

6.6 BIODEGRADATION

In addition to abiotic processes \rightarrow Biodegradation of hydrocarbons
Biofilm + Oxygen \rightarrow Aerobic biodegradation
 \rightarrow Growth of microbial population

AEROBIC

Need oxygen sources - dissolved in water
- pumped in for remediation

Monod - function governs rates!

3 rate laws (coupled) (H) Hydrocarbon concentration
(O) Oxygen availability in fluid
(M) Biofilm mass

\rightarrow 3 conservation equations and 3 unknowns
Solve for (H).

ANAEROBIC

Microbes use other metabolic source eg. nitrate available from fertilizer

1 rate law required only } solve for hydrocarbon concentration.
1 conservation equation

BIODEGRADATION - More complex than simple reaction since requires

AEROBIC

3 Growth/Decay laws - inter-related

$$\frac{dH}{dt} = -M_A \left(\frac{H}{K_A + H} \right) \left(\frac{O}{K_O + O} \right) \quad (3.59)$$

$$\frac{dO}{dt} = -M_A \left(\frac{H}{K_A + H} \right) \left(\frac{O}{K_O + O} \right) \quad (3.60)$$

$$\frac{dM_A}{dt} = M_A \left(\frac{H}{K_A + H} \right) \left(\frac{O}{K_O + O} \right) + k_d M_A - bM_A \quad (3.61)$$

where

- H = hydrocarbon concentration in pore fluid (ML⁻³)
- O = oxygen concentration in pore fluid (ML⁻³)
- M_A = total aerobic microbial concentration (ML⁻³)
- A₀ = maximum hydrocarbon utilization rate per unit mass of aerobic microorganisms (T⁻¹)
- Y = microbial yield coefficient (g cells/g hydrocarbon)
- K_A = hydrocarbon half saturation constant (ML⁻³)
- K_O = oxygen half saturation constant (ML⁻³)
- k_d = first order decay rate of natural organic carbon
- C₀ = natural organic carbon concentration (ML⁻³)
- b = microbial decay rate (T⁻¹)
- G = ratio of oxygen to hydrocarbon consumed

The microorganisms will grow on both naturally occurring organic carbon as well as hydrocarbon contaminants. The microorganisms tend not to move in the aquifer because they generally adhere to aquifer materials (Harvey, Smith, and George 1984). Even if the microbes are free to move, the natural tendency of the aquifer matrix will be to filter them out. There will be some tendency for microbes to transfer from the solid surface to solution. As a first approximation this can be considered to be a linear function of the total mass of microorganisms.

We can combine Equations 3.59, 3.60, and 3.61 individually with Equation 3.1 to obtain solute transport equations for hydrocarbon, oxygen and microorganisms. The hydrocarbon is assumed to sorb onto the solid surfaces following a linear sorption

3 Conservation equations - inter-related

isotherm. The resulting equations are (Borden and Bedient 1986)

$$\frac{\partial H}{\partial t} + \frac{1}{\tau_s} \left(D_x \frac{\partial^2 H}{\partial x^2} - v_x \frac{\partial H}{\partial x} \right) - \frac{k_d M_A}{\tau_s} \left(\frac{H}{K_A + H} \right) \left(\frac{O}{K_O + O} \right) \quad (3.62)$$

$$\frac{\partial O}{\partial t} + \frac{1}{\tau_s} \left(D_x \frac{\partial^2 O}{\partial x^2} - v_x \frac{\partial O}{\partial x} \right) - \frac{1}{\tau_s} M_A \left(\frac{H}{K_A + H} \right) \left(\frac{O}{K_O + O} \right) \quad (3.63)$$

$$\frac{\partial M_A}{\partial t} + \frac{1}{\tau_s} \left(D_x \frac{\partial^2 M_A}{\partial x^2} - v_x \frac{\partial M_A}{\partial x} \right) + k_d M_A \left(\frac{H}{K_A + H} \right) \left(\frac{O}{K_O + O} \right) - bM_A \quad (3.64)$$

where

- M_A = concentration of aerobic microbes in solution
- τ_s = retardation factor for hydrocarbon
- τ_s = microbial retardation factor
- v_x = average linear ground water velocity

ANAEROBIC

Some microorganisms can degrade hydrocarbons in the absence of oxygen. These microbes use another electron acceptor, such as nitrate (Major, Mayfield, and Barber 1988). Anaerobic decomposition of hydrocarbons can be described by another variation of the Monod function, which describes two-step catalytic chemical reactions (Bouwer and McCarty 1984). This function is

$$\frac{dH}{dt} = -k_d M_A \left(\frac{H}{K_A + H} \right) \quad (3.65)$$

where

- M_A = total mass of anaerobic microbes
- k_d = maximum hydrocarbon utilization rate per unit mass of anaerobic microbes
- K_A = half maximum rate concentration of the hydrocarbon for anaerobic decay

The solute transport and decay equation for anaerobic biodegradation in the aqueous phase is

$$\frac{\partial H}{\partial t} = \frac{1}{\tau_s} \left(D_x \frac{\partial^2 H}{\partial x^2} - v_x \frac{\partial H}{\partial x} \right) - \frac{k_d M_A}{\tau_s} \left(\frac{H}{K_A + H} \right) \quad (3.66)$$

If the concentration of the hydrocarbon, H, is much less than K_A, the half-maximum rate concentration, then Equation 3.65 can be simplified to a linear form by neglecting H in the denominator (Bouwer and McCarty 1984). This results in a first-order decay term.

$$\frac{dH}{dt} = - \left(\frac{k_d M_A}{K_A} \right) H \quad (3.67)$$

Under these conditions the solute-transport equation with anaerobic biodegradation becomes

$$\frac{\partial H}{\partial t} = \frac{1}{\tau_s} \left(D_x \frac{\partial^2 H}{\partial x^2} - v_x \frac{\partial H}{\partial x} \right) - \left(\frac{k_d M_A}{\tau_s K_A} \right) H \quad (3.68)$$

Reaction term to equation.

LINEARIZED ANAEROBIC

Hydrocarbon conc $\ll K_A$
then linearizes as

$$\frac{dH}{dt} = -k_d M_A \left(\frac{H}{K_A + H} \right) \Rightarrow -k_d M_A \frac{H}{K_A}$$