DRAFT! Advection, Diffusion & Reaction Modeling

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[1]

The movement of compounds in the environment is driven by two processes, advection and diffusion. The compounds are also subject to transformations or reactions. Thus, to monitor the fate and transport of compounds in the environment, we can capitalize on mathematical models that have been used to describe advection, diffusion, and reaction.

Introduction

Fate and Transport Processes

The fate and transport of compounds in the environment is subject to an array of processes. For example, pollutants might carried by the wind (advection) and spread out (dispersion or diffusion). In addition, the pollutant might be transformed into different compounds (reaction). Together, these three processes, advection, diffusion, and reaction (Figure 1).

These three processes have profound implications – they provide the a framework to understand and quantify the fate and transport of pollutants in the environment (Figure 2), the movement of nutrients in the soil, and the movement of solutes in the human body. By understanding of these processes, we have tools to characterize environmental quality and its implications on human and non-human populations. Moreover, by modeling these processes, we can develop more effective policy, regulation, and mitigation strategies.

Because these processes are complex and are often difficult to measure, we rely on models to help us understand the movement of solutes in the environment. These models are based on the fundamental mathematical equations to describe advection, diffusion, and reaction.
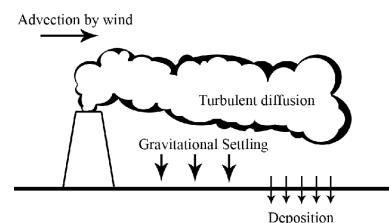

Figure 1: A simple diagram of advection and diffusion that inclues how "solutes" might be deposited downwind of a stationary source if air pollution. At the scale analyzed there, the term turbulant diffusion is different than molecular diffusion, but might be modelled in a similar way.

The Processes

As an example of the three processes consider a droplet of dye in water as a dose in a solution. The dye will move with the bulk motion of the water (advection), spread out by random molecular motion (diffusion)(Figure 3), and disappear as it reacts with the water (reaction).
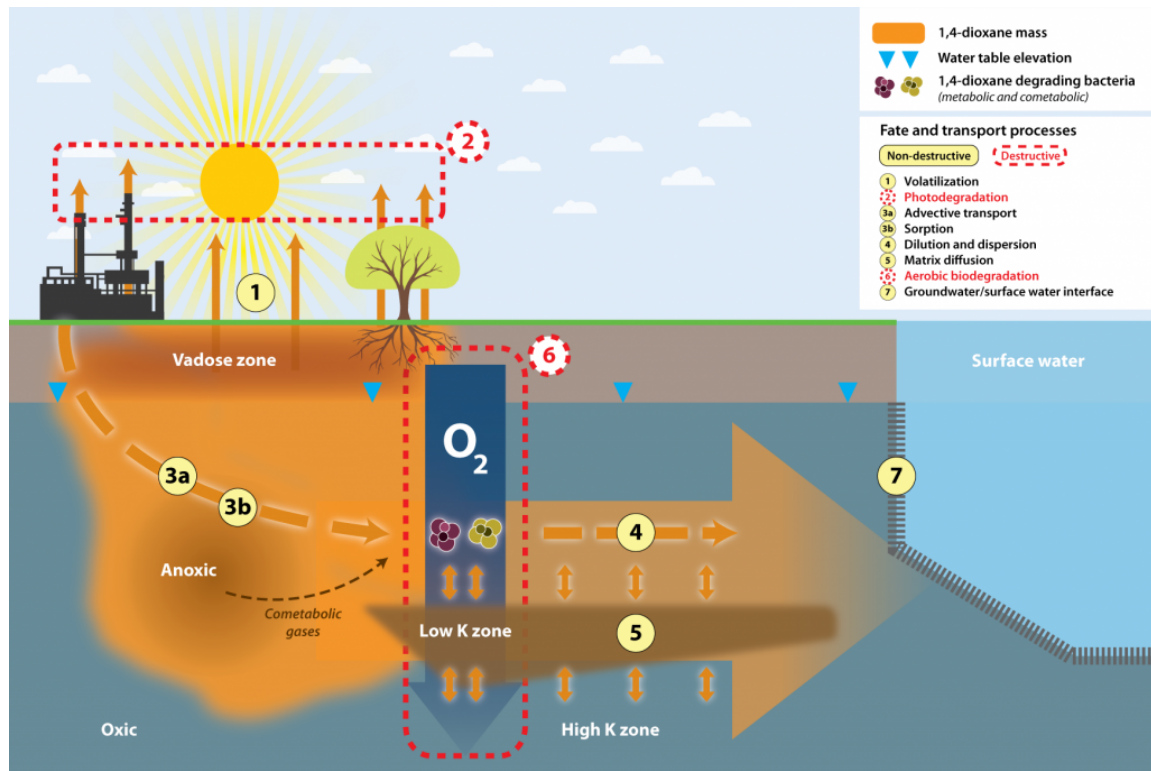
Generalized figure for the fate and transport of 1,4-dioxane: In the absence of water or soil moisture 1,4-dioxane volatilizes ① to the atmosphere where it is rapidly photodegraded ②. In the presence of water advective flow drives 1,4-dioxane into groundwater systems or plants via uptake through plant root systems ③ₐ with little retardation from sorption into organic matter ③ᵦ. In the saturated zone, attenuation of 1,4-dioxane occurs via dilution and dispersion ④, matrix diffusion ⑤, or aerobic biodegradation mediated by microbes ⑥. Transport of undegraded 1,4-dioxane to surface water may occur through groundwater–surface water interfaces ⑦.

Figure 2: A diagram of the major processes that influence the fate and transport of a dioxane plume from a ce in the environment (Source: https://14d-1.itrcweb.org/environmental-fate-transport-and-investigative-str 1,4-Dioxane is often referred to as a "forever" compound.

Advection and diffusion govern the transport of solutes in the environment. Advection is the transport of a solute by the bulk motion of the fluid. Advection depends on velocity or v in this session. Diffusion is the transport of a solute by random molecular motion. Diffusion depends on the diffusion coefficient and the concentration gradient or $\frac{\partial^2 C}{\partial x^2}$ in this session. Notice that this is the second derivative.

Reaction is the transformation of a solute into a different compound. Reaction depends on the reaction rate or k in this session.

In the case of air pollution, we are interested in the pollutant in the context of the air – or the media of air (Figure 1). And for air pollution, the chemical transormations are a critical part of our regulatory framework (Figure **??**). In the case of water, we might think about solutes in the water as a media. For example, the movement of a nutrient in a river is driven by the bulk motion of the water (advection) through the water column and the sediments (two types of media) and the random motion of the molecules (diffusion) and the reactions that might occur in the water column and sediments (Figure5).

Figure 3: A simple diagram of 2D diffusion. To solve these equations, we'll use a numerical approach and descretize the media into a grid. We'll then solve the equations for each grid cell.
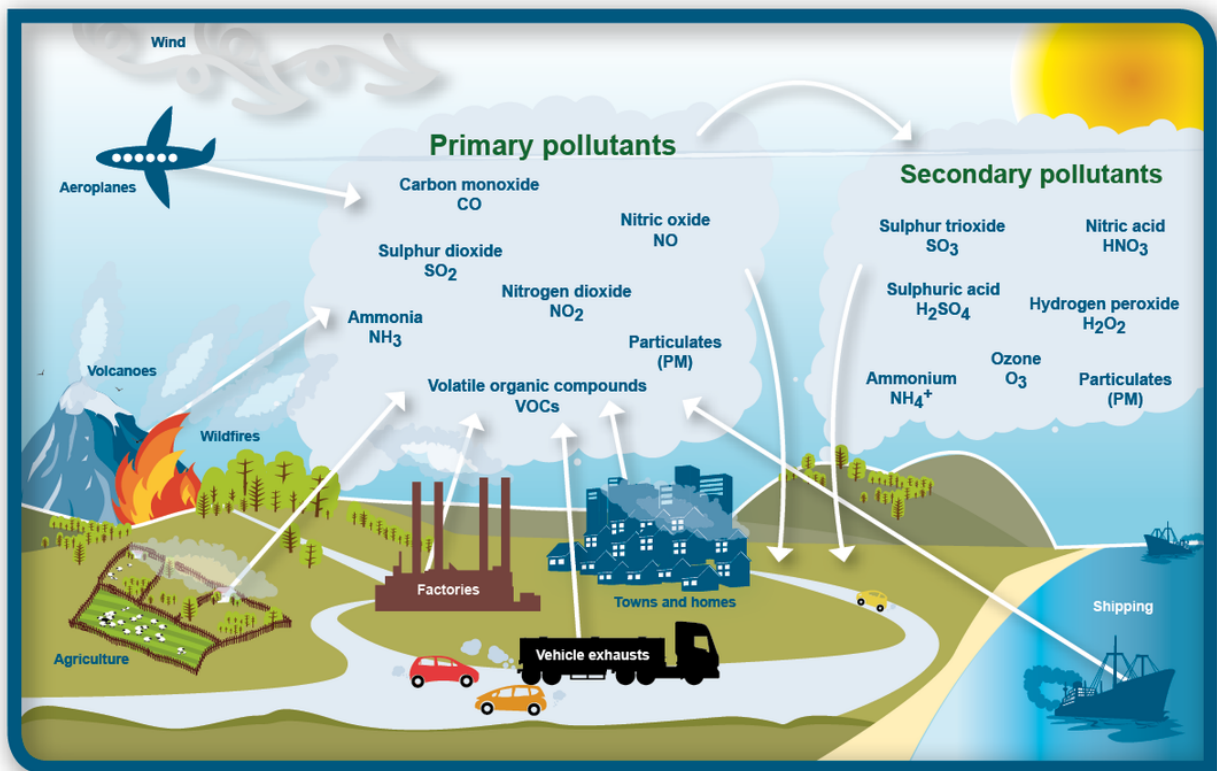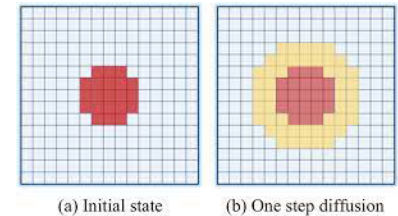

(a) Initial state   (b) One step diffusion

Figure 4: A simple diagram of advection and diffusion in the context of air pollution.

jk

Nutrient Cycling vs. Spiraling

1) Cycling in closed systems

2) Cycling in open ecosystems [creates spirals]

Inorganic forms

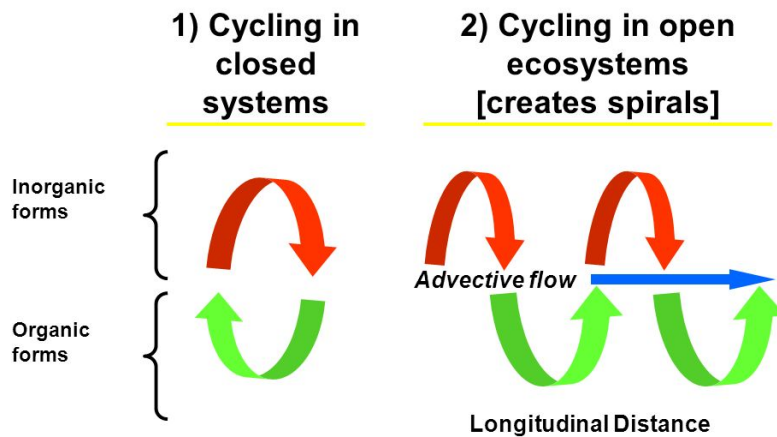Organic forms

Advective flow

Longitudinal Distance

Figure 5: A simple diagram of advection and nutrient reactions (organic substances and inorganic substances) in a river. Although not shown, you might also think about how diffusion might influence the movement of nutrients in the river and in the sediments. The zone where water moves into the sediment bed is called the hyperreic zone. The porosity of the sediments will allow more advective flow that might influence the reaction capacity of solutes in the sediments.

Session Goals

We will not become experts in advection-diffusion-reaction modeling, but we will become familiar with the processes and the equations that describe them. Moreover, we'll see a bit more about how R can be used to model these processes. After this session, I hope you can do the following:

1. Describe the physical processes of advection and diffusion and solute reaction
2. Describe the equations used to model A-D-R.
3. Analyze 1-dimensional movement using advection equations in R.
4. Describe diffusion mathematically
5. Analyze 1-dimensional adveecton-diffusion using R.
6. Appreciate how two-dimensional analysis of advection-diffusion can be modeled in R.

   In this session, we'll want to think about the movement of solutes in the porous media, i.e. a soil with air space, sediments with water between the particles. We will refer to the porousity as ξ, which is a proportion between 0 and 1.

Equations to Describe Processes

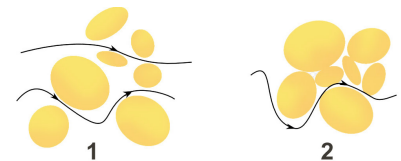AN EQUATION THAT OFTEN CREATES ANXIETY

1 **2**

Figure 6: Notice how the porosity of the media can influence the path of the fluid. In ground water, this is measured as permeability and can be used to evaluate the flow chacterstitics in aquifers and oil fields. The permeability is a function of the porosity and the connectivity of the pores.

The advection equation is a partial differential equation that describes the movement of a substance in a fluid. The equation is derived from the conservation of mass. The equation is:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 \zeta_x C}{\partial x^2} + D_y \frac{\partial^2 \zeta_y C}{\partial y^2} + D_z \frac{\partial^2 \zeta_z C}{\partial z^2} - v_x \frac{\partial \zeta_x C}{\partial x} - R \qquad (1)$$

Here D is the "diffusion coefficient", v is the "advection rate" (or velocity), and A_x and ζ are the surface area and volume fraction, respectively.

As you complete the first part of this handout, please do some reflecting:

> What you look at this equation, think about how it makes you feel. It's a bit intimidating, to say the least. But that's only part of the story. I believe these equations, when put in front of is generates anxiety – and this anxiety can be a barrier to learning. While it's easy to claim we can just put this anxiety away seems to be be a disservice and acknoweldgement of our emotional responses. Before moving forward, let's take a moment to acknowledge the anxiety and see where in your body you are feeling that. Take a deep breath and let it out several times before moving forward.

First, let's simplify this to 1-D (in one direction, x). And assume that the volume fraction is 1 ($xi = 1$). The movement of compounds in the environment is driven by two processes, advection and diffusion – these terms associated with ∂x define movement. The third term on the right, R, is the reaction term.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - R \qquad (2)$$

Left side: $\frac{\partial C}{\partial t}$

The left side of the equation describes the change in concentration over time. This is the rate of change of the concentration of the solute in the fluid. In steady state, this term is zero, which will use use to model the steady state concentration of the solute in the fluid.

First term on the right side: $D \frac{\partial^2 C}{\partial x^2}$

The first term on the right side of the equation describes the movement of the solute due to diffusion. This is the rate of change of the concentration of the solute in the fluid due to the movement of the solute from areas of high concentration to areas of low concentration.

Second term on the right side: $-v\frac{\partial C}{\partial x}$

The second term on the right side of the equation describes the movement of the solute due to advection. This is the rate of change of the concentration of the solute in the fluid due to the movement of the fluid.

Third term on the right side: $-R$

The third term on the right side of the equation describes the rate of change of the concentration of the solute in the fluid due to reactions. This is the rate of change of the concentration of the solute in the fluid due to the reaction of the solute with other compounds in the fluid.

> **Pause for a moment:** Reflect on your emotional state. What are you feeling? Where are you feeling it? Take a deep breath and let it out several times. You have completed the reading for Wednesday's class.

2/21 Handout Update

Quatifying Advective Transport

$$J = C \cdot v \tag{3}$$

J is the "flux density" of the solute, which is the amount of solute that moves through a unit area in a unit time. With units of $mass/(area \cdot time)$, the equation returns the rate of movement of the solute in the fluid.

We can take the derivative of the flux density with respect to the distance to get the "flux rate" and then derive the concentration change with respect to time: [2]

$$\frac{\partial J}{\partial x} = v\frac{\partial C}{\partial t} \tag{4}$$

of the solute, which is the amount of solute that moves through a unit area in a unit time. With units of $mass/(area \cdot time)$, the equation returns the rate of movement of the solute in the fluid.

[2] How dows J become C??

Diffusion

Fick's First Law and Three Types of Diffusion

There are three types of diffusion: turbulent (eddy) diffusion, dispersion and molecular diffusion. Each of the operate at different scales,

but have similar effects and are describe by the same equation:

$$J = -D\frac{dC}{dx} \tag{5}$$

Equation 5 ss known as Fick's first law. The negative sign indicates that the solute moves from areas of high concentration to areas of low concentration. The equation returns the rate of movement of the solute in the fluid.

Turbulent or Eddy diffusion is the movement of solutes due to the movement of the fluid. In this case, D is the "eddy diffusion coefficient".

Dispersion is the movement of solutes due to the random movement of the solute through a porous media where D is the "dispersion coefficient".

Molecular diffusion is the movement of solutes due to the random movement of the solute molecules where D is the "molecular diffusion coefficient".

Fick's Second Law – Rate of Change

STILL WORKING ON THIS...

Fick's Second Law is based on the conservation of mass, where the rate of change of the concentration of the solute in the fluid due to the movement of the solute from areas of high concentration to areas of low concentration is described by the equation:

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x}J = 0 \rightarrow \frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}(D\frac{\partial}{\partial x}C) = 0 \tag{6}$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{7}$$

which can be written as

$$\frac{\partial C}{\partial t} + D\frac{\partial^2 C}{\partial x^2} = 0 \tag{8}$$

We can rearrange Fick's first law to get the rate of change of the concentration of the solute in the fluid due to the movement of the solute from areas of high concentration to areas of low concentration:

$$\frac{\partial C}{\partial t} + D\frac{\partial^2 C}{\partial x^2} \tag{9}$$

Based on the conservation of mass, we can derive the rate of change of the concentration of the solute in the fluid due to the

movement of the solute from areas of high concentration to areas of low concentration:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{10}$$

This equation is known as Fick's second law. It describes the rate of change of the concentration of the solute in the fluid due to the movement of the solute from areas of high concentration to areas of low concentration.

Applications using R

ReacTran Package

Soetaert et al. (2017) have developed a nice library in R that solves these equations using finite-difference solutions.

The ReacTran package is a collection of functions for modeling solute transport in 1D, 2D, and 3D. The package includes functions for solving the advection-diffusion equation, the advection-diffusion-reaction equation, and the advection-diffusion-reaction equation for multi-phase systems.

The package also includes functions for solving:

- Advection-diffusion equations in 1D, 2D, and 3D
- Advection-diffusion-reaction equations in 1D, 2D, and 3D
- Advection-diffusion-reaction equations for multi-phase systems

Using R as a Modelling Environment to Solve PDEs and ODEs

We can use R to solve the advection-diffusion equation. The 'deSolve' package to solve the ReacTran library functions decomposing the partial differential equatation (PDE) into a descretized by space and solving be ordinary differential equations (ODE).

```
library(ReacTran) # Load the ReacTran package

## Loading required package:  rootSolve
## Loading required package:  deSolve
## Loading required package:  shape

library(deSolve) # Load the deSolve package
library(xtable) # Load the xtable package to help format tables outputs
```

Much of the complexity for modeling solute transport in 1D, 2D, and 3D is in the boundary conditions, initial conditions, and the rate of reaction. If these are not carefully considered, the model, which is an interative process, may not "converge" to a solution.

Grid and Time Step

Setting up the grid and time step is the first step in solving the advection-diffusion equation. The grid is the spatial domain over which the solute is transported, and the time step is the time domain over which the solute is transported. The grid and time step are used to discretize the advection-diffusion equation, which is a partial differential equation that describes the rate of change of the concentration of the solute in the fluid due to the movement of the solute from areas of high concentration to areas of low concentration.

Here are some rules of thumb for setting up the grid and time step:

- The grid should be fine enough to capture the spatial variation of the solute in the fluid.
  General equation??
- The time step should be small enough to capture the temporal variation of the solute in the fluid.
  General equation??

Steady-state vs. Transient State

The advection-diffusion equation can be solved in either the steady-state or transient state.

The steady-state solution is used to determine the concentration of the solute in the fluid at a given time, while the transient state solution is used to determine the concentration of the solute in the fluid over time.

Boundary Conditions

The boundary conditions are used to specify the concentration of the solute in the fluid at the boundaries of the grid. The boundary conditions are used to specify the concentration of the solute in the fluid at the inlet and outlet of the grid, and at the top and bottom of the grid.

Initial Conditions

The initial conditions are used to specify the concentration of the solute in the fluid at the start of the simulation. The initial conditions are used to specify the concentration of the solute in the fluid at the start of the simulation, and at the start of each time step.

Rate of Reaction

```
parms <- c(v = v, D = D, dx = dx, nx = nx)
```

```
C <- ode(y = C, times = t, func = solute_transport, parms = parms)
```

Implemeting Some 1D Examples in R

Plug Flow – Salts in a River

Pulse Injection – Tracer Test

Tracer test are used to determine the flow velocity of a fluid. The tracer is injected into the fluid and the concentration of the tracer is measured at a downstream location. The time it takes for the tracer to travel from the injection point to the downstream location is used to determine the flow velocity of the fluid.

The advection-dispersion model is used to predict the concentration of the tracer at the downstream location. The model is based on the advection-diffusion equation, which describes the movement of the tracer through the fluid. The advection-dispersion model is a partial differential equation that describes the rate of change of the concentration of the tracer in the fluid due to the movement of the tracer from areas of high concentration to areas of low concentration.

The advection-dispersion model is based on the conservation of mass, where the rate of change of the concentration of the tracer in the fluid due to the movement of the tracer from areas of high concentration to areas of low concentration is described by the equation:

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x} J = 0 \rightarrow \frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}\left(D\frac{\partial}{\partial x}C\right) = 0 \tag{11}$$
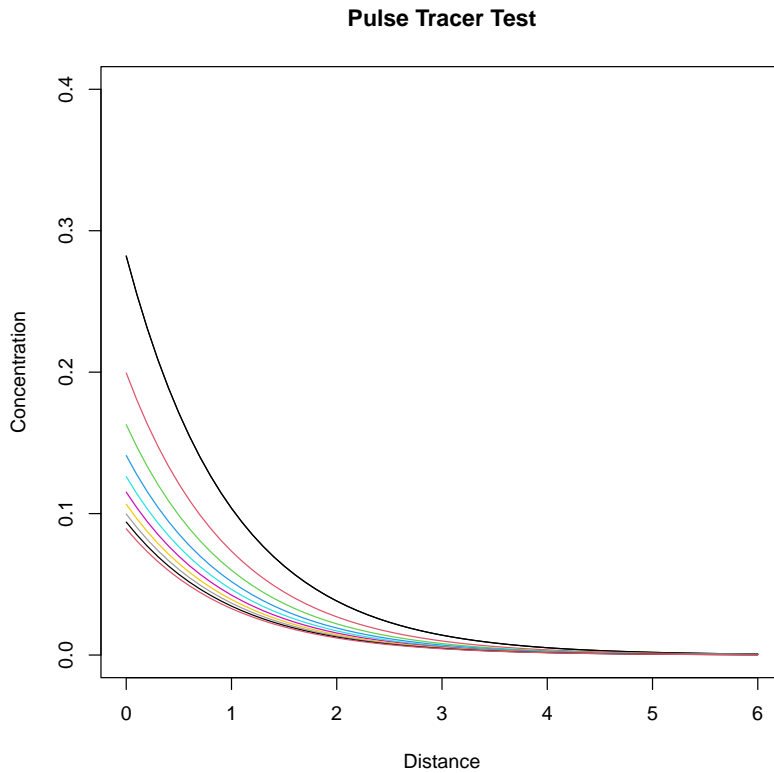
```
# pulse tracer test in water without decay
# simple diffusion portion?? not sure where...
pulseTracer <- function(x, t, D, v, C0) {
  C <- C0 * exp(-v * x / D) / sqrt(4 * pi * D * t)
  return(C)
}


# Solve
x <- seq(0, 6, .1)
t <- 1
D <- 1
v <- 1
C0 <- 1
```

```
C <- pulseTracer(x, t, D, v, C0)
plot(x, C, type = "l", xlab = "Distance", ylab = "Concentration", main = "Pulse Tracer Test", ylim=c(0, 0.
for(t in seq(1, 10, 1)) {
  C <- pulseTracer(x, t, D, v, C0)
  lines(x, C, col = t)
}
```

Pulse Tracer Test

Pulse Injection – Tracer Test with Decay

The impacts of matrix diffusion on the initial breakthrough of the solute plume and on later cleanup are illustrated in Figure 7).

The lower graph in Figure 7 shows the predicted cleanup concentration profiles following complete elimination of a source area. The advection-dispersion model (gray line) predicts a clean-water front arriving at a time corresponding to the average groundwater velocity. The advection-diffusion model (black line) predicts that concentrations will start to decline more rapidly than expected (based on the average groundwater velocity) as clean water rapidly migrates through the highest-permeability strata. However, low but significant contaminant concentrations linger much longer (tailing) due to dif-
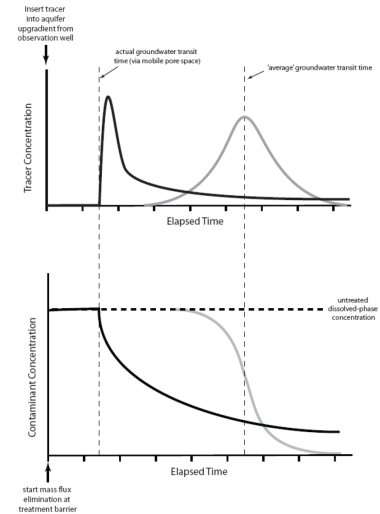

Figure 7: Using a traditional advection-dispersion model, the breakthrough curve for a pulse tracer injection appears as a bell-shaped (Gaussian) curve (gray line on the right side of the upper graph) where the peak arrival time corresponds to the average groundwater velocity. Using an advection-diffusion approach, the breakthrough curve for a pulse injection is asymmetric (solid black line) with the peak tracer concentration arriving earlier than would be expected based on the average groundwater velocity, but with a long extended tail to the flushout curve.

fusive contaminant mass exchange between zones of high and low
permeability.

$$\frac{dCv_vc}{dt} = \Sigma Q_{in} \cdot C_{in} - \Sigma Q_{out} \cdot C_{out} + \Sigma RV_{cv} \tag{12}$$

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} \tag{13}$$

$$C(x,t) = \frac{M}{A\sqrt{4\pi D_d t}} \cdot \exp[\frac{x'^2}{4D_d t}] \tag{14}$$

Where:

M = mass of conservative material in the spike

Dd = axial dispersion coefficient [L2/T],

xâĂŹ = x - Ut, U = longitudinal advective velocity in the reactor,

A is the cross-sectional area of the reactor.

First we make a one-dimensional grid and define the parameters
of the problem.[3]

```
# working on this

L <- 1 # length of the grid, 10 meters
nx <- 100 # number of grid cells
dx <- L/nx # length of each grid cell
x <- seq(0, L, by=dx) # grid
D <- 0.1 # diffusion coefficient
```

Next, we define the initial and boundary conditions. We will as-
sume that the concentration of the solute is zero at the beginning of
the experiment and that the concentration of the solute is constant at
the boundaries of the grid.

```
# working on this

v <- 0.1 # advection velocity
t <- 0.1 # times
C <- 0 # concentration of the solute
```

Next we define the functions that will be used to solve the advection-
diffusion equation.

```
# working on this
# define the solute transport function
solute_transport <- function(t, C, parms) {
  with(as.list(c(parms, C)), {
    dC <- -v * (C - C[-1])/dx - D * (C[-1] - 2 * C + C[-nx])/dx^2
```

```
    list(dC)
  })
}
```

We solve the advection-diffusion equation using the 'ode' function from the 'deSolve' package.

```
# working on this
# solve the advection-diffusion equation
# error hmax = must be a non-ngative value... ??

parms <- c(v = v, D = D, dx = dx, nx = nx)
C <- ode(y = C, times = t, func = solute_transport, parms = parms)

## Warning in max(abs(diff(times))):  no non-missing arguments
to max; returning -Inf
## Error in checkInput(y, times, func, rtol, atol, jacfunc,
tcrit, hmin, :  'hmax' must be a non-negative value
```

Finally, we visualize the results.

```
# working on this
```

Dissolved Oxygen Consumed in a Porous Media

We will be modeling the consumption of oxygen in a "sand-sized" porous spherical particle. The model is based on the following equation:

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} - k(C)$$

where C is the concentration of oxygen, D is the diffusion coefficient, v is the velocity of the fluid, and $k(C)$ is the rate of oxygen consumption.

At this scale the velocity will be zero. Thus, we will rely on diffusion to for the oxygen movement to where it is consumed.

We start with defining the size and porosity of the particle and use R to create a grid to solve the advection-diffusion-reaction equation.

Parameter	Description	Typical Range	Modelled Value
R	Radius of the particle	$0.005 - 0.2$ cm	0.025 cm
Porosity	Proportion of void space	$0.005 - 0.7$	0.7

Table 1: Chararacteristics of the Particle

We will create a grid to model the particle with Radius R and N (= 100) grid points. We will also define the properties of the particle such as porosity, diffusion coefficient (D = 400), and the rate of oxygen consumption, $R_{02} = 10^6$.

Although we are modeling a one-dimensional system, we will need to create a grid surface as a circle to effectively model the particle surface area changes as O2 diffuses into the particle and is consumed by the reactions in the particle.

```
grid <- setup.grid.1D(x.up=0, L = R, N = N) # Grid definition
por.grid <- setup.prop.1D(value=por, grid=grid) # Porosity
D.grid <- setup.prop.1D(value=D, grid=grid) # Diffusion coefficient

sphere.surf <- function(x) 4*pi*x^2 # Surface area of a sphere
A.grid <- setup.prop.1D(func=sphere.surf,  grid=grid) # Surface area
```

Finally, we need to define the O2 concentration at the surface of the particle and the O2 consumption rate of the particle.

Parameter	Description	Typical Range	Modelled Value
C_{ow}	Concentration of O2 in Water	$0.1 - 0.3 \ \mu\text{mols/cm}^{-3}$	0.25 $\mu\text{mols/cm}^{-3}$
R_{02}	Rate of oxygen consumption	$10^5 - 10^6 \ \mu\text{mols/cm}^{-3}$ /year	$10^6 \ \mu\text{mols/cm}^{-3}$/year
K_s	O2 saturation	$0.001 - 0.01 \ \mu\text{mols/cm}^{-3}$	0.005 $\mu\text{mols/cm}^{-3}$

Table 2: Model Calculation in the Particle

Note, we often measure oxygen using ppm (parts per million), but the model uses $\mu\text{mols/cm}^{-3}$. The conversion is 1 ppm = 0.0224 $\mu\text{mols/cm}^{-3}$, thus, we are modeling Ks within a range of 2.24 - 6.72 ppm, using Ks = 0.22 $\mu\text{mols/cm}^{-3}$.

Next we create a function to model the oxygen consumption in the, particle that relies on We will use the `tran.1D` function to solve the advection-diffusion equation and the `steady.1D` function to solve the steady state solution of the advection-diffusion-reaction equation.

```
Aggregate.Model <- function(time, O2, pars) {
  tran <- tran.1D(C = O2, C.down = C.ow.O2, D = D.grid,
          A=A.grid, VF = por.grid, dx = grid)
    reac <- - R.O2 * (O2 /(Ks + O2))
    return(list(dCdt= tran$dC + reac, reac = reac,
                flux.up=tran$flux.up, flux.down=tran$flux.down))
}



O2.agg <- steady.1D(y = runif(N), func=Aggregate.Model,
                  nspec=1, positive=TRUE, atol = 1e-10)
```

The plot shows the oxygen concentration in the particle. The concentration is highest at the surface and decreases as it moves into the particle. The concentration is zero at the center of the particle.

Next steps: figure out how to create a 3D sphere with the oxygen concentration changes as we enter the sphere...
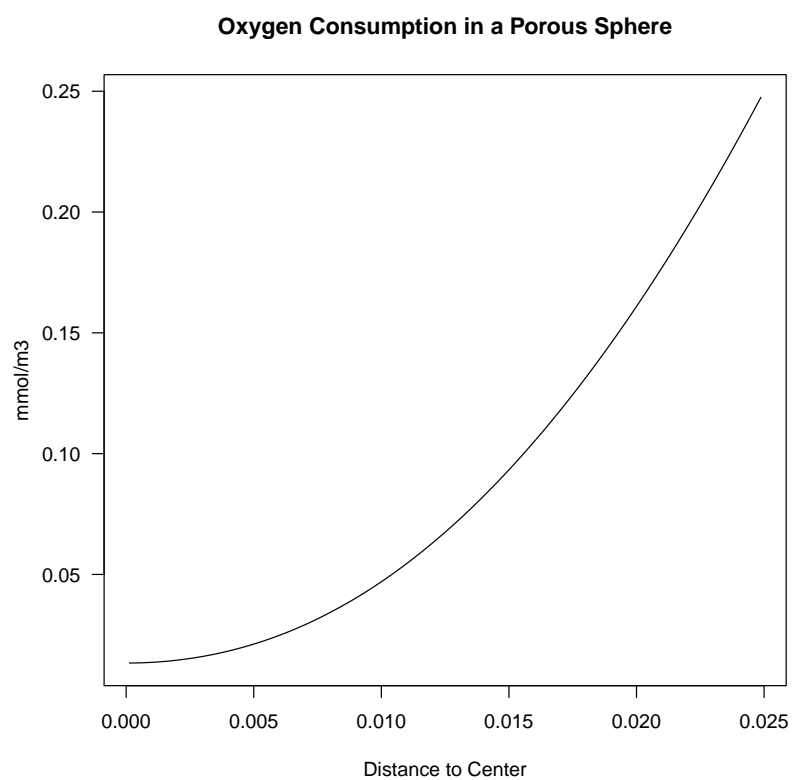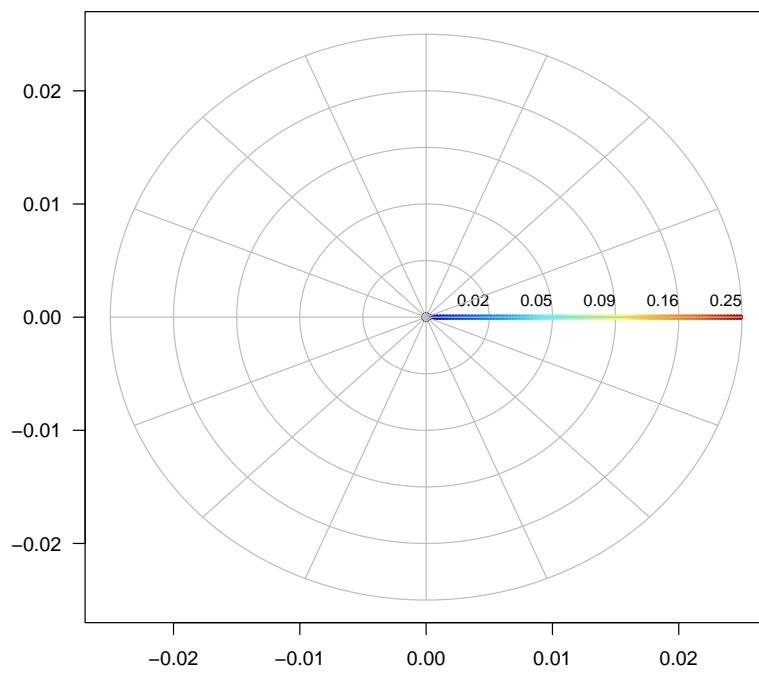
Figure 8: Oxygen Consumption in a Porous Sphere

Oxygen Consumption in a Porous Sphere

2D Examples

Modeling vehicle pollution from cars on a freeway that does in a west to east direction, while pollution moved in a north to south direction. The cars are pollution makers, and the wind is the advection term. The diffusion term is the natural spread of the pollution. The reaction term is the removal of pollution from the air. We'll model this as a steady state, where $\frac{\partial C}{\partial t} = 0$.

Where v_x is the velocity in the x direction, v_y is the velocity in the y direction, D is the diffusion coefficient, and R is the reaction term.

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) - R \qquad (15)$$

OR? with C as a fuction of y would be better! Not working yet!

```
# Create a function to model the pollution

Pollution.Model <- function(time, C, pars) {
  tran <- tran.2D(C = C, C.down = C.ow, D = D.grid,
          A=A.grid, VF = por.grid, dx = grid)
    reac <- - R * (C /(Ks + C))
    return(list(dCdt= tran$dC + reac, reac = reac,
               flux.up=tran$flux.up, flux.down=tran$flux.down))
}

# Create a 2D grid

grid <- expand.grid(x = seq(0, 100, length = 100),
                    y = seq(0, 100, length = 100))

# Define Initial Conditions
???

# Create a 2D model

Pollution.2D <- steady.2D(y = runif(nrow(grid)), func=Pollution.Model,
                   nspec=1, positive=TRUE, atol = 1e-10)


# Plot the 2D model

plot(Pollution.2D, grid = grid, xlab = "Distance to Center", ylab = "mmol/m3",
     las=1, main="Pollution in a 2D Grid")
```

3D Examples

Conclusion

References

https://en.wikipedia.org/wiki/Convection%E2%80%93diffusion_
equation

References

Soetaert, K., Meysman, F., and Soetaert, M. K. (2017). Package âĂŸre-
    actranâĂŹ.