieve equilibrium rapidly with respect to the rate of transport through the system, and the other is not. Nonequilibrium sorption is modeled using a standard first-order mass transfer relation [Kanney *et al.*, 2003a]. We write this system in one spatial dimension as

$$\frac{\partial C^a}{\partial t} + \frac{\theta^f \rho^f}{\theta^a} \frac{\partial \omega^f}{\partial t} + \frac{\partial(v^a C^a)}{\partial x} = \frac{\partial}{\partial x} \left(D^a \frac{\partial C^a}{\partial x} \right) + f^a(x, t) - \frac{\theta^s \rho^s k_s^{s,a}}{\theta^a} [\omega_e^s(C^a) - \omega^s] \quad (1)$$

$$\frac{d\omega^s}{dt} = k_s^{s,a} [\omega_e^s(C^a) - \omega^s] \text{ on } \Omega \times [0, T] \quad (2)$$

$$\omega^f = \omega_e^f(C) \quad (3)$$

where the superscript a denotes the aqueous phase. The superscripts s and f refer to the slowly sorbing and the rapidly sorbing solid phase compartments, respectively. C^a is the aqueous phase solute concentration, while ω^s and ω^f are the solute mass fractions for the solid phase. θ^α is the volume fraction and ρ^α is the density for $\alpha = a, s, f$. v^a and D^a are the mean pore velocity and dispersion coefficient, respectively. f^a represents continuous sources and sinks in the aqueous phase.

The initial aqueous phase concentration and solid phase mass fractions are given by $C^{a,0}(x)$, $\omega^{s,0}(x)$, and $\omega_e^f(C^{a,0})$, respectively. For simplicity, we restrict ourselves to a total flux condition on the inflow boundary and zero dispersive flux along the outflow boundary

$$\begin{aligned} \left(v^a C^a - D^a \frac{\partial C^a}{\partial x} \right) \cdot n &= q^b(x, t) \text{ for } x \in \Gamma_I, \\ \frac{\partial C^a}{\partial x} \cdot n &= 0 \text{ for } x \in \Gamma_O \end{aligned} \quad (4)$$

where $\Gamma_I \cup \Gamma_O = \partial\Omega$, $\Gamma_I \cap \Gamma_O = \emptyset$, and $\partial\Omega$ is the boundary of Ω . The outward unit normal on $\partial\Omega$ is n , with $v \cdot n < 0$ on Γ_I and $v \cdot n \geq 0$ on Γ_O .

In order to simplify notation, we drop the a superscript where possible and normalize the solid phase mass fractions and isotherms

$$\varphi(C) = \rho^f \theta^f / \theta^a \omega_e^f(C), \quad \phi(C) = \rho^s \theta^s / \theta^a \omega_e^s(C), \quad \text{and } S = \rho^s \theta^s / \theta^a \omega^s \quad (5)$$

Eqn (1) and eqn (2) can then be written

$$\frac{\partial M(C, S)}{\partial t} + \frac{\partial(vC)}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) + f(x, t) \quad (6)$$

$$\frac{\partial S}{\partial t} = k_s^{s,a} [\phi(C) - S], \quad \text{with} \quad (7)$$

$$M(C, S) = C + \varphi(C) + S \quad (8)$$

To obtain a weak formulation, we first we multiply eqns (6) and (7) by test functions $w(x, t)$ and $z(x, t)$, respectively. We integrate over $\Omega \times [0, T]$ and expand to obtain

$$\begin{aligned} \int_{\Omega} \int_0^T \left\{ \frac{\partial[M(C, S)w]}{\partial t} - M(C, S) \frac{\partial w}{\partial t} \right\} dt dx + \int_0^T \int_{\Omega} \frac{\partial}{\partial x} \left[w \left(vC - D \frac{\partial C}{\partial x} \right) \right] dx dt \\ - \int_0^T \int_{\Omega} \left(vC \frac{\partial w}{\partial x} - D \frac{\partial C}{\partial x} \frac{\partial w}{\partial x} \right) dx dt = \int_0^T \int_{\Omega} f w dx dt \end{aligned} \quad (9)$$

$$\int_{\Omega} \int_0^T z \frac{\partial S}{\partial t} dt dx = \int_{\Omega} \int_0^T z k_s^{s,a} [\phi(C) - S] dt dx \quad (10)$$

To collect terms, eqn (9) can be rearranged

$$\begin{aligned} \int_{\Omega} \int_0^T \frac{\partial[M(C, S)w]}{\partial t} dt dx + \int_0^T \int_{\Omega} D \frac{\partial C}{\partial x} \frac{\partial w}{\partial x} dx dt \\ + \int_0^T \int_{\Omega} \left[\frac{\partial}{\partial x} \left(vCw - D \frac{\partial C}{\partial x} w \right) \right] dx dt = \\ \int_0^T \int_{\Omega} \left[M(C, S) \frac{\partial w}{\partial t} + vC \frac{\partial w}{\partial x} \right] dx dt + \int_0^T \int_{\Omega} f w dx dt \end{aligned} \quad (11)$$

We next divide the temporal domain $[0, T]$ into intervals $[t^n, t^{n+1}]$ and require that the test functions w, z disappear for $t \notin [t^n, t^{n+1}]$. As in *Farthing et al.* [2006], we choose $w(x, t)$ to satisfy the adjoint equation

$$M(C, S) \frac{\partial w}{\partial t} + vC \frac{\partial w}{\partial x} = 0 \quad (12)$$

over $[t^n, t^{n+1}]$, which is nonlinear in C and S but linear in w . A simpler structure is assumed for z . That is, z is independent of t for $t \in [t^n, t^{n+1}]$ and zero otherwise. Assuming that C and S are continuous over the interval $[t^n, t^{n+1}]$ and applying Green's formula, we obtain a mass-conservation statement for the contaminant species in the entire system

combined with one for the nonequilibrium solid phase fraction

$$\begin{aligned} \int_{\Omega} M[C(x, t^{n+1}), S(x, t^{n+1})]w(x, t^{n+1}) dx + \int_{t^n}^{t^{n+1}} \int_{\Omega} D \frac{\partial C}{\partial x} \frac{\partial w}{\partial x} dx dt \\ + \int_{t^n}^{t^{n+1}} \int_{\partial\Omega} \left(vCw - D \frac{\partial C}{\partial x} w \right) \cdot n ds dt = \int_{t^n}^{t^{n+1}} \int_{\Omega} fw dx dt \\ + \int_{\Omega} M[C(x, t^n), S(x, t^n)]w(x, t^n) dx \end{aligned} \quad (13)$$

$$\int_{\Omega} \int_{t^n}^{t^{n+1}} z(x) \frac{\partial S}{\partial t} dt dx = \int_{\Omega} \int_{t^n}^{t^{n+1}} z(x) k_s^{s,a} [\phi(C) - S] dt dx \quad (14)$$

Looking at eqn (13), we see that it consists, as in the equilibrium model from [Farthing *et al.*, 2006], of five integrals corresponding to the total mass at the new time level, physical dispersion, contributions from the physical boundary, contributions from sources and sinks, and mass at the old time level.

Integrating the left-hand side of eqn (14) gives

$$\int_{\Omega} z(x)S(x, t^{n+1}) dx - \int_{\Omega} z(x)S(x, t^n) dx = \int_{t^n}^{t^{n+1}} \int_{\Omega} z(x)k_s^{s,a}[\phi(C) - S] dx dt \quad (15)$$

As with other ELLAM formulations, global mass conservation for the system can be obtained by requiring that the test functions w and z sum to one at any point in (x, t)

$$\begin{aligned} \int_{\Omega} M[C(x, t^{n+1}), S(x, t^{n+1})] dx + \int_{t^n}^{t^{n+1}} \int_{\partial\Omega} \left(vC - D \frac{\partial C}{\partial x} \right) \cdot n ds dt = \\ \int_{\Omega} M[C(x, t^n), S(x, t^n)] dx + \int_{t^n}^{t^{n+1}} \int_{\Omega} f dx dt, \quad \text{and} \end{aligned} \quad (16)$$

$$\int_{\Omega} S(x, t^{n+1}) dx - \int_{\Omega} S(x, t^n) dx = \int_{t^n}^{t^{n+1}} \int_{\Omega} k_s^{s,a} [\phi(C) - S] dx dt \quad (17)$$

3. SOLUTION APPROACH

The formulation detailed in §2 is a natural extension of the equilibrium sorption model in [Farthing *et al.*, 2006]. As a result, many aspects of the discretization can be carried over with little or no modification. We first apply a temporal discretization to eqns (13) and (15). A backward Euler approximation is again used for the dispersion and source terms in eqn (13). For the right-hand side of eqn (15), we consider a simple linear weighting. The resulting semi-discrete system is then

$$\begin{aligned} \int_{\Omega} M[C(x, t^{n+1}), S(x, t^{n+1})]w(x, t^{n+1}) dx + \int_{\Omega} \Delta t(x) D \frac{\partial C}{\partial x}(x, t^{n+1}) \frac{\partial w}{\partial x}(x, t^{n+1}) dx \\ + \int_{t^n}^{t^{n+1}} \int_{\partial\Omega} \left(vCw - D \frac{\partial C}{\partial x} w \right) \cdot n ds dt = \int_{\Omega} M[C(x, t^n), S(x, t^n)]w(x, t^n) dx \\ + \int_{\Omega} \Delta t(x) f(x, t^{n+1})w(x, t^{n+1}) dx \end{aligned} \quad (18)$$

and

$$\begin{aligned}
\int_{\Omega} z(x)S(x, t^{n+1}) \, dx &= \int_{\Omega} z(x)S(x, t^n) \, dx \\
&+ a\Delta t \int_{\Omega} z(x)k_s^{s,a} \{\phi[C(x, t^{n+1})] - S(x, t^{n+1})\} \, dx \\
&+ (1-a)\Delta t \int_{\Omega} z(x)k_s^{s,a} \{\phi[C(x, t^n)] - S(x, t^n)\} \, dx \quad (19)
\end{aligned}$$

Here $\Delta t = \Delta t^{n+1} = t^{n+1} - t^n$, except for points near the inflow boundary, where the time step is set to the smaller of Δt^{n+1} and the time required to track back to the physical boundary. a is assumed to be in the interval $[0, 1]$, with $a = 1/2$ corresponding to the trapezoidal rule (Crank-Nicolson) and $a = 1$ a backward Euler approximation.

In the following we consider an FE-ELLAM approximation for eqns (18) and (19). We introduce a discrete mesh \mathcal{M}^h for the spatial domain $\Omega = [x_L, x_R]$ containing vertices $x_i, i = 0, \dots, n_e$ and $\Omega_i = [x_i, x_{i+1}]$ with $|\Omega_i| = \Delta x_i$. The trial solutions are

$$C(x, t) \approx \hat{C}(x, t) = \sum_{i=0}^{n_e} C_i(t)\psi_i(x), \quad \text{and} \quad S(x, t) \approx \hat{S}(x, t) = \sum_{i=0}^{n_e} S_i(t)\psi_i(x) \quad (20)$$

where ψ_i is the standard linear Lagrangian shape function associated with node i . Below, we use $C(x, t)$ and $S(x, t)$ to denote the trial solutions wherever possible. As is commonly done for ELLAM formulations, we write the test functions w as $\{w_i^{n+1}\}$ to reinforce the notion that they are aligned with \mathcal{M}^h at t^{n+1} . We do not include the superscript for $\{z_i\}$, since we have assumed that they are time independent

$$w_i^{n+1}(x, t^{n+1}) = \psi_i, \quad z_i(x) = \psi_i, \quad \text{for } t \in [t^n, t^{n+1}] \quad (21)$$

where $i = 0, \dots, n_e$

3.1. Evaluation of integrals.

3.1.1. *Species mass conservation equation.* In principle, approximation of the five integrals eqn (18) can proceed exactly as in the equilibrium model with the understanding that the total (normalized) mass variable is now $M = M(C, S)$ [Farthing et al., 2006]. The dispersion and source term integrals are the same as those for a linear transport problem, while the first term is a standard Eulerian integral for the mass at the new time level. We approximate these integrals using composite trapezoidal rule quadrature with NS intervals [Russell and Celia, 2002].

The Lagrangian aspect of an ELLAM formulation primarily enters through the boundary integral and the integral accounting for the total mass at the old time level. Approximating these terms requires characteristic tracking and so can be considerably more complex. In the two-site model considered here, characteristics for the adjoint equation, eqn (12) are given by

$$\frac{dx}{dt} = \lambda_a[C(x, t), S(x, t), x, t], \quad \text{with} \quad \lambda_a = \frac{vC}{C + \varphi(C) + S} \quad (22)$$

As in [Farthing et al., 2006], we use a forward tracking procedure to evaluate the first term on the right hand side of eqn (18). The boundary integral is also approximated following

the approach taken in [Farthing *et al.*, 2006], which involves forward tracking for inflow boundary terms and a trapezoidal rule approximation at the outflow.

3.1.2. *Nonequilibrium solid phase mass conservation equation.* The four terms in eqn (19) all involve standard Eulerian spatial integrals, since $z_i = \psi_i$. These can be approximated using numerical quadrature rules. As with eqn (18), we employ the composite trapezoidal rule, but allow a potentially different number (NSS) of subintervals. Specifically, the use of one interval in eqn (19) can decouple the equations for S_i , $i = 0, \dots, n_e$ in space.

3.2. **Tracking methods.** Approximating integrals for the mass at t^n and boundary contributions requires tracking integration points along characteristics defined by eqn (22). Here, we consider a second-order, explicit Runge-Kutta scheme (RK2-S) that requires solution values at t^n and t^{n+1} only. This tracking scheme is simple and performed well for Courant numbers up to 4.5 in Farthing *et al.* [2006].

3.3. **Operator splitting.** While we have focused on a fully coupled ELLAM formulation to this point, reactive transport models are often solved within an operator splitting framework [Barry *et al.*, 2002]. Operator splitting is, itself, a very broadly defined notion and encompasses a host of alternative solution strategies [Kanney *et al.*, 2003b]. Over a step from t^- to t^+ with input C^- and S^- , a basic first-order splitting for eqns (6)–(8) can be written

$$\begin{aligned} M(C^*, S^*) &= M(C^-, S^-) \\ \frac{\partial S^*}{\partial t} &= k_s^{s,a} [\phi(C^*) - S^*], \quad \text{for } t \in [t^-, t^+] \end{aligned} \quad (23)$$

and

$$\begin{aligned} \frac{\partial M(C^+, S^+)}{\partial t} + \frac{\partial(vC^+)}{\partial x} &= \frac{\partial}{\partial x} \left(D \frac{\partial C^+}{\partial x} \right) + f(x, t) \\ S^+(x, t) &= S^*(x, t^+), \quad \text{for } t \in [t^-, t^+] \end{aligned} \quad (24)$$

An ELLAM approximation for eqns (23) and (24) can be formulated in a manner analogous to the fully coupled approach outlined above. In addition, the order of eqns (23) and (24) can be reversed, or they can be interleaved to obtain a formally second-order alternating split operator algorithm.

4. RESULTS

To evaluate the approach outlined in §2 and §3, a series of numerical experiments were performed for different target Courant numbers (Cr) and different mass transfer rates, $k_s^{s,a}$. In addition to a fully coupled approximation (FC), a first-order noniterative operator splitting (SNI) and a second-order alternating split operator (ASO) algorithm were evaluated. NS and NSS were set to six for the FC approximation, while NSS was set to one for the split-operator algorithms. The nonlinear system resulting from the FC formulation was solved using Newton's method and an ℓ_2 relative residual convergence test with tolerance of 10^{-8} . The same nonlinear solution approach was used for the discrete approximation of eqn (24) in the operator splitting methods, while the nodal equations

for eqn (23) were solved using the variable order, variable step size differential algebraic equation solver developed in *Kees and Miller [1999]*.

The spatial domain was the unit interval and the temporal domain was $[0, 0.5]$. The initial condition was a slug of unit height spread over $[0.15, 0.35]$ [*Farthing et al., 2006*, eqn. (40)]. Table 1 summarizes the remaining physical and simulation parameters for the first and second test problems, PA and PB. Figure 1 presents results for the fully coupled and operator-splitting solution strategies for PA. Figure 2, shows the fully coupled solution for PB, while Figure 3 shows the corresponding results for the operator-splitting methods. The “exact” solutions were obtained using a temporally accurate, finite difference solution on a spatial grid with 20001 nodes.

Table 1. Simulation Parameters

	PA	PB
v	1	1
D	10^{-3}	10^{-3}
$k_s^{s,a}$	0.1	100
$\varphi(C)$	$0.50085 \times C^{0.7}$	$0.50085 \times C^{0.7}$
$\phi(C)$	$0.50085 \times C^{0.7}$	$0.50085 \times C^{0.7}$
n_e	100	100
Cr	6.5	3.5

Figure 1. PA

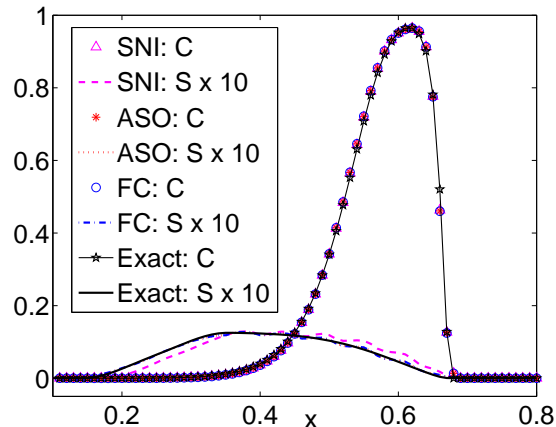


Figure 2. PB: FC solution

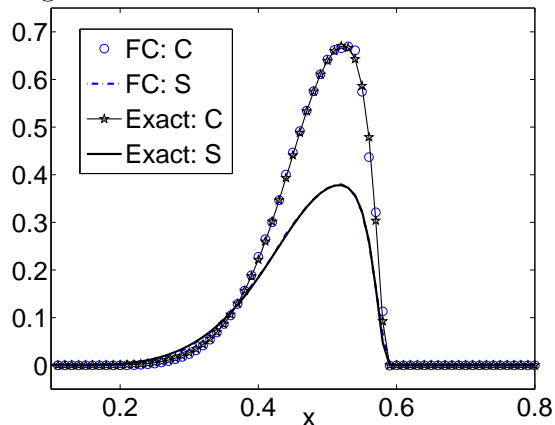
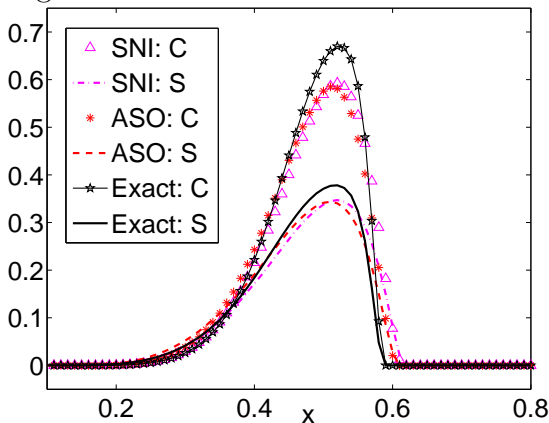


Figure 3. PB: SNI and ASO solutions



5. DISCUSSION

For the first test problem, which had a low nonequilibrium mass transfer rate, all three solution strategies performed well for a time step that was many times larger than what is typically required for stability with explicit Eulerian advection schemes. The SNI solution was less accurate than the FC or ASO results, but still reasonably good. As the nonequilibrium mass transfer rate increased, the time step required for the fully coupled algorithm to obtain accurate results decreased, but was still several times larger than the

standard Eulerian advection limit. On the other hand, the splitting error in the SNI and ASO schemes was significant at $Cr = 3.5$ on a mesh with $n_e = 100$ elements.

Acknowledgments. This work was supported in part by the National Science Foundation through grants DMS-0112069 and EAR-0440211, Department of Energy grant DE-FG02-02ER63369, and grant 5-P42-ES005948-0913 from the National Institute of Environmental Health Sciences. This work was also supported by the Countermine Phenomenology Program at the US Army Engineer Research and Development Center. Permission was granted by the Chief of Engineers to publish this information.

REFERENCES

- Barry, D. A., H. Prommer, C. T. Miller, P. K. Engesgaard, A. Brun, and C. Zheng (2002), Modelling the fate of oxidisable organic contaminants in groundwater, *Advances in Water Resources*, 25(8–12), 945–983.
- Bell, L., and P. Binning (2004), A split operator approach to reactive transport with the forward particle tracking Eulerian-Lagrangian localized adjoint method, *Advances in Water Resources*, 27, 323–334.
- Binning, P., and M. Celia (2002), A forward particle tracking Eulerian-Lagrangian Localized Adjoint Method for solution of the contaminant transport equation in three dimensions, *Advances in Water Resources*, 25, 147–157.
- Dahle, H. K., R. E. Ewing, and T. F. Russell (1995), Eulerian-Lagrangian localized adjoint methods for a nonlinear advection-diffusion equation, *Computer Methods in Applied Mechanics and Engineering*, 122(3-4), 223–250.
- Farthing, M. W., C. E. Kees, T. F. Russell, and C. T. Miller (2006), An ELLAM approximation for advective-dispersive transport with nonlinear sorption, *Advances in Water Resources*, 29, 657–675.
- Kanney, J. F., C. T. Miller, and D. A. Barry (2003a), Comparison of fully coupled approaches for approximating nonlinear transport and reaction problems, *Advances in Water Resources*, 26(4), 353–372.
- Kanney, J. F., C. T. Miller, and C. T. Kelley (2003b), Convergence of iterative split-operator approaches for approximating nonlinear reactive transport problems, *Advances in Water Resources*, 26(3), 247–261.
- Kees, C. E., and C. T. Miller (1999), C++ implementations of numerical methods for solving differential-algebraic equations: Design and optimization considerations, *Association for Computing Machinery, Transactions on Mathematical Software*, 25(4), 377–403.
- Russell, T. F., and M. A. Celia (2002), An overview of research on Eulerian-Lagrangian localized adjoint methods (ELLAM), *Advances in Water Resources*, 25(8-12), 1215–1231.
- Russell, T. F., C. Heberton, L. Konikow, and G. Hornberger (2003), A finite-volume ELLAM for three-dimensional solute-transport modeling, *Ground Water*, 41(2), 258–272.
- Våg, J., H. Wang, and H. Dahle (1996), Eulerian-lagrangian localized adjoint methods for systems of nonlinear advective-diffusive-reactive transport equations, *Advances in Water Resources*, 19(5), 297–315.