Environmental Water Quality BAE 452/552

Session 20

Groundwater Waste Loads (continued)

1

Transport of Pollutants & Loading Calculations

- Mass balance & hydrologic components
- Erosion and sediment transport
- Loading calculations
- Solid-phase and dissolved chemical loads
- Distributed-phase chemical loads
- Salt loads in irrigation return flows & urban runoff loads
- Ground water waste loads ←

2

Leaching of Organic Chemicals

- Adsorption
- Degradation
- Ground water contamination is minimal when a chemical is strongly adsorbed, rapidly degraded, and the water table is well below the soil surface
- Reverse: weak adsorption, slow degradation, and high water table

3

Retardation Factor

The retardation factor (R) is a general indication of a chemical's mobility in the soil compared to the water velocity

- $R = u/u_s$

where

- u = mean water velocity (cm yr^{-1})
- u_s = mean chemical velocity (cm yr^{-1})

4

Retardation Factor

- For a nonadsorbed ion such as Cl^- or NO_3^-, R approaches unity
- For a strongly adsorbed chemical, R will be much greater than 1, and movement through soil will be slow ($u_s << u$)
- R can also be taken as the ratio of the total to dissolved chemical in the soil

5

From Session 10

$c_T = c_d + c_p$

- In soil: $c_d = \theta_v C_d$

  $c_p = \rho_{dry} C_s$

where θ_v is volumetric moisture content (-), ρ_{dry} is dry bulk density (kg m^{-3})

6

Retardation Coefficient

What is C_d in soil if $C_s = K_d C_d$?

- $C_T = c_d + c_p = \theta_v C_d + \rho_{dry} C_s = C_d(\theta_v + \rho_{dry} K_d)$

$$C_d = \left(\frac{1}{\theta_v + \rho_{dry} K_d}\right) C_T$$

So, R can be expressed as:

$$R = \frac{C_T}{C_d} = \theta_v + \rho_{dry} K_d = 1 + \frac{\rho_{dry} K_d}{\theta_v}$$

7

Chemical Displacement

The retardation factor (R) can be used to determine the distance which a chemical moves in t years:

$R = ut/u_s t = Z/X$

where

Z = water displacement during time t (cm)

X = chemical displacement during time t (cm)

8

Water Displacement

In unsaturated soil: $Z = \frac{Q}{\theta_{fc}}$

In saturated soil: $Z = \frac{Q}{\theta_s}$

In EPA document: $Z = \frac{Q}{w}$

where

- Q = water flow per unit area (cm)
- θ_{fc}, θ_s = moisture content at field capacity and saturation, respectively ($cm^3\ cm^{-3}$)
- w = available water capacity (fc - wp)

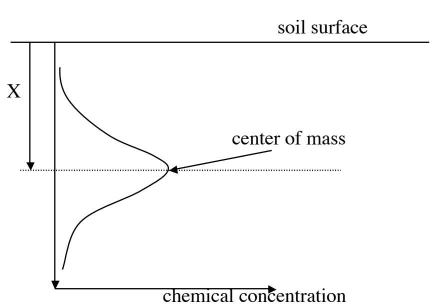
9

Chemical Displacement

- Unsaturated zone: $X = \frac{Q}{\theta_{fc} + \rho_{dry} K_d}$
- Saturated zone: $X = \frac{Q}{\theta_s + \rho_{dry} K_d}$
- EPA document: $X = \frac{Q/w}{1 + \rho_{dry} K_d / \theta_v}$
- X indicates the location of the center of mass after percolation Q

10

Downward Movement of Chemical in Soil



11

Mean Travel Time

- The time required for the chemical's center of mass to reach the aquifer, and hence the mean travel time of the chemical through the unsaturated zone is:
- T = 100H/X
- where
- T = mean travel time (yr)
- H = depth to the water table (m)

12

Degradation

- The degree of ground water pollution by an organic chemical is very much influenced by degradation and decay rates
- Assuming a 1st order process: $C(t) = C(0)e^{-k_s t}$

where

- $C(t)$ = chemical in the soil at time t (g ha^{-1})
- $C(0)$ = initial chemical at the soil surface (g ha^{-1})
- k_s = decay rate (yr^{-1})

13

Degradation

To calculate the chemical mass entering the water table T years after leaching begins:

$$C(T) = C(0)e^{-k_s T}$$

where

- $C(T)$ = chemical mass entering water table after T years (g ha^{-1})

14

Ground Water Loads of Organic Chemicals

Equations are providing "order of magnitude" estimates due to effects of dispersion, uncertainty in decay rates, and the assumption of homogeneous porous media.

15

Example III-12

Napthalene Leaching from a Waste Storage Site:

50,000 g ha^{-1} of napthalene is leaching from an abandoned waste disposal site. The site is on a sandy loam with 1% OM. Water table depth is 1.5 m. Mean annual percolation is 40 cm. K_{ow} = 2300 and a half-life of 1700 days

How much napthalene will reach the water table aquifer and what will be the resulting napthalene concentration at the water table surface?

16

Example III-12 solution

Session 11:

$K_{oc} = 0.66K_{ow}^{1.029} = 0.66(2300)^{1.029} = 1900$

%OC = 0.59(%OM) = 0.59(1) = 0.59

$K_d = K_{oc}$ (%OC/100) = 1900(0.59/100) = 11.2

Table III-27:

bulk density ρ_{dry} = 1.5 g cm^3

moisture at fc: θ_{fc} = 0.22 cm^3cm^{-3}

available water capacity: w = 0.22 - 0.08 = 0.14

17

Example III-12 solution

Annual napthalene movement:

$$X = \frac{Q/w}{1+\rho_{dry}K_d/\theta_v} = \frac{40/0.14}{1+1.5(11.2)/0.22} = 3.7 cm/yr$$

Average time to reach the water table aquifer:

- T = 100H/X = 100(1.5)/3.7 = 40.5 yr

18

Example III-12 solution

- To calculate the napthalene remaining after 40.5 years, use:

$$C(T) = C(0)e^{-k_s T}$$

- To obtain k_s:

$$0.5 = e^{-(1700/365)k_s}$$

$$k_s = -\ln(0.5)/4.66 = 0.149\,yr^{-1}$$

19

Example III-12 solution

- To calculate the napthalene remaining after 40.5 years, use:

$$C(T) = C(0)e^{-k_s T}$$

$$C(T) = 50{,}000e^{-0.149(40.5)} = 120\ \ g\ \ ha^{-1}$$

20

Example III-12 solution

- To determine the napthalene concentration in water at the aquifer surface, we need to divide the 120 g ha^{-1} into dissolved and adsorbed amounts using the retardation factor:

$$R = \frac{C_T}{C_d} = 1 + \frac{\rho_{dry}K_d}{\theta_v} = 1 + \frac{1.5(11.2)}{0.22} = 77$$

$$C_d = \frac{C_T}{R} = \frac{120}{77} = 1.56\ \ g\ \ ha^{-1}$$

21

Example III-12 solution

- Assuming the 1.56 g ha^{-1} is dissolved into one year's percolation flow, 40 cm = 4000 m^3 ha^{-1}, the concentration is:
- 1.56/4000 = 0.00039 g m^{-3} = 0.39 μg L^{-3}

22

Physical Processes

- Convective-dispersion equation (CDE)
- Breakthrough curves
- Piston flow
- Hydrodynamic dispersion, Mechanical dispersion, Molecular diffusion√
- Mobile-immobile regions in soils
- Preferential flow

23

Solute Transport in Soils

Applications:

- Design of optimum pesticide and fertilizer application
- Reclamation of saline or sodic soils
- Ground water contamination issues

24

Solute Conservation Equation

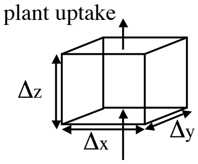
For a chemical located in a small volume element of soil $V = \Delta x \Delta y \Delta z$ over a small period Δt:

mass of solute entering V during Δt =

mass of solute leaving V during Δt +

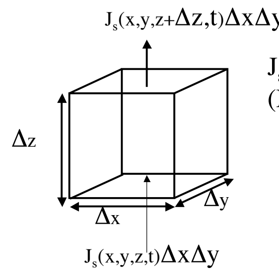
increase in solute mass stored in V during Δt +

disappearance of solute from V during Δt by chemical or biological reactions or by plant uptake



25

Solute Conservation Equation



J_s = total solute flux (M/T)

26

Solute Conservation Equation

$J_s(x,y,z,t+1/2\Delta t)\ \Delta x \Delta y \Delta t =$

$J_s(x,y,z+\Delta z,t+1/2\Delta t)\ \Delta x \Delta y \Delta t +$

$(C_T(x,y,z+1/2\Delta z,t+\Delta t)-C_T(x,y,z+1/2\Delta z,t))\ \Delta x \Delta y \Delta z$ +

$k_r(x,y,z+1/2\Delta z,t+1/2\Delta t)\ \Delta x \Delta y \Delta t$

where

$C_T = \rho_{dry} C_s + \theta_v C_d + (n - \theta_v) C_g$ (M/L^3)

k_r = reaction rate per volume (loss of solute per soil volume per unit time)

27

Solute Conservation Equation

divide by $\Delta x \Delta y \Delta z \Delta t$ and rearranging:

$$\frac{J_s[x,y,z+\Delta z,\bar{t}]}{\Delta z} + \frac{C_T[x,y,\bar{z},t+\Delta t] - C_T[x,y,\bar{z},t]}{\Delta z} + k_r(\bar{z},\bar{t}) = 0$$

where

$\bar{z}, \bar{t}$ are the average values of z and t, respectively.

Taking the limit Δx, Δy, Δz, Δt => 0, we obtain

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_s}{\partial z} + k_r = 0$$

28

Solute Flux through Soil

The chemical can move in dissolved and vapor phase (sorbed phase is stationary):

$$J_s = J_l + J_g$$

where

J_l = flux of dissolved solute

J_g = flux of solute vapor

29

Dissolved Solute Flux

We will only develop the dissolved solute flux:

- convection of dissolved chemical with flowing solution (bulk transport), J_{lc}
- diffusive flux of dissolved solute moving by molecular diffusion, J_{ld}

$$J_l = J_{lc} + J_{ld}$$

30

Convection Term

The solute convection term is expressed as:

$J_{lc} = J_w C_d + J_{lh}$

where

J_w = the water flux

J_{lh} = hydrodynamic dispersion flux: $J_{lh} = -D_{lh}\frac{\partial C_d}{\partial z}$

where

D_{lh} = the hydrodynamic dispersion coefficient ($cm^2 day^{-1}$)

31

Diffusion Term

The solute diffusion term is expressed as:

$$J_{ld} = -D_l^s \frac{\partial C_d}{\partial z}$$

where

D_l^s = the soil liquid diffusion coefficient ($cm^2\ day^{-1}$)

32

Dissolved Solute Flux

The total flux of dissolved solute in a convection-dispersion model now becomes:

$$J_l = J_w C_d - D_{lh}\frac{\partial C_d}{\partial z} - D_l^s \frac{\partial C_d}{\partial z}$$

which is commonly written as:

$$J_l = J_w C_d - D_e \frac{\partial C_d}{\partial z}$$

where

D_e is the effective diffusion-dispersion coefficient

33

Convection-Dispersion Equation

Substituting C_T, J_s (= $J_l + J_g$) into the solute conservation equation,

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_s}{\partial z} + k_r = 0$$

the solute transport equation (without vapor phase):

$$\frac{\partial}{\partial t}(\rho_{dry} C_s + \theta_v C_d) = \frac{\partial}{\partial z}(J_w C_d) - \frac{\partial}{\partial z}\left(D_e \frac{\partial C_d}{\partial z}\right) - k_r$$

34

Convection-Dispersion Equation (CDE)

A typical experiment: water is flowing uniformly at steady state through a homogeneous soil column of length L at a constant water content.

For inert, non-adsorbing chemicals ($C_s = 0$, $k_r = 0$)

$$\frac{\partial C_d}{\partial t} = D\frac{\partial^2 C_d}{\partial z^2} - v\frac{\partial C_d}{\partial z}$$

where

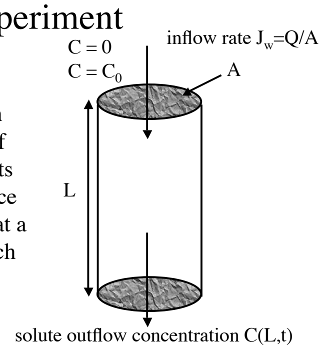
$D = D_e/\theta_v$

v = water velocity (J_w/θ_v)

35

Experiment

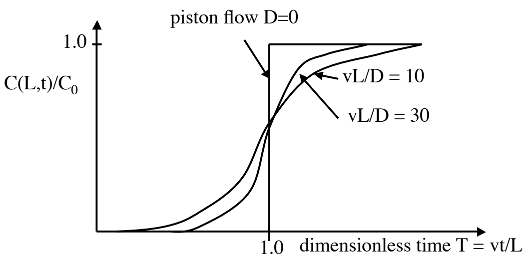
At t = 0, we instantaneously switch the water inlet valve of the soil column from its initial solute-free source to a chloride solution at a concentration C_0, which continues to flow at J_w through the column



36

The Breakthrough Curve

Plot of outflow concentration versus time, which are mathematical solutions to the convective-dispersion equation



37

Breakthrough Time

The center of each of the solute fronts, for different values of D, arrive at the outflow end of the column at the same time $t_b = L/v$, called the breakthrough time

When dispersion is neglected (D = 0), all solutes move at the same velocity, and the front arrives as one discontinuous jump to the final concentration C_0. This is called ‘piston flow’

38

Effect of Dispersion

As can be seen in the breakthrough curves, the effect of dispersion is to cause some early and late arrival of chloride with respect to breakthrough time.

This deviation is due to diffusion and small-scale convection ahead of and behind the front moving at v, and becomes more pronounced as D becomes larger

39

Pore Volumes

Instead of plotting outflow concentration as a function of time, concentration can be plotted against cumulative water drainage d_w passing through the outflow end of the column. At steady state: $d_w = J_w t$

At breakthrough time, $d_{wb} = J_w t_b = J_w L/v = L\theta_v$

$L\ \theta_v$ is called a ‘pore volume’, so it requires approximately one pore volume of water to move a mobile solute through a soil column

40

Transport of Pulses through Soil

In many cases, a narrow pulse of solute, rather than a front, might be added to the inlet at t=0

A solution to the CDE is then:

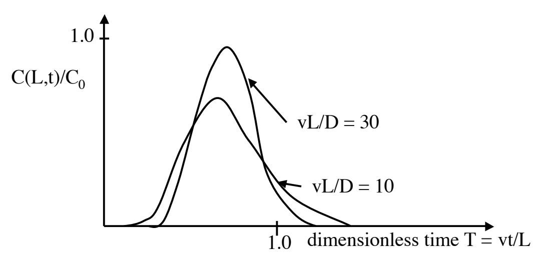
$$C(L,t) = \frac{C_0 L}{2\sqrt{\pi D t^3}} e^{\left(-\frac{(L-vt)^2}{4Dt}\right)}$$

As D becomes larger, the pulse becomes more spread out

41

The Breakthrough Curve

Plots of outflow concentration versus time, which are mathematical solutions to the convective-dispersion equation



42

Inert, Adsorbing Chemicals

- For chemicals that partition between solid phase and dissolved phase, the transport equation is written as:

$$\frac{\rho_{dry}}{\theta_v}\frac{\partial C_s}{\partial t} + \frac{\partial C_d}{\partial t} = D\frac{\partial^2 C_d}{\partial z^2} - v\frac{\partial C_d}{\partial z}$$

- Using a linear partition coefficient, K_d:

$$\frac{\partial C_s}{\partial t} = K_d\frac{\partial C_d}{\partial t}$$

43

Inert, Adsorbing Chemicals

- Combining previous two equations:

$$\left(1 + \frac{\rho_{dry}K_d}{\theta_v}\right)\frac{\partial C_d}{\partial t} = D\frac{\partial^2 C_d}{\partial z^2} - v\frac{\partial C_d}{\partial z}$$

- where the retardation factor R is:

$$R = \left(1 + \frac{\rho_{dry}K_d}{\theta_v}\right)$$

44

Inert, Adsorbing Chemicals

- If we divide through by R:

$$\frac{\partial C_d}{\partial t} = D_R\frac{\partial^2 C_d}{\partial z^2} - v_R\frac{\partial C_d}{\partial z}$$

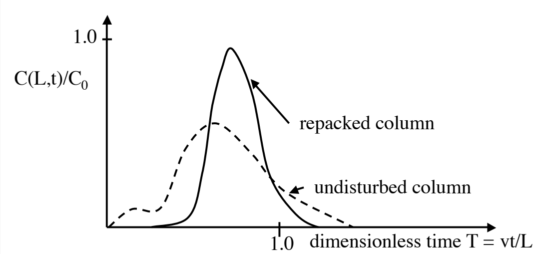
where $D_R = D/R$, and $v_R = v/R$

- Breakthrough time, $t_{bR} = L/v_R = RL/v = Rt_b$
- Dispersion is greater than for non-adsorbing chemical because while the dispersion coefficient is reduced by R, travel time is increased

45

Effect of Soil Structure on Transport

- Soil structure can create preferential flow channels for water and dissolved solutes



46

Preferential Flow Effects

- The early arrival of solute may be attributed to preferential flow of water through the larger channels of the wetted pore space (large channels and wetted regions between finer pores in an aggregated soil)
- Water in the finer pores is more stagnant and do not contribute to solute transport, except for diffusion exchange, explaining the later arrival

47

Mobile-immobile Water Model

- A model that represents the wetted pore space with two water contents:
- a mobile water content, θ_m, through which water is flowing
- an immobile water content, θ_{im}, which contains stagnant water
- $\theta_{im} = \theta_v - \theta_m$

48

Mobile-immobile Water Model

- Solute concentration is divided into an average concentration C_m in the mobile region and a second C_{im} in the immobile region
- In the mobile region, solute is transported by a convective-dispersive process
- In the immobile region, a rate-limited diffusion process exchanges solute with the mobile region

49

Mobile-immobile Water Model

- For an inert, non-reactive solute, the conservation equation is now written as:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = D_e \frac{\partial^2 C_m}{\partial z^2} - J_w \frac{\partial C_m}{\partial z}$$

- where
- $C_T = \theta_m C_m + \theta_{im} C_{im}$

50

Preferential Flow

- Macropores
- Funnel flow
- Fingering

51

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Session 21

Groundwater Waste Loads (continued)

52