Mass Transfer Processes

In a conservative pollutant, pollutant enters the domain of interest at the boundaries or at an interior location using a fluid source/sink term (actually on internal boundary, but far easier to treat as a source/sink).

Non-conservative pollutants can enter the domain of interest at boundaries and fluid sources — but also they enter and leave through mass transfer mechanisms

- chemical reactions
- adsorbtion
- volatilization
- dissolution

- precipitation
- radioactive decay
- biological decay (actually a reaction, but often modeled as decay)

Traditionally these "different" mechanisms are treated separately — however from a Reynolds transport point of view or cell balance point of view they can all be treated as an additional flux component or mass accumulation component depending on which makes more modeling sense.

Adsorption in a porous medium is a good example to illustrate how to incorporate non-conservative mass transfer terms into the pollutant balance equations.

Starting with advection - dispersion equation we can add fluid source/sink terms as

$$\frac{\partial c}{\partial t} = \nabla \cdot (\underline{D} \cdot \nabla c - c\underline{v}) + q_s C_s - q_w C$$

$$q_s = \frac{\text{volume of fluid added}}{\text{unit volume (cell volume)}}$$

$$C_s = \text{source concentration}$$

$$q_w = \frac{\text{volume of fluid withdrawl}}{\text{unit volume}}$$

The assumption is that $\underline{v}$ is determined after effects of q_s and q_w are considered.

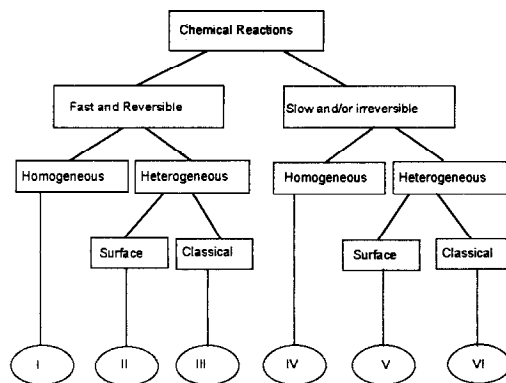Observe that $q_s C_s$ & $q_w C$ are just additional terms in the flux integrals.

To add mass transfer terms we add additional terms to the flux integral(s).

The result will be something like

$$\frac{\partial c}{\partial t} = \nabla \cdot (\underline{D} \nabla c - c\underline{v}) + q_s C_s - q_w C + \sum_{k=1}^{N} R_k$$

where k represents the different mass transfer processes of interest.

Mass Transfer Hierarchy

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                    ┌──────────────────┐
                    │ Chemical Reactions│
                    └──────────────────┘
              ┌───────────────┴───────────────┐
    ┌──────────────────┐          ┌──────────────────────┐
    │ Fast and Reversible│        │ Slow and/or irreversible│
    └──────────────────┘          └──────────────────────┘
       ┌──────┴──────┐               ┌──────┴──────┐
 ┌───────────┐ ┌─────────────┐  ┌───────────┐ ┌─────────────┐
 │Homogeneous│ │Heterogeneous│  │Homogeneous│ │Heterogeneous│
 └───────────┘ └─────────────┘  └───────────┘ └─────────────┘
        │      ┌────┴────┐            │      ┌────┴────┐
        │  ┌──────┐ ┌────────┐        │  ┌──────┐ ┌────────┐
        │  │Surface│ │Classical│      │  │Surface│ │Classical│
        │  └──────┘ └────────┘        │  └──────┘ └────────┘
        │      │        │             │      │        │
      ( I )  ( II )   ( III )       ( IV )  ( V )   ( VI )
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Adsorbtion - solute clings to surface due to various attractive forces - usually electrostatic.

Ion-Exchange - ions are attracted to mineral surfaces substitute themselves into the mineral structure.

Chemisorption - solute is incorporated into a sediment by chemical reaction.

Absorbtion - solute diffuses into solid matrix and clings to interior surfaces.

All these reactions are controlled to a great extent by solution pH, EH, and salinity.

Adsorption describes a process where solute clings to the surface of solids (immobile) in the flow field because of attractive forces.

Isotherm is the name given to a set of data that describe a solute-solid interaction at a constant temperature

Adsorption Isotherms

Several jars of water with known C_0 of solute are prepared
Different masses of same solid are added to each jar
Jars sealed and agitated for sufficient time to reach equilibrium
After equilibrium, concentration in each jar is measured C_e.
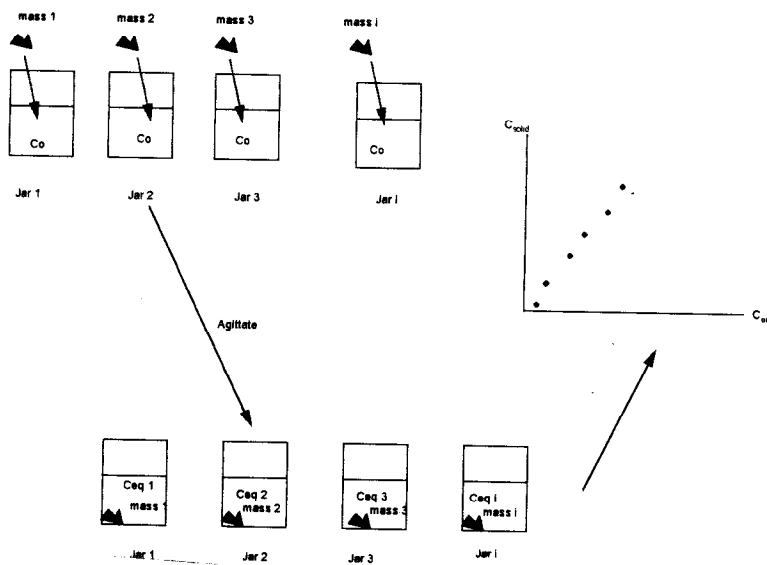Amount of mass transferred to solid is

$$M_s = \forall (C_0 - C_e)$$

Solid phase concentration is $\quad C_s = \dfrac{M_s}{m_{solid}}$

Plot of C_s versus C_e is called an equilibrium adsorption isotherm

If the procedure is done using different agitation times
so equilibrium is not reached, then kinetic effects can
be studied.

Isotherms are usually drawn using massic concentrations

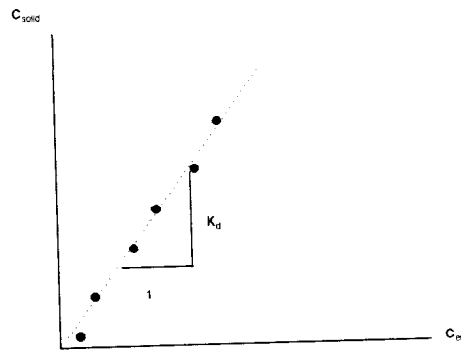Linear Isotherm, Freundlich Isotherm, Langmuir Isotherm

•If the data exhibits a straight-line relationship when plotted on arithmetic graph paper, then the isotherm is called a *linear equilibrium isotherm*.

•If, in addition to the linear relationship, the system assumes new equilibrium conditions very fast relative to the transport processes involved, then the isotherm is called an *instantaneous linear equilibrium isotherm*.
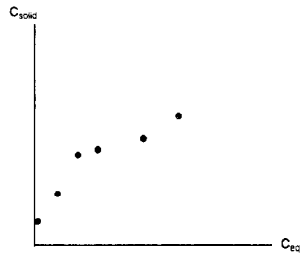
•The slope of the isotherm is called the distribution coefficient, K_d.

•The equation of the isotherm is: $C_{solid} = K_d C_{aq}$

•Expressed as a rate equation: $dC_{solid}/dt = K_d \, dC_{aq}/dt$

•If the data exhibits a straight-line relationship when plotted on log-log graph paper, then the isotherm is called a _Freundlich Isotherm._
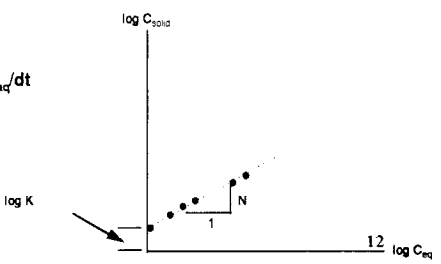
•If, in addition to the log-log linear relationship, the system assumes new equilibrium conditions very fast relative to the transport processes involved, then the isotherm is called an _instantaneous Freundlich equilibrium isotherm._
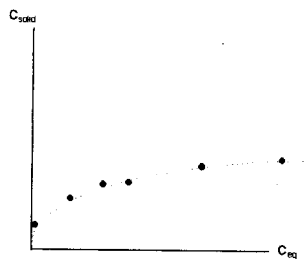
•The slope of the isotherm is called Freundlich exponent, N, and the intercept is called the Freundlich distribution coefficient, K.

•The equation of the isotherm is : $C_{solid} = K C_{aq}^N$

•Expressed as a rate equation: $dC_{solid}/dt = KN C_{aq}^{N-1} dC_{aq}/dt$

•If the data exhibits a straight-line relationship when C_{aq}/C_{solid} is plotted versus C_{aq} on arithmetic paper, then the isotherm is called a _Langmuir Isotherm_.

•If, in addition to the linear relationship of C_{aq}/C_{solid} versus C_{aq}, the system assumes new equilibrium conditions very fast relative to the transport processes involved, then the isotherm is called an _instantaneous Langmuir equilibrium isotherm_.
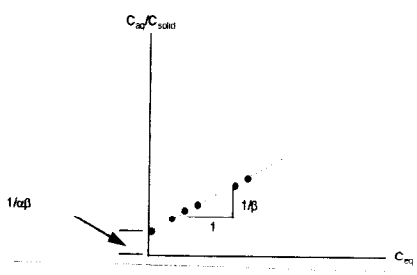
•The equation of the isotherm is:
$$C_{aq}/C_{solid} = 1/ab + C_{aq}/b$$

where a is an adsorbtion constant related to binding energy and b is the maximum amount of solute that can be adsorbed.
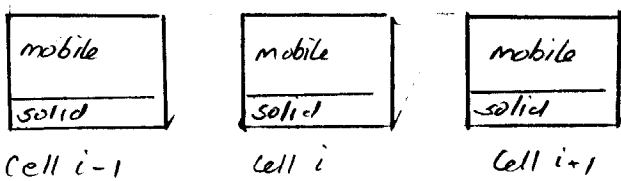
•To express as a rate equation rearrange as

$C_{solid} = [abC_{aq}]/[1 + a C_{aq}]$

$dC_{solid}/dt = ([ab]*[1 + a C_{aq}]^{-2})dC_{aq}/dt$

Incorporation of Isotherms into pollutant balance equations

Consider a cell balance

mobile		mobile		mobile
solid		solid		solid

Cell i-1   Cell i   Cell i+1

two compartments:
mobile & immobile
(solid)

Isotherm provides following relationship

$$\frac{\partial C_s}{\partial t} = K_d \frac{\partial C_w}{\partial t} \qquad (\text{linear isotherm})$$

Cell geometry & porosity provide

$$\mathcal{V}_{cell} = \Delta x \Delta y \Delta z \qquad \mathcal{V}_{pore} = n \Delta x \Delta y \Delta z \qquad m_{water} = \rho_w \, n \Delta x \Delta y \Delta z$$

$$\mathcal{V}_{solid} = (1-n) \Delta x \Delta y \Delta z \qquad\qquad m_{solid} = \rho_s (1-n) \Delta x \Delta y \Delta z$$

Total solute (pollutant) balance for any cell

$$m_{solute} = m_{solute-mobile} + m_{solute-immobile}$$

$$= C_w \, n \Delta x \Delta y \Delta z + C_s \rho_s (1-n) \Delta x \Delta y \Delta z$$

Now the rate of change of m_{solute} in each cell is

$$\frac{dm_{solute}}{dt} = \frac{\partial C_w}{\partial t} n \Delta x \Delta y \Delta z + \frac{\partial C_s}{\partial t} \rho_s (1-n) \Delta x \Delta y \Delta z$$

The isotherm relates the second term to the first as $\frac{\partial C_s}{\partial t} = K_d \frac{\partial C_w}{\partial t}$.

Finally because $\frac{dm_{solute-immobile}}{dt}$ has its only source as mobile phase loss, the rates can be related in the two compartments. The result is

$$\frac{\partial C_w}{\partial t} = \nabla \cdot (\underline{D} \nabla C - C \underline{V}) + q_s C_s - q_w C - K_d \frac{\partial C_w}{\partial t} \rho_s \frac{(1-n)}{n}$$

In this term velocity is the pore velocity, and volume is aquifer volume. More on these distinctions later —
What is important is that the mass transfer term is just another "flux" from the Reynolds Transport point of view.