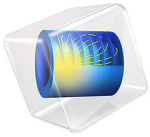


Pesticide Transport and Reaction in Soil

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.

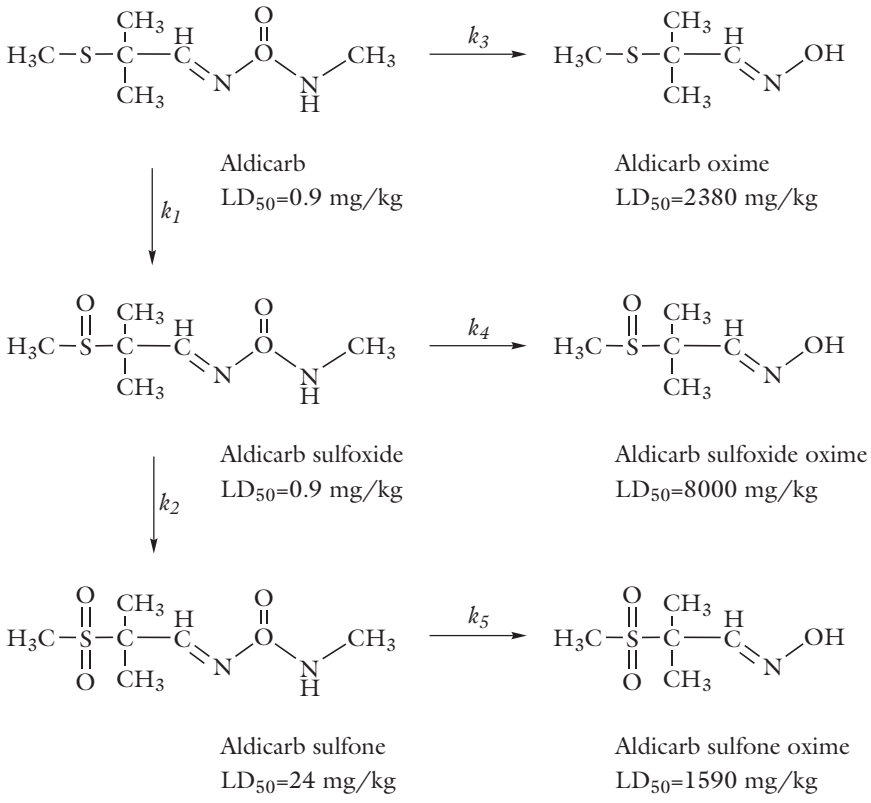


Figure 1: Reaction pathways of aldicarb degradation.

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 convection, 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.

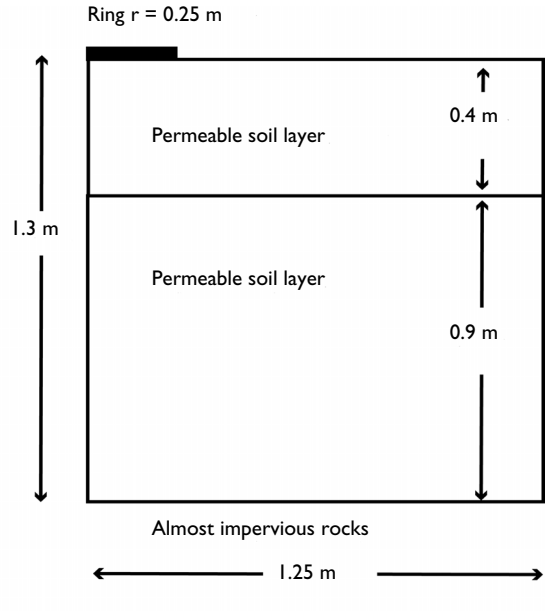


Figure 2: Geometry of the infiltration ring and soil column.

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}. Model the problem with 2D axisymmetry and track the solute transport for 10 days. The vertical axis to the left is the symmetry axis. Add infinite elements to the right axis such that the solutes can freely leave the soil column with the fluid flow.

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

$$(C_{\mathrm{m}} + S_{\mathrm{e}} S_{\mathrm{p}}) \frac{\partial H_p}{\partial t} + \nabla \cdot (-K \nabla (H_p + D)) = 0$$

where C_{m} denotes specific moisture capacity (m^{-1}); $\mathrm{S_e}$ is the effective saturation of the soil (dimensionless); S_{p} 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: $1/\mathrm{m}^2$) and hydraulic conductivity K (SI unit: m/s) are related to the viscosity μ (SI unit: Pa·s) and density ρ (SI unit: $\mathrm{kg/m}^3$) of the fluid, and the acceleration of gravity g (SI unit: $\mathrm{m/s}^2$) by

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

In this problem, $S_{\mathrm{p}} = (\theta_{\mathrm{s}} - \theta_{\mathrm{r}})/(1\ \mathrm{m} \cdot \rho g)$ 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.

$$\frac{\partial}{\partial t}(\theta c) + \frac{\partial}{\partial t}(\rho_{\mathrm{b}} c_{\mathrm{P}}) + \mathbf{u} \cdot \nabla c + \nabla \cdot (-\theta D_{\mathrm{L}} \nabla c) = \Sigma R_{\mathrm{L}} + \Sigma R_{\mathrm{P}} + S_{\mathrm{c}} \qquad (1)$$

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

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

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

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	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
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 as well as the sum of the three most toxic species — aldicarb, aldicarb sulfoxide, and aldicarb sulfone (see Figure 1 for LD_{50} values). Only small amounts of aldicarb remain after 10 days. Considering the

summed-up contributions, contamination levels clearly remain high even after several months.

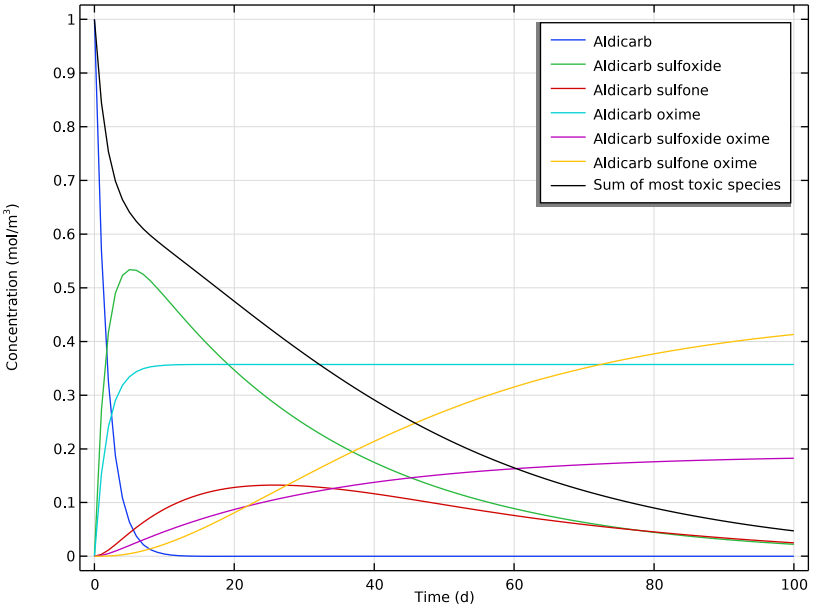


Figure 3: Concentration profiles as reactions occur during a 100 day time period.

The following results come from the space- and time-dependent model setup. Figure 4 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.

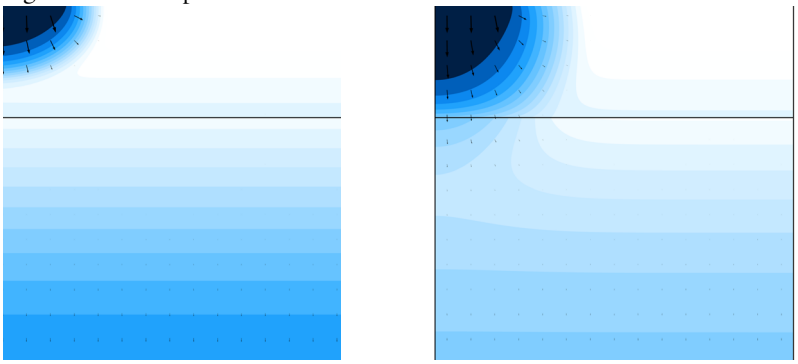


Figure 4: The effective saturation (surface plot), pressure head (contours), and flow velocity (arrows) in a variably saturated soil after 0.3 days (left) and 1 day (right).

Figure 5 through Figure 7 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.

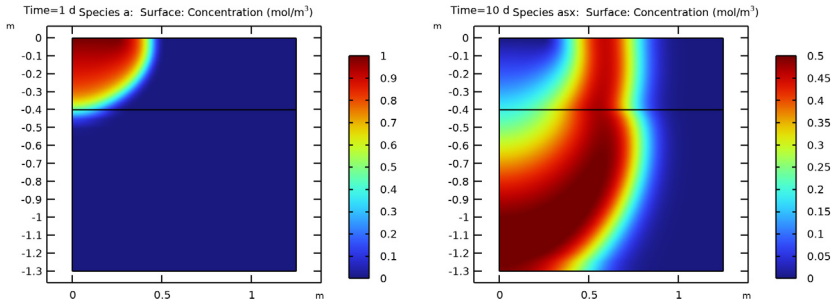


Figure 5: Concentration of aldicarb (left) and aldicarb sulfoxide (right) after 1 day (note the differing color ranges).

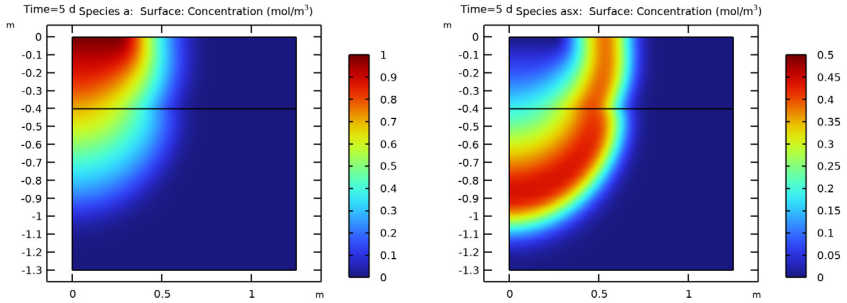


Figure 6: Concentration of aldicarb (left) and aldicarb sulfoxide (right) after 5 days.

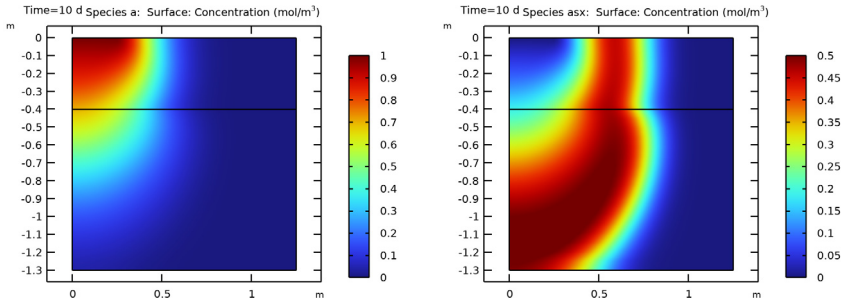


Figure 7: Concentration of aldicarb (left) and aldicarb sulfoxide (right) after 10 days.

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 3). 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.

Notes About the COMSOL Implementation

This model makes use of the **Infinite Element Domain** feature. It performs a coordinate scaling to the selected domain such that boundary conditions on the outside of the infinite element layer are effectively applied at a very large distance. Therefore unwanted effects of artificial boundary conditions on the region of interest are suppressed. This allows to model details in an area which is actually very large or infinite.

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 **General Studies>Time Dependent**.

6 Click **Done**.

GLOBAL DEFINITIONS

Load the rate constants from file.

Rate constants

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

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

3 Click **Load from File**.

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

5 In the **Label** text field, type `Rate constants`.

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

GLOBAL ODES AND DAES (GE)

Global Equations 1 (ODE1)

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 (ODE1)**.

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

3 Click **Load from File**.

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

5 Locate the **Units** section. Click **Select Dependent Variable Quantity**.

6 In the **Physical Quantity** dialog box, type `concentration` in the text field.

7 Click **Filter**.

8 In the tree, select **General>Concentration (mol/m^3)**.

9 Click **OK**.

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

11 Click **Select Source Term Quantity**.

12 In the **Physical Quantity** dialog box, type `reactionrate` in the text field.

13 Click **Filter**.

14 In the tree, select **Transport>Reaction rate (mol/(m^3*s))**.

15 Click **OK**.

STUDY 1

Step 1: Time Dependent

1 In the **Model Builder** window, under **Study 1** 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 **Output times** text field, type `range(0,1,100)`.

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

RESULTS

Concentration of species (100 days)

A plot showing the time dependent concentration is added automatically. Edit this plot to reproduce Figure 3 with the following steps:

1. In the **Settings** window for **1D Plot Group**, type `Concentration of species (100 days)` in the **Label** text field.
2. Click to expand the **Title** section. From the **Title type** list, choose **None**.
3. Locate the **Plot Settings** section.
4. Select the **y-axis label** check box. In the associated text field, type `Concentration (mol/m<sup>3</sup>)`.

Global 1

1. In the **Model Builder** window, expand the **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**.

   The concentration for all species is added automatically. Add the expression for the sum of the three most toxic species to the table.
6. Locate the **y-Axis Data** section. In the table, enter the following settings:

Expression	Unit	Description
`cpm_a+cpm_asn+cpm_asx`	`mol/m^3`	`Sum of most toxic species`

7. In the **Concentration of species (100 days)** toolbar, click **Plot**.

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

ADD PHYSICS

1. In 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 1** in the window toolbar.

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

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

8 In the **Concentrations (mol/m³)** table, enter the following settings:

c_a
c_asx
c_asn

9 In the table, clear the **Solve** check box for **Study 1**.

10 Click **Add to Component 1** in the window toolbar.

11 In the **Home** toolbar, click **Add Physics** to close the **Add Physics** window.

ADD STUDY

1 In 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 **Global ODEs and DAEs (ge)**.

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

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

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

STUDY 2

Step 1: Time Dependent

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

GLOBAL DEFINITIONS

Transport parameters

1 In the **Home** toolbar, click **Parameters** and choose **Add>Parameters**.

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

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `pesticide_transport_parameters_2.txt`.

5 In the **Label** text field, type `Transport parameters`.

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 In the **Geometry** toolbar, click **Rectangle**.

2 In the **Settings** window for **Rectangle**, locate the **Size and Shape** section.

3 In the **Width** text field, type `1.5`.

4 In the **Height** text field, type `0.9`.

5 Locate the **Position** section. In the **z** text field, type `-1.3`.

6 Click to expand the **Layers** section. Select the **Layers to the right** check box.

7 Clear the **Layers on bottom** check box.

8 In the table, enter the following settings:

Layer name	Thickness (m)
Layer 1	0.25

This additional layer to the right will later be used to define an **Infinite Element Domain**. Read more about it in the Notes About the COMSOL Implementation section. Proceed with the second soil layer.

9 Right-click **Rectangle 1 (r1)** and choose **Duplicate**.

Rectangle 2 (r2)

1 In the **Model Builder** window, click **Rectangle 2 (r2)**.

2 In the **Settings** window for **Rectangle**, locate the **Size and Shape** section.

3 In the **Height** text field, type `0.4`.

4 Locate the **Position** section. In the **z** text field, type `-0.4`.

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

Point 1 (pt1)

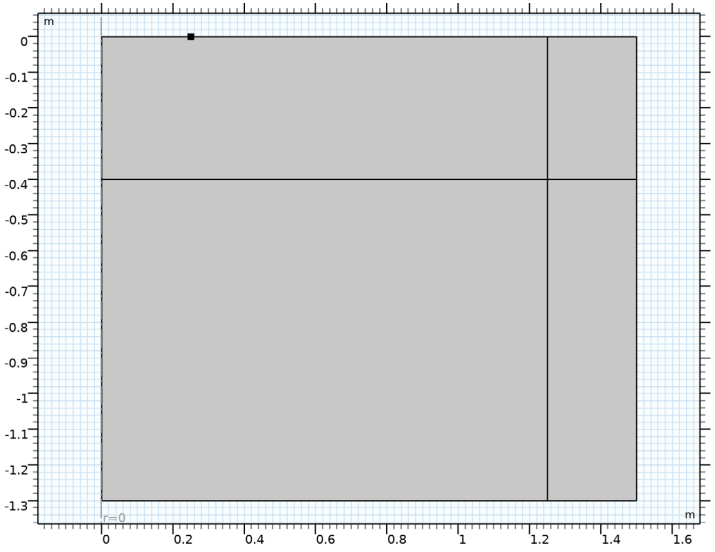
1 In the **Geometry** toolbar, click **Point**.

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**.

5 Click the **Zoom Extents** button in the **Graphics** toolbar.



Now, define the **Infinite Element Domain**.

DEFINITIONS

Infinite Element Domain 1 (ie1)

1 In the **Definitions** toolbar, click **Infinite Element Domain**.

2 Select Domains 3 and 4 only.

3 In the **Settings** window for **Infinite Element Domain**, locate the **Geometry** section.

4 From the **Type** list, choose **Cylindrical**.

Variables 1

1 In the **Definitions** toolbar, click **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 model'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 **Unsaturated Porous Medium** node, then duplicate this node and modify the domain selection and properties to match the top layer.

Unsaturated Porous Medium 1

1. In the **Model Builder** window, under **Component 1 (comp1)>Richards' Equation (dl)** click **Unsaturated Porous Medium 1**.
2. In the **Settings** window for **Unsaturated Porous Medium**, locate the **Porous Medium** section.
3. From the **Storage model** list, choose **User defined**. In the S_p text field, type `Sp_1`.

Porous Matrix 1

1. In the **Model Builder** window, click **Porous Matrix 1**.
2. In the **Settings** window for **Porous Matrix**, locate the **Matrix Properties** section.
3. From the **Permeability model** list, choose **Hydraulic conductivity**.
4. In the K_s text field, type `Ks_1`.
5. Locate the **Retention Model** section. In the α text field, type `alpha_1`.
6. In the n text field, type `n_1`.
7. In the θ_r text field, type `thetar_1`.

Unsaturated Porous Medium 1

In the **Model Builder** window, right-click **Unsaturated Porous Medium 1** and choose **Duplicate**.

Unsaturated Porous Medium 2

1. In the **Model Builder** window, click **Unsaturated Porous Medium 2**.
2. Select Domains 2 and 4 only.
3. In the **Settings** window for **Unsaturated Porous Medium**, locate the **Porous Medium** section.
4. In the S_p text field, type `Sp_2`.

Porous Matrix 1

1. In the **Model Builder** window, expand the **Unsaturated Porous Medium 2** node, then click **Porous Matrix 1**.
2. In the **Settings** window for **Porous Matrix**, locate the **Matrix Properties** section.
3. In the K_s text field, type `Ks_2`.

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

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

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

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**.

Initial Values 1

1 In the **Model Builder** window, 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)`.

5 Right-click **Initial Values 1** and choose **Duplicate**.

Initial Values 2

1 In the **Model Builder** window, click **Initial Values 2**.

2 Select Domains 2 and 4 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 In 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`.

Pervious Layer 1

1 In the **Physics** toolbar, click **Boundaries** and choose **Pervious Layer**.

2 Select Boundaries 2 and 8 only.

3 In the **Settings** window for **Pervious Layer**, locate the **Pervious Layer** section.

4 In the H_b text field, type `-2`.

5 In the R_b text field, type `1/5[d]`.

TRANSPORT OF DILUTED SPECIES IN POROUS MEDIA (TDS)

Now, set up the transport equation for an unsaturated porous medium, accounting for adsorption, dispersion and volatilization.

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

Unsaturated Porous Medium 1

1 In the **Physics** toolbar, click **Domains** and choose **Unsaturated Porous Medium**.

2 In the **Settings** window for **Unsaturated Porous Medium**, locate the **Domain Selection** section.

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

Liquid 1

1 In the **Model Builder** window, click **Liquid 1**.

2 In the **Settings** window for **Liquid**, locate the **Saturation** section.

3 From the list, choose **Liquid volume fraction**.

4 In the θ_l text field, type `dl.theta_l`.

This corresponds to the liquid volume fraction.

5 From the **Liquid fraction time change** list, choose **Time change in pressure head**.

6 From the dH_p/dt list, choose **Time change in pressure head (dl)**.

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

8 Locate the **Convection** section. From the $\mathbf{u}$ list, choose **Total Darcy velocity field (dl)**.

The diffusion coefficients are the same for all species.

9 Locate the **Diffusion** section. In the $D_{L,ca}$ text field, type `Dl`. Also type `Dl` in the text fields for the liquid diffusion coefficients of aldicarb sulfoxide and aldicarb sulfone.

Gas 1

Again, the diffusion coefficients are the same for all species.

1 In the **Model Builder** window, click **Gas 1**.

2 In the **Settings** window for **Gas**, locate the **Diffusion** section.

3 In the $D_{G,ca}$ text field, type `Dg`. Also type `Dg` in the text fields for the gas diffusion coefficients of aldicarb sulfoxide and aldicarb sulfone.

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

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

Unsaturated Porous Medium 1

In the **Model Builder** window, click **Unsaturated Porous Medium 1**.

Adsorption 1

1. In the **Physics** toolbar, click **Attributes** and choose **Adsorption**.
2. In the **Settings** window for **Adsorption**, locate the **Adsorption** section.
3. From the **Adsorption isotherm** list, choose **User defined**.
4. Select the **Species c_a** check box.
5. In the $c_{\mathrm{P,ca}}$ text field, type `kp_a*c_a`.
6. Select the **Species c_asx** check box.
7. In the $c_{\mathrm{P,casx}}$ text field, type `kp_asx*c_asx`.
8. Select the **Species c_asn** check box.
9. In the $c_{\mathrm{P,casn}}$ text field, type `kp_asn*c_asn`.

Unsaturated Porous Medium 1

In the **Model Builder** window, click **Unsaturated Porous Medium 1**.

Dispersion 1

1. In the **Physics** toolbar, click **Attributes** and choose **Dispersion**.
2. In the **Settings** window for **Dispersion**, locate the **Dispersion** section.
3. From the **Dispersion tensor** list, choose **Dispersivity**.
4. From the **Dispersivity model** list, choose **Transverse isotropic**.
5. In the α table, enter the following settings:

`alphar`
`alphaz`

Reactions 1

1. In 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_l*(-r_1-r_3)`.
5. In the R_{casx} text field, type `dl.theta_l*(r_1-r_2-r_4)`.
6. In the R_{casn} text field, type `dl.theta_l*(r_2-r_5)`.

Outflow 1

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

2 Select Boundaries 2, 8, 12, and 13 only. This corresponds to the right and bottom boundaries.

Concentration 1

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

2 Select Boundaries 6 and 11 only.

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

4 In the h_c text field, type `Dg/d_s`.

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

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

MATERIALS

Some required material properties have not yet been defined. This is indicated by a small red cross at the material node. Continue as follows to add the missing properties.

Porous Material: Lower Layer

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Materials** and choose **More Materials>Porous Material**.

2 In the **Settings** window for **Porous Material**, type `Porous Material: Lower Layer` in the **Label** text field.

3 Locate the **Phase-Specific Properties** section. Click **Add Required Phase Nodes**.

Fluid 1 (pmat1.fluid1)

1 In the **Model Builder** window, click **Fluid 1 (pmat1.fluid1)**.

2 In the **Settings** window for **Fluid**, locate the **Material Contents** section.

3 In the table, enter the following settings:

Property	Variable	Value	Unit	Property group
Density	rho	`rhof`	kg/m³	Basic

Solid 1 (pmat1.solid1)

1 In the **Model Builder** window, click **Solid 1 (pmat1.solid1)**.

2 In the **Settings** window for **Solid**, locate the **Solid Properties** section.

3 In the θ_s text field, type `1-poro_1`.

4 Locate the **Material Contents** section. In the table, enter the following settings:

Property	Variable	Value	Unit	Property group
Density	rho	`rhob`	kg/m³	Basic

Porous Material: Lower Layer (pmat1)

In the **Model Builder** window, right-click **Porous Material: Lower Layer (pmat1)** and choose **Duplicate**.

Porous Material: Upper Layer

1 In the **Model Builder** window, under **Component 1 (comp1)>Materials** click **Porous Material: Lower Layer 1 (pmat2)**.

2 In the **Settings** window for **Porous Material**, type `Porous Material: Upper Layer` in the **Label** text field.

3 Select Domains 2 and 4 only.

Solid 1 (pmat2.solid1)

1 In the **Model Builder** window, expand the **Component 1 (comp1)>Materials> Porous Material: Upper Layer (pmat2)** node, then click **Solid 1 (pmat2.solid1)**.

2 In the **Settings** window for **Solid**, locate the **Solid Properties** section.

3 In the θ_s text field, type `1-poro_2`.

MESH 1

Using a mapped mesh is a good idea for this geometry. It uses less mesh elements while keeping the accuracy compared to using a triangular mesh with the same mesh size.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Mesh 1**.

2 In the **Settings** window for **Mesh**, locate the **Physics-Controlled Mesh** section.

3 From the **Element size** list, choose **Finer**.

Mapped 1

In the **Mesh** toolbar, click **Mapped**.

Size 1

1 Right-click **Mapped 1** and choose **Size**.

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

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

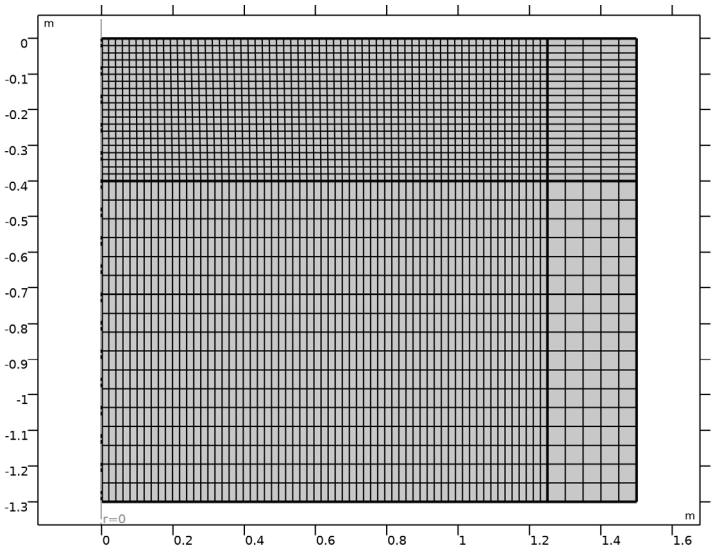
4 Select Domain 2 only.

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

6 Locate the **Element Size Parameters** section.

7 Select the **Maximum element size** check box. In the associated text field, type `0.02`.

8 In the **Model Builder** window, right-click **Mesh 1** and choose **Build All**.



STUDY 2

Step 1: Time Dependent

1 In the **Model Builder** window, under **Study 2** 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 **Output times** text field, type `range(0,0.1,0.9) range(1,1,10)`.

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

RESULTS

Study 2/Solution 2 (sol2)

Flownet, pressure, and concentration plots are created per default. Pressure and concentration are also visualized on a revolved 3D geometry. Visualizing the results on the infinite element domains does not add value to the plots. Focus on the region close to the source and therefore hide the infinite element domains from the plots with the following steps.

Selection

1. In the **Model Builder** window, expand the **Results>Datasets** node.
2. Right-click **Study 2/Solution 2 (sol2)** and choose **Selection**.
3. In the **Settings** window for **Selection**, locate the **Geometric Entity Selection** section.
4. From the **Geometric entity level** list, choose **Domain**.
5. Select Domains 1 and 2 only.

Proceed as follows to plot the effective saturation, pressure head, and velocity field at different times.

A plot for the effective saturation is available as a predefined plot.

ADD PREDEFINED PLOT

1. In the **Home** toolbar, click **Windows** and choose **Add Predefined Plot**.
2. Go to the **Add Predefined Plot** window.
3. In the tree, select **Study 2/Solution 2 (sol2)>Richards' Equation>Effective Saturation (dl)**.
4. Click **Add Plot** in the window toolbar.
5. In the **Home** toolbar, click **Add Predefined Plot** to close the **Add Predefined Plot** window.

RESULTS

Effective Saturation (dl)

1. In the **Model Builder** window, click **Effective Saturation (dl)**.
2. In the **Settings** window for **2D Plot Group**, locate the **Data** section.
3. From the **Time (d)** list, choose **0.3**.

Arrow Surface 1

Right-click **Effective Saturation (dl)** and choose **Arrow Surface**.

Contour 1

1 In the **Settings** window for **Contour**, locate the **Levels** section.

2 In the **Total levels** text field, type `15`.

3 In the **Effective Saturation (dl)** toolbar, click **Plot**.

Arrow Surface 1

1 In the **Model Builder** window, click **Arrow Surface 1**.

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

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

4 In the **Effective Saturation (dl)** toolbar, click **Plot**.

Compare the plot in the **Graphics** window with that in the left panel of Figure 4.

Effective Saturation (dl)

1 In the **Model Builder** window, click **Effective Saturation (dl)**.

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

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

4 In the **Effective Saturation (dl)** toolbar, click **Plot**.

Compare with the right panel of Figure 4.

The fourth and fifth default plots show the solute concentration after 10 days. Follow the steps below to reproduce the plots shown in Figure 5-Figure 7.

Concentration, aldicarb

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

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

Streamline 1

1 In the **Model Builder** window, expand the **Concentration, aldicarb** node.

2 Right-click **Streamline 1** and choose **Disable**.

Surface 1

1 In the **Model Builder** window, click **Surface 1**.

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`.

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

5 Click ← **Plot Previous** to plot the concentration after 9 days. Repeat to plot the concentration after 5 and 1 day.

Concentration, aldicarb sulfoxide

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

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

Streamline 1

1 In the **Model Builder** window, expand the **Concentration, aldicarb sulfoxide** node.

2 Right-click **Streamline 1** and choose **Disable**.

Surface 1

1 In the **Model Builder** window, click **Surface 1**.

2 In the **Settings** window for **Surface**, locate 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 `0.5`.

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

Concentration, aldicarb sulfoxide

1 In the **Model Builder** window, 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 In the **Concentration, aldicarb sulfoxide** toolbar, click **Plot**.

Repeat to plot the aldicarb sulfoxide concentration after 10 days.

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, WebM, and AVI format. Alternatively, add Player features with animations contained inside the model MPH-file as follows:

Concentration, a, 3D (tds)

In the **Model Builder** window, click **Concentration, a, 3D (tds)**.

Animation 1

In the **Concentration, a, 3D (tds)** toolbar, click **Animation** and choose **Player**.