

Analytical Solutions to the Problem of Natural Attenuation

by

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Abstract

An analytical one-dimensional model of natural attenuation is proposed. The asymptotical expansion for large time of analytical solutions in one dimension are found. Approximate analytical solutions of the solute-transport equation for an arbitrary source of contamination are analyzed. A graphical method of building the solution of the solute-transport equation is demonstrated.

1 Introduction

The process of natural attenuation defined as the process of reduction of the level of contamination due to biodegradation, dispersion, sorption or volatilization, has been modeled by different equations all of which are derivatives from the generic mass balance equation in porous media. The main difference between existing models is in their ability to model the actual process of natural attenuation: some assume a constant source of contamination [1,2], some postulate exponentially decreasing in time source of contamination [3,4], however none of the existing models have solved analytically the equation describing natural attenuation for a generic time-dependent source of contamination. We propose a new analytical method of solving the solute-transport equation by approximating a time dependent source with a multiple step-functional sources. In addition, we derive asymptotic expressions for a constant and a step-functional source in the large time approximation. This approximation is especially useful when predicting the extent and time of contamination decrease below allowable safety standards.

One of the most frequently encountered problems in the environmental research is to correctly describe a contamination source. In practical applications, frequently the source behavior is unknown and thus impossible to describe. We propose a new method in dealing with this problem: instead of estimating the source which in case of groundwater contamination is almost impossible, we propose to install a monitoring well in the direction of the flow of groundwater at the edge of the contaminated soil area. This way the well will serve as a point of contamination source for more remote areas down the stream. Measuring contamination in the “source well” will provide needed information for our model to predict contamination at any location for any time.

Groundwater is believed to be flowing in the direction of the gradient under the action of gravitational force. However, we believe that there is evidence that groundwater does not always flow “downhill”. Then the only explanation of this phenomenon is to attribute the flow of groundwater to the existence of the underground reservoir of water whence the groundwater originates. In our model we assume that the speed of groundwater is independent of distance. This is a good approximation for horizontally flowing groundwater. However, for mountainous

areas where groundwater may have a varying speed, the assumption of constancy of the speed becomes invalid and our model will have to be modified to give realistic results.

2 The Differential Equation for the Solute Transport

The solute transport in groundwater is described by the following equation:

$$\begin{aligned}
 R \frac{\partial C}{\partial t} = & - \frac{\partial}{\partial x} \left(v_x C - D_x \frac{\partial C}{\partial x} \right) \\
 & - \frac{\partial}{\partial y} \left(v_y C - D_y \frac{\partial C}{\partial y} \right) \\
 & - \frac{\partial}{\partial z} \left(v_z C - D_z \frac{\partial C}{\partial z} \right) \\
 & - \lambda C
 \end{aligned} \tag{1}$$

Concentration of the contamination changes due to the change of the flux through space and biodegradation. Assuming $v_y = v_z = 0$, $D_y = D_z = 0$, and the speed and dispersivity are same everywhere in space, equation (1) reduces to the following equation:

$$R \frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - \lambda C \tag{2}$$

where R is the coefficient of retardation, C is the contaminant concentration, λ is the first-order biodegradation decay rate, v_x is speed, D_x is the coefficient of hydrodynamic dispersion defined by the equation:

$$D_x = \alpha_x v_x + wD \tag{3}$$

where α_x is the longitudinal dispersivity, w is an empirical constant, and D is the coefficient of diffusion. The first term in Eq(3) is a contribution of mechanical dispersion while the second term is a correction due to molecular dispersion.

3 The Analytical Model

We shall assume that the solute motion is described by the equation:

$$\frac{\partial C}{\partial t} = -v_c \frac{\partial C}{\partial x} + D_R \frac{\partial^2 C}{\partial x^2} - \lambda_R C \quad (4)$$

where $v_c = v_x/R$, $D_R = D_x/R$, $\lambda_R = \lambda/R$ are the velocity, dispersion and biodegradation rate of the retarded contaminant.

To solve the solute-transport equation (4), one has to define the boundary conditions: $C_0(t) = C(x = 0, t)$, $C(x = \infty, t)$, $C(x, t = 0)$. The first condition defines the source. The second condition defines the asymptotic value of contamination, the third condition defines the initial condition before the source is turned on.

The exact solution of the solute-transport equation is known only for a very limited configurations of the source. However, we can approximate arbitrary function $C_0(t)$ by its discrete values connected with a step-function. The total solution will be given by the superposition of each individual solutions:

$$C(t, x) \cong \sum C_i(t, x) \quad (5)$$

The total amount of contamination over the period of time T is

$$M_{tot} \sim \int_0^T C_0(t) dt = \sum C_0(t_i^c) \Delta t_i^c \quad (6)$$

Where t_i^c is moment in time when the source contamination becomes $C_0(t_i^c)$, and Δt_i^c is the interval of time corresponding to the duration of that discrete value.

3.1 Constant Source Solutions

We shall assume that molecular diffusion is zero ($D=0$). For constant source $C_0(t) = C_0$, contamination $C(t, x)$ can be calculated as [1,2] (see Figure 1 and Figure 2)

$$C(t, x) = \left(\frac{C_0}{2}\right) \exp\left[\frac{x}{2\alpha_x}(1 - \gamma)\right] \cdot \operatorname{erfc}\left(\frac{x - v_c t \gamma}{2\sqrt{D_R t}}\right) + \left(\frac{C_0}{2}\right) \exp\left[\frac{x}{2\alpha_x}(1 + \gamma)\right] \cdot \operatorname{erfc}\left(\frac{x + v_c t \gamma}{2\sqrt{D_R t}}\right) \quad (7)$$

Where

$$\gamma = \sqrt{1 + \frac{4\lambda_R \alpha_x}{v_c}} \quad (8)$$

$$\operatorname{erfc}(y) = 1 - \operatorname{erf}(y) = 1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-t^2} dt \quad (9)$$

And $D_R = \alpha_x v_c$ is the coefficient of mechanical dispersion.

If the source concentration varies in time exponentially: $C_0(t) = C_0 e^{-kt}$, $C(t, x)$ is given by (7) where instead of λ_R one has to substitute $(\lambda_R - k)$ [3,4].

For large y , $\operatorname{erfc}(y)$ can be asymptotically expanded as

$$\operatorname{erfc}(y) = \frac{e^{-y^2}}{y\sqrt{\pi}} \sum_{n=0}^{\infty} (-1)^n \frac{(2n-1)!!}{(2y^2)^n} \quad (10)$$

Asymptotic expansion for large $t \gg x/(v_c \gamma)$ and $x \geq 4\alpha_x$

$$C(t, x) = C_0 \exp\left[\frac{x}{2\alpha_x}(1 - \gamma)\right] - 2C_0 \frac{\sqrt{D_R}}{(v_c\gamma)^2} x \cdot \exp\left[\frac{x}{2\alpha_x}\right] \cdot t^{-3/2} \exp\left[-\frac{(v_c\gamma)^2}{4D_R}t\right] \quad (11)$$

Small Dispersion Approximation. Assuming that the mechanical dispersion is small: $D_R \ll \frac{v_c^2}{\lambda_R}$ (i.e. $\frac{\lambda_R \alpha_x}{v_c} \ll 1$ or $\gamma \cong 1 + \frac{2\lambda_R \alpha_x}{v_c}$), one can analytically calculate the asymptotic expansion of the solution for large time t ($t \gg t_0$) and distances greater than dispersion scale ($x > 4a_x$) (see Figure 2.)

$$C(t, x) = C_0 \exp\left[-\frac{\lambda_R}{v_c}x\right] - 2C_0 \exp\left[\frac{x}{2\alpha_x}\right] \frac{x\sqrt{a_x v_c}}{v_c^2} t^{-3/2} \exp\left[-\lambda_R t - \frac{v_c}{4\alpha_x}t\right] \quad (12)$$

Large Biodegradation Approximation. If the rate of biodegradation is large: $\lambda_R \gg \frac{v_c^2}{D_R}$ (i.e. $\frac{\lambda_R \alpha_x}{v_c} \gg 1$ or $\gamma \cong 2\sqrt{\frac{\lambda_R \alpha_x}{v_c}}$), for large time t ($t \gg t_0$) and distances greater than dispersion scale ($x > 4a_x$)

$$C(t, x) = C_0 \exp\left[-\sqrt{\frac{\lambda_R \alpha_x}{v_c}} \frac{x}{\alpha_x}\right] - \frac{1}{2} C_0 \exp\left[\frac{x}{2\alpha_x}\right] \cdot \frac{x}{\lambda_R \sqrt{a_x v_c}} t^{-3/2} \exp[-\lambda_R t] \quad (13)$$

3.2 The Generic Solution

The generic solution for an arbitrary source $C_0(t)$ can be calculated as the sum step-functional components of $C_0(t)$ (see Figure 3 and Figure 4):

$$C(t, x) = \sum (C(t - t_i^c, x) - C(t - t_i^c - \Delta t_i^c, x)) \quad (14)$$

$$\begin{aligned}
C(t, x) = & \sum \left\{ \left(\frac{C_0(t_i^c)}{2} \right) \exp \left[\frac{x}{2\alpha_x} (1 - \gamma) \right] \cdot \operatorname{erfc} \left(\frac{x - v_c(t - t_i^c)\gamma}{2\sqrt{D_R(t - t_i^c)}} \right) \right. \\
& + \left(\frac{C_0(t_i^c)}{2} \right) \exp \left[\frac{x}{2\alpha_x} (1 + \gamma) \right] \cdot \operatorname{erfc} \left(\frac{x + v_c(t - t_i^c)\gamma}{2\sqrt{D_R(t - t_i^c)}} \right) \\
& - \left(\frac{C_0(t_i^c)}{2} \right) \exp \left[\frac{x}{2\alpha_x} (1 - \gamma) \right] \cdot \operatorname{erfc} \left(\frac{x - v_c(t - t_i^c - \Delta t_i^c)\gamma}{2\sqrt{D_R(t - t_i^c - \Delta t_i^c)}} \right) \\
& \left. - \left(\frac{C_0(t_i^c)}{2} \right) \exp \left[\frac{x}{2\alpha_x} (1 + \gamma) \right] \cdot \operatorname{erfc} \left(\frac{x + v_c(t - t_i^c - \Delta t_i^c)\gamma}{2\sqrt{D_R(t - t_i^c - \Delta t_i^c)}} \right) \right\}
\end{aligned} \tag{15}$$

For large $t \gg t_i^c + \Delta t_i^c + t_0$:

$$C(t, x) = 2 \frac{\sqrt{D_R}}{(v_c \gamma)^2} \sum C_0(t_i^c, \Delta t_i^c) x \cdot \exp \left[\frac{x}{2\alpha_x} \right] t^{-3/2} \exp \left[-\frac{(v_c \gamma)^2}{4D_R} t \right] \tag{16}$$

Where

$$C_0(t_i^c, \Delta t_i^c) = C_0(t_i^c) \left(1 - \exp \left[-\frac{(v_c \gamma)^2}{4D_R} \Delta t_i^c \right] \right) \tag{17}$$

From equation (16), one can derive the formula for the plume evolution (the contamination change in time at any location of the plume):

$$C(t + \Delta t, x) = C(t, x) \exp \left[-\frac{(v_c \gamma)^2}{4D_R} \Delta t \right] \tag{18}$$

3.3 Analytical Study of the Generic Solution

The solution (15), which is the generic solution to the solute-transport equation in one dimension with a step-functional source, can be studied analytically by employing the analytical form of the error function [5]

$$\operatorname{erfc}(x) = 1 - \operatorname{sgn}(x) \sqrt{1 - \exp\left(-x^2 \frac{4/\pi + \alpha x^2}{1 + \alpha x^2}\right)} \quad (19)$$

where $\alpha = 0.147$.

Analytical solutions are depicted graphically for various values of the parameters: $\lambda, v_c, a_x, C_0, X, T, t_c$ in Figures 3-6.

Time dependency of the contamination for a step-functional source for different locations is depicted in Figure 3. As expected, contamination reaches the closest location first. It increases slowly (approximately for 1000 days), reaches its maximum and then begins to decrease at a slower rate (for approximately 1500 days) until it reaches zero. The farther the location, the smaller is the maximum value of the contamination reached, while the duration of contamination stays approximately the same.

Movement of contamination in space is depicted in Figure 4. Its amplitude decreases exponentially with distance: damping of the amplitude occurs at the rate of 1% between 700 m and 1400 m and approximately 99% between the source (0 m) and 700 m.

Time dependency of contamination for a step-functional source for various values of λ, v_c, a_x is depicted in Figure 5. λ and a_x only very slightly affect the time it takes for the contamination to reach a certain location in space. They only influence the amplitude of the contamination: the smaller λ and the greater a_x , the greater the amplitude. The speed, on the other hand, influences both – the time it takes for the contamination to reach a certain location and its amplitude: the greater the speed, the smaller the time and the greater the amplitude.

Distribution of contamination in space for a step-functional source for various values of parameters λ, v_c, a_x is depicted in Figure 5. λ has no effect on the extent of contamination. It influences the magnitude of contamination: the greater the λ , the smaller the magnitude of contamination. a_x , on the other hand, has affect on the extend as well as the amplitude of contamination: the greater the a_x , the great the extent and the amplitude of contamination. The speed influences only the location of contamination and its amplitude, and has no effect on the extent of contamination. The greater the speed, the farther the contamination and the greater its amplitude.

3.4 1,2-DCP Model

We have applied the developed model to realistic set of data of 1,2-Dichloropropane (1,2-DCP) (See Table 1 below). The data for 1,2-DCP was collected between July 2000 and Jan 2004. We have approximated the contamination rate before July 2000 and after Jan 2004. In addition, we have assumed that the biodegradation rate is equal to 0.1 yr^{-1} , the groundwater velocity is 50 m/yr and the mechanical dispersivity is 10 m.

Table 3.1. The Data Set.

Jul-00	Nov-00	Mar-01	Jul-01	Oct-01	Feb-02	May-02	Jul-02	Oct-02	Feb-03	May-03	Aug-03	Jan-04
112	188	168	254	322	2,300	4100	5100	5700	6200	6300	6000	2700

In Figure 6A, time dependency of 1,2-DCP at $x=660\text{m}$ is depicted. In November 2030, 1,2-DCP concentration reaches the MCL level (5 ug/L) (The value obtained graphically).

In Figure 6B, the distribution of 1,2-DCP in space in December 2016 is depicted. At $x = 1170 \text{ m}$ DCP concentration drops below the MCL level.

4 Conclusions

A generic solution to the solute-transport equation with a constant source was studied asymptotically. For large t ($t \gg t_0$), we saw that, in the approximation of small dispersion ($D_R \ll \frac{v_c^2}{\lambda_R}$) the plume dissipates with distance as $\exp\left[-\frac{\lambda}{v_c}x\right]$ and degrades in time as $t^{-3/2}\exp\left[-\lambda t - \frac{v_c}{4\alpha_x}t\right]$. In the approximation of large biodegradation rate ($\lambda \gg \frac{v_c^2}{D_x}$), the plume dissipates with distance as $\exp\left(-\sqrt{\frac{\lambda\alpha_x}{v_c}}\frac{x}{\alpha_x}\right)$ and degrades in time as $t^{-3/2}\exp[-\lambda t]$.

Using a constant-source solution, we derived an analytical form of a generic solution for an arbitrary source $C_0(t)$. For large t ($t \gg t_i^c + \Delta t_i^c + t_0$), we saw that the plume degrades in time as $t^{-3/2}\exp\left[-\frac{(v_c\gamma)^2}{4D_R}t\right]$.

We used analytical form of the $erfc(x)$ function to analyze graphically generic solutions for arbitrary time for a realistic set of data to predict the time and distance of dropping contamination concentration below MCL level.

Groundwater contamination is one of the most notorious problems in the environmental sciences. It is one of the most difficult to monitor as well. Our approach to this problem can be summarized as:

1. Identify the area where the contamination occurred. Install a groundwater monitoring well at the edge of contamination zone. Monitor contamination in this “source well”. It will provide necessary information about the rate at which the groundwater is contaminated.
2. Measure the hydrogeologic parameters: the speed of groundwater, dispersivity.
3. Measure the first-order rate of biodegradation. One of the ways to calculate the biodegradation rate is by using the formula for the plume evolution (equation (18)).
4. Use the analytical formula

$$C(t, x) = 2 \frac{\sqrt{D_R}}{(v_c \gamma)^2} \sum C_0(t_i^c) x \cdot \exp\left[\frac{x}{2\alpha_x}\right] t^{-3/2} \exp\left[-\frac{(v_c \gamma)^2}{4D_R} t\right] \quad (20)$$

To calculate the level of contamination along the direction of the flow of groundwater. In equation (20) we assumed that the time is much larger than time it takes for the groundwater to reach the point x since the level of contamination in the “source well” has become non-detectable.

To calculate concentration of contaminants at arbitrary time at any location, one can use the graphical method like we did for the dataset in Table 1 (see Figure 6 A and B).

References

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- [1] Van Genuchten, M. Th. (1981) Analytical Solutions for chemical transport with simultaneous adsorption, zero-order production and first-order decay. Journal of Hydrology 49: 213-233
- [2] Bear, J. (1972) Dynamics of fluids in porous media. American Elsevier Publishing Co., New-York.
- [5] Winitzki, S. (2008) A handy approximation for the error function and its inverse.

APPENDIX A

A Constant Source Plots

Contamination vs. Time

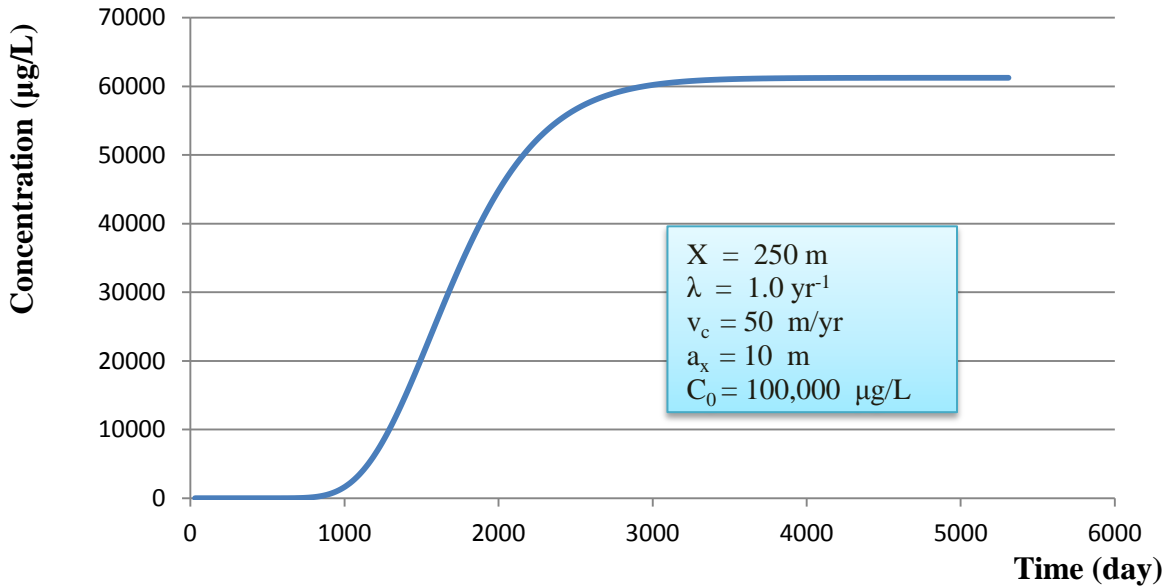
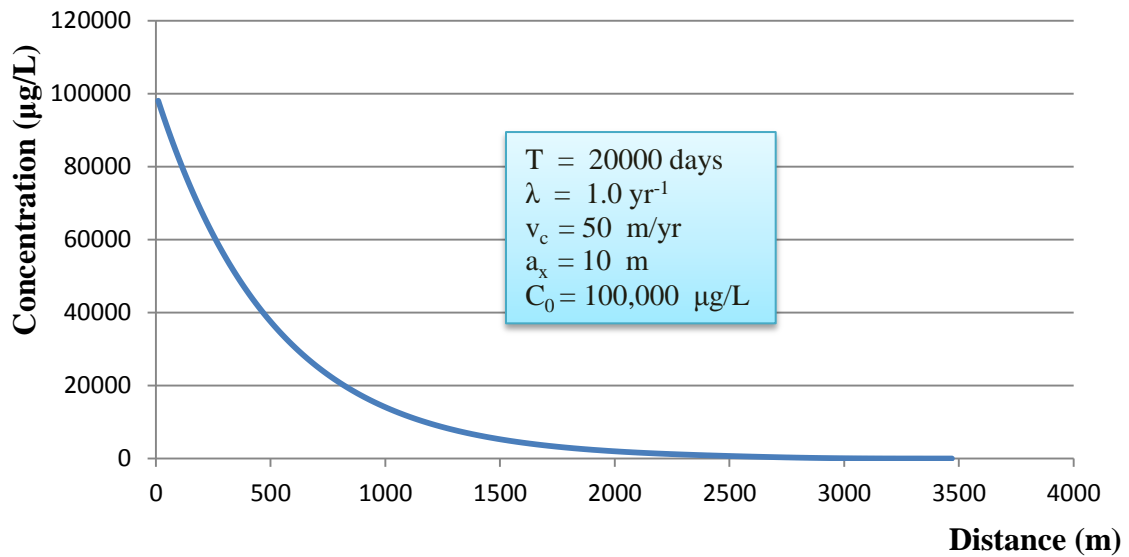


Figure A1. Contamination $C(t, x)$ vs. Time t plot.

Contamination vs. Distance



APPENDIX B

A Step-Functional Source Plots

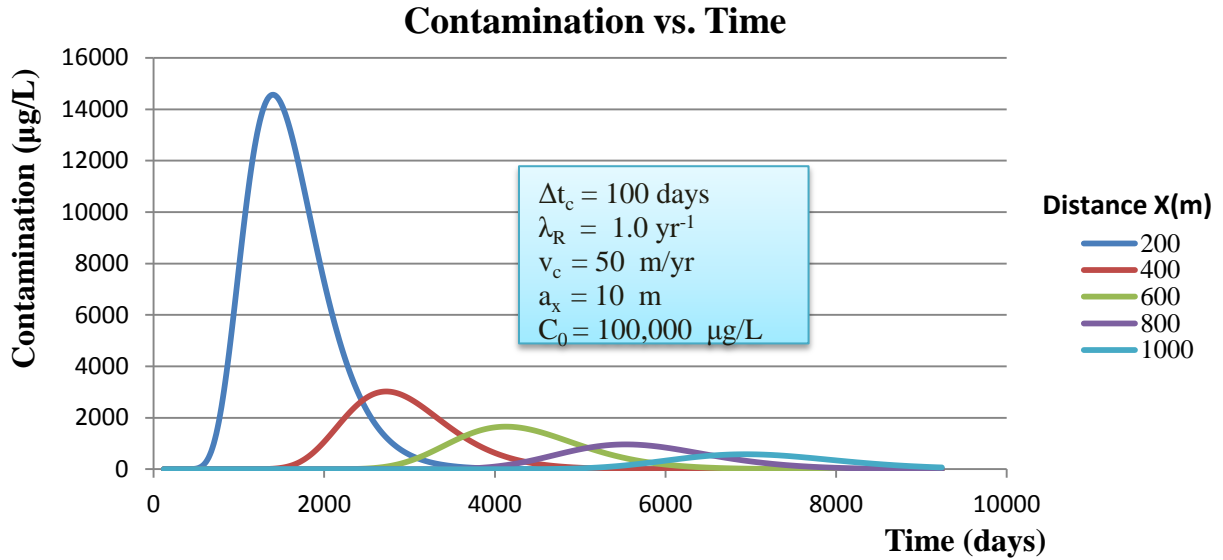


Figure B1. Contamination $C(t, x)$ vs. Time t plot for a step-functional source.

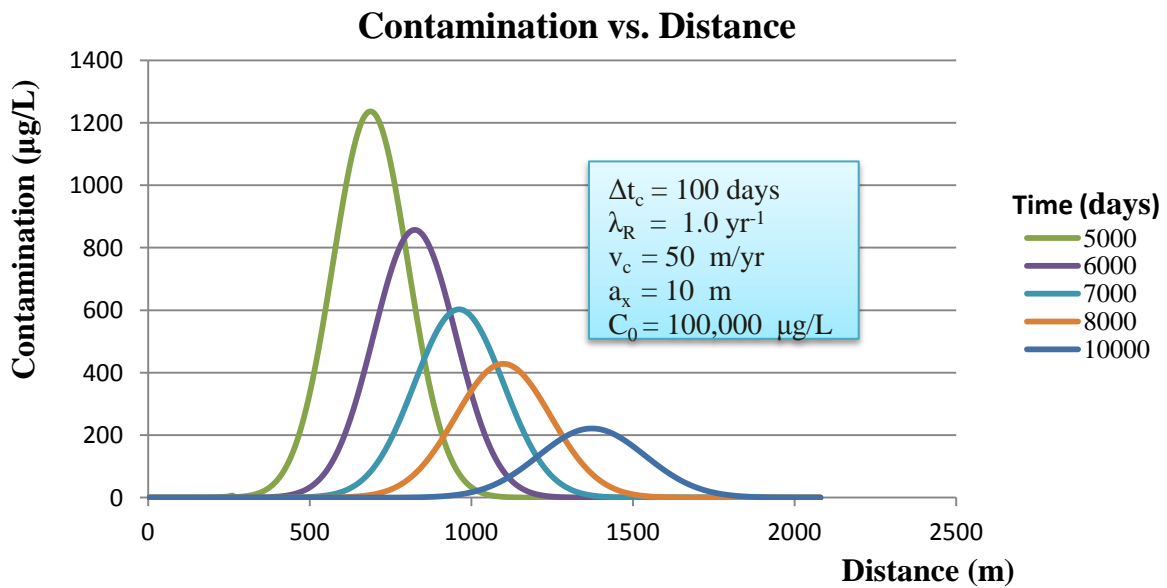
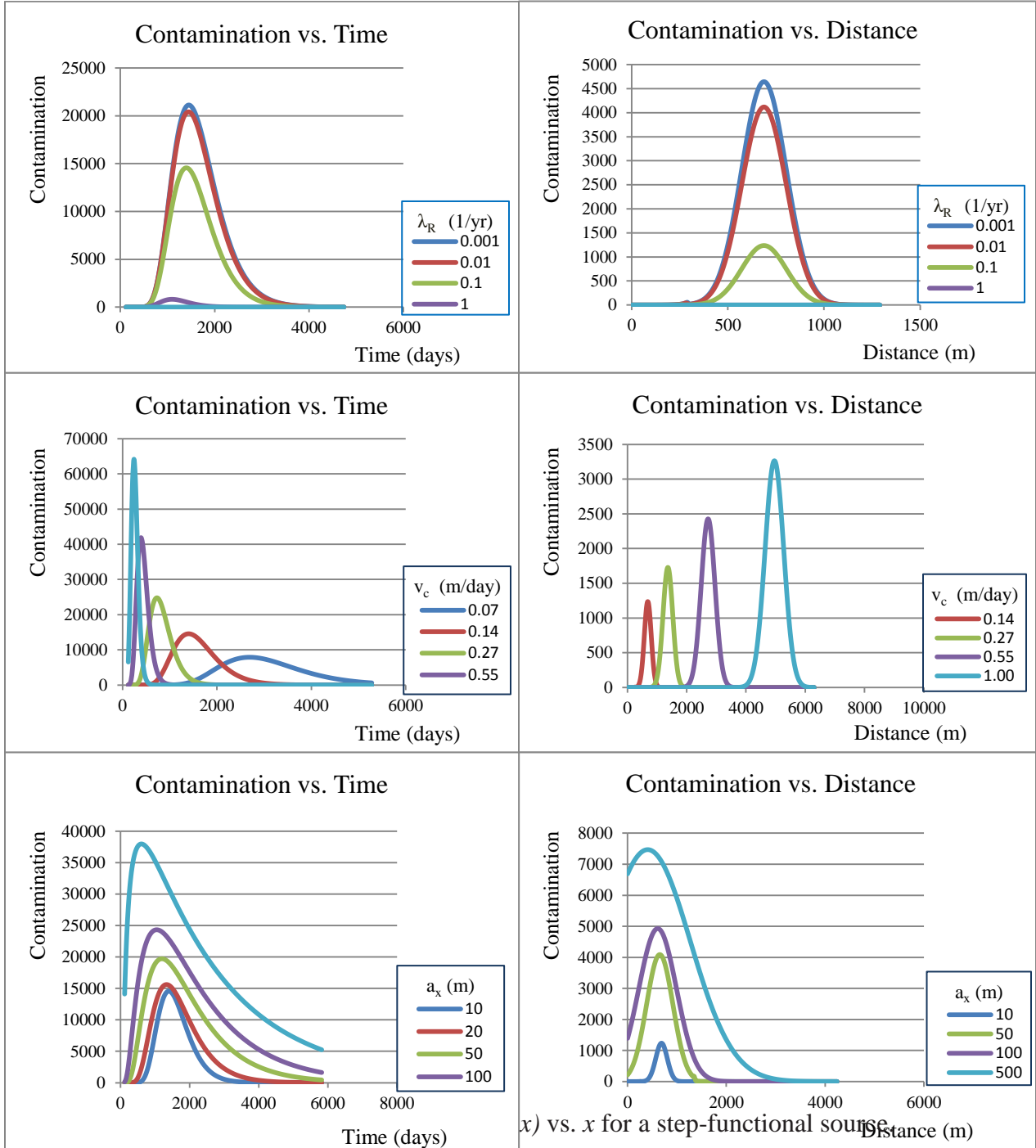


Figure B2. Contamination $C(t, x)$ vs. Distance x plot for a step-functional source.

APPENDIX C

Parameter Dependence of Step-Functional Source Plots



APPENDIX D

1,2-DCP Plots

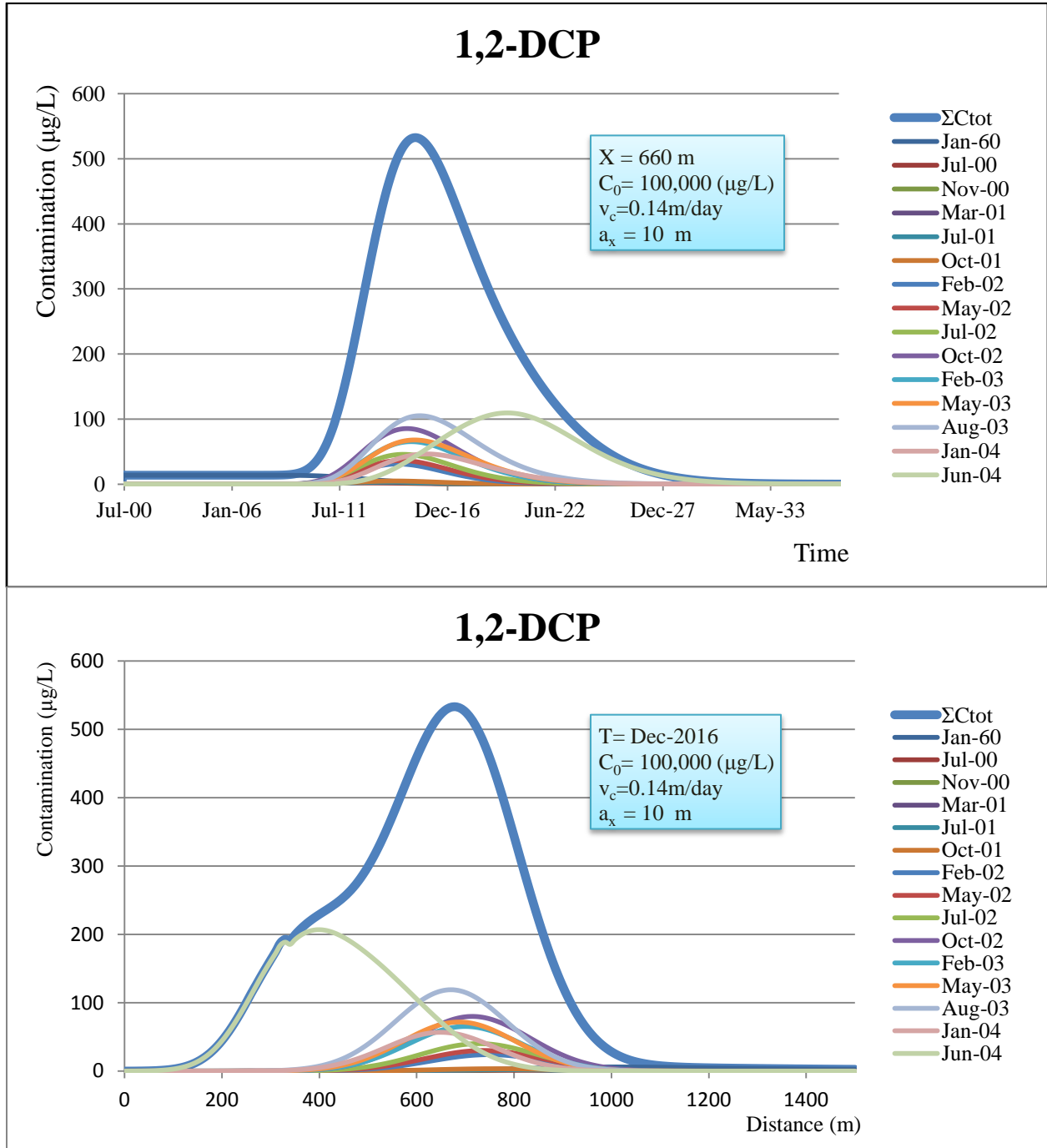


Figure D1-D2. 1,2-DCP