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Research paper

Analytical solutions and approximation errors of 3D contaminant transport models with exponential source decay

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Article Impact Statement: A 3D closed form solution of advection-dispersion-equation for reacting solute with source decay, suitable for Tier I risk analysis.

Abstract

Despite the availability of numerical models, interest in analytical solutions of multi-dimensional advection-dispersion systems remains high. Such models are commonly used for performing Tier I risk analysis and are embedded in many regulatory frameworks dealing with ground water contamination. In this work we develop a closed form solution of the 3D advection-dispersion-equation (ADE) with exponential source decay, first order reaction and retardation, and present an approach based on some ease of use diagrams to compare it with the integral open form solution and with earlier versions of the closed form solution. The comparison approach focuses on the relative differences associated with source decay and the effect of simulation time. The analysis of concentration contours, longitudinal sections and transverse sections confirms that the closed form solutions studied can be used with acceptable approximation in the central area of a plume bound transversely within the source width, both behind and beyond the advective front and for concentration values up to two orders of magnitude less than the initial source concentration. Since the proposed closed form model can be evaluated without nested numerical computations and with simple mathematical functions, it can be very useful in risk assessment procedures.

Introduction

Analytical and semi-analytical solutions are efficient tools widely used for modeling fate and transport of contaminants in groundwater. These solutions are useful for testing complex numerical transport models under particular simplified subsurface and boundary conditions and for performing risk analysis of polluted sites resulting from accidental spills and waste disposal

activities. Modern numerical transport models are capable of handling multi-contaminant systems with complex reaction chains in non-homogeneous and anisotropic media, under a multitude of initial and boundary conditions. Unfortunately, complex numerical models require defining parameters which are often not well known, leading to model outputs that are highly uncertain. This uncertainty in some cases could diminish the advantages of adopting a more detailed approach. During the past decades a great number of analytical solutions of the advection-dispersion equation for both conservative and reacting solutes have been developed. These solutions have been developed to provide physical insights into transport problems and they are also preferred by governments and some companies to perform Tier I risk assessments because of their ease of use and low costs for implementation (Ford et al, 2007).

Sagar (1982), Wexler (1992), Batu (1993) proposed exact 3D analytical solutions in integral open form. Batu (1996, 2006) proposed a generalized open form 3D analytical solution containing series; Leij et al. (2000) provided a useful collection of 3D solutions by applying Green's Function Method (GFM). Park and Zhan (2001) and Wang and Wu (2009) provided one-, two- and three dimensional analytical solutions in both closed form and integral open form in an aquifer of finite thickness by using GFM. Wang et al. (2011) proposed a stepwise superposition approach for the analytical solution in infinite and finite domains expressed as sums rather than integrals.

A major limitation in all the aforementioned multi-dimensional analytical solutions in finite-infinite domains and under first or third type boundary conditions include integrals in their expression or infinite series, which need to be solved numerically. The numerical solutions can introduce approximation errors, can be computationally demanding and may explain why models using the same input parameters can generate very different results.

Domenico and Robbins (1985), Domenico (1987), Martin-Hayden and Robbins (1997) proposed some 3D approximated analytical solutions in closed form. The key advantage of the Domenico and Robbins (1985) approach and its derived extensions included in US EPA tools as BIOSCREEN (1996), BIOCHLOR (Aziz et al., 2000), currently used in risk assessment procedures, is that it provides a closed form solution that can be evaluated with much less significant numerical computations since it contains only complementary error functions. The latest version of the Domenico-Robbins-based solutions is valid for linear sorption, pollutant first order decay and a variety of plane and linear source boundary conditions. These analytical solutions, identified by the authors as based on the "extended-pulse-approximation", have received much attention in the literature, given their adoption by regulatory agencies.

By recalling the principal steps followed by Domenico and Robbins (1985), it can be noticed that they propose a closed form 3D solution by multiplying the 1D solution in the flow direction with the two transverse spreading solutions, in which time t is replaced by an averaged time taken as x/v, where x is the coordinate in the flow direction and v is the average pore scale velocity. Wexler (1992) provided an exact analytical solution of the equation proposed in Domenico (1987), this solution was already contained in the work by Sagar (1982). Srnivasan et al. (2007) performed a limiting analysis of the approximated Domenico (1987) solution and proved that it relaxes to the Wexler (1992) analytical solution for axial dispersivity tending to zero. Srinivasan et al. (2007) concluded that the Domenico and Robbins (1985) approach forces a quasi-steady state condition in transverse direction at all times, and for this reason it introduces significant errors for longitudinal-dominated problems. They performed some comparison by varying dispersivities and space velocity by an order of magnitude, showing the possibility of

high errors in the centerline. Also West et al. (2007) performed comparisons with the Domenico and Robbins-modified solutions, along the centerline, by varying the source dimension and dispersion coefficients. Their results gave errors of about 40-80% at small simulation times. Guyonnet and Neville (2004) performed a comparison method using non-standard dimensionless groups and on the axial Peclet number, finding errors in the transverse direction greater than in the axial one.

In this work we present a new closed form solution of the 3D problem with first order reaction and retardation but unlike past solutions allows for exponential source decay. The model being suitable for treating continuous source dissipation with time owing to dilution by precipitation or source removal or remediation. We also suggest a novel approach to compare models using some ease of use diagrams that include all the previous analytical solutions. The comparison approach can be extended to other solutions in finite domain and different shaped sources. The particular solution here analyzed in detail refers to a plane source with first type boundary condition, semi-finite domain in x direction and infinite domain in y and z directions. Concentration at the source is defined as a decaying exponential function of time.

Model derivation

The governing equation for the three-dimensional advection-dispersion of a solute subject to a first order decay (also valid for a pseudo-first order reaction in homogeneous phase where the contaminant is the controlling reactant, i.e. other reactants are in excess) and linear sorption, instantaneous and reversible, can be written as:

$$R\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D_x\frac{\partial^2 c}{\partial x^2} + D_y\frac{\partial^2 c}{\partial y^2} + D_z\frac{\partial^2 c}{\partial z^2} - \lambda c \qquad (1)$$

where $c(x,y,z,t)$ is the solute concentration [ML^{-3}], x is the longitudinal coordinate, y and z are the horizontal transverse and the vertical coordinates, respectively, v is the average pore scale velocity of the fluid [LT^{-1}], taken unidirectional along x, D_x is the longitudinal dispersion coefficient [L^2T^{-1}], D_y and D_z are the horizontal transverse and the vertical transverse dispersion coefficients [L^2T^{-1}], respectively, t is time [T], λ is the first order decay constant [T^{-1}], and R is the retardation factor [-].

The retardation factor can be eliminated from the term on the left by replacing D_x, D_y, D_z with D_x/R, D_y/R, D_z/R; v with v/R and, λ with λ/R.

Eqn. (1) can be written as a linear operator on concentration:

$$L(C(x,y,z,t)) = 0 \quad (2)$$

By applying the GFM it is possible to obtain different solutions depending on different boundary and initial conditions (Greenberg 1971, Roach 1982). It is possible to use GFM if the following conditions occur:

1) homogeneous and anisotropic porous medium;
2) constant velocity in x direction;
3) horizontally infinite or semi-finite domains; vertically semi-finite or finite domains;
4) initial condition set as $c(x,y,z,0) = 0$
5) point, linear, plane, volumetric source (regular or irregular).

The source of contamination can be usually placed as:

i. a source generation term r [$ML^{-3}T^{-1}$] inside the domain (GFM general approach) and in this case an infinite domain in x and y is usually considered;

ii. a boundary condition of the first type and expressed as concentration, or a boundary condition of the third type and expressed as a mixed flux/concentration in a semi-finite domain.

If we consider case i), i.e. the source term inside the domain, usually we put:

$$c(\infty, y, z, t) = 0 \tag{3}$$

$$c(x, \pm\infty, z, t) = 0 \tag{4}$$

$$c(x, y, \pm\infty, t) = 0 \quad \left(\text{or } \frac{\partial c}{\partial z} = 0 \text{ in z direction, where the domain is finite}\right) \tag{5}$$

The specific source generation term (source strength) can be defined as:

$$r = \begin{cases} r_0 f(t) & 0 < x < x_0;\ y_0 < y < y_1;\ z_0 < z < z_1 \\ 0 \end{cases} \tag{6}$$

where r is a function of x,y,z and can be a linear or non-linear function of t; r_0 [$ML^{-3}T^{-1}$] is the initial volumetric mass released by the source per unit of time, f(t) is a dimensionless known function. The specific source generation term exists only in the space occupied by the source, otherwise is zero. The specific source generation term cannot depend on C.

Since eqn. (1) is linear, the superposition principle allows us to write each appropriate Green's function as the sum of a fundamental solution and a causal solution. The fundamental (or source) solution is found by solving eqn. (1) under homogeneous boundary conditions at infinity and with an added generation term r, discontinuous inside the domain and defined by:

$$r = r_0 \delta(x - x_0)\delta(y - y_0)\delta(z - z_0)\delta(t - t_0) \tag{7}$$

The causal (or forced) solution is given by solving eqn. (1) under inhomogeneous boundary conditions. Subsequently, it is possible to find the solution for distributed and/or continuous generation terms as the superposition of the solutions obtained by describing the

generation terms as an infinite number of pulse functions. In summary, by knowing the solution for the instantaneous point source (solved for infinite, semi-finite or finite domains), we can extend it to a more complex source knowing that:

A. The 3D solution for a point instantaneous source is the product of the 3 directional solutions;
B. The 3D solution for a finite instantaneous source can be obtained by integration of the 3D point source solution into the source domain;
C. The 3D solution for a continuous (point or not-point) source can be obtained by integration of the 3D source solution in time.

In case of finite boundaries it is possible to use the method of images (or reflection method) to find the Green's function: starting from the free space solution we can add to it some other solutions of eqn. (2) in order to get the required boundary condition. To do this, we can suppose that there is an image of the source outside of the domain, with opposite sign and exactly at the same distance away from the boundary as the source is (like a mirror). The goal is to cancel the values of the free space solution that are on the boundaries. This method is used to find solutions of the ADE for finite z domain (usually from 0 to L).

The analytical solution of eqn. (1) for the instantaneous point source centered in (x_0, y_0, z_0) at time t_0 subject to (3), (4) and (5) is obtained by applying (A) to the well known 1D directional solutions:

$$c(x,y,z,t) = \frac{M}{8\sqrt{\pi^3 D_x D_y D_z (t-t_0)^3}} \exp\left[-\lambda(t-t_0)\right] \exp\left\{-\frac{\left[(x-x_0)-v(t-t_0)\right]^2}{4D_x(t-t_0)}\right\} \exp\left[-\frac{(y-y_0)^2}{4D_y(t-t_0)}\right] \exp\left[-\frac{(z-z_0)^2}{4D_z(t-t_0)}\right] \quad (8)$$

where M is the total mass inserted by the instantaneous point source per unit time (Baetsle, 1969). A class of solutions for the point source in different domains can be obtained by changing equations (3), (4), (5) with different ones. Finally, it is possible to obtain analytical solutions for complex sources in space and time by integrating the class of point solutions in space and time.

If we consider case ii), i.e. the source term is a boundary condition of the first type or third type, the generation term *r* is zero and we have, respectively:

$$c(0,y,z,t)=\begin{cases} c_0 f(t) \\ \\ 0 \end{cases} \quad \text{or} \quad -D\frac{\partial c(0,t)}{\partial x}+vc(0,t)=vg(t) \qquad y_1 < y < y_2;\ z_1 < z < z_2 \tag{9}$$

$$c(\infty,y,z,t)=0 \quad \text{or} \quad \frac{\partial c(L_0,t)}{\partial x}=0 \quad \text{or} \quad \frac{\partial c(\infty,t)}{\partial x}=0 \tag{10}$$

$$c(x,\pm\infty,z,t)=0 \tag{11}$$

$$c(x,y,\pm\infty,t)=0 \quad (\text{or} \quad \frac{\partial c}{\partial z}=0 \quad \textit{in z direction, where the domain is finite}) \tag{12}$$

where c_0 [ML^{-3}] is the initial source concentration, *f(t)* is a dimensionless time function, *g(t)* is a time function and L_0 [L] is the length of the finite x domain.

Sagar (1982) and Wexler (1992) derived the analytical solution of the 3D ADE for a plane source described by a boundary condition of the first type at constant concentration c_0, and the remaining boundary conditions expressed as concentration tending to zero at infinite domain (terms on the left of eqns. (10), (11) and (12)).

The solution can be found by using traditional integration transform methods or GFM. The final analytical solution is:

$$c(x,y,z,t)=\frac{C_0 x'}{8\sqrt{\pi D_x}}\int_0^t \exp\left[-\lambda\tau-\frac{(x'-v\tau)^2}{4D_x\tau}\right] \left[erfc\frac{y-y_2}{2\sqrt{D_y\tau}}-erfc\frac{y-y_1}{2\sqrt{D_y\tau}}\right]\left[erfc\frac{z-z_2}{2\sqrt{D_z\tau}}-erfc\frac{z-z_1}{2\sqrt{D_z\tau}}\right]\frac{1}{(\tau)^{3/2}}\,\mathrm{d}\tau \quad (13)$$

where $\tau = t - t_0$; $x' = x - x_0$.

It is important to remark that since Eqn. (13) satisfies the initial condition $c(x,y,z,0)=0$, the solution predicts a concentration equal to zero at $x'=0$ for every y and z and $t = 0$, as already observed by Wang et al. (2011). So the solution is valid for all $x'>0$.

Eqn.(13) is in open form and the integral in time has to be numerically evaluated. Wang et al. (2011) introduced a stepwise superposition approach to handle eqn.(13) by discretizing the time interval in N steps and by approximating the contribute of Gy×Gz by its weighted average.

Martin-Hayden and Robbins (1997) proposed an analytical solution for a plane source in closed form by adopting the approximation of Domenico (1987), this solution is referred by Srinivasan et al. (2007) as the "modified-Domenico" solution. This analytical solution takes into account the first order decay and is contained in BIOCHLOR (Aziz et al., 2000):

$$c(x,y,z,t)=\frac{C_0}{8}\left\{\exp\left[\frac{(v-u')x'}{2D_x}\right]\mathrm{erfc}\left(\frac{x'-u't}{2\sqrt{D_x t}}\right)+\exp\left[\frac{(v+u')x'}{2D_x}\right]\mathrm{erfc}\left(\frac{x'+u't}{2\sqrt{D_x t}}\right)\right\} \left[\mathrm{erfc}\frac{y-y_2}{2\sqrt{D_y\tau_m}}-\mathrm{erfc}\frac{y-y_1}{2\sqrt{D_y\tau_m}}\right]\left[\mathrm{erfc}\frac{z-z_2}{2\sqrt{D_z\tau_m}}-\mathrm{erfc}\frac{z-z_1}{2\sqrt{D_z\tau_m}}\right] \quad (14)$$

where $u'=\sqrt{v^2+4\lambda D_x}$, $\tau_m = x/v$ and the first term of the product is the mono-dimensional solution derived by Bear (1975).

If we have a plane source generating contamination with exponential decay, being λ_s the decaying constant of the source, i.e.:

$$r = r_0 f(t_0) = r_0 f(t-\tau) = r_0 \exp(-\lambda_s (t-\tau)) \tag{15}$$

eqn.(13) can be extended as:

$$c(x,y,z,t) = \frac{C_0 x'}{8\sqrt{\pi D_x}} \int_0^t \exp(-\lambda_s (t-\tau) \exp\left[-\lambda\tau - \frac{(x'-v\tau)^2}{4D_x\tau}\right] \left[erfc\frac{y-y_2}{2\sqrt{D_y\tau}} - erfc\frac{y-y_1}{2\sqrt{D_y\tau}}\right]\left[erfc\frac{z-z_2}{2\sqrt{D_z\tau}} - erfc\frac{z-z_1}{2\sqrt{D_z\tau}}\right]\frac{1}{(\tau)^{3/2}}\,d\tau \tag{16}$$

that is the solution in integral open form for a plane source with exponential decay as a boundary condition of the first type. This solution is used in BIOSCREEN-AT (Karanovic et al., 2007).

The proposed 3D solution for a plane source with exponential decay

The closed form solution developed here is based on the "extended pulse approximation" that uses spatial extensions of the well known instantaneous finite pulse models. This approximated solution can be easily derived by following the approach proposed in Domenico and Robbins (1985) and Martin-Hayden and Robbins (1997). Alternatively, the proposed solution can be obtained from the instantaneous pulse solution, by following the three steps defined in rules (A), (B) and (C) and by making some simplifying hypothesis.

The closed form approximate solution can be written as:

$$c(x,y,z,t) = \frac{C_0}{8}\{g_x(t)\}\{g_y(t)\}\{g_z(t)\} \tag{17}$$

To construct the 3D solution of eqn.(1) subject to (9), (10), (11) and (12), where $f(t) = \exp(-\lambda_s t)$, i.e. valid for semi-finite domain in x, infinite domain in y and z, and subject

213 to a first type boundary condition described as a finite plane decaying source, we can use the
214 following functions:

215 i) in eqn. (17) the term g_x is taken from the solution $c(x,t) = \frac{c_0}{2} g_x$ of the 1D ADE (obtained by
216 eliminating terms in y and z from eqn.(1)) subject to a first type boundary condition described
217 as an exponential decaying source. This solution was given in the most general case by Van
218 Genuchten and Alves (1982) and named C13, and it was later proposed by Williams and
219 Tomasko (2008) for a particular case;

220 ii) the two terms g_y and g_z come from the solutions $c(y,t) = \frac{c_0}{2} g_y$ and $c(z,t) = \frac{c_0}{2} g_z$ of two
221 independent 1D equations with dispersion, no advection and no reaction, valid for infinite
222 domain and subject to instantaneous finite linear sources, defined respectively in $y_1 \le y \le y_2$
223 and in $z_1 \le z \le z_2$.

224 Since the proposed approximation combines the solution in x obtained for a continuous source
225 with the solutions in y and z obtained for instantaneous sources to construct the final solution, a
226 fixed time $\underline{t}$ has to be defined to calculate at each x the contribution of the instantaneous
227 spreading terms in y and z. By following the Domenico and Robbins (1985) approximation, g_y
228 and g_z in eqn.(17) are computed at the apparent residence time $\tau_m = x / v$ and the contribute of
229 these two spreading terms in diluting concentration during time is calculated as at steady state.
230 The physical meaning of this choice was explained by the plug flow model approximation in
231 Domenico (1987).

232 The final solution is:

$$c(x,y,z,t) = \frac{C_0}{8}\left\{\exp\left[\frac{(v-u)x'}{2D_x} - \lambda_s t\right]\operatorname{erfc}\left(\frac{x'-ut}{2\sqrt{D_x t}}\right) + \exp\left[\frac{(v+u)x'}{2D_x} - \lambda_s t\right]\operatorname{erfc}\left(\frac{x'+ut}{2\sqrt{D_x t}}\right)\right\}$$

$$\left[\operatorname{erfc}\frac{y-y_2}{2\sqrt{D_y \tau_m}} - \operatorname{erfc}\frac{y-y_1}{2\sqrt{D_y \tau_m}}\right]\left[\operatorname{erfc}\frac{z-z_2}{2\sqrt{D_z \tau_m}} - \operatorname{erfc}\frac{z-z_1}{2\sqrt{D_z \tau_m}}\right] \quad (18)$$

with $u = \sqrt{v^2 + 4D_x\lambda - 4D_x\lambda_s}$.

The alternative method to obtain eqn. (18) uses GFM and rules (A), (B) and (C) to derive the open integral form solution given by eqn. (16). Then the simplifying hypothesis consists in "reinterpreting time t as x/v for a moving coordinate system, as is common in all transverse spreading models" (Domenico and Robbins 1985). This translates in the substitution of time t in the transverse spreading terms of eqn. (16) with the apparent residence time $\tau_m = x / v$. With this substitution the two last terms of eqn. (16) do not depend on time, and the integration in time of eqn.(16) reduces to the integration in time of the 1D ADE, with first order reaction and subject to an exponential source decay as a first type boundary condition, that again leads to eqn.(17).

Evaluation of Model Relative Errors

We want to compare eqn. (18), i.e. the approximated 3D analytical solution here proposed in closed-form for a plane source with exponential source decay, and eqn. (16), i.e. the 3D analytical solution in open form under the same conditions. We suggest an approach different from those adopted by Srinivasan et al. (2007) and West et al. (2007).

The main goal is to quantify relative errors in order to propose a short-cut method, based on simple diagrams, that allows the users of the closed form models to correct their results or to evaluate uncertainty of model output. Since the analytical solution here proposed in eqn. (18) and eqn. (16) are more general than the existing ones, the method is valid also for error analysis of

254 the analytical solutions contained in BIOSCREEN and BIOCHLOR. However, to show and
255 compare results of the method, we use the same values adopted in Srinivasan et al. (2007), even
256 if it could be observed that some chosen values are not consistent with some dispersivity
257 estimates.

Parameter	**Value**	
Longitudinal dispersivity (α_x)	42.58	m
Transverse dispersivity (α_y)	8.43	m
Transverse dispersivity (α_z)	0.00642	m
velocity (v)	0.2151	m/d
Source width in Y direction (Y)	240.0	m
Source width in Z direction (Z)	5.0	m
Source concentration (C_0)	850	mg/l
Simulation time (t_m)	5110	d
First order reaction constant (λ)	0.001	s^{-1}

258 **Table 1**. Simulation data

259 As shown in Gelhar et al. (1992) and Zheng and Bennett (2002), high-reliability
260 estimates of longitudinal dispersivities range from about 0.5 to 4 m and high-reliability estimates
261 of horizontal transverse dispersivities range from about 0.02 to 0.1 m. The values of
262 dispersivities here adopted to quantify relative errors are more than one order of magnitude
263 greater than the expected ones for real cases. Since Srnivasan et al. (2007) proved that the
264 approximated closed form solution of eqn. (14) relaxes to the Wexler (1992) analytical solution
265 for axial dispersivity tending to zero, the choice of a very high value of axial dispersivity is
266 conservative for this study, since the effects on relative errors will be increased with respect to
267 the real ones. Furthermore, since West et al. (2007) proved that for small transverse dispersivities
268 errors reduce in the centerline, simulations here proposed with a value of horizontal transverse

dispersivity almost two orders of magnitude greater than the expected one will produce higher relative errors in the centerline than the expected real ones.

Dispersion coefficients used in this analysis are expressed by the product of dispersivities and velocity.

Simulations are performed at different values of the exponential source decay constant λ_s; in this way also the comparison of the Domenico-modified closed-form solution given in eqn.(14) with the Wexler (1992) analytical open form solution given in eqn. (13) are included. Values of λ_s and λ are chosen in order to analyze all the known particular solutions included in eqn. (16) and eqn. (18).

For certain uncommon values of λ_s the term under the square root defining $u = \sqrt{v^2 + 4D_x\lambda - 4D_x\lambda_s}$, also present in the well known one-dimensional solution proposed by van Genuchten and Alves (1982), can be negative. In this case eqn. (18) must be computed by using tools that treat complex exponential and complex error functions, such as Maple™ (trademark of Waterloo Maple Inc.), so that concentration is always a real number.

Simulation cases here reported are shown in table 2:

Parameters		Case	Corresponding simplified solutions
λ [s^{-1}]	λ_s [s^{-1}]		
0.0	0.0	a $u=u'=v$	conservative solute, no source decay.
0.001	0.0	b $u=u'>v$	eqns. (13) and (14).
0.001	0.0008	c $u>v$	

0.001	0.001	d $u=v$
0.001	0.0018	e $u<v$
0.001	0.0023	f $u=0$

Table 2. values of the decay constants and relative cases.

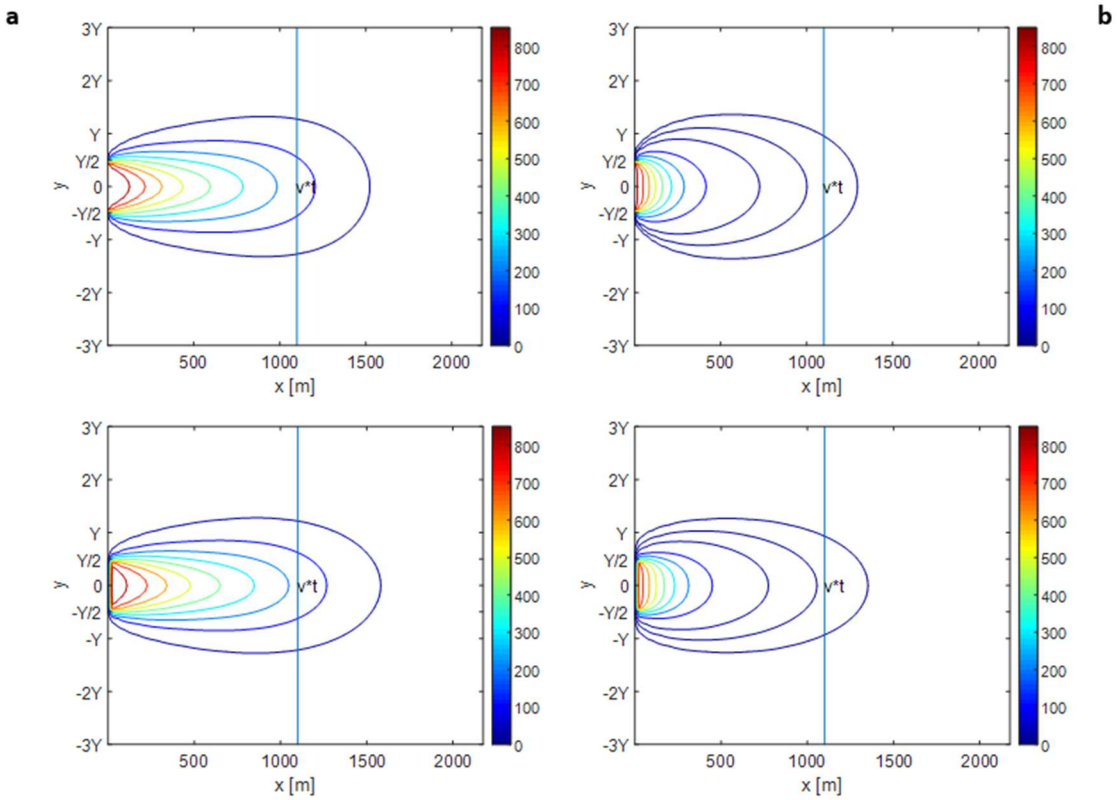
Concentration field

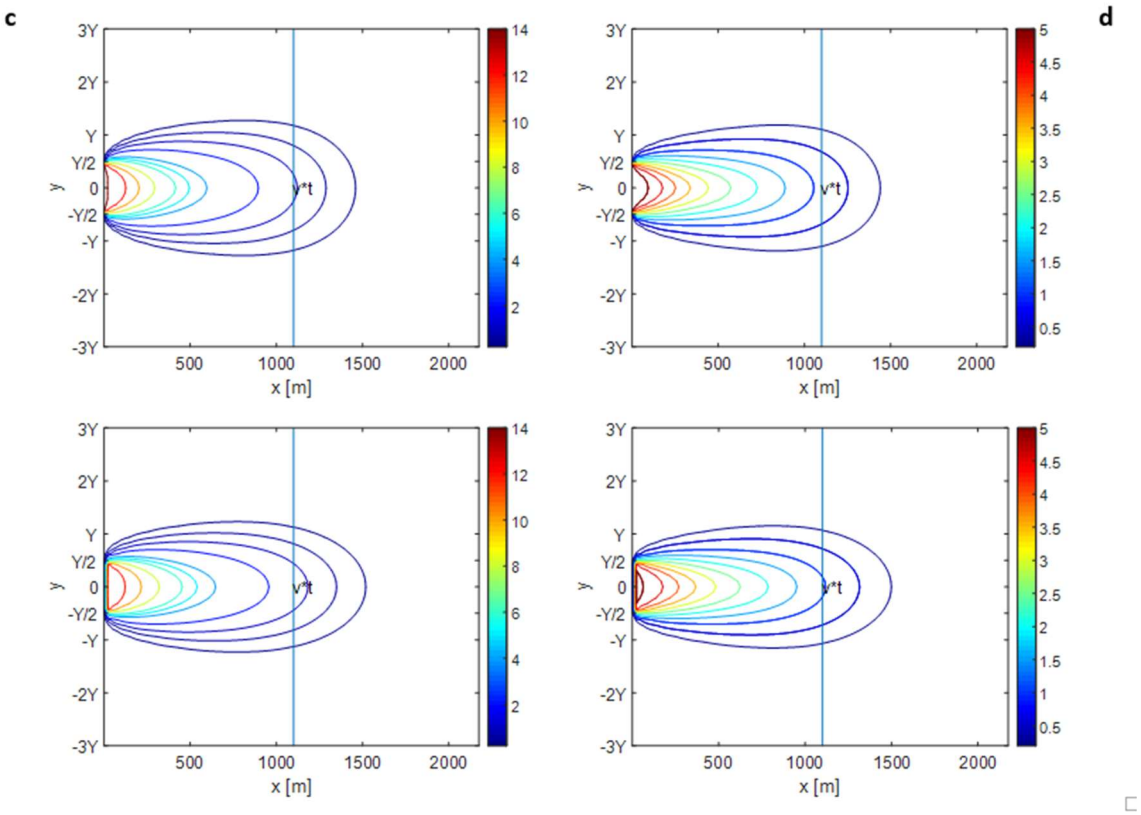
Some concentration fields evaluated by eqn. (18) and eqn. (16) at changing λ_s are plotted in the (x,y) plane and reported in figure 1. Since in this study we considered the analytical 3D solutions with infinite z domain, no differences between the contour shapes in y and z are to be outlined, apart the obvious influence of the different source extensions and dispersion coefficients. Hence concentration fields in (x,z) plane are essentially identical.

The numerical integration of eqn. (16) was made by adaptive Gauss-Kronrod quadrature method (available in QUADPACK library, GNU Scientific Library, Matlab QUADGK, NAG Numerical Libraries and R). For each subplot of figure 1 the upper concentration contour map was developed using the approximate closed form proposed in eqn. (18) and the lower one is evaluated by the exact open integral form expressed by eqn. (16). The vertical line is the advective front, i.e. the distance $\underline{x}$ from the source where a conservative contaminant injected with a Dirac function would be found without dispersion effects at $t=t_m$.

Case a) represents model outputs in the simple situation of advection-dispersion of a conservative solute released at constant concentration by a plane source. Case b) compares models outputs for a non-conservative solute underlying a first order decay and released at

constant concentration by a plane source. Finally, cases c), d), e), f) represent concentration contours for a non-conservative solute subject to first order decay, released by decaying plane sources with varying decay constants and effective velocities.

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3Y
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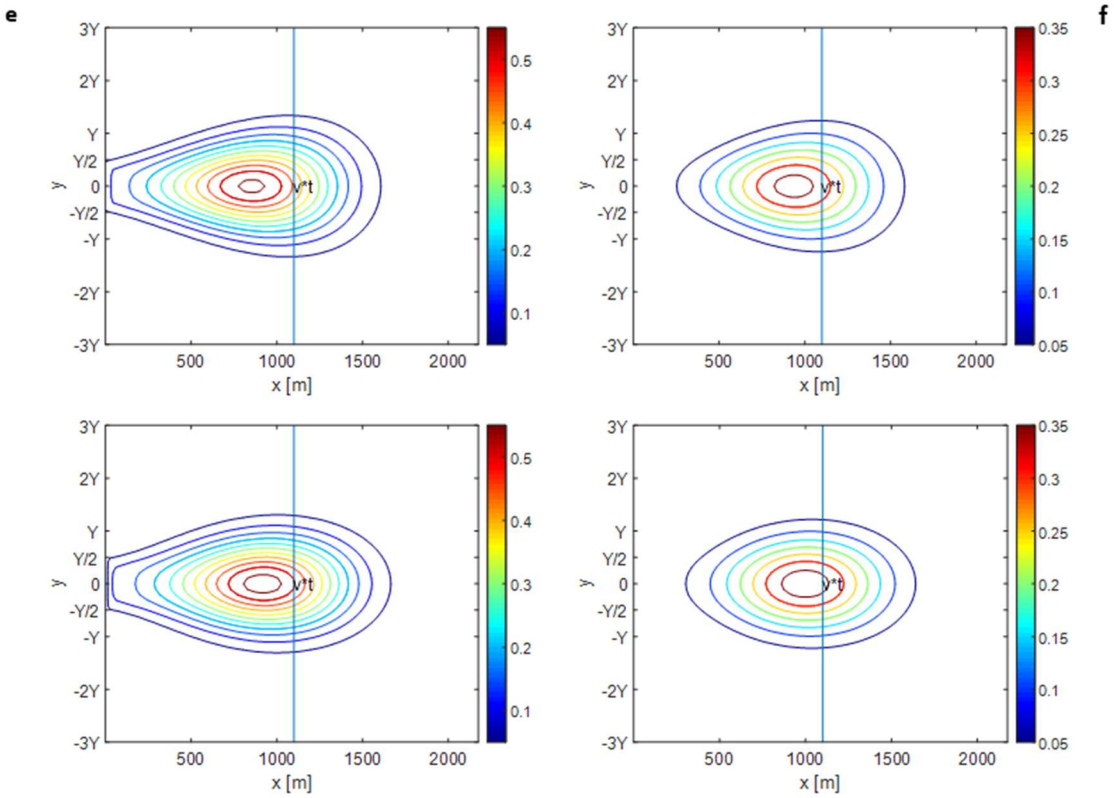


305 **Figure 1**. Concentration maps. Approximated closed form (top) versus integral open form
306 (bottom). Case a) conservative solute, no source decay. Case b) reacting solute, no source decay.
307 Cases c) to f) reacting solute, source decay.

308

309 It can be observed that concentration distributions evaluated by eqn. (18), are more
310 delayed with respect to the advective front than distributions obtained by eqn. (16). The graphs
311 show that the delay increases with λ_s. By observing cases e) and f) at simulation time t_m=5110
312 [s], when the source is already consumed, the centre of the plume, i.e. the point at maximum
313 concentration, evaluated with the closed form solution, lags behind with respect to the
314 concentration profiles computed by eqn. (16).

315 The initial value of concentration is set at C_0=850mg/l; case a) is the one with the higher
316 concentration in the domain since a conservative contaminant is considered. By comparing the
317 well known case a) and case b) at equal distance from the source, graphs confirm the effect of
318 first order decay in reducing contaminant concentration in the domain. The effect of the first
319 order reaction in mean contracting the shape of the iso-concentration curves can be also noticed.
320 This effect can be directly correlated to the value of the effective velocity u' appearing in eqn.
321 (14), where u' is higher than v.

322 By looking at cases c) and d) it's interesting to observe how the shape of concentration
323 contours in the domain stretches again under the reduction of the effective velocity u appearing
324 in eqn. (18). This decrease is due to the term containing the zero order source decay, that has
325 opposite sign with respect to the first order reaction term, both contained in the expression of the
326 effective velocity appearing in eqn. (18). Consequently, for case d), in which $\lambda=\lambda_s$, giving u=v,
327 the shape of the iso-concentration distributions are identical to case a).

328 Finally, in cases e) and f) for which u is less than v, the shape of concentration contours
329 changes again allowing to observe the effect of source diminishment.

330

331 **Relative differences**

332 Relative differences between the closed form solution and the integral one, expressed as:

333 $$E_r = \frac{C - I}{I} \qquad (18)$$

334 are shown in the ray-shaped diagrams of figure 2. The symbol C indicates the closed form
335 solution with the same type of approximation adopted by Martin-Hayden and Robbins (1997),
336 also called Domenico modified; and the symbol I the integral open form solution. Diagrams in

figure 2 are plotted at fixed simulation time t=5110 days and at changing λ_s. The vertical line in the figure is the advective front, as previously defined. The reported cases are the same as illustrated in figure 1.

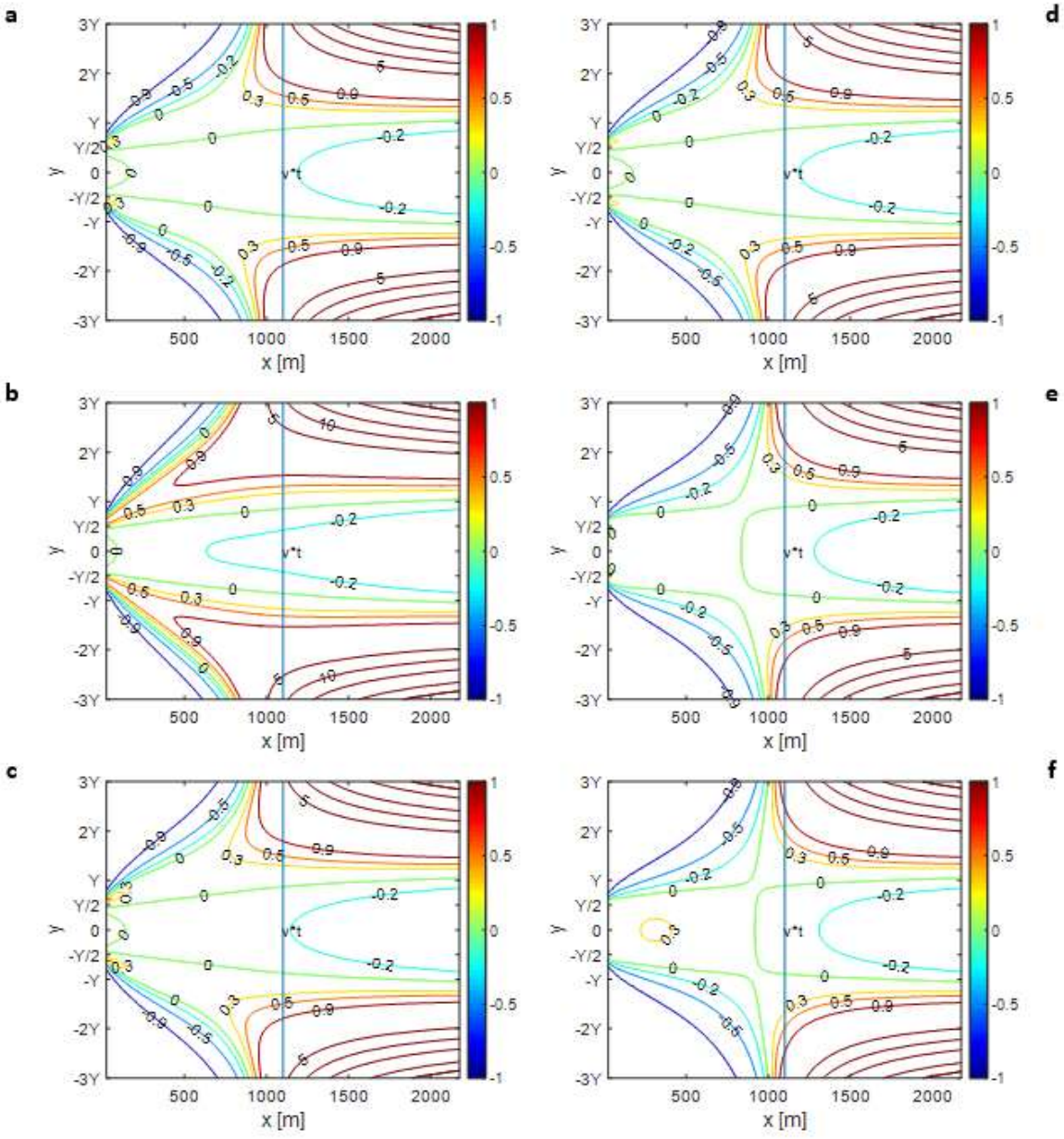


Figure 2. Diagrams of relative errors at fixed simulation time. Case a) conservative solute, no source decay. Case b) reacting solute, no source decay. Cases c) to f) reacting solute, source decay.

Three error zones can be distinguished in figure 2. The first one lies along the centerline and extends in the y direction for a width slightly greater than the source width Y. The other two zones are separated by the vertical line describing the advective front and posed at $\underline{x} = v*t_m$. This vertical line is an asymptote for the relative errors contours at y tending to ±infinity. The existence of this asymptote is due to the fact that both the solutions satisfy the boundary condition at y tending to infinity. In the zone on the left of the asymptote, the closed form approximated solution underestimates the concentration, however in the zone on the right of the asymptote the approximated solution overestimates the concentration. It is very important to notice that in these two zones concentration values are more than three orders of magnitude lower than the source concentration.

Along the centerline in figure 2, the relative error is always negative for cases a) to d), where the effective velocity u is greater (or equal) than the pore space velocity v. For these four cases the approximate closed form solution underestimates concentrations on the centerline and also in the domain space of width Y along the centerline. However, the maximum underestimation is only 10% for concentration values up to two orders of magnitude lower than the source concentration value. Cases e) and f), when u is less than the pore space velocity v, show a particular behaviour behind the advective front: the relative error is positive and the approximated closed form solution can overestimate concentration values. Looking at the lateral zone behind the advective front and on the left of the asymptote, negative relative errors have to be weighted in comparison to concentration values. For all the six cases a) to f) the underestimation of the transverse dispersion effects on concentration produced by eqn. (18) gives

366 relative errors, which, when greater than 20%, are related to values of concentration less than
367 two orders of magnitude of the initial concentration of the source.

368 Finally, as regards the lateral zone beyond the advective front and on the right of the
369 asymptote where the closed form solution overestimates concentration levels, very high relative
370 errors are related to concentration values that are more than four orders of magnitude less than
371 the initial concentration, hence these errors are insignificant. As regards cases c) tof) subject to
372 the decaying source, it has to be noted that concentration values are not very high also on the
373 centerline, so the relative errors observed in the two zones are related to concentration values that
374 are very small. As an example, in case f) the centre of the plume, i.e. the point at maximum
375 concentration, has a concentration value of about 0.45mg/l.

376 It is interesting to outline that ray diagrams of case a) and case d) are identical, so the
377 effective velocity u can be used as a parameter influencing relative error diagrams.

378 With reference to table 1, a complete analysis of relative errors should take into
379 consideration six chemical-physical parameters, i.e. the three dispersivities, space velocity and
380 the two decay constants; three parameters derived from initial and boundary conditions, i.e.
381 source widths Y and Z and initial concentration C_0; simulation time t_m.

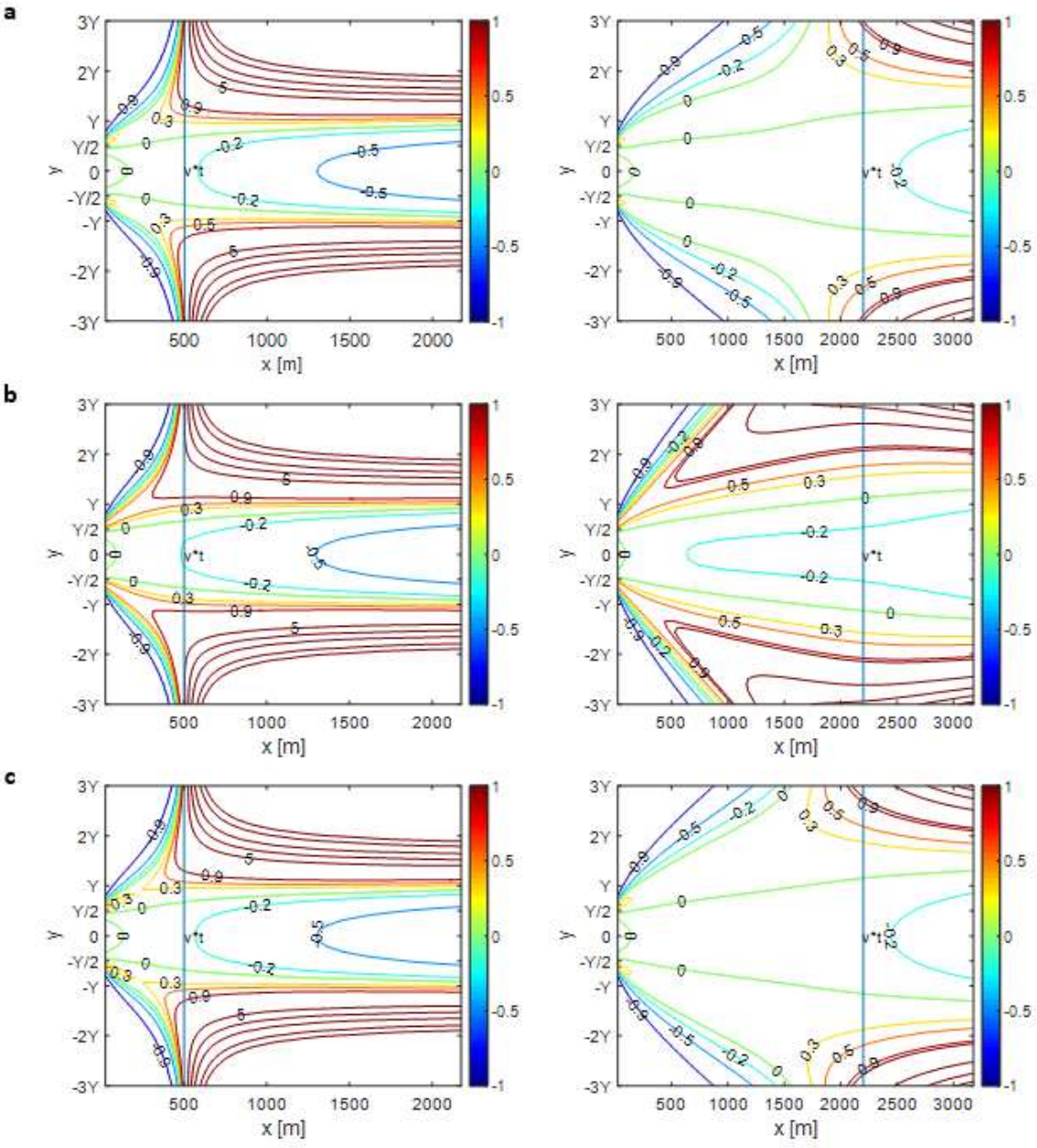
382 Since simulation time t_m is not correlated with dimensionless numbers but it is very
383 important for the validity of the Domenico and Robbins approximation, we report here its effects
384 at different λ_s values.

385

386 Time dependence

387 Some simulations have been carried out in order to observe how the diagrams vary at

388 changing t_m. In figure 3 and figure 4 ray-diagram modifications at $t_m/2$ and $2t_m$ are shown.



389

390 **Figure 3**. Diagrams of relative errors at half simulation time (left) and double simulation time

391 (right). Case a) conservative solute, no source decay. Case b) reacting solute, no source decay.

392 Case c) reacting solute, source decay.

393

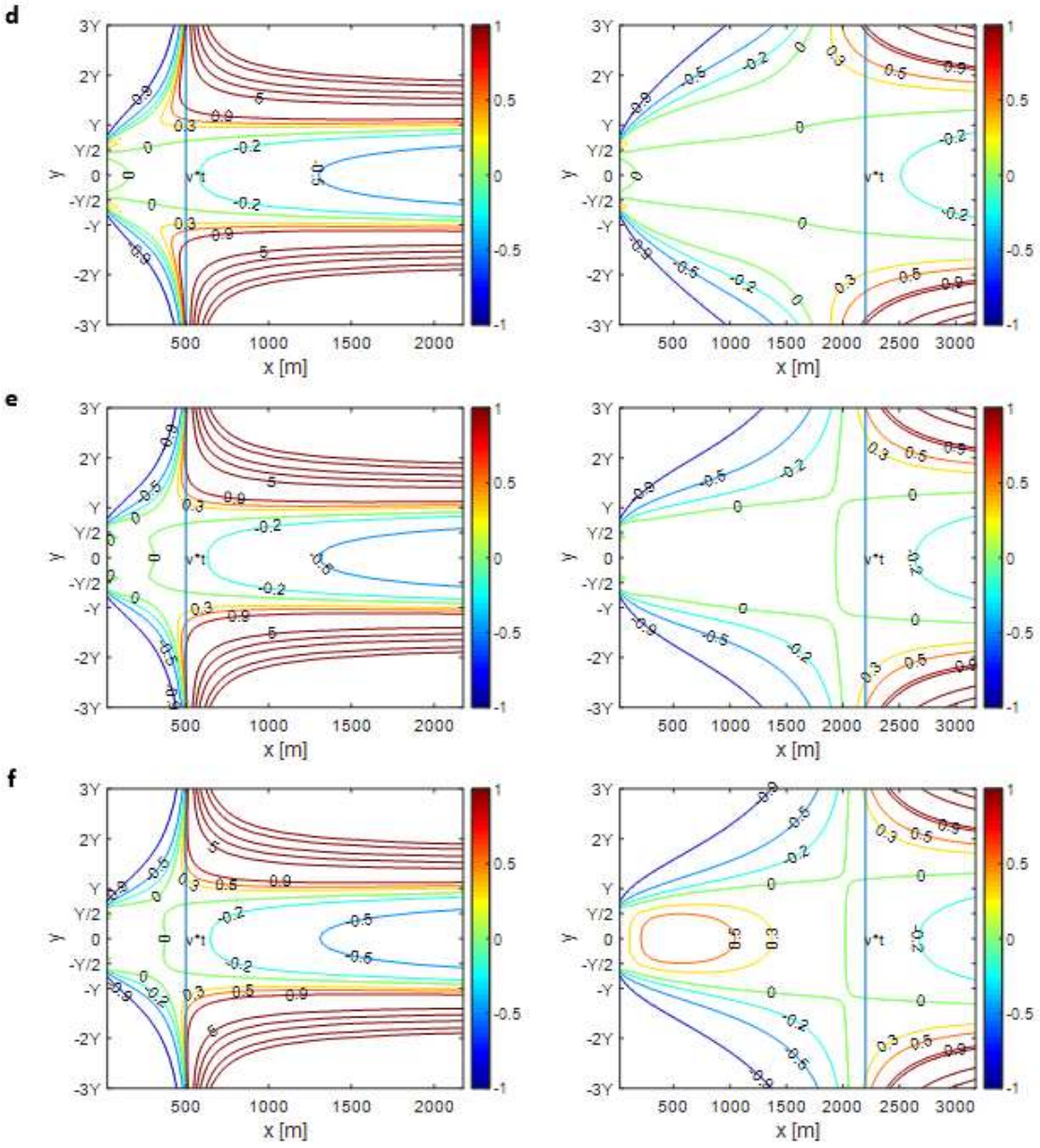


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Figure 4. Diagrams of relative errors at half simulation time (left) and double simulation time (right). Cases d) to f) reacting solute, source decay.

In the zone of width Y along the centerline, at half simulation time $t= t_m/2$, small relative errors behind the advective front can be observed. On the contrary, negative relative errors are observed far from the centerline and on the left hand side of the asymptote are present. Overestimation errors are observed far from the centerline and on the right hand side of the asymptote. If the amplitude of relative errors is again evaluated with reference to the ratio between the actual concentration and the initial one, it is easy to observe that the supposed higher relative errors, for example in figure 3 case c) at x=600, y=-2Y where Er=5, are related to lower concentration values as $c=2*10^{-4}$ mg/l).

Ray diagrams of case a), i.e. conservative solute, and case d) in which u=v, are identical. For double simulation time, it's important to notice how the approximate solution overestimates concentration in the zone along the centerline and behind the advective front and underestimates beyond the advective front in cases e) and f), i.e. when u is less than v and the plume detaches from the boundary. Again cases a) and d) have the same relative error.

Centerline profiles near source

In order to better analyze the results of the proposed solution for small simulation times and near the source of contamination, some concentration profiles in the centerline are presented in figure 5 for cases of table 2 at changing simulation times.

Concentration profiles at different values of λ_s are plotted as a continuous line for the exact integral solution and as a dotted line for the approximated closed form solution.

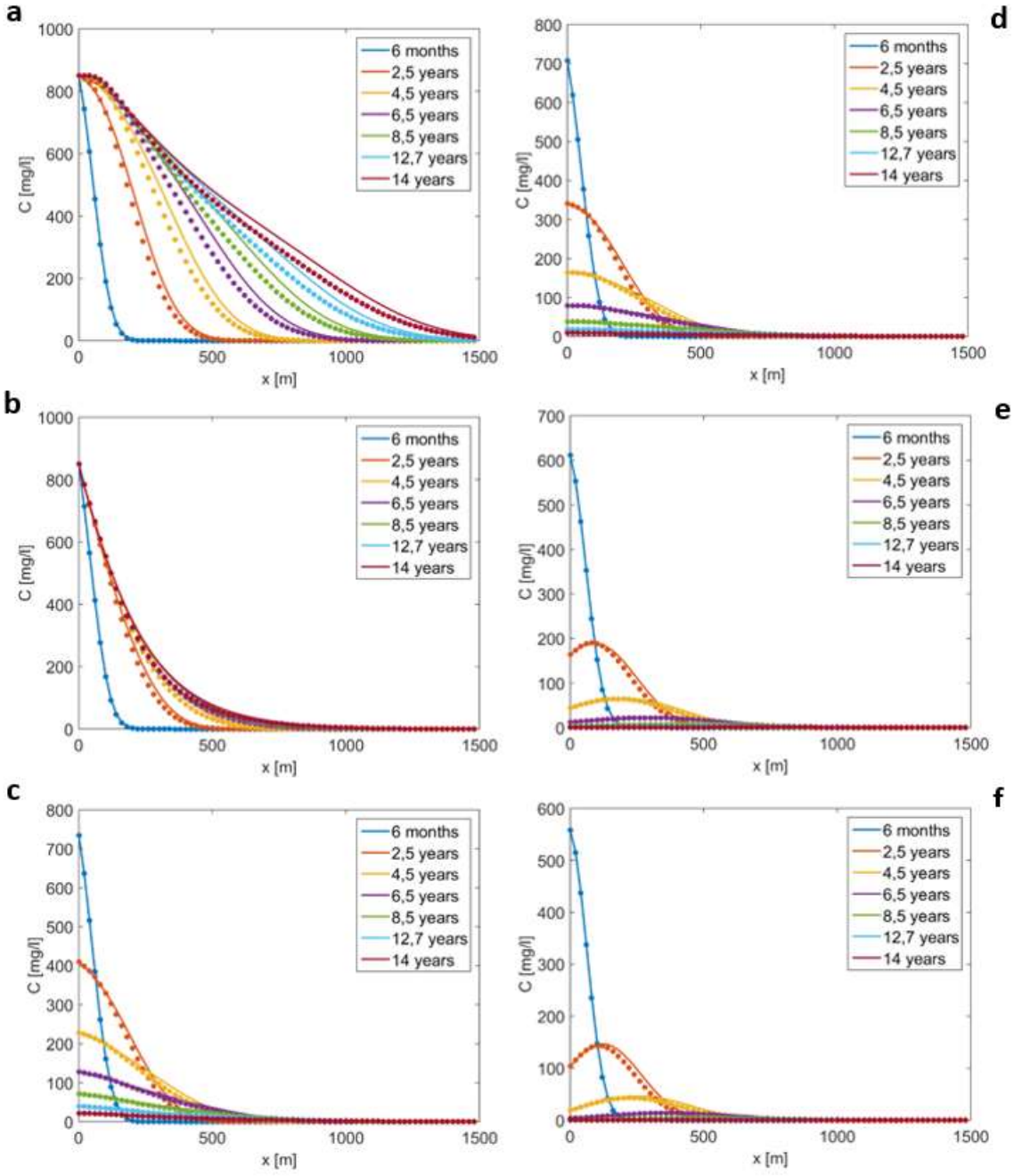

Figure 5. Concentration profiles in the centerline at changing simulation time. Approximated closed form (dotted) versus integral form (continuous). Case a) conservative solute, no source decay. Case b) reacting solute, no source decay. Cases c) to f) reacting solute, source decay.

Transverse profiles

Transverse profiles were analyzed with respect to the advective front, i.e. the distance $\underline{x}$ from the source where a conservative contaminant injected with a Dirac function would be found without dispersion effects at $t=t_m$. In figure 6 three transverse sections at $x=x/2$, $x=x=v*t_m$ and $x=2x$ are plotted, where concentration profiles at different values of λ_s are represented as a continuous line for the exact integral solution and as a dotted line for the approximate closed form solution.

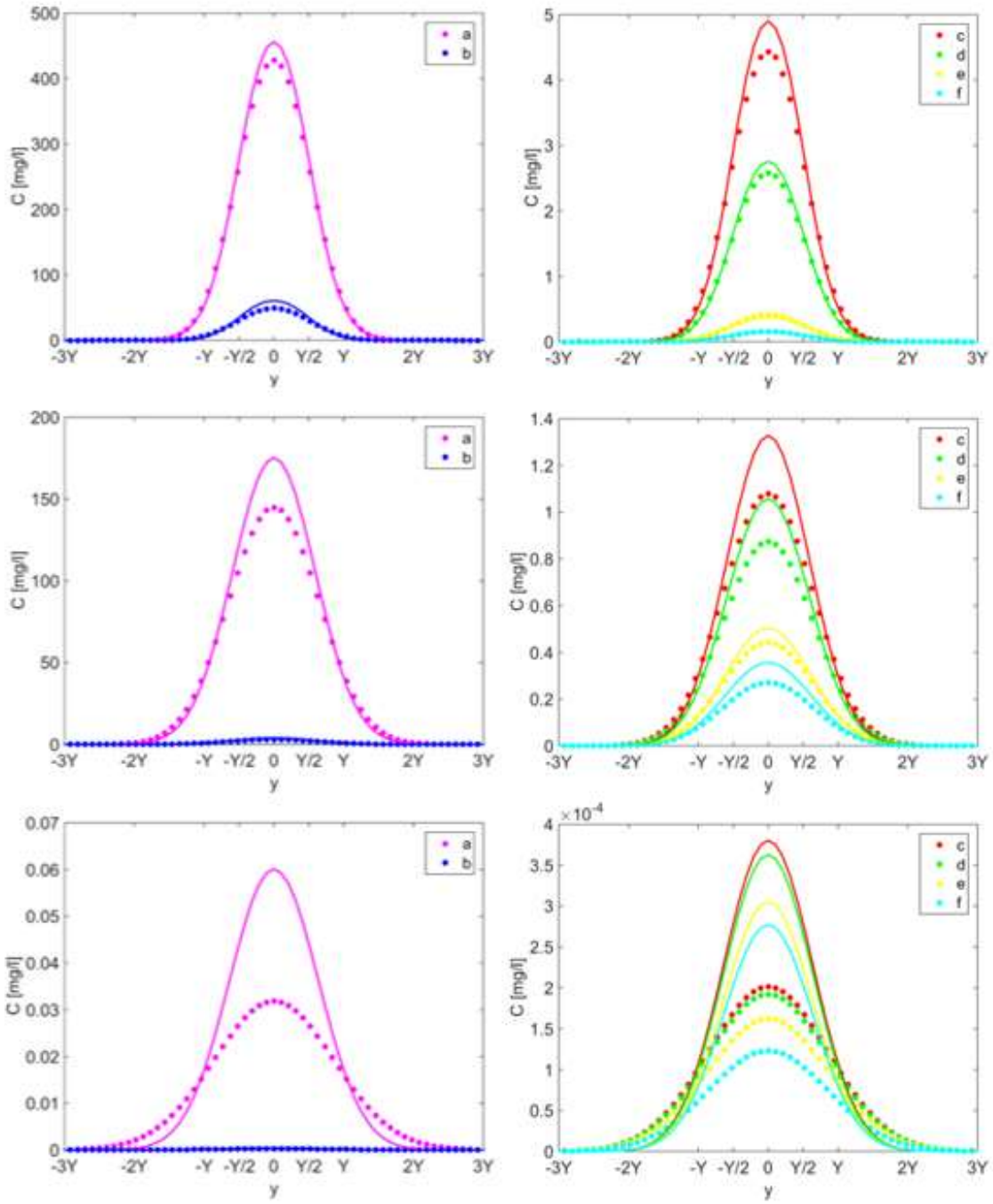

Figure 6. Concentration profiles in three transverse sections at x=$\underline{x}$/2 (top), x=$\underline{x}$=v*t_m (center) and x=2$\underline{x}$ (bottom) for the approximated closed form (dotted) and the integral form (continuous). Case a) conservative solute, no source decay. Case b) reacting solute, no source decay. Cases c) to f) reacting solute, source decay.

435

436 Cases a) and b) are plotted on the left hand side of figure 6 and cases c) to f) on the right
437 hand side. Cases c) to f) are plotted in different graphs since concentration values are much
438 smaller than in cases a) and b), due to source consumption in time.

439 In the region of space far from the centerline the closed form solution overestimates
440 concentration values. This effect increases with values of λ_s but at lower concentration values.

441 By observing figure 6 for all cases a) to f) the value of y where the two solutions
442 converge can be determined. It lies in the intervals (-2Y, -Y/2) and (Y/2, 2Y).

443

444 ## Conclusions

445 A three-dimensional approximate closed form solution with source decay has been
446 presented and compared with the exact solution contained in BIOCHLOR-AT. Relative error
447 diagrams are presented that define areas in the flow field where use of the closed form solution
448 results in minimum error. The study focused on the errors associated with source decay and the
449 effect of simulation time. The concentration profiles given in the form of contours, longitudinal
450 sections and transverse sections, confirm that the closed form solution can be used with
451 acceptable errors in the entire central area of a width at least equal to the source width, both
452 behind and beyond the advective front and with underestimation maximum errors of 20-25% for
453 concentration values up to two orders of magnitude less than the initial source concentration. In
454 the case of source decay, at high simulation times an overestimation error sometimes appears
455 near the source of up to 50% but in these cases concentration values are about three orders of
456 magnitude lower than the initial source concentration. It is finally confirmed that the closed and

457 the open form models give different results far from the centerline beyond the advective front,
458 but this situation corresponds again to negligible values of concentration.

459

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466

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