Environmental Water Quality
BAE 452/552

Session 9

Fate of Contaminants in Soil, Isotherms

1

Main Course Components

- Definitions
- Receiving water impacts
- Sources of Pollutants ←
- Transport of Pollutants
- Loading Functions
- Control of non-point source pollution

2

Sources of Pollutants

- Pollutant interaction with soils
- Basic soil & water relationships
- Fate of contaminants in soils, isotherms
- Degradation and transformations
- Specific pollutants and interaction in soils
- Atmospheric deposition

3

Pollutant Interaction with Soils

- Balanced soil systems: great for water quality

Accumulations have occurred for the last 2000 years:

- Mining related activities (metals)
- Industrial Revolution (industrial, agricultural, commercial, and domestic)

4

Pollutant Interaction with Soils

- Return waste to soil instead of water. “soil has infinite capacity to assimilate pollutants”?
- Soil’s capacity is limited!
- What we add: 20 to 200 kg N per hectare, 10 to 50 kg P per hectare, pesticides, herbicides, etc.
- “Chemical time bomb” concept

5

Pollutant Interaction with Soils

- Interaction between solid and liquid phase in soils occurs in the A-horizon, in sediments with the overlying waters
- Organic matter is important component of soil’s buffering capacity (-> microorganisms)
- Organic matter (%) ≈ 1.67 x organic carbon (%)

6

Pollutant Interaction with Soils

Three phases:

- Solid phase: precipitated and/or adsorbed
- Liquid phase: dissolved in water or soil moisture
- Gaseous phase: volatilized or gasified

7

Pollutant Interaction with Soils

- Solid phase contaminants are transported by soil erosion and overland flow transport (except for some colloidal transport in the vadose zone)
- Liquid or dissolved phase contaminants can be transported by either surface runoff and interflow
- Liquid phase contaminants also can reach ground water and reappear in base flow

8

Basic Soil-Water Relationships

- Volume of soil sample: $V_t = V_s + V_w + V_a$
- Total mass of soil sample: $m_t = m_s + m_w + m_a$
- Volume of voids: $V_v = V_w + V_a$
- Porosity: $n = \frac{V_v}{V_t}$
  (typical value 0.35-0.50)

9

Basic Soil-Water Relationships

- Gravimetric moisture content:

$$\theta_g = \frac{m_w}{m_s} \left(= \frac{m_{wet} - m_{dry}}{m_{dry}}\right)$$

- Volumetric moisture content:

$$\theta_v = \frac{V_w}{V_t}$$

10

Basic Soil-Water Relationships

- Bulk density: $\rho_{dry} = \frac{M_s}{V_t}$
  (typical value 1.35 g/cm^3)
- Particle density: $\rho_p = \frac{M_s}{V_s}$
  (typical value 2.65 g/cm^3)
- Degree of saturation: $S = \frac{V_w}{V_v}$
  - If a soil is dry, S=0
  - If a soil is saturated, S=1

11

Basic Soil-Water Relationships

- Other useful relationships:
- Porosity: $n = 1 - \frac{\rho_{dry}}{\rho_p}$
- Moisture content: $\theta_v = \theta_g \frac{\rho_{dry}}{\rho_w}$ ρ_w is density of water (1 g/cm^3)

$$\theta_v = Sn$$

12

Fate of Contaminants in Soils

- If a contaminant in soil is not subject to degradation, volatilization, or chemical breakdown, its mass does not change with time, and we classify them as *conservative*
- Contaminants which changes mass over time (excluding effects of convection and dispersion), are classified as *non-conservative*

13

Fate of Contaminants in Soils

Transformation processes:

- Sorption-desorption
- Volatilization
- Bio-degradation
- Plant uptake
- Leaching & transport (later in course)

14

Sorption

Definitions:

- Sorption: process by which a dissolved substance is transferred to and becomes associated with solid material
- Sorption includes adsorption and absorption:
- Adsorption: accumulation on surfaces of solids
- Absorption: interpenetration or intermingling with solids

15

Sorption

Definitions:

- Sorbate: substance that is sorbed (also particulate form)
- Sorbent: the solid
- Desorption: process by which sorbed substance is released from a solid particle

16

Sorption Mechanisms

Neutral organics:

- Hydrophobic effects
- Weak surface interactions (van der Waals, dipole-dipole, and other intermolecular forces)
- Surface reactions resulting in bonding

Charged toxins:

- Ion exchange

17

Isotherms

Experiment:

- Mix a mass of solids in a well-stirred container with a quantity of dissolved chemical
- At intervals, take samples and determine chemical on solids and in solution
- After minutes to hours, equilibrium will be reached
- Can be repeated for different concentration levels

18

Isotherms

Dissolved fraction:

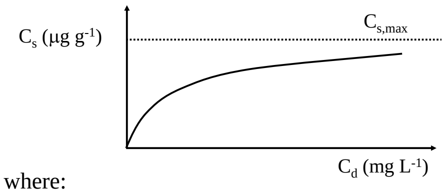
- Determine through chemical analysis in laboratory

Sorbed fraction:

- $C_s = (C_{d,initial} - C_d)$/dry weight of solids

19

Isotherms



where:

- C_s is sorbed concentration of substance
- C_d is dissolved concentration of substance
- Plot is called ‘isotherm’

20

Isotherms Models

Three models to describe data:

- Freundlich
- Langmuir
- Linear

21

Freundlich Isotherm

$$C_s = K_f C_d^{1/n}$$

where:

- K_f is the Freundlich adsoption coefficient
- n is an empirical coefficient

Obtain K_f and n by plotting log C_s vs log C_d:

$$\log C_s = \log K_f + (1/n) \log C_d$$

22

Langmuir Isotherm

$$C_s = \frac{C_{s,max} K_l C_d}{1 + K_l C_d}$$

where:

- K_l is the Langmuir constant (L µg^{-1})
- $C_{s,max}$ is adsorption maximum at fixed temperature (µg g^{-1})

23

Langmuir Isotherm

$$C_s = \frac{C_{s,max} K_l C_d}{1 + K_l C_d}$$

Obtain K_l and $C_{s,max}$ by plotting (C_d/C_s) vs C_d:

$$\frac{C_d}{C_s} = \frac{1}{C_{s,max} K_l} + \frac{C_d}{C_{s,max}}$$

slope = $\frac{1}{C_{s,max}}$ intercept = $\frac{1}{C_{s,max} K_l}$

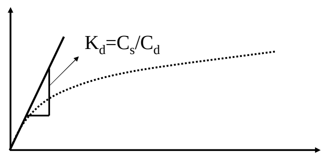
24

Linear Isotherm

$$C_s = K_d C_d$$

where:

- K_d is the partition coefficient or soil distribution coefficient ($m^3\ \mu g^{-1}$)



Example

Determine the appropriate adsorption model and associated coefficients for the data provided:

Mass of solid (g) dissolved in 1.0 L of water	Residual contaminant concentration (C_d, g L^{-1})
0.0	20*
0.9	13
1.7	10
4.0	6
7.0	4
10.0	3

* $C_{d,initial}$

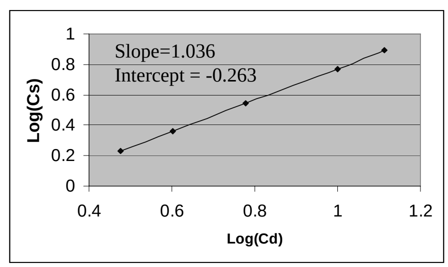
Example Solution

Determine $C_s = (C_{d,initial} - C_d)$/dry weight of solids

M_{solid} (g)	C_d (g L^{-1})	C_s (g g^{-1})
0.9	13	7.8
1.7	10	5.9
4.0	6	3.5
7.0	4	2.3
10.0	3	1.7

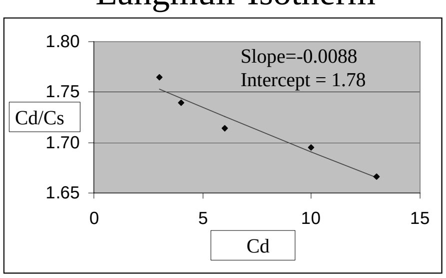
* $C_{d,initial}$= 20 (g L^{-1})

Freundlich Isotherm



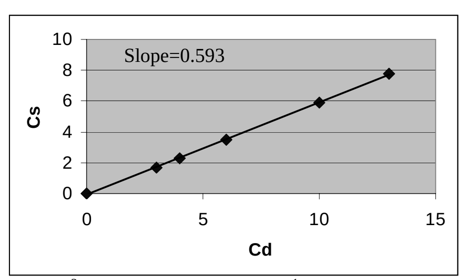
Regression: $r^2 = 0.9999$; $n = 1/1.036 = 0.97$; $K_f = 10^{-0.263} = 0.55$

Langmuir Isotherm



Regression: $r^2 = 0.97$; $C_{s,max} = 1/-0.0088 = -113.9$ (g g^{-1});
$b = 1/(-113.8*1.78) = -0.005$ (L g^{-1})

Linear Isotherm



Regression: $r^2 = 0.9994$; $K_d = 0.593$ (L g^{-1})

Langmuir at Low Concentrations

- At low concentrations, Langmuir isotherms and linear isotherms are similar:

$$C_s = \frac{C_{s,max} K_l C_d}{1 + K_l C_d} \rightarrow C_s = C_{s,max} K_l C_d$$

$$K_d = C_{s,max} K_l$$

31

Estimating Partition Coefficients

For neutral organic chemicals:

- $K_d = f_{oc} K_{oc}$

where K_{oc} = the organic-carbon partition coefficient (mg gC^{-1})(mg m^{-3}) and f_{oc} = weight fraction of the total carbon in solid matter (gC g^{-1})

- $K_{oc} = 6.17 \times 10^{-7} K_{ow}$

where K_{ow} = octanol-water partition coefficient (mg m$^{-3}_{octanol}$)(mg m$^{-3}_{water}$)

32

Octanol-Water Partition Coefficient

- Measure
- From published tables
- Computed from formulas

33

Octanol-Water Partition Coefficient

- Add chemical to mixture of pure octanol (nonpolar solvent) and pure water (polar solvent)
- Agitate until equilibrium, analyze both phases for the chemical
- K_{ow} is ratio of chemical concentration in octanol phase to that in water phase.

34

Finding Dissolved Concentration

- Also note that total concentration C_T is the sum of dissolved concentration (c_d) and particulate concentration (c_p):

$$C_T = c_d + c_p$$

35

Finding Dissolved Concentration

$C_T = c_d + c_p$

- In soil: $c_d = \theta_v C_d$
  $c_p = \rho_{dry} C_s$
- In water: $c_d = C_d$
  $c_p = TSS\ C_s$

where θ_v is volumetric moisture content (-), ρ_{dry} is dry bulk density (kg m^{-3}), and TSS is total suspended solids (mg L^{-1})

36

Finding Dissolved Concentration

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

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

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

What is C_d in water if $C_s=K_dC_d$?

- $C_T = c_d + c_p = C_d + TSS\, C_s = C_d(1 + TSS\, K_d)$

$$C_d = \left(\frac{1}{1 + TSSK_d}\right)C_T$$

37

Volatilization

- Loss of chemicals in vapor form from soil or water surfaces to the atmosphere
- Process involves concentrations in air and water interfaces above soil and water surfaces
- We use the dimensionless form of Henry's constant: $C_d = K_H C_g$

where C_d=concentration in (pore) water solution, and C_g = concentration in vapor phase (vapor density) ($\mu g\ L^{-1}$)

38

Finding Dissolved Concentration

What is C_d in soil if $C_s=K_dC_d$ and $C_d=K_HC_g$?

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

$= C_d[\theta_v + \rho_{dry} K_d + (n - \theta_v)/K_H]$

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

If soil is dry: adsorption dominates
If soil is wet: diffusion dominates
In between: volatilization can be significant

39

Bio-degradation

- Bio-degradation: breakdown of chemical by living organisms to more simple compounds (CO_2, H_2O, and other end products)
- Bio-transformation: change to another form (e.g., DDT to DDE)

40

Bio-degradation

Microorganisms and fungi needed:

- Heterotrophic: energy, organic C, nutrients
- Autotrophic: need sunlight and CO_2
- Chemotrophic: exothermic chemical reaction and CO_2

41

Bio-degradation

Conditions can be:

- Aerobic (oxygen-rich aerated soils): oxidation processes
- Anaerobic (saturated soils w/out oxygen): reduction processes

42

Bio-degradation

Monod model: $$\frac{dC_d}{dt} = \frac{-\mu_m S C_d}{k_s + C_d}$$

where

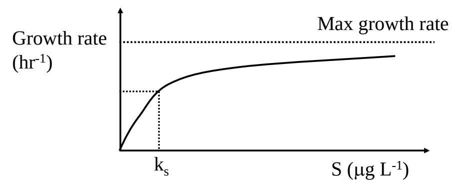
μ_m = maximum growth rate when food is abundant ($\mu g\ L^{-1} day^{-1}$)

S = substrate concentration ($\mu g\ L^{-1}$)

k_s = half-saturation constant for chemical ($\mu g\ L^{-1}$)

43

Microbial Growth Rate



44

Bio-degradation

For small concentrations ($C_d << k_s$):

$$\frac{dC_d}{dt} = -k_b C_d$$

which is a 1st order reaction rate equation

45

Other Transformations

- Chemical oxidation-reduction reactions
- Hydrolysis
- Photochemical transformations

46

Half-Life

- For organic chemicals without a specific degradation rate, the half-life is used
- Half-life: number of days required for 50% of the original chemical to degrade in soil
- 1st order reaction rate accepted model

$$P(t) = P(0)e^{-k_t t}$$

47

Half-Life

1st order reaction rate model:

$$P(t) = P(0)e^{-k_t t} \quad \rightarrow \quad t_{1/2} = -\frac{\ln(0.5)}{k_t} = \frac{0.69}{k_t}$$

where P(t) and P(0) = chemical mass, k_t = degradation rate coefficient, t = time

48