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MEMORANDUM

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SUBJECT: FUMIGANT TRANSPORT MODELING USING HYDRUS: 2. COMPARISON
OF MODEL SIMULATIONS TO ANALYTICAL SOLUTIONS OF FICK'S
SECOND LAW OF DIFFUSION

ABSTRACT

HYDRUS1-D and HYDRUS2/3D numerical simulations of gas phase diffusion in porous media were compared to analytical solutions of Fick's second law of diffusion for two sets of boundary and initial conditions. The numerical simulations included cases using different water-solid and water-air partition coefficients and different water contents. There was close agreement between the numerical and analytical solutions for concentration and flux, demonstrating the computational integrity of the HYDRUS programs for describing the combined vapor phase diffusion/partition process and the first order mass transfer surface volatilization process.

INTRODUCTION

The Department of pesticide Regulation (DPR) has been evaluating several models for simulating post-application fumigant volatilization from soil. These include PRZM, LEACHM, CHAIN2D, HYDRUS1D, and HYDRUS2/3D. While every transport model has some limitations, it is evident that the shortcomings of certain models argue against their general use for simulating fumigant volatilization in the regulatory environment. For example, PRZM relies on a simplified "tipping bucket" scheme for describing water movement in soil as opposed to the more rigorous Richard's equation. This is problematic because soil-water dynamics have a strong influence on simulated vapor phase diffusive transport, so accurate description of soil water movement is critical (Spurlock, 2008). Additional model shortcomings include limited or no on-going support (CHAIN2D, LEACHM), limited or no ability to represent complex geometries (CHAIN2D, HYDRUS1D, LEACHM, PRZM) and poor and/or outdated documentation (CHAIN2D). A few attempts have been made to adapt or modernize older models such as LEACHM (Chen et al., 1995) and CHAIN2D (with modifications as described in Dawson and Smith, 2008). However, problems with lack of support remain for these older models, certain of the modifications included the use of novel and complex algorithms without



review by qualified independent scientists, and the modified models were not adequately validated (Johnson, 2008). The latter shortcomings are severe for a fumigant regulatory program.

In contrast, both HYDRUS1D and HYDRUS2/3D have extensive support (e.g. <<http://www.pc-progress.com/en/Default.aspx?support>>) and continue to be extensively used by vadose modelers around the world to simulate water, heat and solute movement under a variety of conditions. Available at: <<http://www.pc-progress.com/en/Default.aspx?h3d-references>>. Based on these observations, DPR currently considers the most promising models for simulating fumigant movement and volatilization from soils to be HYDRUS1D for simple application geometries and HYDRUS2/3D for more complex problems.

All of the previously mentioned vadose zone transport models, including the HYDRUS models, claim the ability to simulate gas phase transport and surface volatilization. However, even for HYDRUS relatively few studies exist that demonstrate these abilities. DPR has begun to critically examine the ability of HYDRUS to simulate gas phase diffusion and volatilization from soils (e.g. Spurlock, 2008), and this memorandum is one step in that process. The work described here tested HYDRUS' computational integrity by comparing HYDRUS predicted concentrations to those obtained from analytical solutions of Fick's second law of diffusion for two cases with different boundary and initial conditions. These comparisons also included the effect of variable water content and phase partitioning on diffusion.

It has been suggested that advective transport of soil-applied fumigants due to diurnal barometric pressure fluctuations may be significant under certain circumstances (Chen et al., 1995). This question remains open, and may be a topic for future analysis of model capabilities. However, mass flow in the soil gas phase (advection) is not considered in the HYDRUS models or in any of the previously mentioned models. Thus the analysis here is focused solely on gas phase diffusion.

METHODS

Crank (1955) provides analytical solutions of Fick's second law of diffusion (Equation 1) for several initial conditions, boundary conditions and geometries.

$$[1] \quad \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

In Equation 1, C is concentration, D is the diffusion coefficient (assumed constant in both examples here), t is time and x is the distance coordinate. Solutions for two cases were compared to HYDRUS numerical simulation modeling results.

Analytical solutions to the diffusion equation

Case 1. Diffusion inside an infinite column ($-\infty < x < \infty$).

The first example is diffusion from an initial “plug” of solute in an infinite column (Figure 1a).

$$[2] \quad \begin{aligned} C &= C_0 & -w < x < w \\ &= 0 & \text{otherwise} \end{aligned}$$

Practically speaking, the “infinite” condition on column length means that the analytical solution is applicable to a finite system as long as concentration at the system boundaries does not increase above the initial concentration of zero. The solution for $C(t)$ is (Crank, 1955).

$$[3] \quad C = \frac{C_0}{2} \left[\operatorname{erf} \frac{(w-x)}{(4Dt)^{0.5}} + \operatorname{erf} \frac{(w+x)}{(4Dt)^{0.5}} \right]$$

In [3], erf is the “error function”

$$[4] \quad \operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} d\eta$$

where η is a dummy variable.

Case 2. Surface evaporation from a semi-infinite column.

The second example that was investigated was surface evaporation from a semi-infinite medium (Figure 1b). For this case the initial condition is a constant initial solute concentration C_0 throughout the column. The surface evaporation boundary condition is

$$[5] \quad J = -D \frac{\partial C}{\partial x} = \alpha(C_\infty - C_s)$$

In Equation 5, J is the solute flux density, C_S is the concentration at the surface at any time, C_∞ is the concentration in the atmosphere “remote” from the surface, and α is a proportionality constant. All calculations in this paper assumed $C_\infty=0$. In that case, the analytical solution describing the total amount of solute volatilized per unit of cross-sectional area at time t ($=M_t$) is

$$[6] \quad M_t = -\frac{C_0}{h} [\exp(h^2 Dt) \operatorname{erfc}(h\sqrt{Dt}) - 1 + \frac{2}{\sqrt{\pi}} h\sqrt{Dt}]$$

The parameter $h = \alpha/D$, and erfc is the complementary error function: $\operatorname{erfc}(z) = 1 - \operatorname{erf}(z)$. For large values of $[h/(Dt)^{0.5}]$ it is not possible to calculate Equation 6 directly using commonly available software such as Excel or SAS. Crank (1955) provides a convenient asymptotic formula for “large” $h/(Dt)^{0.5}$ as an aid in calculating Equation 6.

$$[7] \quad e^{z^2} \operatorname{erfc}(z) = \frac{1}{z\sqrt{\pi}} \left[1 + \sum_{n=1}^{\infty} (-1)^n \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{(2z^2)^n} \right] = \frac{1}{\pi^{1/2}} \left(\frac{1}{z} - \frac{1}{2z^3} + \frac{1 \cdot 3}{2^2 \cdot z^5} - \cdots \right)$$

Crank (1955) provides no guidance for what “large” is. However, Weber and Arfken (2003) discuss the use of an asymptotic expansion very similar to Equation 7 to estimate $\operatorname{erf}(z)$. They derive an upper bound for error in a partial sum asymptotic estimate for $\operatorname{erf}(z)$ based on the number of terms n included in the expansion. Using their result (page 316), the following upper bound for the error in using Equation 7 to estimate $e^{z^2} \operatorname{erfc}(z)$ can be easily derived.

$$[8] \quad \max \text{ error} = \frac{1}{\sqrt{\pi}} \frac{(2n+1)!!}{2^{n+1} z^{2n+3}}$$

where “!!” refers to the double factorial function. Equation 8 was used to assess the error in the asymptotic expansion for the smallest values of $[h/(Dt)^{0.5}]$, i.e. $= z$) used in Equation 6. The upper bound error yielded an estimate for percent error in flux of $\ll 10^{-10}$ in all cases.

Numerical solutions calculated using HYDRUS1-D and HYDRUS2/3D

For both cases, a horizontal soil column at constant water content with zero water flux at all boundaries was used in HYDRUS for simulations. Solute aqueous phase diffusion coefficients were set to zero to meet the objective of comparing evaluate model simulation results vs analytical solutions for *gaseous phase diffusion.*, so the solute aqueous phase coefficient was set to zero. Gas phase diffusion was the only transport process simulated.

The HYDRUS2/3D simulations were essentially two-dimensional simulations of one-dimensional problems. Preliminary simulations demonstrated that the (arbitrary) choice of column width z (Figure 1) had no effect on the solute distribution in the x direction or flux density in the case of the surface evaporation example.

Comparing numerical solutions of diffusion in a porous medium to analytical solutions.

To compare numerical model solutions to the analytical solution for diffusion within a porous medium (Equation 3), both the solute concentration and diffusion coefficient in the porous medium need to be expressed in volume-averaged terms. For a volatile solute diffusing in a porous medium, the *effective* diffusion coefficient in the medium is lower than it would be in air due to tortuosity and the partitioning of the solute among different soil phases (gas, liquid, solid). The effective diffusion coefficient D_{eff} is:

$$[9] \quad D_{eff} = D_0 \tau_g R_g$$

where D_0 is the solute diffusion coefficient in air, τ_g is the gas phase tortuosity and R_g is the gas phase retardation factor. The D_{eff} can be considered the volume average diffusion coefficient in the sense that it would be the equivalent overall diffusion coefficient in the medium if diffusive transport were occurring throughout the entire medium instead of just in the air-filled porosity.

Most models, including HYDRUS1D and HYDRUS2/3D, account for tortuosity using a relationship based on the work of Millington and Quirk (1961).

$$[10] \quad \tau_g = \frac{a^{(7/3)}}{\theta_s^2}$$

In Equation 10, θ is the volumetric water content, θ_s is saturated water content and a is the volumetric air-filled porosity, typically taken as $(\theta_s - \theta)$. It is evident from Equations 9 and 10 that increases in water content yield lower effective diffusion coefficients by increasing tortuosity.

The gas-phase retardation factor R_g accounts for partitioning.

$$[11] \quad R_g = \frac{aK_H}{(aK_H + \theta + \rho_b K_D)}$$

In Equation 11 ρ_b is soil bulk density, K_D is the soil-water partition coefficient and K_H is the dimensionless air-water partition coefficient (Henry's law constant). Conceptually, the retardation factor may be viewed as the fraction of total solute molecules that are in the gas phase in a given volume of soil.

The HYDRUS programs' output report aqueous concentrations C_w , whereas the analytical solutions are based on total concentration in the medium (total solute mass/total volume). Consequently, conversion of C_w to total volume-averaged concentration C is required before comparison with an analytical solution.

$$[12] \quad C = C_w (aK_H + \theta + \rho_b K_D)$$

After converting to total volume-averaged concentration, numerical solutions of Equation 1 subject to Equation 2 can be easily compared for consistency to Crank's analytical solution—or to each other—by using dimensionless variables. When HYDRUS simulations are conducted using different soil water content θ , Henry's law constant K_H and/or sorption coefficient K_D , the net effect of changing those variables is to modify the effective diffusion coefficient in the medium D_{eff} by changing the gas phase retardation factor (Equations 9 and 11). However, plots of dimensionless concentration $C^* = C/C_0$ vs. dimensionless distance x/w will be congruent for any fixed value of dimensionless time $(D_{eff}t/w^2)^{0.5}$ (Crank, 1955)—regardless of the actual values of the dimensioned variables.

In the second case, the surface evaporation boundary condition for the analytical solution (Equation 5) is similar to the surface boundary layer condition for volatile solutes used in both HYDRUS models.

$$[13] \quad J = \frac{D_0 [C^g(\infty) - C^g(0)]}{d}$$

The parameter d is a measure of diffusive resistance at the surface and is called the boundary layer thickness (Jury et al., 1986). Large values of d correspond to high diffusive resistance and may be used, for example, to simulate the presence of diffusive barriers such as tarps. In Equation 13, $C^g(0)$ is the *gas phase* concentration at the surface (i.e. $x = 0$, Fig. 1b). In many modeling applications, the atmospheric concentration distant from the surface $C^g(\infty)$ is often assumed to be zero. That assumption was employed here for all simulations and the analytical solution calculations (i.e. $C^g(\infty) = C_\infty = 0$).

In the surface evaporation boundary condition, α is a first order mass transfer coefficient (Equation 5) and the parameter $h = \alpha/D$. Comparing Equations 5, 6, and 12, it is evident that for any given HYDRUS simulation the corresponding analytical solution can be calculated using the following substitutions in Equation 6:

$$[14] \quad h = \frac{1}{d} \quad \text{and} \quad D = D_0$$

RESULTS

Case 1. Diffusion from an initial “plug” distribution inside an infinite column

Two different examples were simulated using both HYDRUS1D and HYDRUS2/3D for the case of diffusion from an initial “plug” distribution inside an infinite column. In example 1a, the set of input data given in Table 1 were used in both HYDRUS1-D and HYDRUS2/3D to calculate solute distributions in the column for a given time. The resultant distributions for the two models were essentially identical to each other, and also identical to the analytical solution (Figure 2). For example, peak concentrations in Figure 2 were 0.2151, 0.2149 and 0.2145 for HYDRUS1D, HYDRUS2/3D and the analytical solution, respectively. For both models, the correlation between model simulations and analytical solution were nearly equal to unity (> 0.99999). The mean percent difference between HYDRUS-modeled concentrations and the analytical solution in Figure 2 was 0.3 percent.

For example 1b of diffusion from an initial “plug” distribution inside an infinite column, three different sets of the variables K_D , θ , θ_s , a , τ_g and K_H were created (Table 2), and each set assigned to either HYDRUS1D, HYDRUS2/3D or the analytical solution calculation method. Solute distributions were then calculated for a given fixed dimensionless time $(D_{eff}t/w^2)^{0.5} = 2.598$. Although different values of the input variables were used for each calculation method, the solute distributions from both models were very close to the analytical solution when plotted as dimensionless variables (Figure 3). For example, peak concentrations in Figure 2 were 0.2149, 0.2149 and 0.2145 for HYDRUS1D, HYDRUS2/3D and the analytical solution, respectively. Other triplicate sets of input data also yielded nearly essentially identical results (results not shown).

Table 1. Inputs for case 1a simulations/calculation. Actual units are arbitrary.

Model Inputs	
gas phase diffusion coefficient D_0 ($L^2 T^{-1}$)	24.98
soil volumetric water content θ (-)	0.171
soil saturated water content θ_s (-)	0.400
soil bulk density ρ_b ($M L^{-3}$)	1.5
soil-water partition coefficient K_D ($L^3 M^{-1}$)	0.33
air-water partition coefficient K_H (-)	0.035
HYDRUS1D: half-width of initial solute distribution w (L)	1.054
HYDRUS2D: half-width of initial solute distribution w (L)	1.125
Derived Variables	
air-filled porosity a (-)	0.229
effective diffusion coefficient D_{eff} ($L^2 T^{-1}$)	0.060
gas phase retardation factor R_g (-)	0.0119
gas phase tortuosity τ_g (-)	0.201
duration of simulation: dimensionless time (-)	2.598

L = length, M= mass, T=time

Table 2. Inputs for case 1b simulations/calculation. Units as in Table 1. Duration of all simulations/calculation= 2.598 = dimensionless time = $(D_{eff} t/w^2)^{0.5}$.

Model Inputs	HYDRUS1D	HYDRUS2D	ANALYTICAL SOLUTION
D_0	13.926	51.409	362.446
θ	0.1706	0.0694	0.120
θ_s	0.400	0.400	0.350
ρ_b	1.50	1.50	1.175
K_D	1	5	2
K_H	0.20	0.30	0.05
h	1.054	0.625	1.5
Derived Variables			
a	0.229	0.330	0.230
D_{eff}	0.075	0.1054	0.3037
R_g	0.0267	0.00435	0.00317
τ_g	0.2014	0.4719	0.2646

Case 2. Surface evaporation from a semi-infinite column.

For this example, HYDRUS1D and HYDRUS2/3D simulations were conducted using the parameters in Table 3. The analytical solution (Equation 6) was calculated using $\alpha = D_0/d = 2000$, where those values of D_0 , and d are those used in the modeling simulations (Table 3). The cumulative HYDRUS flux results were taken directly from model output files. The two model simulations and the analytical solution yielded very similar results (Figure 4), with pairwise correlations >0.99999 . The mean percent difference between the HYDRUS predicted fluxes and the analytical results in Figure 4 was 1.3 percent (mean of [(HYDRUS-analytical) / analytical]).

Table 3. Inputs for case 2 “surface evaporation condition” simulations/calculation. Both models and analytical solution used identical inputs.

Input Variables	
D_0	1000
boundary layer thickness for HYDRUS models, d	0.5
θ	0.0694
θ_s	0.40
ρ_b	1.50
K_D	2.5
K_H	0.3
initial uniform conc in medium C_0 ($M L^{-3}$)	1
constant of proportionality, Equation [7] α ($L T^{-1}$)	2000
Derived Variables	
a	0.3306
D_{eff}	11.955
R_g	0.0253
τ_g	0.4723
h ($=\alpha/D_{eff}$, L^{-1})	167.29

CONCLUSION

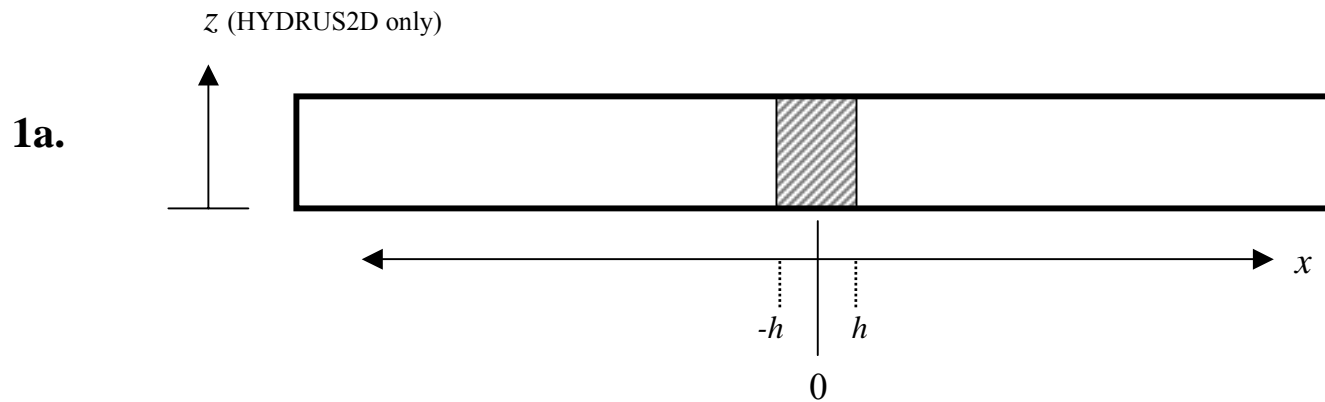
In the first case of volatile solute redistribution by gaseous diffusion from an initial “plug” inside an infinite column, the two HYDRUS1D and HYDRUS2/3D models provided solute distributions that were indistinguishable from the analytical solutions. In addition, the effect of both phase partitioning and water content on modeled gas phase diffusive transport within the porous medium was as expected from first principles (Equations 9 thru 11).

In a second example, the models were used to simulate volatilization from the boundary of a semi-infinite medium at constant initial concentration and using the standard HYDRUS volatile solute boundary condition. This “volatile” boundary condition describes solute volatilization

using first-order mass transfer kinetics (Šimůnek et al., 2007; Šimůnek et al. 2008). The HYDRUS time series predictions of cumulative solute volatilized were essentially identical to the analytical solution. In summary, no computational problems or inaccuracies were observed in any of the comparisons between the HYDRUS models and the analytical solutions.

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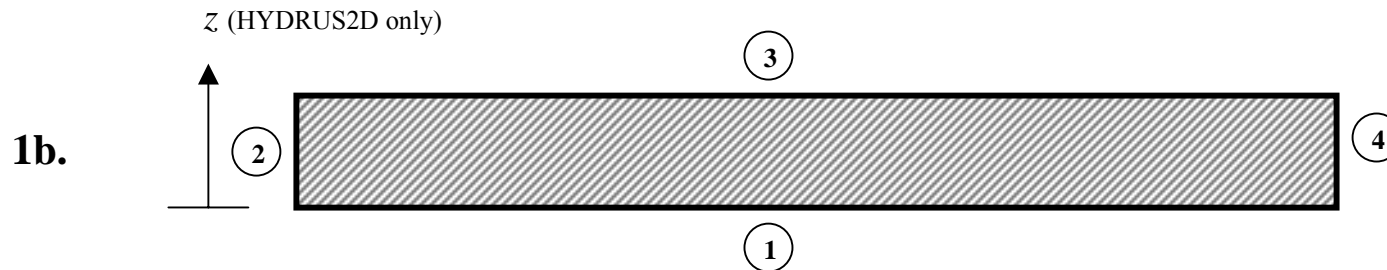
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Boundary conditions

all boundaries

- * water – zero flux
- * solute – zero flux



Boundary conditions

boundaries 1-3:

- * water – zero flux
- * solute – zero flux

boundary 4

- * water – zero flux
- * solute – volatile solute^A

^A Šimůnek et al., 2007
Šimůnek et al. 2008

Figure 1. (a) Case 1. Diffusion inside an infinite column. Initial solute distribution: $\text{conc} = C_0, -h < x < h; = 0$ elsewhere.

(b) Case 2. Volatilization from semi-infinite column at constant initial concentration throughout. Volatilization modeled as first-order mass –transfer process.

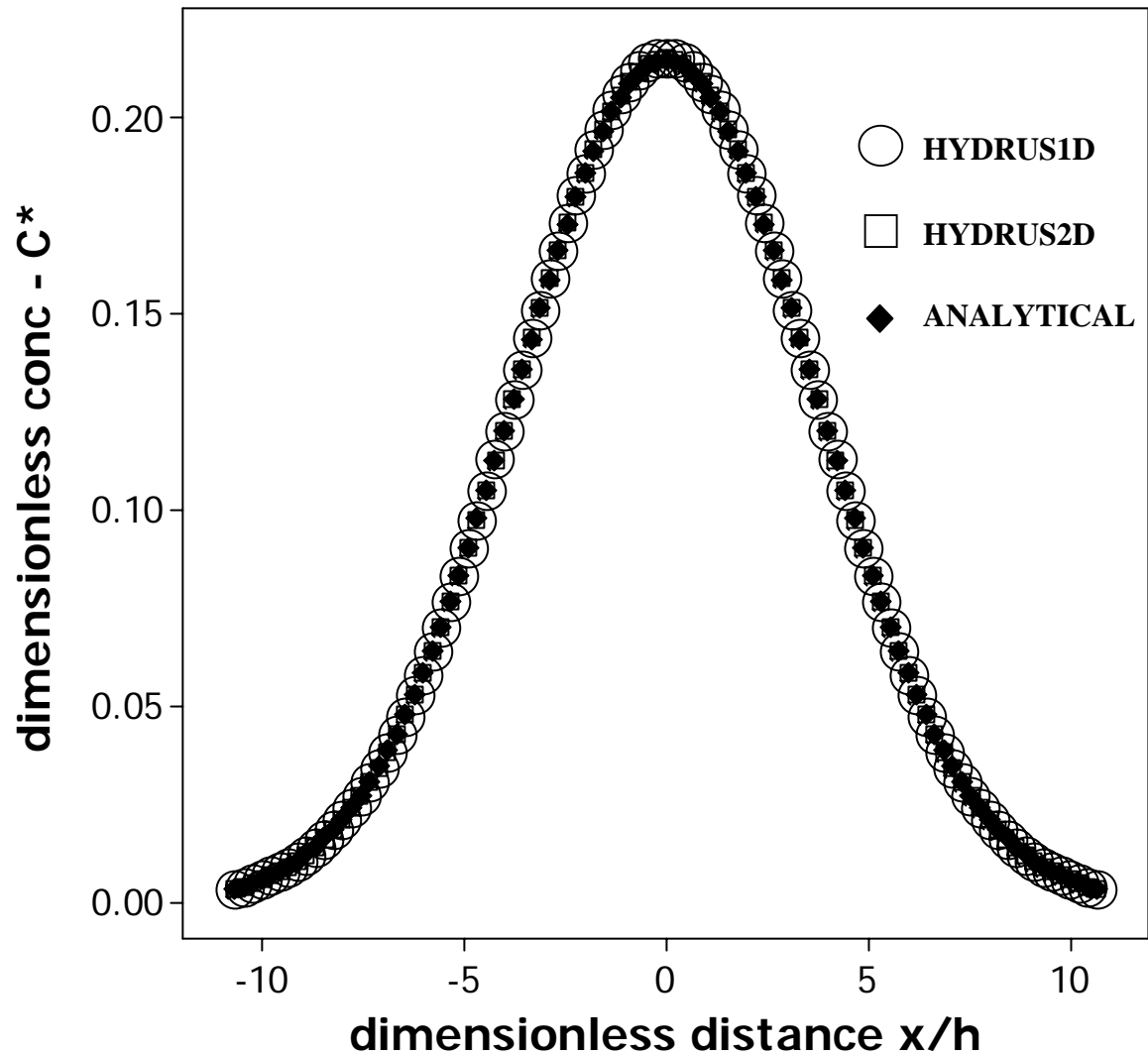


Figure 2. Comparison of solute distributions for Case 1, example 1a. Model outputs and analytical solution for diffusion of initial “plug” solute distribution within a semi-infinite column obtained using identical variables in Table 1.

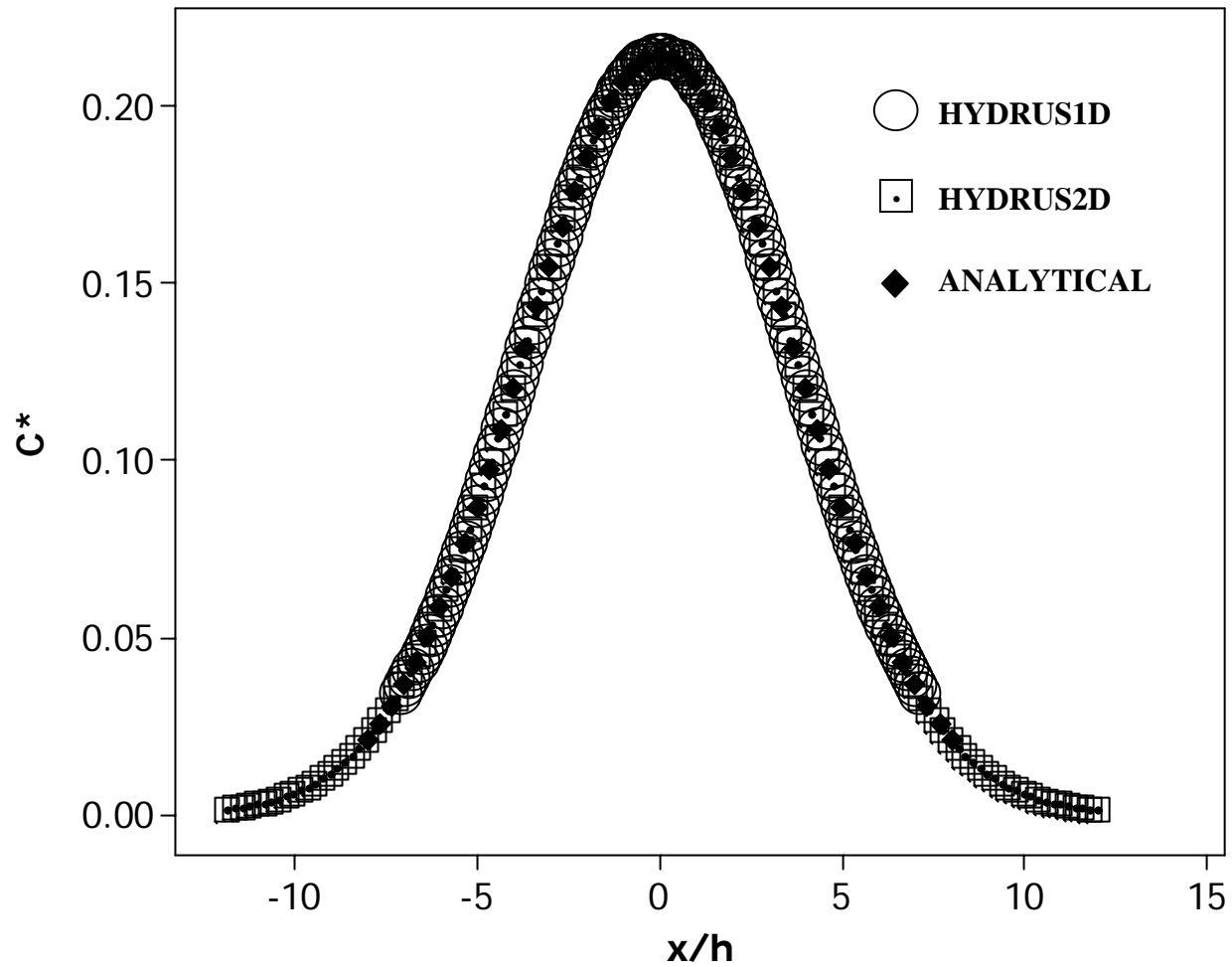


Figure 3. Comparison of solute distributions for Case 1, example 1b. Model outputs and analytical solution for diffusion of initial “plug” solute distribution within a semi-infinite column obtained using various data given in Table 2.

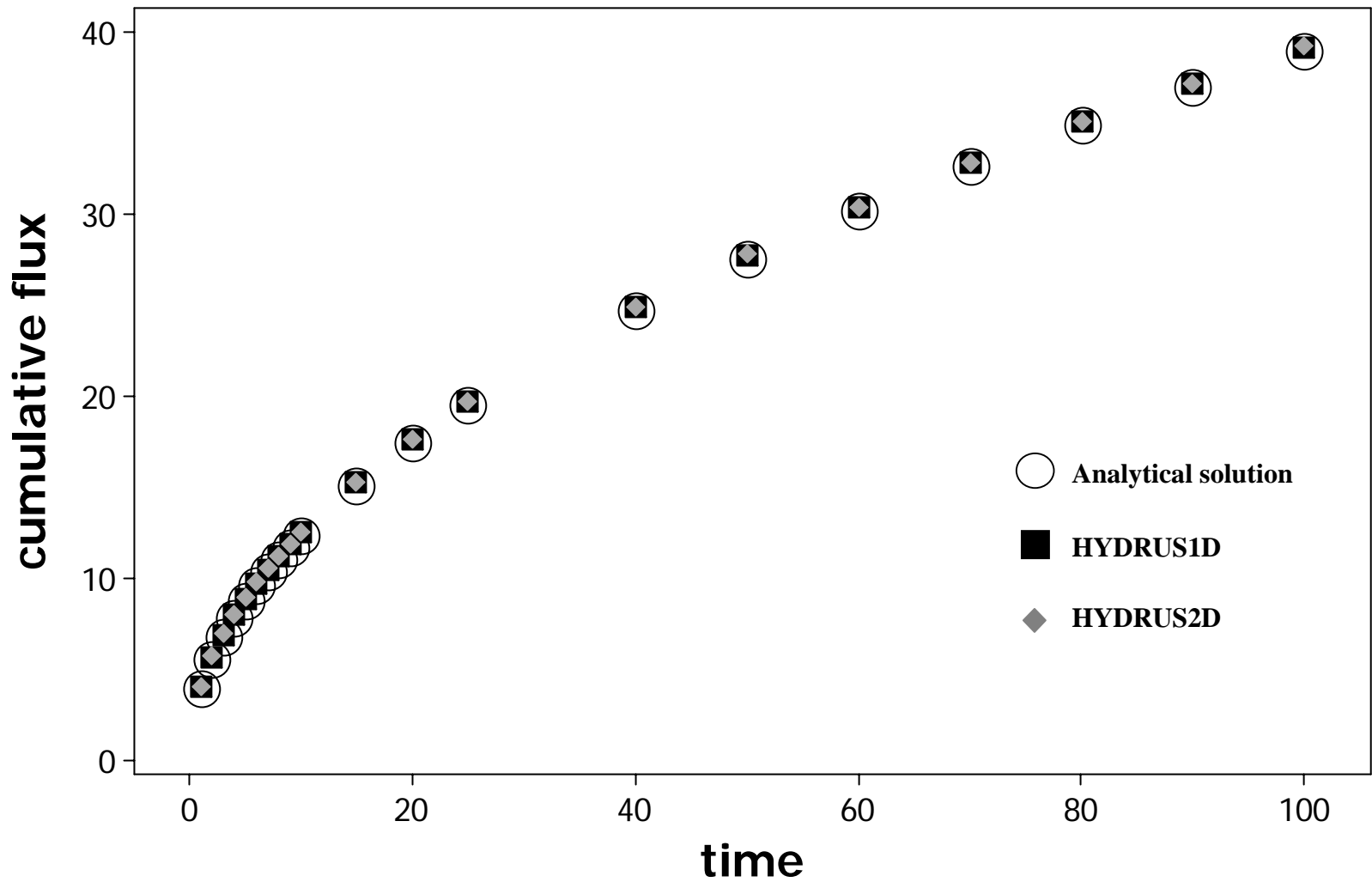


Figure 4. Cumulative volatilization ($M L^{-2} T^{-1}$, arbitrary units) from semi-infinite column at uniform initial concentration. Comparison of cumulative flux time series for Case 2. Variables used for analytical solution and modeling given in Table 3.