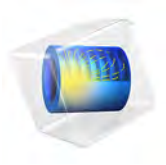


Pesticide Transport and Reaction in Soil

Introduction

Aldicarb is a commercial pesticide, used on a variety of crops, including cotton, sugar beet, citrus fruits, potatoes, and beans. The general population may be exposed to aldicarb primarily through the ingestion of contaminated water and foods.

This example looks at the degradation kinetics of aldicarb and its toxic by-products, investigating both the degradation time-scale as well as the spatial concentration distribution of toxic components. In the first model the chemicals are contained in a water pond, treated as a perfectly mixed system. The second model tracks the detailed distribution of chemicals in soil as the pesticide leaches out of the pond and is transported in water through the ground.

Model Definition

Aldicarb degrades by transformation to the corresponding sulfoxide and the sulfone (both of which are toxic), and is detoxified by hydrolysis to oximes and nitriles. The chain of reactions is illustrated in Figure 1. The toxicity of a chemical species is indicated by its LD_{50} value, signifying the median lethal dose (mg/kg) to half of a test population of rats. As indicated, both the sulfoxide and sulfone analogues of aldicarb are also relatively toxic.

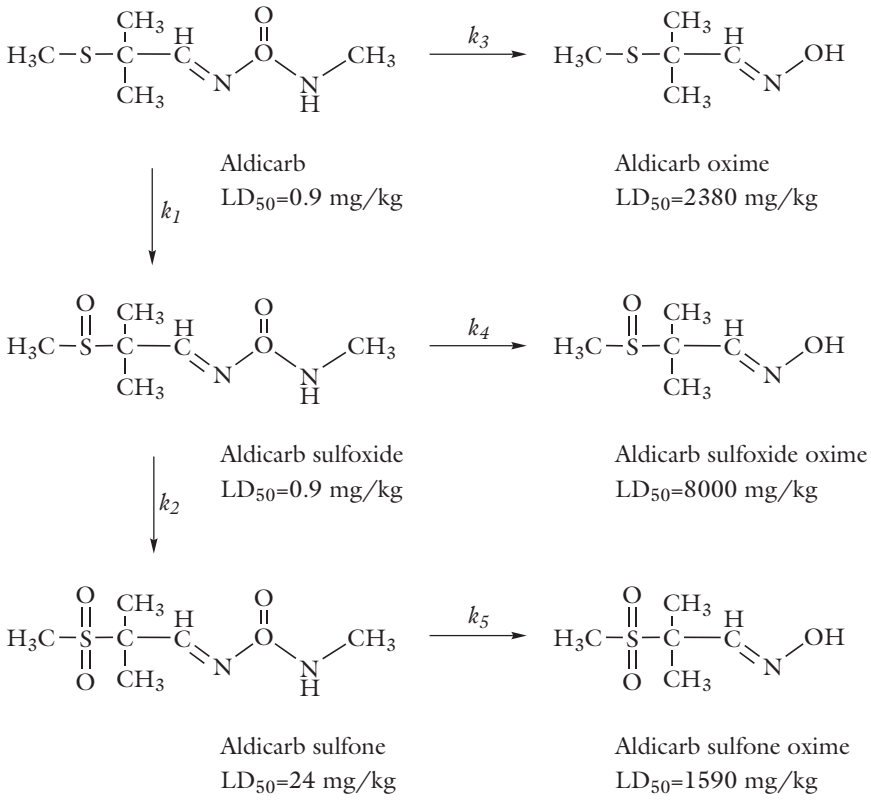


Figure 1: Reaction pathways of aldicarb degradation.

Each of the j unimolecular reactions outlined above has a rate expression of the form

$$r_j = k_j c_i$$

Note that in this example the concentration unit is mol/m^3 and the rate constants are expressed in 1/day.

PERFECTLY MIXED SYSTEM

The first model solves for the decomposition kinetics of aldicarb occurring in a water pond. The pond is treated as a closed and perfectly mixed system. The reaction mechanism illustrated in Figure 1 translates into the following mass balance equations:

- For aldicarb (a)

$$\frac{dc_a}{dt} = -r_1 - r_3$$

- For aldicarb sulfoxide (asx)

$$\frac{dc_{\text{asx}}}{dt} = r_1 - r_2 - r_4$$

- For aldicarb sulfone (asn)

$$\frac{dc_{\text{asn}}}{dt} = r_2 - r_5$$

- For aldicarb oxime (ao)

$$\frac{dc_{\text{ao}}}{dt} = r_3$$

- For aldicarb sulfoxide oxime (asxo)

$$\frac{dc_{\text{asxo}}}{dt} = r_4$$

- For aldicarb sulfone oxime (asno)

$$\frac{dc_{\text{asno}}}{dt} = r_5$$

Solving this set of coupled ODEs provides information on the time scales of the degradation processes.

SPACE- AND TIME-DEPENDENT SYSTEM

In a more detailed model, assume that aldicarb moves from the pond into relatively dry soil. In the soil, the aldicarb decomposes according to the mechanism illustrated in Figure 1. In addition, the pesticide and its decay products are transported by advection, dispersion, sorption, and volatilization.

Geometry

Water is ponded by a ring sitting on the ground. The soil is layered and rests on rocks, with the top layer slightly less permeable than the bottom one. Water moves through the bottom of the ring into the soil. The water level in the ring is known, as is the initial distribution of pressure heads in the soil. There is no flow through the vertical walls or the surface outside of the ring.

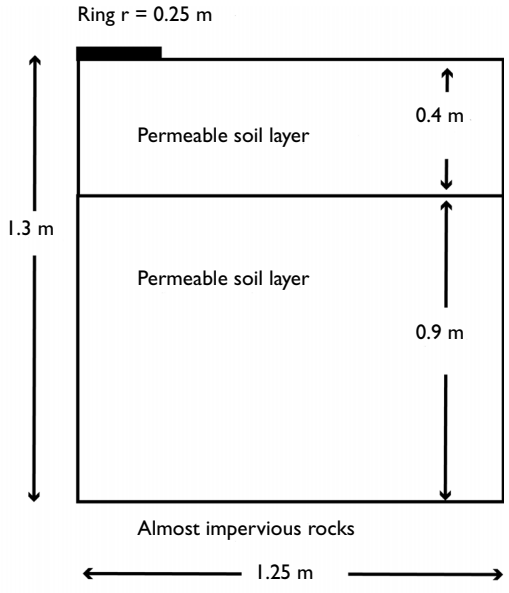


Figure 2: Geometry of the infiltration ring and soil column.

Aldicarb moves with water from the pond into the soil at a constant concentration. In the soil, the chemicals react and also adsorb onto soil particles. Aldicarb and the aldicarb sulfone volatilize to the atmosphere. The sorption, biodegradation, and volatilization proceed in linear proportion to the aqueous concentrations. The soil is initially pristine with zero concentration of the involved chemicals. At the ground surface outside the ring there is volatilization to the atmosphere for c_{a} and c_{asn}. The vertical axis is a line of symmetry. The other boundaries are posed such that the solutes can freely leave the soil column with the fluid flow. Model the problem with 2D axisymmetry and track the solute transport for 10 days.

Fluid Flow

Richards' equation governs the saturated-unsaturated flow of water in the soil. The soil pores are connected to the atmosphere, so you can assume that pressure changes in the air do not affect the flow and use Richards' equation for single-phase flow. Given by Ref. 1, Richards' equation in pressure head reads

$$(C_m + \mathrm{Se}S)\frac{\partial H_p}{\partial t} + \nabla \cdot (-K\nabla(H_p + D)) = 0$$

where C_m denotes specific moisture capacity (m^{-1}); Se is the effective saturation of the soil (dimensionless); S is a storage coefficient (m^{-1}); H_p is the pressure head (m), which is proportional to the dependent variable, p (Pa); t is time; K equals the hydraulic conductivity (m/s); D is the direction (typically, the z direction) that represents vertical elevation (m).

To be able to combine boundary conditions and sources with the Darcy's Law formulation, COMSOL Multiphysics converts Richards' equation to SI units and solves for the pressure (SI unit: Pa). Hydraulic head, H, pressure head, H_p, and elevation D are related to pressure p as

$$H_p = \frac{p}{\rho g}; \qquad H = H_p + D$$

Also, the permeability κ (SI unit: $1/m^2$) and hydraulic conductivity K (SI unit: m/s) are related to the viscosity μ (SI unit: Pa·s) and density ρ (SI unit: kg/m^3) of the fluid, and the acceleration of gravity g (SI unit: m/s^2) by

$$\frac{\kappa}{\mu} = \frac{K}{\rho g}$$

In this problem, $S = (\theta_s - \theta_r)/(1\ \text{m}\cdot\rho g)$ where θ_s and θ_r denote the volume fraction of fluid at saturation and after drainage, respectively. For more details see The Richards' Equation Interface in the *Subsurface Flow Module User's Guide*.

Mass Transport

The governing equation for solute transport describes advection and dispersion of a sorbing, volatilizing, and decaying solute in variably saturated soil.

$$\frac{\partial}{\partial t}(\theta c) + \frac{\partial}{\partial t}(\rho_b c_P) + \mathbf{u}\cdot\nabla c + \nabla\cdot(-\theta D_L \nabla c) = \Sigma R_L + \Sigma R_P + S_c \qquad (1)$$

The Transport of Diluted Species in Porous Media interface implements Equation 1. It describes the time rate of change in two terms: c denotes dissolved concentration (mol/m^3) and c_P is the mass of adsorbed contaminant per dry unit weight of solid (mg/kg). Further, θ denotes the volume fraction of fluid (porosity), and ρ_b is the bulk density (kg/m^3). Because ρ_b amounts to the dried solid mass per bulk volume of the solids and pores together, the term $\rho_b c_P$ gives solute mass attached to the soil as the concentration changes with time.

Solute spreading now includes mechanical dispersion in water plus molecular diffusion for water and air. These three processes appear in the liquid-gas dispersion tensor, whose entries are

$$\theta D_{\mathrm{LG}ii} = \alpha_1 \frac{u_i^2}{|\mathbf{u}|} + \alpha_2 \frac{u_j^2}{|\mathbf{u}|} + \theta \frac{D_\mathrm{m}}{\tau_\mathrm{L}} + \alpha_\mathrm{v} \frac{D_\mathrm{G}}{\tau_\mathrm{G}} k_\mathrm{G}$$

$$\theta D_{\mathrm{LG}ij} = \theta D_{\mathrm{LG}ji} = (\alpha_1 - \alpha_2) \frac{u_i u_j}{|\mathbf{u}|}$$

In these equations, $D_{\mathrm{LG}ii}$ are the principal components of the liquid-gas dispersion tensor; $D_{\mathrm{LG}ij}$ and $D_{\mathrm{LG}ji}$ are the cross terms; α is the dispersivity (m) where the subscripts "1" and "2" denote longitudinal and transverse dispersivities, respectively; D_m and D_G (m^2/d) are molecular diffusion coefficients; and τ_L and τ_G give the tortuosity factors for liquid (water) and gas (air), respectively.

The three solutes—aldicarb, aldicarb sulfoxide, and aldicarb sulfone—have different decay terms, $R_{\mathrm{L}i}$, partition coefficients, $k_{\mathrm{P}i}$, and volatilization constants, $k_{\mathrm{G}i}$. All of the solutes adsorb to soil particles, but only two of the solutes volatilize; sulfoxide does not.

Model Data

The following table provides data for the fluid-flow model:

VARIABLE	UNIT	DESCRIPTION	UPPER LAYER	LOWER LAYER
K_s	m/d	Saturated hydraulic conductivity	0.298	0.454
θ_s		Porosity/void fraction	0.399	0.339
θ_r		Residual saturation	0.001	0.001
α	m^{-1}	alpha parameter	1.74	1.39
n		n parameter	1.38	1.60
H_{p0}	m	Pressure head in ring	0.01	
$H_{p,\mathrm{init}}$	m	Initial pressure head	-(z+1.2) -0.2(z+0.4)	-(z+1.2)

The inputs needed for the solute-transport model are:

VARIABLE	UNITS	DESCRIPTION	VALUE
ρ_b	$\mathrm{kg/m}^3$	Bulk density	1400
k_p	m^3/kg	Partition coefficient	0.0001
D_m	m^2/d	Coefficient of molecular diffusion	0.00374

VARIABLE	UNITS	DESCRIPTION	VALUE
α_r	m	Longitudinal dispersivity	0.005
α_z	m	Transverse dispersivity	0.001
ϕ_L	d^{-1}	Decay rate in liquid	0.05
ϕ_P	d^{-1}	Decay rate on solid	0.01
c_0	mol/m^3	Solute concentration in ring	1.0

Results and Discussion

First, review the results of the perfectly mixed reactor model. Figure 3 shows the concentration profiles of aldicarb and all of its decay products. Only small amounts of aldicarb remain after 10 days. Figure 4 shows the concentration transients of the three most toxic species—aldicarb, aldicarb sulfoxide, and aldicarb sulfone—as well as their sum (see Figure 1 for LD_{50} values). Considering the summed-up contributions, contamination levels clearly remain high even after several months.

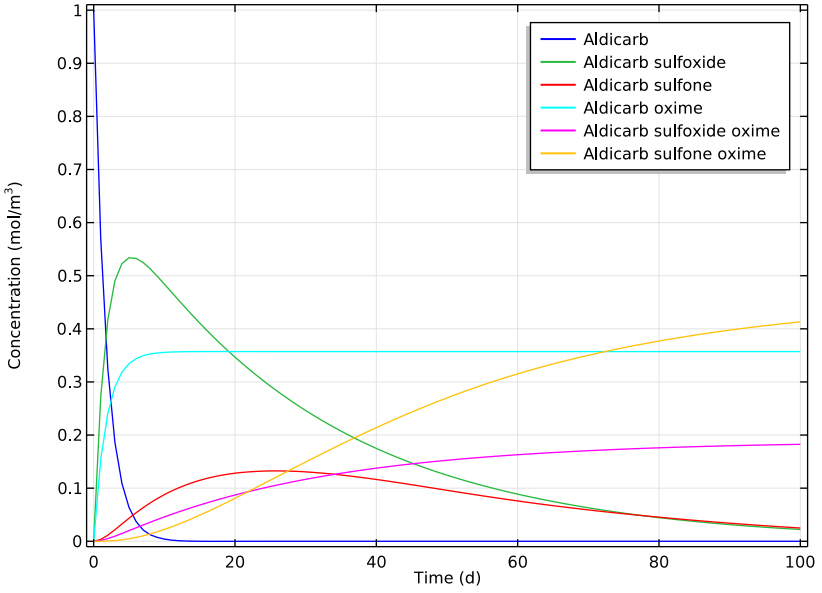


Figure 3: Concentration profiles as reactions occur during a 100 day time period.

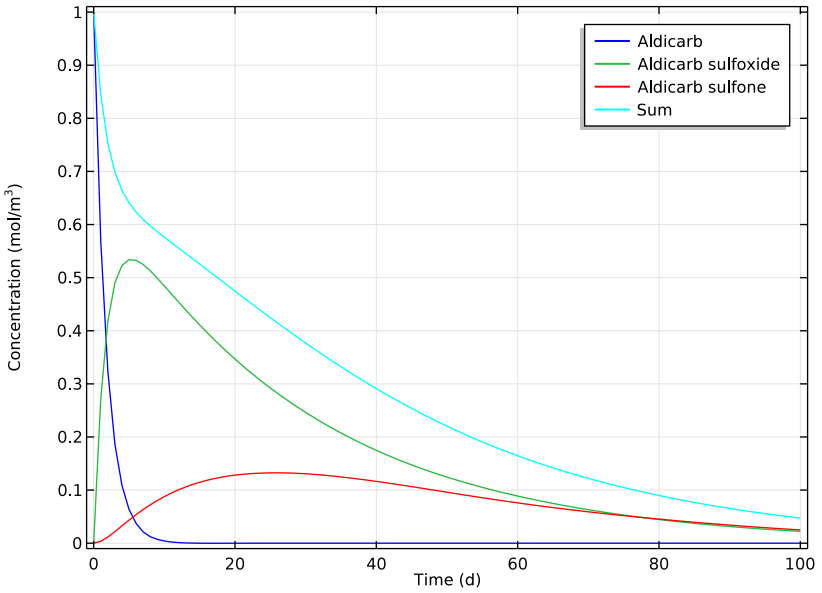


Figure 4: Concentration transients of the most toxic species, aldicarb (c_a), aldicarb sulfoxide (c_asx), and aldicarb sulfone (c_asn).

The following results come from the space- and time-dependent model setup. Figure 5 shows the fluid flow in soil after 0.3 days (left) and 1.0 day (right). The plots illustrate the wetting of the soil with time. As indicated by the arrows, the fluid velocities are relatively high beneath the ponded water.

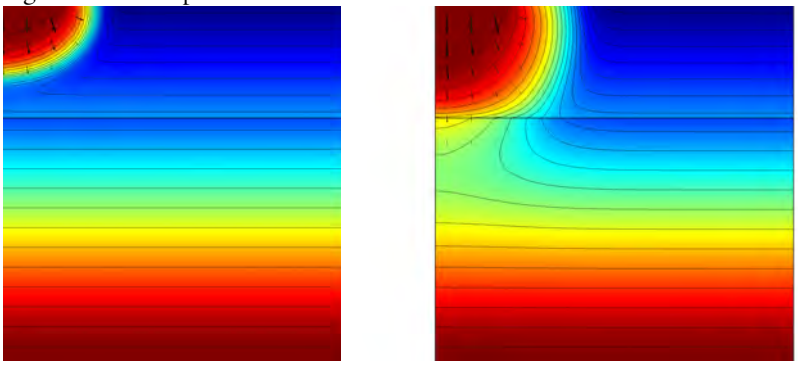


Figure 5: The effective saturation (surface plot), pressure head (contours), and flow velocity (arrows) in a variably saturated soil after 0.3 days (left) and 1 day (right).

Figure 6 through Figure 8 show the concentration distributions of aldicarb and the equally toxic aldicarb sulfoxide after 1, 5, and 10 days of infiltration. Consistent with the evolving flow field, the main direction of transport is in the vertical direction.

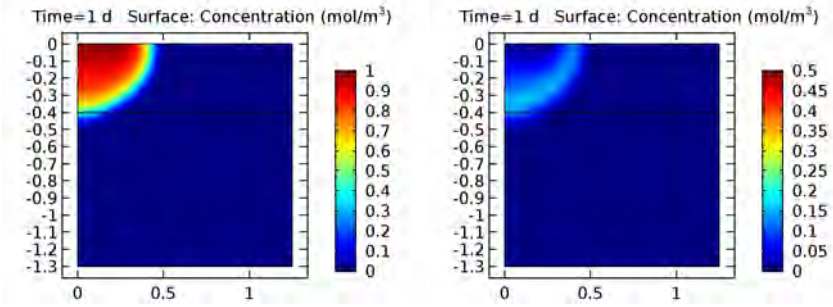


Figure 6: Concentration of aldicarb (left) and aldicarb sulfoxide (right) after 1 day (note the differing color ranges).

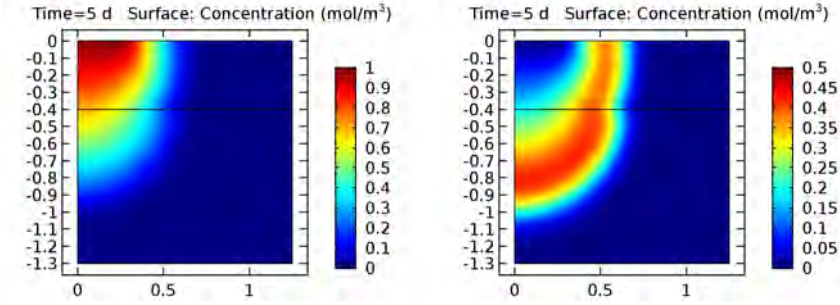


Figure 7: Concentration of aldicarb (left) and aldicarb sulfoxide (right) after 5 days.

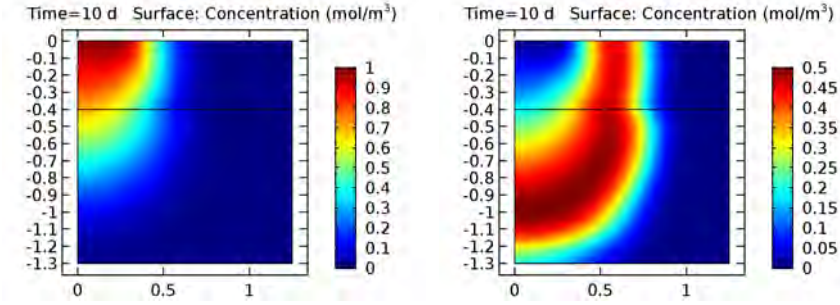


Figure 8: Concentration of aldicarb (left) and aldicarb sulfoxide (right) after 10 days.

The distribution of aldicarb has clearly reached steady-state conditions after 10 days, a time frame that was also predicted by the ideal reactor model (see Figure 4). Results also show that the soil contamination is rather local with respect to the aldicarb source. The aldicarb sulfoxide, on the other hand, can be expected to affect a considerably larger soil volume for a significantly longer time.

References

1. J. Bear, *Hydraulics of Groundwater*, McGraw-Hill, 1978.

2. M.Th. van Genuchten, "A closed-form equation for predicting the hydraulic of conductivity of unsaturated soils," *Soil Sci. Soc. Am. J.*, vol. 44, pp. 892–898, 1980.

Application Library path: `Subsurface_Flow_Module/Solute_Transport/pesticide_transport`

Modeling Instructions

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1. In the **Model Wizard** window, click **2D Axisymmetric**.
2. In the **Select Physics** tree, select **Mathematics>ODE and DAE Interfaces>Global ODEs and DAEs (ge)**.
3. Click **Add**.
4. Click **Study**.
5. In the **Select Study** tree, select **Preset Studies>Time Dependent**.
6. Click **Done**.

GLOBAL DEFINITIONS

Load the rate constants from file.

Parameters

1. On the **Home** toolbar, click **Parameters**.

2 In the **Settings** window for Parameters, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the application's Application Libraries folder and double-click the file `pesticide_transport_parameters_1.txt`.

First consider the aldicard decomposition kinetics in the the water pond treated as a perfectly mixed system.

GLOBAL ODES AND DAES (GE)

Global Equations 1

Read in a set of the equations defining the reactions.

1 In the **Model Builder** window, under **Component 1 (comp1)>Global ODEs and DAEs (ge)** click **Global Equations 1**.

2 In the **Settings** window for Global Equations, locate the **Global Equations** section.

3 Click **Load from File**.

4 Browse to the application's Application Libraries folder and double-click the file `pesticide_transport_reactions.txt`.

5 Locate the **Units** section. Find the **Dependent variable quantity** subsection. From the list, choose **Concentration (mol/m^3)**.

6 Find the **Source term quantity** subsection. From the list, choose **Reaction rate (mol/(m^3*s))**.

STUDY 1

Step 1: Time Dependent

1 In the **Model Builder** window, expand the **Study 1** node, then click **Step 1: Time Dependent**.

2 In the **Settings** window for Time Dependent, locate the **Study Settings** section.

3 From the **Time unit** list, choose **d**.

4 In the **Times** text field, type `range(0,1,100)`.

5 On the **Home** toolbar, click **Compute**.

RESULTS

1D Plot Group 1

1 In the **Model Builder** window, under **Results** click **1D Plot Group 1**.

2 In the **Settings** window for 1D Plot Group, type `Concentration of species (100 days)` in the **Label** text field.

Reproduce Figure 3 with the following steps:

3 Click to expand the **Title** section. From the **Title type** list, choose **None**.

4 Locate the **Plot Settings** section. Select the **y-axis label** check box.

5 In the associated text field, type `Concentration (mol/m<sup>3</sup>)`.

Global 1

1 In the **Model Builder** window, expand the **Results>Concentration of species (100 days)** node, then click **Global 1**.

2 In the **Settings** window for Global, locate the **x-Axis Data** section.

3 From the **Parameter** list, choose **Expression**.

4 In the **Expression** text field, type `t`.

5 From the **Unit** list, choose **d**.

6 Click to expand the **Legends** section. On the **Concentration of species (100 days)** toolbar, click **Plot**.

Concentration of species (100 days)

To plot the concentration of the most toxic species, as in Figure 4, proceed as follows:

1 In the **Model Builder** window, under **Results** right-click **Concentration of species (100 days)** and choose **Duplicate**.

Concentration of species (100 days) 1

In the **Settings** window for 1D Plot Group, type `Concentration of toxic species (100 days)` in the **Label** text field.

Global 1

1 Delete the expressions for `cpm_ao`, `cpm_asno`, and `cpm_asxo`.

2 In the **Model Builder** window, expand the **Results>Concentration of toxic species (100 days)** node, then click **Global 1**.

3 In the **Settings** window for Global, locate the **y-Axis Data** section.

4 In the table, enter the following settings:

Expression	Unit	Description
`cpm_a+cpm_asn+cpm_asx`	`mol/m^3`	Sum

5 On the **Concentration of toxic species (100 days)** toolbar, click **Plot**.

Now solve the time- and space-dependent transport and reaction problem in the soil.

ADD PHYSICS

1 On the **Home** toolbar, click **Add Physics** to open the **Add Physics** window.

2 Go to the **Add Physics** window.

3 In the tree, select **Fluid Flow>Porous Media and Subsurface Flow>Richards' Equation (dl)**.

4 Find the **Physics interfaces in study** subsection. In the table, clear the **Solve** check box for **Study 1**.

5 Click **Add to Component** in the window toolbar.

ADD PHYSICS

1 Go to the **Add Physics** window.

2 In the tree, select **Chemical Species Transport>Transport of Diluted Species in Porous Media (tds)**.

3 Click to expand the **Dependent variables** section. Locate the **Dependent Variables** section. In the **Number of species** text field, type 3.

4 In the **Concentrations** table, enter the following settings:

c_a
c_asx
c_asn

5 Find the **Physics interfaces in study** subsection. In the table, clear the **Solve** check box for **Study 1**.

6 Click **Add to Component** in the window toolbar.

7 On the **Home** toolbar, click **Add Physics** to close the **Add Physics** window.

ADD STUDY

1 On the **Home** toolbar, click **Add Study** to open the **Add Study** window.

2 Go to the **Add Study** window.

3 Find the **Physics interfaces in study** subsection. In the table, clear the **Solve** check box for the **Global ODEs and DAEs (ge)** interface.

4 Find the **Studies** subsection. In the **Select Study** tree, select **Preset Studies>Time Dependent**.

5 Click **Add Study** in the window toolbar.

6 On the **Home** toolbar, click **Add Study** to close the **Add Study** window.

Load the parameters defining the material properties and the geometry from file.

GLOBAL DEFINITIONS

Parameters

1. In the **Model Builder** window, under **Global Definitions** click **Parameters**.
2. In the **Settings** window for Parameters, locate the **Parameters** section.
3. Click **Load from File**.
4. Browse to the application's Application Libraries folder and double-click the file `pesticide_transport_parameters_2.txt`.

GEOMETRY 1

The modeling domain is made up of the two permeable soil layers, each of which is represented by a rectangular domain in 2D axisymmetry.

Rectangle 1 (r1)

1. On the **Geometry** toolbar, click **Primitives** and choose **Rectangle**.
2. In the **Settings** window for Rectangle, locate the **Size and Shape** section.
3. In the **Width** text field, type `1.25`.
4. In the **Height** text field, type `0.9`.
5. Locate the **Position** section. In the **z** text field, type `-1.3`.

Rectangle 2 (r2)

1. Right-click **Rectangle 1 (r1)** and choose **Build Selected**.
2. On the **Geometry** toolbar, click **Primitives** and choose **Rectangle**.
3. In the **Settings** window for Rectangle, locate the **Size and Shape** section.
4. In the **Width** text field, type `1.25`.
5. In the **Height** text field, type `0.4`.
6. Locate the **Position** section. In the **z** text field, type `-0.4`.
7. Right-click **Rectangle 2 (r2)** and choose **Build Selected**.
8. Click the **Zoom Extents** button on the **Graphics** toolbar.

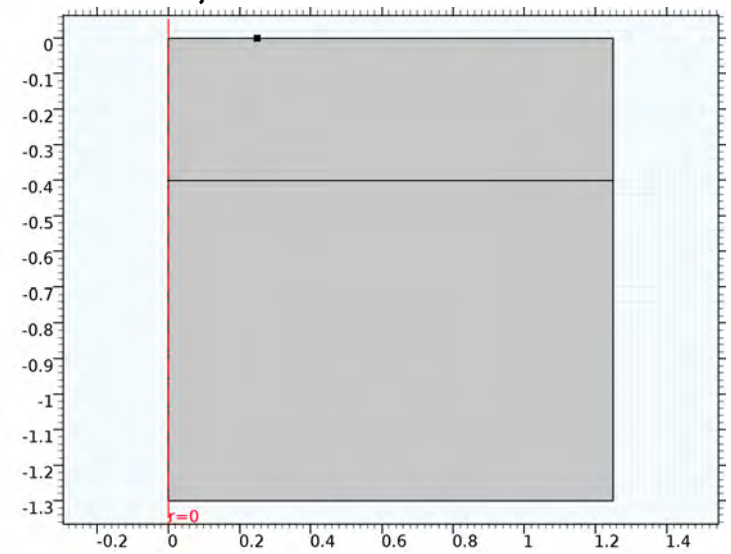
To finish the model geometry, add a point on the top boundary marking the pond's outer rim.

Point 1 (pt1)

1. On the **Geometry** toolbar, click **Primitives** and choose **Point**.
2. In the **Settings** window for Point, locate the **Point** section.

3 In the **r** text field, type `0.25`.

4 Click **Build All Objects**.



DEFINITIONS

Variables 1

1 On the **Home** toolbar, click **Variables** and choose **Local Variables**.

Load the rate expressions from file.

2 In the **Settings** window for Variables, locate the **Variables** section.

3 Click **Load from File**.

4 Browse to the application's Application Libraries folder and double-click the file `pesticide_transport_variables.txt`.

RICHARDS' EQUATION (DL)

Begin by specifying the properties for the bottom soil layer in the default Richards Equation Model node, then duplicate this node and modify the domain selection and properties to match the top layer.

Richards' Equation Model 1

1 In the **Model Builder** window, expand the **Richards' Equation (dl)** node, then click **Richards' Equation Model 1**.

2 In the **Settings** window for Richards' Equation Model, locate the **Fluid Properties** section.

3 From the ρ list, choose **User defined**. In the associated text field, type `rho`.

4 Locate the **Matrix Properties** section. From the **Permeability model** list, choose **Hydraulic conductivity**.

5 In the K_s text field, type `Ks_1`.

6 In the θ_s text field, type `thetas_1`.

7 In the θ_r text field, type `thetar_1`.

8 Locate the **Storage Model** section. From the **Storage** list, choose **User defined**. In the S text field, type `Ss_1`.

9 Locate the **Retention Model** section. In the α text field, type `alpha_1`.

10 In the n text field, type `n_1`.

Richards' Equation Model 2

1 Right-click **Component 1 (comp1)>Richards' Equation (dl)>Richards' Equation Model 1** and choose **Duplicate**.

2 Select Domain 2 only.

3 In the **Settings** window for Richards' Equation Model, locate the **Matrix Properties** section.

4 In the K_s text field, type `Ks_2`.

5 In the θ_s text field, type `thetas_2`.

6 In the θ_r text field, type `thetar_2`.

7 Locate the **Storage Model** section. In the S text field, type `Ss_2`.

8 Locate the **Retention Model** section. In the α text field, type `alpha_2`.

9 In the n text field, type `n_2`.

Initial Values 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Richards' Equation (dl)** click **Initial Values 1**.

2 In the **Settings** window for Initial Values, locate the **Initial Values** section.

3 Click the **Pressure head** button.

4 In the H_p text field, type `-(z+1.2)`.

Initial Values 2

1 Right-click **Component 1 (comp1)>Richards' Equation (dl)>Initial Values 1** and choose **Duplicate**.

2 Select Domain 2 only.

3 In the **Settings** window for Initial Values, locate the **Initial Values** section.

4 In the H_p text field, type `-(z+1.2)-0.2*(z+0.4)`.

Pressure Head 1

1 On the **Physics** toolbar, click **Boundaries** and choose **Pressure Head**.

2 Select Boundary 5 only.

3 In the **Settings** window for Pressure Head, locate the **Pressure Head** section.

4 In the H_{p0} text field, type `Hp0`.

Mass Flux 1

1 On the **Physics** toolbar, click **Boundaries** and choose **Mass Flux**.

2 Select Boundary 2 only.

3 In the **Settings** window for Mass Flux, locate the **Mass Flux** section.

4 In the N_0 text field, type `-N0`.

Gravity 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Richards' Equation (dl)** click **Gravity 1**.

2 In the **Settings** window for Gravity, locate the **Gravity** section.

3 From the **Specify** list, choose **Elevation**.

TRANSPORT OF DILUTED SPECIES IN POROUS MEDIA (TDS)

On the **Physics** toolbar, click **Richards' Equation (dl)** and choose **Transport of Diluted Species in Porous Media (tds)**.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Transport of Diluted Species in Porous Media (tds)**.

2 In the **Settings** window for Transport of Diluted Species in Porous Media, locate the **Transport Mechanisms** section.

3 Select the **Adsorption in porous media** check box.

4 Select the **Dispersion in porous media** check box.

5 Select the **Volatilization in partially saturated porous media** check box.

Partially Saturated Porous Media 1

1 On the **Physics** toolbar, click **Domains** and choose **Partially Saturated Porous Media**.

2 In the **Settings** window for Partially Saturated Porous Media, locate the **Domain Selection** section.

3 From the **Selection** list, choose **All domains**.

4 Locate the **Model Inputs** section. From the $\mathbf{u}$ list, choose **Darcy's velocity field (dl)**.

5 Locate the **Matrix Properties** section. From the ε_p list, choose **User defined**. In the associated text field, type `dl.thetas`.

6 From the ρ list, choose **User defined**. In the associated text field, type `rhob`.

7 Locate the **Saturation** section. From the list, choose **Liquid volume fraction**.

8 In the θ text field, type `dl.theta`.

9 From the **Fluid fraction time change** list, choose **Time change in pressure head**.

10 From the $dH_{p/dt}$ list, choose **Time change in pressure head (dl)**.

11 In the C_m text field, type `dl.Cm`.

12 Locate the **Diffusion** section. In the $D_{L,\,ca}$ text field, type `Dl`.

13 In the $D_{L,\,casx}$ text field, type `Dl`.

14 In the $D_{L,\,casn}$ text field, type `Dl`.

15 In the $D_{G,\,ca}$ text field, type `Dg`.

16 In the $D_{G,\,casx}$ text field, type `Dg`.

17 In the $D_{G,\,casn}$ text field, type `Dg`.

18 Locate the **Adsorption** section. From the **Species c_a** list, choose **User defined**.

19 In the $k_{P,\,ca}$ text field, type `kp_a`.

20 From the **Species c_asx** list, choose **User defined**.

21 In the $k_{P,\,casx}$ text field, type `kp_asx`.

22 From the **Species c_asn** list, choose **User defined**.

23 In the $k_{P,\,casn}$ text field, type `kp_asn`.

24 Locate the **Dispersion** section. From the **Dispersion tensor** list, choose **Dispersivity**.

25 From the **Dispersivity model** list, choose **Transverse isotropic**.

26 In the α table, enter the following settings:

`alphar`
`alphaz`

27 Locate the **Volatilization** section. In the $k_{G,\,ca}$ text field, type `kg_a`.

28 In the $k_{G,\,casn}$ text field, type `kg_asn`.

Reactions 1

1 On the **Physics** toolbar, click **Domains** and choose **Reactions**.

2 In the **Settings** window for Reactions, locate the **Domain Selection** section.

3 From the **Selection** list, choose **All domains**.

4 Locate the **Reaction Rates** section. In the R_{ca} text field, type `dl.theta*(-r_1-r_3)`.

5 In the R_{casx} text field, type `dl.theta*(r_1-r_2-r_4)`.

6 In the R_{casn} text field, type `dl.theta*(r_2-r_5)`.

Outflow 1

1 On the **Physics** toolbar, click **Boundaries** and choose **Outflow**.

2 Select Boundaries 2, 7, and 8 only.

Concentration 1

1 On the **Physics** toolbar, click **Boundaries** and choose **Concentration**.

2 Select Boundary 5 only.

3 In the **Settings** window for Concentration, locate the **Concentration** section.

4 Select the **Species c_a** check box.

5 In the $c_{0,ca}$ text field, type `c0`.

6 Select the **Species c_asx** check box.

7 Select the **Species c_asn** check box.

Volatilization 1

1 On the **Physics** toolbar, click **Boundaries** and choose **Volatilization**.

2 Select Boundary 6 only.

3 In the **Settings** window for Volatilization, locate the **Volatilization** section.

4 In the d_s text field, type `d_s`.

5 Select the **Species c_a** check box.

6 Select the **Species c_asn** check box.

MESH 1

In the **Model Builder** window, under **Component 1 (comp1)** right-click **Mesh 1** and choose **Free Triangular**.

Free Triangular 1

In the **Model Builder** window, under **Component 1 (comp1)>Mesh 1** right-click **Free Triangular 1** and choose **Size**.

Size 1

1 In the **Settings** window for Size, locate the **Geometric Entity Selection** section.

2 From the **Geometric entity level** list, choose **Domain**.

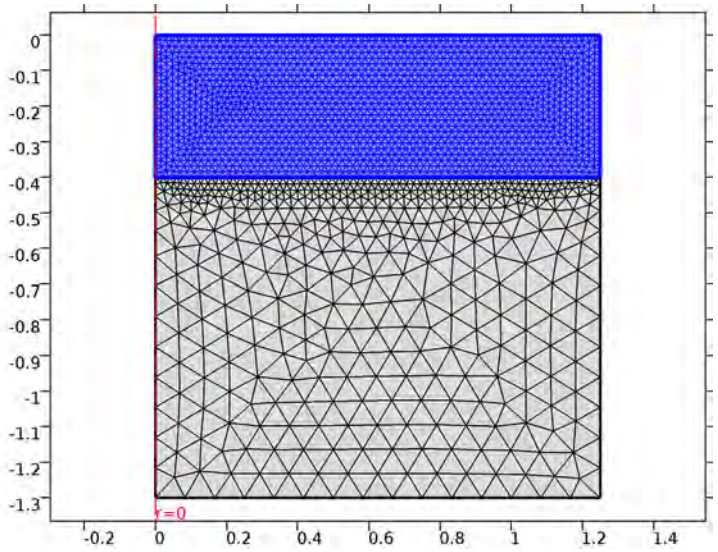
3 Select Domain 2 only.

4 Locate the **Element Size** section. Click the **Custom** button.

5 Locate the **Element Size Parameters** section. Select the **Maximum element size** check box.

6 In the associated text field, type `0.02`.

7 Click **Build All**.



STUDY 2

Step 1: Time Dependent

1 In the **Model Builder** window, expand the **Study 2** node, then click **Step 1: Time Dependent**.

2 In the **Settings** window for Time Dependent, locate the **Study Settings** section.

3 From the **Time unit** list, choose **d**.

4 In the **Times** text field, type `range(0,0.1,0.9) range(1,1,10)`.

5 Locate the **Physics and Variables Selection** section. In the table, clear the **Solve for** check box for the **Global ODEs and DAEs** interface.

6 On the **Home** toolbar, click **Compute**.

RESULTS

Streamline 1

1 In the **Model Builder** window, expand the **Flownet (dl)** node, then click **Streamline 1**.

2 In the **Settings** window for Streamline, locate the **Expression** section.

3 In the **z component** text field, type `dl.w`.

4 On the **Flownet (dl)** toolbar, click **Plot**.

Pressure (dl)

The default plot group contains a surface plot of the pressure distribution. Modify it to show the effective saturation, pressure head, and velocity field at different times.

1 In the **Model Builder** window, under **Results** click **Pressure (dl)**.

2 In the **Settings** window for 2D Plot Group, type `Effective saturation` in the **Label** text field.

3 Locate the **Data** section. From the **Time (d)** list, choose **0.3**.

Surface

1 In the **Model Builder** window, expand the **Results>Effective saturation** node, then click **Surface**.

2 In the **Settings** window for Surface, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Model>Component 1>Richards' Equation> dl.Se - Effective saturation**.

3 Locate the **Coloring and Style** section. Clear the **Color legend** check box.

4 Click the **Zoom Extents** button on the **Graphics** toolbar.

Effective saturation

In the **Model Builder** window, under **Results** right-click **Effective saturation** and choose **Contour**.

Contour 1

1 In the **Settings** window for Contour, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Model>Component 1>Richards' Equation>dl.Hp - Pressure head**.

2 Locate the **Coloring and Style** section. From the **Coloring** list, choose **Uniform**.

3 From the **Color** list, choose **Black**.

4 Clear the **Color legend** check box.

5 Click to expand the **Quality** section. From the **Resolution** list, choose **Finer**.

Effective saturation

Right-click **Effective saturation** and choose **Arrow Surface**.

Arrow Surface 1

1 In the **Settings** window for Arrow Surface, locate the **Coloring and Style** section.

2 From the **Color** list, choose **Black**.

3 On the **Effective saturation** toolbar, click **Plot**.

Compare the plot in the Graphics window with that in the left panel of Figure 5.

Effective saturation

1 In the **Model Builder** window, under **Results** click **Effective saturation**.

2 In the **Settings** window for 2D Plot Group, locate the **Data** section.

3 From the **Time (d)** list, choose **1**.

4 On the **Effective saturation** toolbar, click **Plot**.

Compare with the right panel of Figure 5.

The third default plot shows the solute concentration after 10 days. Follow the steps below to reproduce the plots shown in Figure 6--Figure 8.

Concentration (tds)

1 In the **Model Builder** window, under **Results** click **Concentration (tds)**.

2 In the **Settings** window for 2D Plot Group, type `Concentration, aldicarb` in the **Label** text field.

Surface

1 In the **Model Builder** window, expand the **Results>Concentration, aldicarb** node, then click **Surface**.

2 In the **Settings** window for Surface, click to expand the **Range** section.

3 Select the **Manual color range** check box.

4 In the **Minimum** text field, type `0`.

5 In the **Maximum** text field, type `1`.

These settings give a single color range for all three aldicarb concentration plots.

6 Click to collapse the **Range** section. On the **Concentration, aldicarb** toolbar, click **Plot**.

7 Click the **Zoom Extents** button on the **Graphics** toolbar.

Concentration, aldicarb

1 In the **Model Builder** window, under **Results** click **Concentration, aldicarb**.

2 In the **Settings** window for 2D Plot Group, locate the **Data** section.

3 From the **Time (d)** list, choose **5**.

4 On the **Concentration, aldicarb** toolbar, click **Plot**.

5 From the **Time (d)** list, choose **1**.

6 On the **Concentration, aldicarb** toolbar, click **Plot**.

7 Right-click **Results>Concentration, aldicarb** and choose **Duplicate**.

Concentration, aldicarb 1

In the **Settings** window for 2D Plot Group, type `Concentration, aldicarb sulfoxide` in the **Label** text field.

Surface 1

1 In the **Model Builder** window, expand the **Results>Concentration, aldicarb sulfoxide** node, then click **Surface 1**.

2 In the **Settings** window for Surface, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Model>Component 1>Transport of Diluted Species in Porous Media>c_asx - Concentration**.

3 Click to expand the **Range** section. In the **Maximum** text field, type `0.5`.

Because the maximum concentration for aldicarb sulfoxide is lower, this setting makes better use of the color range.

4 Click to collapse the **Range** section. On the **Concentration, aldicarb sulfoxide** toolbar, click **Plot**.

Concentration, aldicarb sulfoxide

1 In the **Model Builder** window, under **Results** click **Concentration, aldicarb sulfoxide**.

2 In the **Settings** window for 2D Plot Group, locate the **Data** section.

3 From the **Time (d)** list, choose **5**.

4 On the **Concentration, aldicarb sulfoxide** toolbar, click **Plot**.

5 From the **Time (d)** list, choose **10**.

6 On the **Concentration, aldicarb sulfoxide** toolbar, click **Plot**.

You can also visualize the evolution of the concentration distributions with time through animations. By adding **Animation** features under the **Export** node, you can generate movies in GIF, Flash, and AVI format. Alternatively, add Player features with animations contained inside the model MPH-file as follows:

Concentration, aldicarb

1 In the **Model Builder** window, under **Results** click **Concentration, aldicarb**.

2 On the **Concentration, aldicarb** toolbar, click **Animation** and choose **Player**.

Concentration, aldicarb sulfoxide

1 In the **Model Builder** window, under **Results** click **Concentration, aldicarb sulfoxide**.

2 On the **Concentration, aldicarb sulfoxide** toolbar, click **Animation** and choose **Player**.