1 Abstract

The movement of compounds in the environment is driven by two processes, advection and diffusion. Of course, these processes occur in three dimensions, but for this class we'll begin with one dimensional processes before getting to more complecated examples.

2 Introduction

The movement of contaminants through the subsurface is complex and is difficult to predict. Different types of contaminants react differently with soils, sediments, and other geologic materials and commonly travel along different flowpaths and at different velocities. One of the challenges for environmental scientists is to obtain meaningful chemical data from water samples collected from air, surface waters, and groundwater to use to map the distribution of specific contaminants and to use as targets for any models that may be constructed to predict forward or backward in time.

3 Session Outcomes

1. Describe Advection Mathematically
2. Analyze 1-dimensional movement using advection equations
3. Describe Diffuions mathematically
4. Analyze 1-dimensional movement using Fick's law.
5. Two dimensional analysis of advention

4 Material Transport

5 Theory of Pollution Movement

5.1 Diffusion versus Advection

What is diffusion?

Why is diffusion important?

What do we know about diffusion? In free solution and in the absence of any interactions with other macromolecules, the diffusion process is controlled by the size of the macromolecule as described by the Stokes-Einstein relation:

$$D_0 = \frac{k_B T}{6\pi\nu R_H} \tag{1}$$

where k_B is Boltzmann's constant, T the temperature in Kelvin, ν the solvent viscosity, and R_H the hydrodynamic radius.

What are current areas of research concerning diffusion and environmental issues?

6 R as a Calculator

7 One Dimensional Diffusion

7.1 Steady-state solution of 2-D PDEs

within `rootSolve` Package, has a function, `steady.2D()` that can efficiently fine the steady-state of 2-dimensional problems.

(2)

a substance C is consumed at a quadratic rate (r dot C2), while dispersing in X- and Y-direction. At certain positions (x,y) the substance is produced (rate p).

The model is solved on a square (100*100) grid. There are zero-flux boundary conditions at the 4 boundaries.

The term Dx . . . ,

i.e. it is the negative of the ux gradient, where the ux is due to diffusion. In the numerical approximation fo the ux, the concentration gradient is approximated as the subtraction of two matrices, with the columns or rows shifted (e.g. Conc[2:n,]-Conc[1:(n-1),]).

The flux gradient is then also approximated by subtracting entire matrices (e.g. Flux[2:(n+1),]-Flux[1:(n),]). This is very fast. The zero-flux at the boundaries is imposed by binding a column or row with 0-s.

```
> #library(rootSolve)
> diffusion2D <- function(t,conc,par){
+ Conc <- matrix(nr=n,nc=n,data=conc) # vector to 2-D matrix
+ dConc <- -r*Conc*Conc # consumption
+ BND <- rep(1,n) # boundary concentration
+
+ # constant production in certain cells
+ dConc[ii]<- dConc[ii]+ p
+
+ #diffusion in X-direction; boundaries=imposed concentration
+
+ Flux <- -Dx * rbind(rep(0,n),(Conc[2:n,]-Conc[1:(n-1),]),rep(0,n))/dx
+ dConc <- dConc - (Flux[2:(n+1),]-Flux[1:n,])/dx
+
+ #diffusion in Y-direction
```

```
+ Flux <- -Dy * cbind(rep(0,n),(Conc[,2:n]-Conc[,1:(n-1)]),rep(0,n))/dy
+ dConc <- dConc - (Flux[,2:(n+1)]-Flux[,1:n])/dy
+
+ return(list(as.vector(dConc)))
+ }
```

After specifying the values of the parameters, 10 cells on the 2-D grid where there will be substance produced are randomly selected (ii).

Figure 5: Steady-state solution of the nonlinear 2-Dimensional model

```
> # parameters
> dy <- dx <- 1 # grid size
> Dy <- Dx <- 1.5 # diffusion coeff, X- and Y-direction
> r <- 0.01 # 2-nd-order consumption rate (/time)
> p <- 20 # 0-th order production rate (CONC/t)
> n <- 100
> # 10 random cells where substance is produced at rate p
> ii <- trunc(cbind(runif(10)*n+1,runif(10)*n+1))
>
```

The steady-state is found using function steady.2D. It takes as arguments a.o. the dimensionality of the problem (dimens) and lrw=1000000, the length of the work array needed by the solver. If this value is set too small, the solver will return with the size needed. It takes about 0.5 second to solve this 10000 state variable model.

```
> Conc0 <- matrix(nr=n,nc=n,10.)
> # print(system.time(
> # not working yet...
>
> #ST3 <- steady.2D(Conc0,func=diffusion2D,parms=NULL,pos=TRUE,dimens=c(n,n), lrw=1000000,at
>
```

The S3 image method is used to generate the steady-state plot.

```
> #image(ST3,main="2-D diffusion+production", xlab="x", ylab="y")
```

8 Pre-lab Activity

8.1 Pre-assessment: What do you know about diffusion?

8.2 Conceptual Models of Diffusion

8.3 Preparing for the Lab

What can you do to prepare for the lab? Great question.

I have been thinking about this for a few weeks and have some suggestions.

1. Decide how you will make the standard curve before coming to class.
2. Review the recipe to make the agarose and write it out in your laboratory book.
3. Decide how you will sample your agar (spatially) and
4. create some tables to record the data in the lab book before class.
5. The bulk density of the agar is 1.5 g/ml. That means for every 1 gram, you will have a volume of 0.66 mL. You should check this to see how I get this. You will be diluting this volume as you heat them to get the dye into the solution. How will you back calculate the concentration of the dye given a dilution effect in the test tubes that you melt the agar in?
6. What are the possible interferences that you should consider? IMPORTANT: What blanks should you be sure to do?

9 Laboratory Methods

9.1 Preparing Agarose and Sampling Methods

Agarose gels are prepared by adding the desired volume...

The resulting slurry was heated to 90∘C until complete dissolution of agarose, and then slowly cooled. Before gelation, the viscous agarose solution was cast, then slowly cooled at room temperature. The cast are in circular petri dishes (40 cm in diameter).

Samples will be taken from the petri dishes with an exacto knife. Try to sample 1 cm^3. Record the two distances of the agar sampled – and weight sample to obtain a volume (via density).

9.2 Equipment

- Precision Balances
- 20 ml pipettes
- 50 ml beaker
- Weighing boats
- Distilled water
- Saran wrap
- Spec 20?

10 Previous Results

The following are images of notes from a previous lab: I still need to work on translating these into something I can translate. These are over 5 years old and because the results were so ambiguous, I think I never got around to writing this out.

Here are the results: without the T_0 I was completely lost of how to deal with this. But in reality, these are the kind of data we get with groundwater sampling...so, it must be trivial!

10.1 Variations on the Theme

I wonder if we tilt the petri dishes? This would create a preferential flow down gradient. Perhaps a slight tilt?

11 Assessment

12 Diffusion Derivation

a.) From 9.3, Special Case 2, we know that if $A(x,t) = \bar{A}(x) \neq 0$ (if area does not change with time), then the equation can be written as

$$\frac{\partial c(x,t)}{\partial t} = -\frac{1}{\bar{A}(x)}\frac{\partial}{\partial x}[J(x,t)\bar{A}(x)] \pm \sigma(x,t) \tag{3}$$

We now need to find an equation for $\bar{A}(x)$. Since arc length equals radius times angle, we get

$$\bar{A}(r) = \theta r h \tag{4}$$

where θ is the angle of the arc, r is radial distance, and h is height of the section. Therefore we get the equation

$$\frac{\partial c(r,t)}{\partial t} = -\frac{1}{\theta r h}\frac{\partial}{\partial r}[J(r,t)\theta r h] \pm \sigma(r,t) \tag{5}$$

Since θ and h are constants, we can factor them out to get

$$\frac{\partial c(r,t)}{\partial t} = -\frac{1}{r}\frac{\partial}{\partial r}[J(r,t)r] \pm \sigma(r,t) \tag{6}$$

b) Extending the principle applied in part (a), we first need to find $\bar{A}(R)$. Since θ is small, we can approximate cross sectional area by taking horizontal arc length times vertical arc length. Therefore we get the equation

Conc	Distance from Center	Mass
0.035	1	5
0.019	7	5.2
0.001	11	5.3
0.001	15	4.8

Table 1: Results from a Test

$$\bar{A}(R) = \theta_1 \theta_2 R^2 \tag{7}$$

where θ_1 is the horizontal angle of the arc, θ_2 is the vertical angle of the arc, and R is radial distance. Combining this with equation (1) from above, we get

$$\frac{\partial c(R,t)}{\partial t} = -\frac{1}{\theta_1 \theta_2 R^2} \frac{\partial}{\partial R}[J(R,t)\theta_1 \theta_2 R^2] \pm \sigma(R,t) \tag{8}$$

Since θ_1 and θ_2 are constants, we can simplify the equation as such:

$$\frac{\partial c(R,t)}{\partial t} = -\frac{1}{R^2} \frac{\partial}{\partial R}[J(R,t)R^2] \pm \sigma(R,t) \tag{9}$$

c) Part A: In order to obtain the equations in 9.5, we apply Fick's law:

$$J = -\mathcal{D}\nabla c \tag{10}$$

In this case, we use the one-dimensional version:

$$J = -\mathcal{D}\frac{\partial c}{\partial x} \tag{11}$$

Applying this to equation (4), we get

$$\frac{\partial c(r,t)}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}[\mathcal{D}\frac{\partial c}{\partial r}r] \pm \sigma(r,t) \tag{12}$$

Simplifying, and assuming that no particles are created or eliminated at the source, we get:

$$\frac{\partial c(r,t)}{\partial t} = \frac{\mathcal{D}}{r}\frac{\partial}{\partial r}(\frac{\partial c}{\partial r}r) \tag{13}$$

Part B: Once again, we apply Fick's law in one dimension to get

$$\frac{\partial c(R,t)}{\partial t} = \frac{1}{R^2}\frac{\partial}{\partial R}[\mathcal{D}\frac{\partial c}{\partial R}R^2] \pm \sigma(R,t) \tag{14}$$

We again simplify, assuming no particles are created or destroyed at the source.

$$\frac{\partial c(R,t)}{\partial t} = \frac{\mathcal{D}}{R^2}\frac{\partial}{\partial R}(\frac{\partial c}{\partial R}R^2) \tag{15}$$

13 Chang 1997 Key Points

13.1 Data

- Size of halos measured with a ruler over constant time intervals
- Experiment repeated three times to calculate average values used in model

13.2 Methodology

- Mathematical model formed using Fick's law
- c(r,t) = lipase concentration as a function of time and radial distance
- Used regression analysis to fit hindered diffusion coefficients and threshold values of lipase concentration as parameters. The finite difference method outlined in Constantinides, 1987 was used specifically.
- Amount of lipase in plate at each time calculated by numerical integration. The total amount of lipase varied by 2.5%, confirming the appropriateness of the mathematical model used.

14 Discretization

Fick's second law of molecular diffusion, expressed in cylindrical coordinates.

$$\begin{aligned}\frac{\partial C}{\partial t} &= D\Delta^2 C \\ &= D(\frac{1}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2})\end{aligned}$$

Initial conditions:

$$\begin{cases} C = C_0 & \text{for } R_w < r < R_r \\ C = 0 & \text{for } r < R_w \ \& \ R_r < r \end{cases} \tag{16}$$

where D is the effective hindered diffusion coefficient, C_0 is the feed enzyme concentration, R_w is the radius of the well, and R_r is the outer radius of the absorption ring. The lipase concentration as a function of time and radial distance can be solved using the finite difference method.

$$\frac{1}{\Delta t}(C_{i,j+1} - C_{i,j}) = [\frac{1}{i\Delta r}\frac{D}{2\Delta r}(C_{i+1,j} - C_{i-1,j}) + \frac{D}{\Delta r^2}(C_{i+1,j} - 2C_{i,j} + C_{i-1,j})] \tag{17}$$

$$\frac{1}{\Delta t}C_{i,j+1} = \frac{1}{\Delta t}C_{i,j} - \frac{2D}{\Delta r^2}C_{i,j} + \frac{D}{2i\Delta r^2}(C_{i+1,j} - C_{i-1,j}) + \frac{D}{\Delta r^2}(C_{i+1,j} + C_{i-1,j}) \tag{18}$$

$$C_{i,j+1} = (1 - \frac{2D\Delta t}{\Delta r^2})C_{i,j} + \frac{D\Delta t}{\Delta r^2}[(\frac{1}{2i} + 1)C_{i+1,j} - (\frac{1}{2i} - 1)C_{i-1,j}] \tag{19}$$

For convergence, to hold:

$$\frac{D\Delta t}{\Delta r^2} \leq \frac{1}{2} \tag{20}$$

Lastly, the amount of lipase can be calculated using

$$A = \int_{R_w}^{R_r} 2\pi r l C(r)\ dr \tag{21}$$

where A is the total amount of lipase in terms of enzyme activity, R_w and R_h are the radius of well and halo, respectively, $C(r)$ is the concentration at the radial distance of r, and l is the thickness of agar plate.