Answer Sheet

1. (10 pt.)

At low pH: increase in H^+ → react with CO_3^{2-} to form HCO_3 → usually exist as Cd^{2+} (5 pt.)

At high pH: increase in OH^- → react with Cd^{2+} →usually exist as $Cd(OH)_2$ (5 pt.)

2. (10 pt.)

O_2, NO_3^-, SO_4^{2-}, CO_2 (3 pt.)

The energy released taking oxygen as an electron acceptor is the largest. / Since ΔG value for oxygen is the largest (as negative value), it is preferred to be used as first (3 pt.)

Catechol (3 pt.)

Explanation: Aerobic biodegradation by Bacteria of Benzene is following. Hydroxylation occurs due to oxygenase and forms cis-dishydrodiol and catechol. Catechol always forms as the metabolic intermediate. Then, ring fission occurs because of the oxygenase. (1 pt.)

3. (10 pt.)

Key : H_2O_2/Fe^{2+}/OH radical (each 2 pt.)

React with Benzene (1 pt.)

Since carbon of Benzene is reduced carbon and carbon of carbon tetrachloride is oxidized carbon, Benzene is reacted by Fenton oxidation (3 pt.)

4. (10 pt.)

Soil saturated concentration (C_{sat}) is sum of sorbed concentration on soil particles, dissolved concentration by soil pore water, and gas concentration in soil pore space.

$C_{sat} = (\frac{S}{\rho_b}) \times (K_d\rho_b + \theta_W + H'\theta_a)$ (6.5 pt.)

where

C_{sat}: mg/kg (each 0.5 pt.)

S : water solubility, mg/L-water

ρ_b: dry bulk density, kg/L-soil

K_d : sorption coefficient, L/kg

θ_W : water-filled soil porosity, L-water/L-soil

H' : dimensionless value of H. Hx41

θ_a : air-filled soil porosity, L-air/L-soil

5. (10 pt.)

(1) Toxicity reduction

Explanation includes strategies with transformation of valence (As^{3+} to $As^{5+}$and Cr^{6+} to Cr^{3+})(5 pt.)

As^{5+} than As^{3+}, and Cr^{3+} than Cr^{6+} have lower toxicity. Thus, reduction or oxidation has to transform As to As^{5+} and Cr to Cr^{3+} to reduce toxicity of groundwater contaminated with Arsenic and Chromium. Strategies of toxicity reduction includes biological/chemical reduction/oxidation.

(2) Physical removal

As^{5+} exists as oxidized form in groundwater and it has negative (-) charge. Thus, iron oxide or positive (+) charged resin allows As^{5+} to adsorbed on positive (+) charged surface to remove As^{5+}. Cr^{3+} is easier to treat than Cr^{6+} since Cr^{3+} has positive (+) charge in groundwater, it can be removed by allowing absorb on negative (-) charged resin. (5 pt.)

6. (10 pt.)

$P = k \times C$

where

P: partial pressure (atm)

k: Henry's constant (atm·m³/mol)

C: concentration of the compound in water (mol/m³) (1 pt.)

Henry's law is that solubility is proportional to constant partial pressure at constant temperature. If Henry's law constant is regarded as partition coefficient between water and air, Henry's law constant, K, can be explained as: (3 pt.)

$K = \frac{V_P}{S}$

Where

k: Henry's constant (atm·m³/mol)

V_P : Vapor pressure (atm)

S : Water solubility (mol/m^3)

Henry's law constant for methanol is close to 0 since it has high water solubility (1pt.), and this represents low volatility (2 pt.).

However, DDT has trend of volatilization (2 pt.) because DDT has low vapor pressure and low solubility with 7.92X10^{-5} of Henry's law constant (1 pt.).

7. (10 pt.)

Only answers or only order (2 pt.)

pH = pKa : [HA] = [A$^-$]

pH < pKa : [HA] > [A$^-$]

pH > pKa : [HA] < [A$^-$]

At pH of 7 pentachlorophenol and 2,4,6-trichlorophenol exist as [A$^-$] form. As pKa gets lower, possibility of pentachlorophenol adsorption increases because lower pKa represents more ionization. (4 pt.)

In case of aniline, when pH < pKa leads no charge, hydrophobic sorption is primarily occurred so that it does not take part in adsorption process. (4 pt.)

8. (10 pt.)

Although malathion concentration is high at Site A, possibility of contaminant exposure is low due to organic material content is high in the soil. (5 pt.) Thus, risk is also low. (5 pt.)

Other logically proper answers (10 pt.)

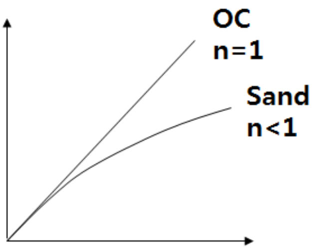
9. (10 pt.)

(1) In case of contaminant X+Y, released enzyme, while grown by X, trnasforms Y to Y' (cometabolism, (2 pt.)), but Y' is not observed because Y' is decomposed by inorganic compounds (CO_2, H_2O) as time passes (3 pt.)

(2) TCE, CH_4 (each 2.5 pt.)

10. (10 pt.)

(each 5 pt.)



11. (10)

ADRE (Advection-Dispersion-Reaction Equation) follows. (From left) dispersion, advection, transformation-reaction term. (4 pt.)

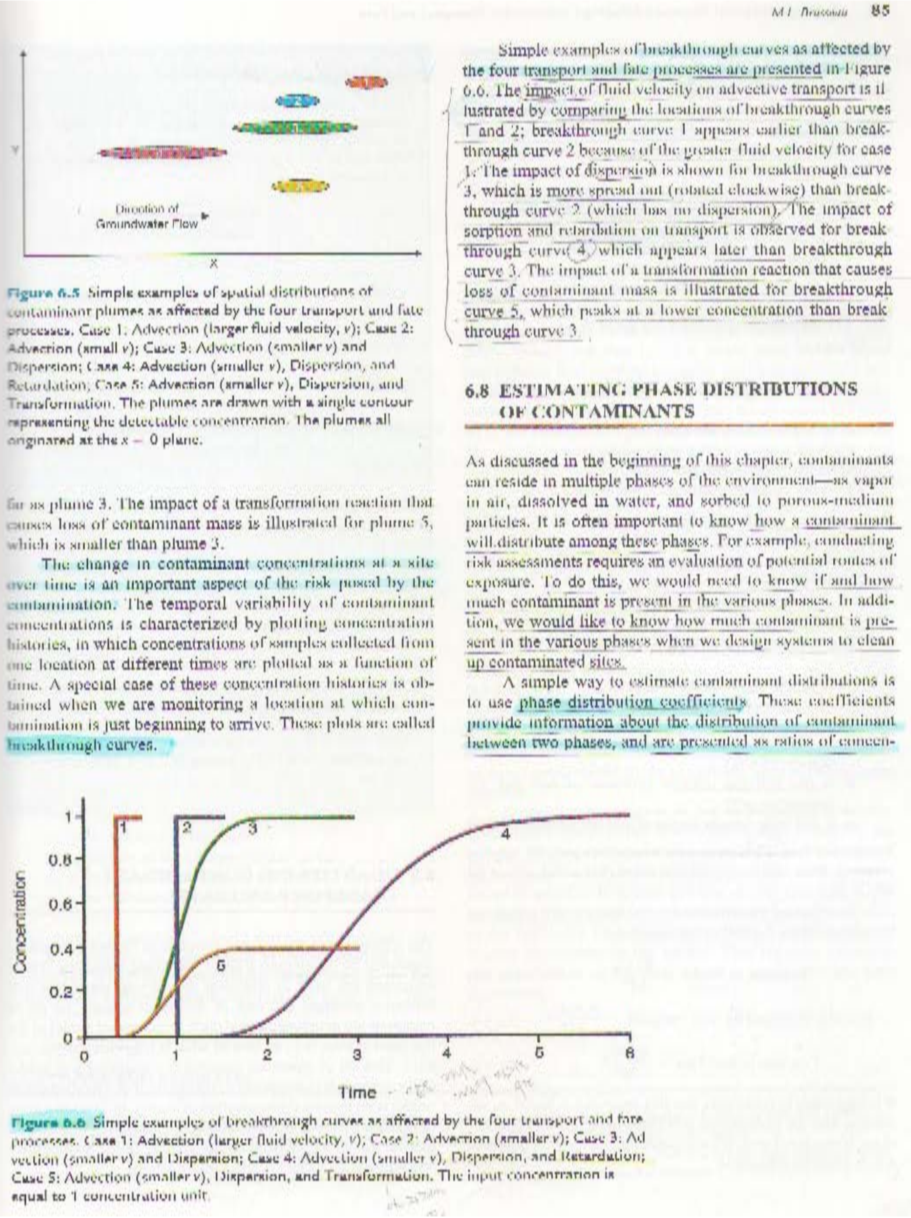


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Figure 6.5 Simple examples of spatial distributions of contaminant plumes as affected by the four transport and fate processes. Case 1: Advection (larger fluid velocity, v); Case 2: Advection (small v); Case 3: Advection (smaller v) and Dispersion; Case 4: Advection (smaller v), Dispersion, and Retardation; Case 5: Advection (smaller v), Dispersion, and Transformation. The plumes are drawn with a single contour representing the detectable concentration. The plumes all originated at the x = 0 plane.

far as plume 3. The impact of a transformation reaction that causes loss of contaminant mass is illustrated for plume 5, which is smaller than plume 3.

The change in contaminant concentrations at a site over time is an important aspect of the risk posed by the contamination. The temporal variability of contaminant concentrations is characterized by plotting concentration histories, in which concentrations of samples collected from one location at different times are plotted as a function of time. A special case of these concentration histories is obtained when we are monitoring a location at which contamination is just beginning to arrive. These plots are called breakthrough curves.

Simple examples of breakthrough curves as affected by the four transport and fate processes are presented in Figure 6.6. The impact of fluid velocity on advective transport is illustrated by comparing the locations of breakthrough curves 1 and 2; breakthrough curve 1 appears earlier than breakthrough curve 2 because of the greater fluid velocity for case 1. The impact of dispersion is shown for breakthrough curve 3, which is more spread out (rotated clockwise) than breakthrough curve 2 (which has no dispersion). The impact of sorption and retardation on transport is observed for breakthrough curve 4, which appears later than breakthrough curve 3. The impact of a transformation reaction that causes loss of contaminant mass is illustrated for breakthrough curve 5, which peaks at a lower concentration than breakthrough curve 3.

6.8 ESTIMATING PHASE DISTRIBUTIONS OF CONTAMINANTS

As discussed in the beginning of this chapter, contaminants can reside in multiple phases of the environment—as vapor in air, dissolved in water, and sorbed to porous-medium particles. It is often important to know how a contaminant will distribute among these phases. For example, conducting risk assessments requires an evaluation of potential routes of exposure. To do this, we would need to know if and how much contaminant is present in the various phases. In addition, we would like to know how much contaminant is present in the various phases when we design systems to clean up contaminated sites.

A simple way to estimate contaminant distributions is to use phase distribution coefficients. These coefficients provide information about the distribution of contaminant between two phases, and are presented as ratios of concen-

Figure 6.6 Simple examples of breakthrough curves as affected by the four transport and fate processes. Case 1: Advection (larger fluid velocity, v); Case 2: Advection (smaller v); Case 3: Advection (smaller v) and Dispersion; Case 4: Advection (smaller v), Dispersion, and Retardation; Case 5: Advection (smaller v), Dispersion, and Transformation. The input concentration is equal to 1 concentration unit.

where

D: Dispersion coefficient

R : Retardation factor

v : velocity

k : first-order reaction constant

Although contaminants in groundwater usually transport by advection as shown in case 1 and case 2, dispersion has to be accounted due to transport depend on variety curved path. Case 3 shows low transferring velocity because of advection and dispersion of case 2. When retardation is also accounted, then contaminant concentration to reach case 1 takes more time. Case 4 shows dispersion of contaminant is slower because of the retardation effect of case 3. Case 5 shows that final contaminant concentration has failed to reach case 1 due to transformation reaction. (case 1 and 2: advection, velocity difference, case 2→3 : change caused by dispersion, case 3→4 : change caused by retardation, case 3→5 :change caused by transformation reaction) (Figure and explanation each 1 pt.)

12. (10 pt.)

Darcy's velocity is the average apparent velocity, considering all pathways through groundwater.

$\frac{\mathrm{Q}}{\mathrm{A}} = \mathrm{vd} = \mathrm{K}\left(\frac{\mathrm{dh}}{\mathrm{dl}}\right)$ (3 pt.)

However the equation does not express the flow through porous medium since this equation only includes hydraulic conductivity and hydraulic slope. Groundwater flows through the porous medium, and the moving distance is much longer than the flow distance through nonporous medium. Thus the hydraulic conductivity is modified with the porosity (n) to calculate the actual velocity (3 pt.). Seepage velocity represents the actual velocity of groundwater in aquifer, and it is the Darcy velocity divided by the porosity.

$v = \frac{K}{n}\left(\frac{dh}{dl}\right)$ (3 pt.)

Where n is $0 < n < 1$, and $\mathrm{v} \geq \mathrm{q}$ (the actual velocity is greater than the average apparent velocity) (1 pt.)

13. (10 pt.)

Definition of soil washing: Soil washing is a mechanical process that uses appropriate washing agents to remove harmful organic pollutants or heavy metals by weakening the surface tension of the harmful organic pollutants that are sorbed on soil or by dissolving heavy metals into aqueous phase. (1 pt.)

There are three major factors that affects the soil washing efficiency.

(1) Particle size (3 pt.)

Soil washing is effective to gravel, sand, and silt, and it is less effective to silt and clay.

(2) Type of contaminant (3 pt.)

Soil washing is effective to semi-volatile organic compounds, total petroleum hydrocarbon (TPH), and heavy metals; however, it is less effective to complex pollutants, such as heavy metal and organic complex compounds.

(3) Washing agent (3 pt.)

Surfactants, coagulants, pH, solid-liquid ratio, etc.

14. (10 pt.)

(1) Retardation factor (R)

It describes the difference of the moving speed caused by sorption, desorption, etc., and it is described by the following equation.

$\text{Retardation Factor (R)} = 1 + \frac{\rho_B}{\theta} K_d = \frac{V_W}{V_P} = \frac{d_w}{d_p}$ (2 pt.)

where

ρ_b: soil bulk density $(\frac{g}{m^3})$

θ: porosity

K_d: soil distribution coefficient $\left(\frac{mL}{g}\right)$

V_W : velocity of the fluid

V_P : velovity of the contaminant

d_W: distance traveled by the fluid

d_P: distance traveled by the contaminant

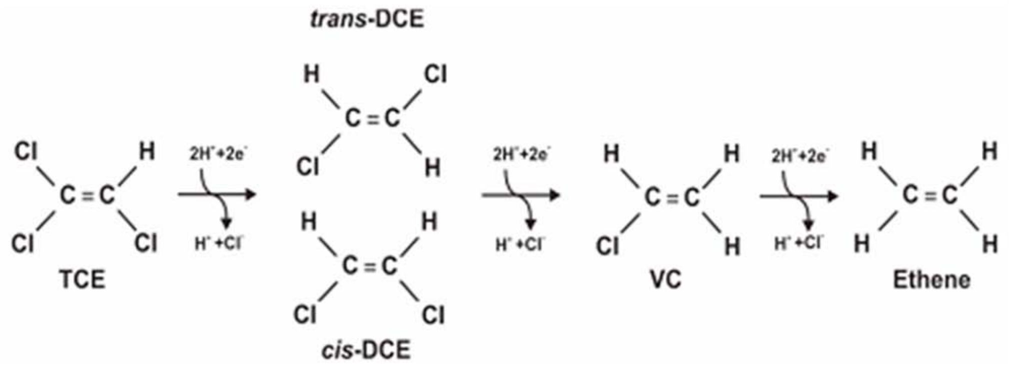
(2) K_d and K_{OC}

K_d (distribution partition coefficient) is the ratio of concentrations of a pollutants in water and pollutants absorbed in soil particles at equilibrium, and the unit is L/kg. (1 pt.)

K_{OC} (organic carbon partition coefficient) is the ratio of concentrations of a pollutants in water and pollutants absorbed in organic carbon at equilibrium. (1 pt.)

$K_d = K_{OC} \times f_{OC}$ (2 pt.)

(3) (4 pt.)



(4) Pseudo-first order reaction

When there is a reaction of two reactants of which the amount of one reactant is much greater than that of the other reactant, one with less can be ignored. The reaction is said to be Pseudo-first order reaction. (2 pt.)

When the amount of B is greater than that of A, the reaction is described with the following equation: $\frac{\mathrm{dA}}{\mathrm{dt}} = -k[A][B] = -k'[A]$, where k' is the Pseudo First-order Reaction rate constant. (2 pt.)

(5) Cation exchange capacity (CEC)

It is the maximum quantity of total cations(Ca, Mg, K, Na, etc.) that a soil is capable of holding available for exchange with the soil solution. (2 pt.) It is expressed as me equivalent, which is the amount of exchangeable cations, for 100g of dry soil, and the unit is me/100g. (2 pt.)