9/14/04

molecular diffusion

$D \approx 10^{-5}$ cm²/s in water
$D \approx 0.2$ cm²/s in air
} ballpark figures – not acct. for chemical species, temperature

turbulent (eddy) diffusion >> molecular

parcels of air/water moving, depends on energy + physical scale

- biological dispersion (West Nile virus, genetic information) can also be modeled (at least qualitatively)

mechanical dispersion – going around obstacles, take paths w/ varying lengths

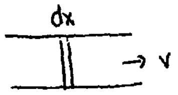
$D_{mech} \approx \alpha \cdot v$ α: dispersivity ≈ grain size

whitewater question: really is lots of advection vectors, but that's impossible to deal with so we assume randomness + represent w/ turbulent diffusion

back-eddies

turbulence and larger-scale structure – (rocks, trees)
lump together + call it "dispersion"

differential control volume



$$\frac{dc}{dt} + \underset{\overset{\uparrow}{\text{advective}}}{v\frac{dc}{dx}} = \frac{\partial}{\partial x}\underset{\overset{\uparrow}{\text{Fickian}}}{\left(D\frac{dc}{dx}\right)} + r \qquad \text{(reaction)}$$

think about each term physically, and sign convention

Chemical Models – predict concentrations

for fast reactions (relative to mechanics), use equil. model
slow reactions – kinetic model

time scales! same goes for air-water exchange, for instance

basic thermo equations:

Gibbs free energy $G = H - TS$

$$Q = \frac{[D]^d[C]^c}{[A]^a[B]^b} \quad \text{reaction quotient}$$

$$\Delta G = \Delta G^\circ + RT\ln Q$$
$$K = e^{-\Delta G^\circ/RT}$$
(where K is Q at equil.)

} think about these

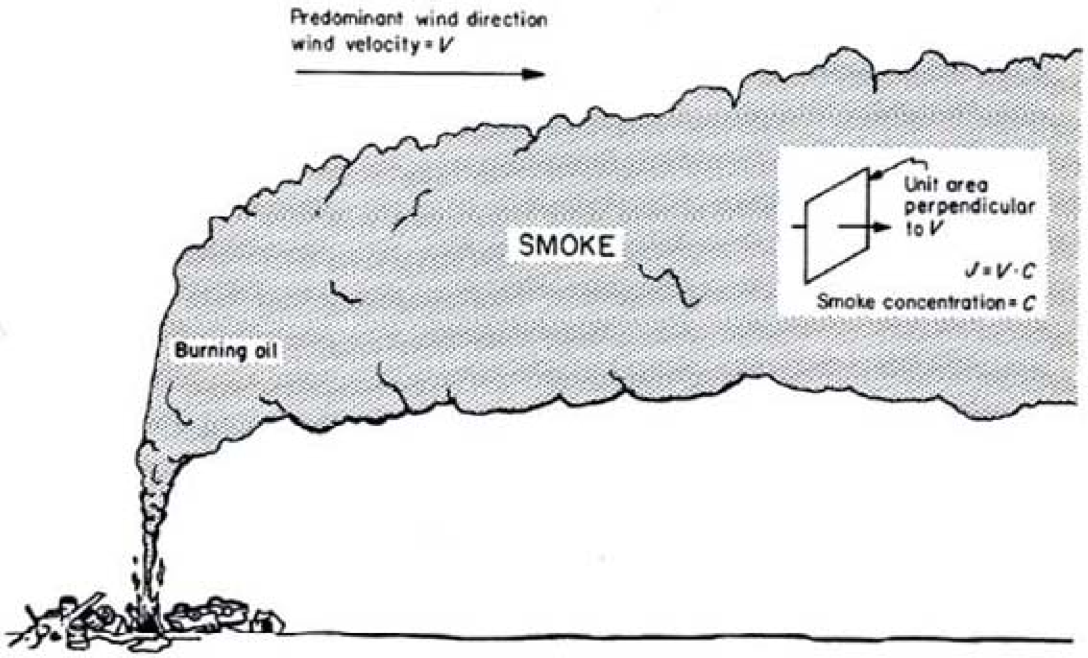


FIGURE 1-5 Advective transport of a smoke plume as shown in Fig. 1-4. The imaginary square frame is oriented perpendicular (⊥) to fluid flow and for convenience has an area of one (in whatever units we prefer—m^2, ft^2, etc.). The flux density of smoke, J, is the product of the wind velocity V and the concentration of smoke in the air, C.

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment*, 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

16 Chapter 1 Basic Concepts

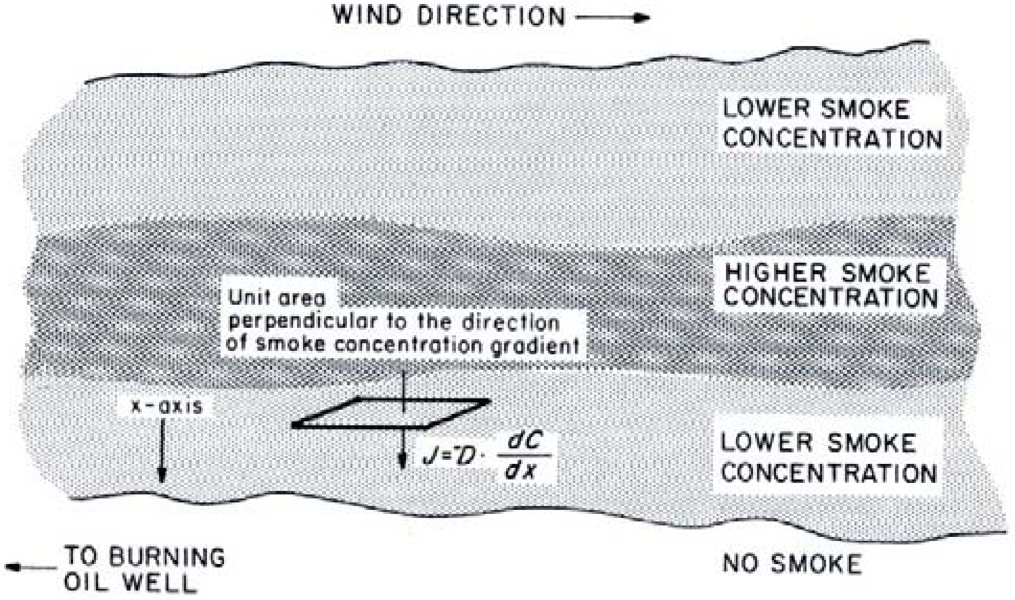


FIGURE 1-6 Fickian transport by turbulent diffusion in a smoke plume as shown in Figure 1-4. As in Figure 1-5, the square frame is of unit area, but in this case is oriented perpendicular to the direction of the concentration gradient (defined as the direction in which the concentration changes the most per unit distance.) In this case the *x*-axis is drawn in the direction of the gradient. The flux density, *J*, is equal to the concentration gradient, *dC/dx*, multiplied by the Fickian transport coefficient *D*. (In this situation, *D* is called a turbulent or eddy diffusion coefficient, because the major agent of Fickian transport is turbulence.)

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment*, 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

example: 0.2M acetic acid

species: HAc, Ac^-, H^+, OH^-

constraints:

1) $\frac{[Ac^-][H^+]}{[HAc]} = 1.75 \times 10^{-5}$ M mass action

2) 0.2M = [HAc] + $[Ac^-]$ mass balance (conservation)

3) $[H^+][OH^-] = K_w = 10^{-14}$ M^2

4) $[H^+] = [Ac^-] + [OH^-]$ electroneutrality

can make simplifications - neglect $[OH^-]$ in #4, for example

in natural waters, ionic strength is important (activity, not conc.)

thermodynamically accurate

$K = \frac{\{H^+\}\{Ac^-\}}{\{HAc\}}$ $\{Ac^-\} = \gamma [Ac]$

in saltwater, this can
make a difference
$\gamma \to 1$ in freshwater

9/16/04

chemistry < reaction (bond breaking + forming)
mov't among phases

steady-state vs. transient for both

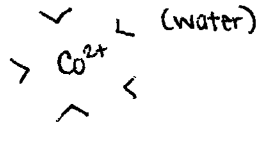
from last time: three types of constraints (mass conservation, electroneutrality, thermo|mass action)

what's a good conceptual way to explain ionic strength?

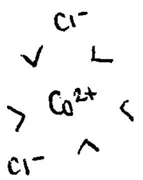
$I = \sum_i \frac{1}{2} c_i z_i^2$ (effect on thermodynamics)

Debye-Huckel: $\log \gamma = -0.5 z^2 \sqrt{I}$

ex. small amount of Co^{2+}



freshwater



seawater

increased I →
lower γ →
$\{Co^{2+}\}$ is less than $[Co^{2+}]$

reaction of Co^{2+} w/EDTA -
less reaction [illegible] in seawater

Davies: $\log \gamma = -0.5 z^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2 I \right)$

for trace metals in
seawater, this can have
effect of up to 10x

continuing the example:

$Co^{2+} + L^{-z} \rightarrow CoL^{-(z-2)}$

bioavailability – microbes care about uncomplexed, not total

complexation reaction (thermo) depends on I...

temp. dependence of $\Delta G | K$ (why both directions?) probably just exothermic | endothermic

kinetics

in closed control volume (cv)

$\frac{d[A]}{dt} = -k[A]$ is one possibility $[A] = [A]_0 e^{-kt}$

rearrange to get $t_{1/2} = \frac{\ln 2}{k}$

DPM - disintegration per minute

DPS – per second; becquerel (Bq)

Ci (curie) = 3.7×10^{10} Bq

} radioactive decay units

also consider energetics of decay, for biological effect

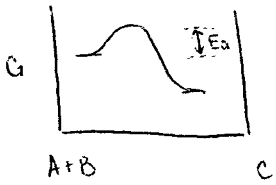
more commonly, $A + B \rightarrow C$

$\frac{d[A]}{dt} = -k[A][B]$ 2nd order units of k are good clue to rxn. order

often try to make pseudo-first-order

if $[B] \approx$ constant ($[B] \gg [A]$, or B is buffered)

$k' = k[B]$ $\frac{d[A]}{dt} = -k'[A]$



(activated complex)

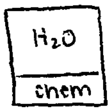
temp. dependence (thermal | dark reactions)

Arrhenius $k = Ae^{-E_a/RT}$

doesn't always hold – ex. ·OH is so fast it's diffusion-limited

or when catalyst is present

Partitioning



pure phase | aqueous – solubility

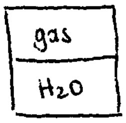
can this be predicted? polarity, size (need to form "hole" in water)

vapor pressure

760 mmHg (torr) = 1 atm   also Pa, bar, psi

Raoult's law for VP of mixtures (gasoline)

so can convert pressure ↔ conc. $\frac{n}{V} = \frac{P}{RT}$



Henry's constant

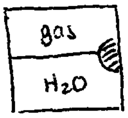
$H \equiv \frac{\text{conc. in gas}}{\text{conc. in water}}$ (dimensionless)

convert w/ RT

is this → partial pressure, not VP?

$H_{dim} = \frac{\text{VP of gas}}{\text{conc. in water}}$ $\left[\frac{\text{atm}}{\text{mol/L}}\right]$ for example

can also back it out: $H_{dim} = \frac{\text{vapor pressure}}{\text{solubility}}$

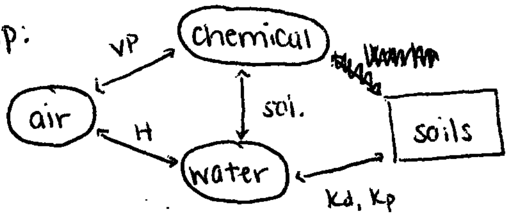


$K_H(CO_2) = \frac{\text{conc. (aq)}}{\text{pressure}}$

next time – partitioning b/t water, solid (K_d is empirical)

9/21/04

recap:

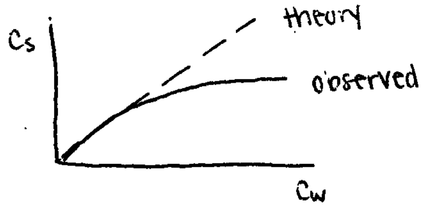


$K_d, K_p \equiv \frac{C_{solid}}{C_{water}}$

this one is more problematic:

1) different kinds of soils

2) is the relationship linear?



$C_s = K_F C_w^n$ (Freundlich isotherm)

different models:

- hydrophobic interaction (into bulk, not surface)
  - how hydrophobic is the soil? % organic content
  - solute? $K_{ow} \equiv \frac{C_{octanol}}{C_{water}}$ → decent surrogate for organic carbon (+ lipids, for pharmaceuticals)

- surface complexation: electrostatic, bonds
- ion exchange (ions diffusing between clay layers?)

} overlap

instead of all the separate partitioning constants, can use fugacity

$f =$ vapor pressure

$C_{medium} = f \cdot Z \leftarrow$ fugacity capacity, ex. $\frac{1}{H}$ for water

(just a rearrangement)

__Rivers__ - movement is dominated by gravity/advection

velocity can be estimated w/ Manning's eqn:

$$V = \frac{1.5 R^{2/3} S^{1/2}}{n} \quad \text{(ft/s)} \qquad R \text{ in ft.} = \frac{A}{P}$$

(wetted perimeter)

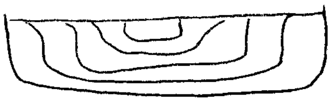
τ at surface resists flow

n is empirical:

smooth concrete $n \approx .010 - .014$

weedy channel $n \approx .075 - .150$

not uniform across channel.

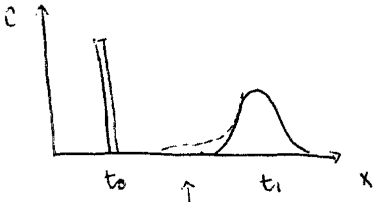


(Aberjona)

dispersion has to do with structure of velocity field - fastest in middle, near surface (as well as eddy diffusion)

velocity may also vary along river, so $\tau_{x_1 \to x_2} = \int_{x_1}^{x_2} \frac{1}{v}\,dx$

pulse injection



Gaussian.

$$Y = \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/2\sigma^2}$$

$\uparrow$ to give unit area

$\uparrow$ tailing - volume that doesn't participate ($\rightarrow$ recirculation)

D as a measure of mixing:

$D_t \equiv$ transverse dispersivity

$D_L \equiv$ longitudinal "

- dispersion due to velocity profile has much greater effect on D_L

what is D, and how does it relate to σ?

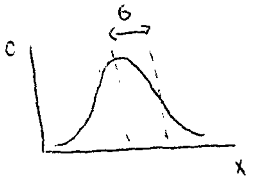
$\sigma^2 = 2Dt$

1-D model: $C(x,t) = \frac{M}{\sqrt{4\pi D_L t}} e^{\frac{-x^2}{4D_L t}}$ ($\times e^{-kt}$ if reaction)

from subst. into Gaussian expression

ways to find D:

1) tracer

observe 

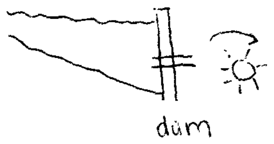
in practice, measure at fixed x as function of t

2) model based on mechanics of river

Fischer, MICW

turbulence - from shear from boundaries, dissipating PE as heat

counterexample



this works b/c of head difference and (more importantly) cuts down on turbulence: large A, small v

τ_0 = bottom stress [force/area]

$u^* = \sqrt{\tau_0/\rho}$

shear/friction velocity

$\Rightarrow$ transverse: $D_t \approx (0.1-0.2)du^*$ ← depth

longitudinal: $D_L = \frac{0.1v^2w^2}{du^*}$

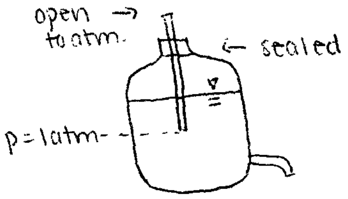
(as v and w increase, get more dispersion - this tends to overcorrect, so u^* on bottom)

9/23/04

Tailing:

tracer should be conservative, non-sorptive

Mariotte bottle - a cool way to do constant injection



so steady flow rate, b/c constant head

74 Chapter 2 Surface Waters

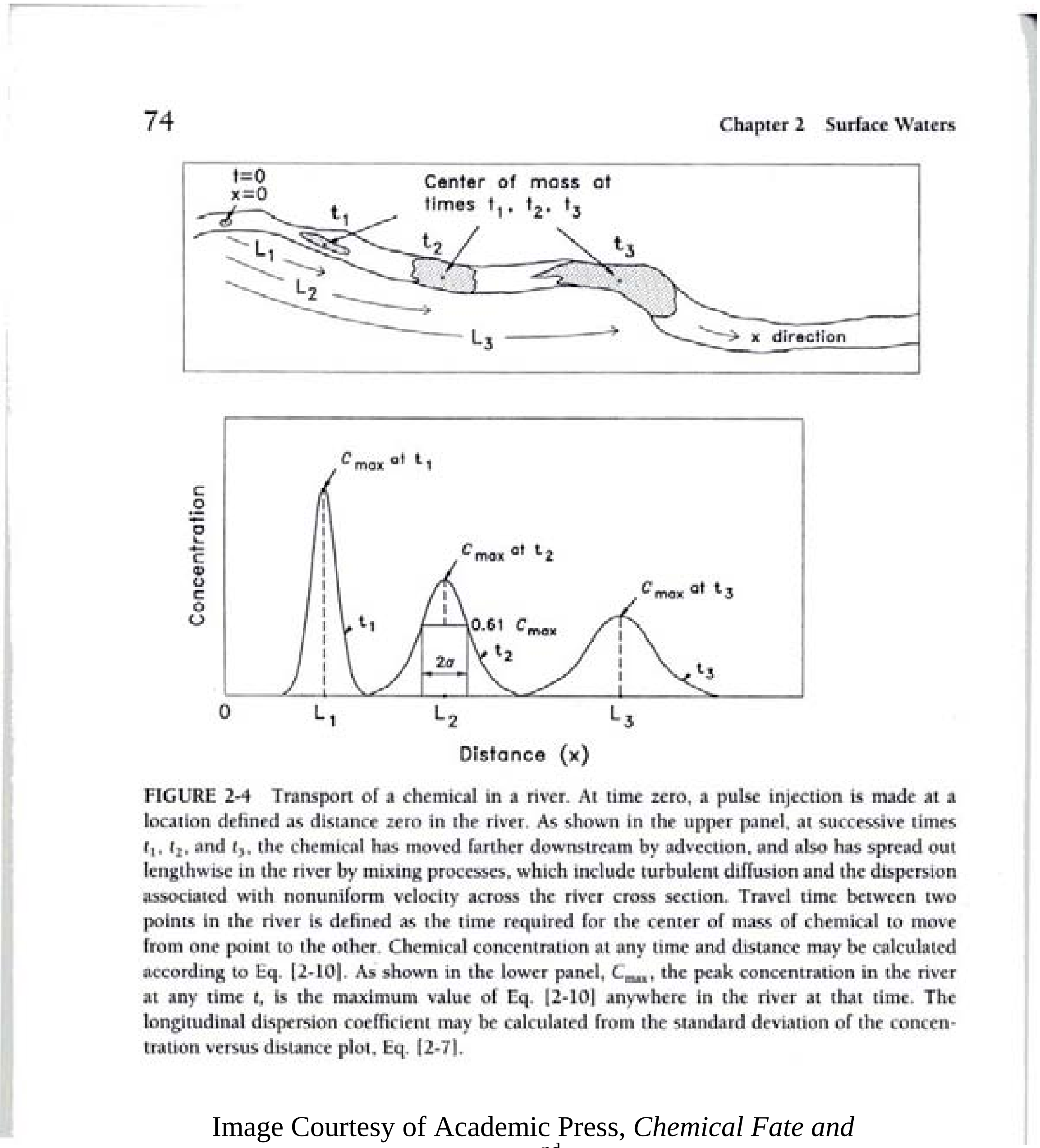


FIGURE 2-4 Transport of a chemical in a river. At time zero, a pulse injection is made at a location defined as distance zero in the river. As shown in the upper panel, at successive times t_1, t_2, and t_3, the chemical has moved farther downstream by advection, and also has spread out lengthwise in the river by mixing processes, which include turbulent diffusion and the dispersion associated with nonuniform velocity across the river cross section. Travel time between two points in the river is defined as the time required for the center of mass of chemical to move from one point to the other. Chemical concentration at any time and distance may be calculated according to Eq. [2-10]. As shown in the lower panel, C_{max}, the peak concentration in the river at any time t, is the maximum value of Eq. [2-10] anywhere in the river at that time. The longitudinal dispersion coefficient may be calculated from the standard deviation of the concentration versus distance plot, Eq. [2-7].

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment*, 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

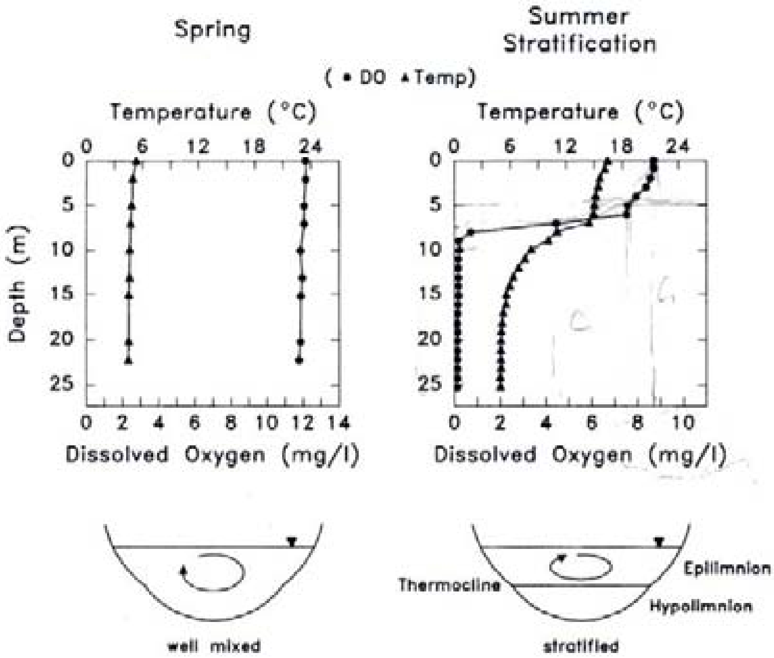


FIGURE 2-7 Measured temperature and oxygen profiles from the Upper Mystic Lake in eastern Massachusetts, on April 1, 1991 and September 30, 1991. (Left) the lake is unstratified and well mixed during turnover, which occurs in spring and fall. (Right) during summer, this eutrophic (productive) lake becomes depleted in oxygen in the lower layer of water (the hypolimnion), while its upper layer (epilimnion) remains well mixed by the wind and oxygenated by photosynthesis and by contact with the atmosphere. An oligotrophic (unproductive) lake may retain its high springtime concentration of oxygen in the hypolimnion throughout the summer [data from Aurilio (1992)].

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment*, 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

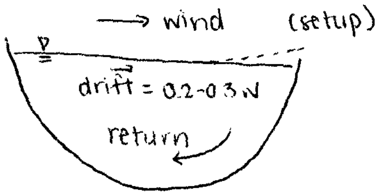
Lakes – fluid motions driven by wind, heat

$\downarrow$

shear stress on surface

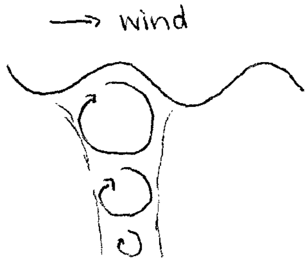
$\tau_0 = 1.9 \times 10^{-6}\, w^2$

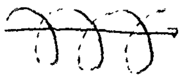
[dy/cm²] [cm/s]



if w doubles, τ increases 4x but drift only doubles – b/c energy goes down, also

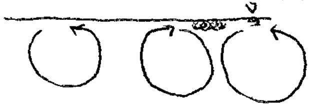
also waves, Langmuir circulation





Langmuir helices

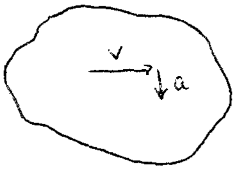
convergence-
stuff collects here



looking down axis of wind

large lake – need to consider Coriolis

looking down at lake (plan view).

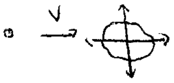


$\bar{a} = 2v\Omega\sin\theta$ ← latitude

↑ rotation speed (?)

Ekman spirals (w/depth) in open ocean

Spreading:



$D_x, D_y \quad (D_x \neq D_y)$

$$C(x,y,t) = \frac{M}{4\pi t\sqrt{D_x D_y}}\, e^{-\left\{\frac{(x-V_x t)^2}{4D_x t} + \frac{y^2}{4D_y t}\right\}}$$

($\times e^{-kt}$ for reaction)

in lake (unlike river) D is scale-dependent

b/c at larger scales, larger water motions are incorporated

rule of thumb: $D \propto L^{4/3}$

Timescales: Damkohler #

$Da = \frac{T_{mix}}{T_{rxn}}$ if $Da \gg 1$, patchiness is seen (like As/UML work)

$T_{rxn} = \frac{1}{k}$

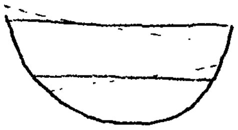
$T_{mix} = \frac{L^2}{D}$

in lake like UML, $D \approx 0.03 - 0.1\ m^2/s$

→ deduce that $k\ (As^{III}/As^{V}) \geq 0.1\ day^{-1}$

useful b/c don't need any microbiology

9/28/04



seiching

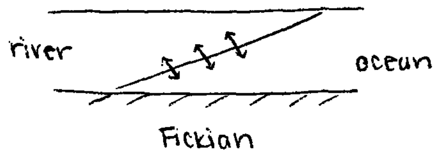
why is internal setup in opposite direction? hydrostatic P

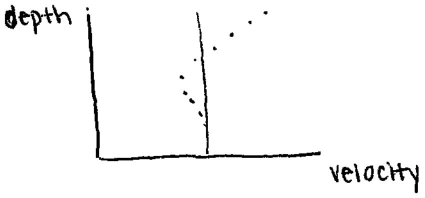
erosion with time - KE input provides an upper limit (increase in PE w/ mixing)

Richardson # : $R_i = \frac{g}{\rho} \frac{(d\rho/dz)}{(dv/dz)^2}$ $R_i \approx 0.25$ is transition

Estuary forces: wind, gravity, buoyancy (salinity), tidal
for large-scale (ex. Chesapeake) also Coriolis

salt wedge





return flow to ensure
"conservation of salt"
(no net change w/time)

wetland - usually O_2 depleted, and dispersive transport is slow
mixing via gas bubbles, and animal burrowing / plant roots

Sediment

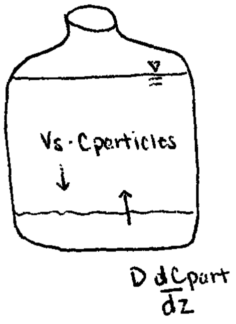
$C_{total} = C_w + \underbrace{(C_w K_d)}_{C_{sed}}$(conc. of sediment)

2 kinds: suspended solids, bed load - classify based on timescales

Stokes' Law - for small objects in laminar flow

$$V_s = \frac{2}{9} \frac{g r^2 (\Delta\rho/\rho)}{\eta}$$

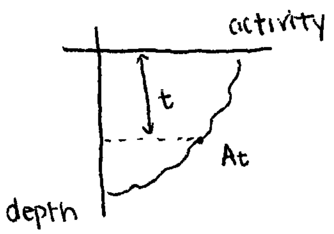
η - kinematic viscosity, ~10^{-2} cm^2/s for water



in a river, D will be much larger

for small enough particles
(ex. clay), can get Brownian
motion

Sediment transport — sediment limited
\ transport limited — cohesionless, load $\propto v^3$
\ cohesive, w/ threshold τ_0(critical) $\propto v^2$



$A_t = A_0 e^{-\lambda t}$

^{14}C for old stuff, $t_{1/2} \approx 5600y$

^{210}Pb, $t_{1/2} \approx 22.3\,y$

$^{226}Ra \rightarrow\rightarrow {}^{222}Rn \rightarrow\rightarrow {}^{210}Pb$
(soil)

9/30/04

nuclear fallout - very useful for dating, ^{137}Cs
(main one in 1963, smaller peak in 1959)

also Chernobyl
- mainly in air (not GW b/c high K_d, tend to sorb - that's why it's good for sediment dating), also sorbed strongly to mosses... poor reindeer...
(some ended up in northern Scandinavia)

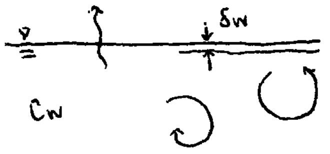
also seasonal, like tree rings
(fine particles in winter, more bedload in spring w/ runoff)
and chemical trends. sulfides, iron etc. at certain times of year

microanalytical techniques - Sebastien's laser ablation, or X-ray beam/fluorescence

wetlands (bogs esp.) are useful for longer time scales, then ^{210}Pb + cultural horizons don't really work, and ^{14}C is needed

mass transfer to atmosphere

simplest case (Ca)



at surface, only molecular diffusion (bottleneck)

bulk - transport done by eddies

shallower ↔ smaller eddies

from Fick's Law, we get $J = -D\frac{(C_w - 0)}{\delta_w}$

rearrange: $J = -\left(\frac{D}{\delta_w}\right) C_w$

k_w, "piston velocity" $\left[\frac{L}{T}\right]$

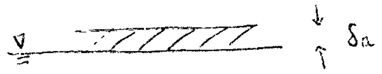
2) inference from fluid mechanics

$\underset{(cm/s)}{k_w} \approx 4\times10^{-4} + 4\times10^{-5}\, \underset{(m/s)}{W_{10}^2}$

$k_a \approx 0.3 + 0.2W_{10}$

not accurate enough to adjust for indiv. chemical based on MW for some chemicals (low VP, prefer being in water), need air-side control

- neglecting water film



- equilibrium right at air-water interface

$$J = -D_a \frac{C_w H}{\delta_a}$$

full versions: ($C_a \neq 0$)

water-side $J = -D_w \frac{(C_w - C_a/H)}{\delta_w}$ air-side $J = -D_a \frac{(C_w H - C_a)}{\delta_a}$

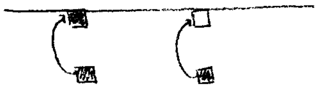
$H > 10^{-2}$ $H < 10^{-2}$ (doesn't like being in air)

equation for transitional ($H \sim 10^{-2}$) case:

$$J = \frac{1}{[\delta_w/D_w + \delta_a/D_a H]} \left[C_w - \frac{C_a}{H}\right]$$

sum of resistances or something...

Thin-Film vs. Surface Renewal
(turbulence from river bottom, more than wind)



how long does parcel hang out at surface?
turns out $J \propto D^{1/2}$ here (why?)

experimentally, D often in the middle ($J \propto D^{0.7}$ or so)

k_w : water-side piston velocity
k_a : air-side "
k_r : reaeration coefficient [for O_2]

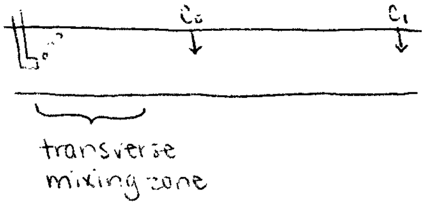
these have different units

$k = \frac{k_w}{\text{depth}}$ $[T^{-1}]$ so $C_t = C_0 e^{-k_r t}$

how to find k values?

1) empirical, tracer-based
propane (C_3H_8) - cheap, widely available, not biodegraded (much), can be measured with GC, not scary...

bubble in continuously



$$\frac{k_w(x)}{k_w(C_3H_8)} \approx \frac{D(x)}{D(C_3H_8)}$$

$$\frac{D_x}{D_{prop}} \approx \sqrt{\frac{MW_{prop}}{MW_x}}$$

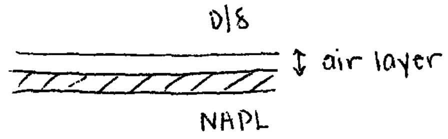
square root for surface renewal

<u>check this!</u>

→ prev. page

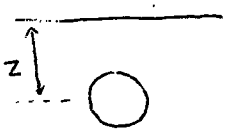
10/5/04

NAPL evaporation also treated w/ thin-film model



convert VP (b/c just above NAPL surface) to concentration

discussion of bubbles



$P_{TOT} = 1 + \rho g z$

$P_{TOT} = \sum C_i H_i$ also

ex. of changing gas concentration:

$NO_3^- + \text{"}CH_2O\text{"} \rightarrow N_2 + CO_2$

rising can be described w/ stokes law

surface tension (surface area/volume?) – very small bubbles should actually collapse, but get started b/c nucleation

Natural water chemistry

one particular bottled water:

high Ca^{2+}, Mg^{2+} – hard water (carbonate rocks)

low NH_4^+, NO_3^- nutrients

other species:

Na^+, K^+, Cl^-, SO_4^{2-}

carbonate system: $CO_{2(aq)} \rightleftharpoons H_2CO_3$

$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+$ $k = 10^{-6.3}$

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$ $K = 10^{-10.3}$

conductivity – weighted total (depends on mobility)

silica $H_4SiO_4 \rightleftharpoons H_3SiO_4^- + H^+$ what diatoms need

phosphate ($H_3PO_4 \rightleftharpoons PO_4^{3-}$) usually a limiting nutrient

but these two aren't really major players (say, in charge balance)

trace metals. Cu, As, Fe, Zn + others

to understand background chemistry, keys are pH and carbonate system

imagine making the water on benchtop

Cl^- from HCl

NO_3^- HNO_3

Ca^{2+} $Ca(OH)_2$

Na^+ NaOH

strong acids + bases

$Alk = \sum[\text{"}Na^+\text{"}] - \sum[\text{"}Cl^-\text{"}]$

where $[\text{"}Na^+\text{"}] = [Na^+] + [K^+] + 2[Ca^{2+}] \ldots$

$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$

electroneutrality.

$Alk = \Sigma Na^+ - \Sigma Cl^- = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$ check signs

$Alk = f_1(pH) + f_2(pH) \cdot C_T$

const. pH lines

10/7/04

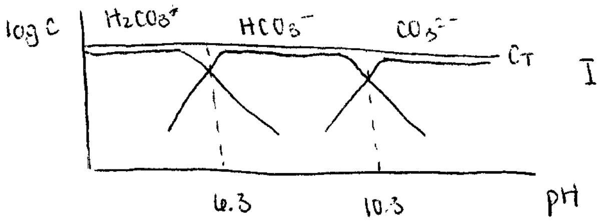
recap: $\Sigma[Na^+] - \Sigma[Cl^-] \equiv Alk = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

$\uparrow$ defn. of alkalinity

└ consequence of electroneutrality

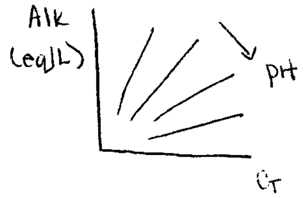
(move everything to one side = 0, then makes sense)

Bjerrum plot



I 0.3 log units

if pH is fixed, then f_1 and f_2 constant. $Alk = a + b \cdot C_T$ → Deffeyes



pH is determined by some sort of basicity (Alk) and how much the effect is cushioned (C_T)

at given Alk, ↑ C_T means ↓ pH

effect of $CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$ ← adds to C_T

$\uparrow$ adds to Alk

we want to find pH (the goal of all this) - pH is the "master variable"

key idea is separating strong acids + bases from weak (which act as buffers)

a final twist. organic acid, H-org (complex mixture of acids)

then $Alk = f_1(pH) + f_2(pH) \cdot C_T + f_3(pH) \cdot Org_T$

└ this is hard to pin down

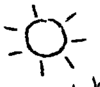
diff. between northeast US (low C_T, acid-susceptible) + Switzerland!

Ecosystems – there are things living in there!

ways to look at ecosystems:

energy flow
chemical cycling } our focus
populations
evolutionary (molecular biology)

Cartoon Version of Energy Flow:



$CO_2 + H_2O \xrightarrow{h\nu}$ "CH_2O" $+ O_2$ stores chemical energy

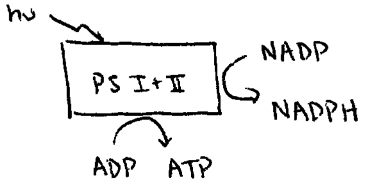
"CH_2O" $+ O_2 \rightarrow CO_2 + H_2O +$ energy
(respiration)

ADP → ATP
energy for lots of processes
(movement, bioluminescence...)

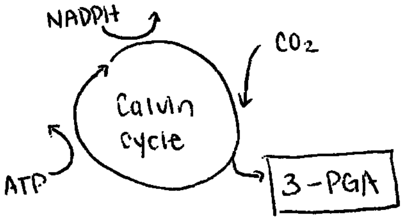
this is *very* simplified – each represents lots of enzymatic reactions

slightly more involved version:

light rxn.

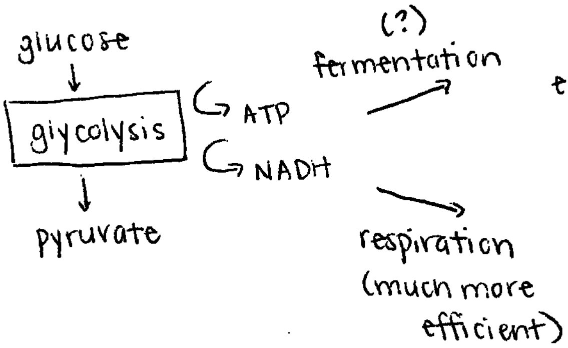


dark rxn. – making plant matter



1st reduced product
(building block for
other C molecules)

respiration side of things:



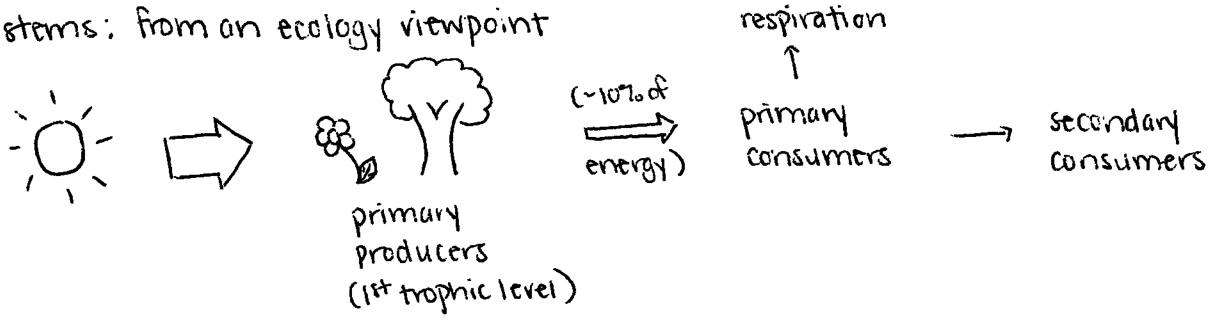
ethanol + CO_2 +
a little energy

TCA cycle,
e⁻ transport system

hmm.
review this.

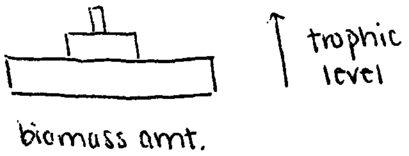
10/12/04

Ecosystems: from an ecology viewpoint



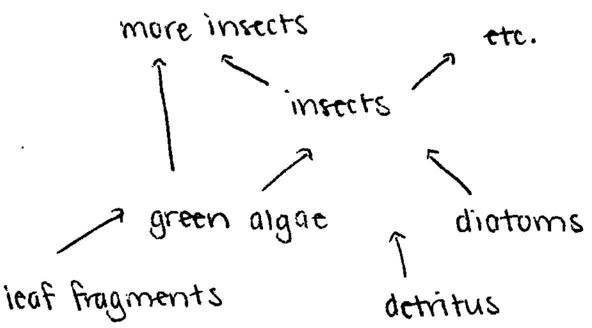
etc.

so higher levels are harder to sustain



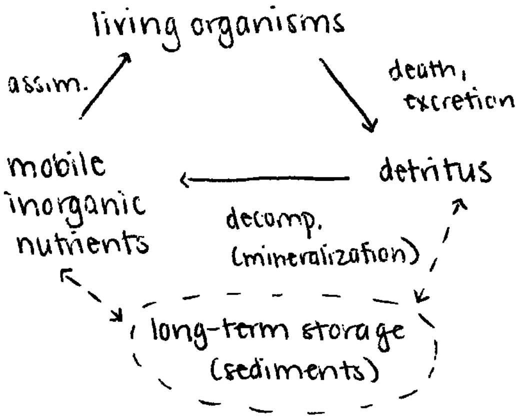
microbial loop – in aquatic systems, detritus often soluble | colloidal
microbes feed upon this, then grazed → energy back into system
(detritus includes organic acids, amino acids, humic|fulvic acids)

example:
(stream)



} from outside the system

cycling of matter:



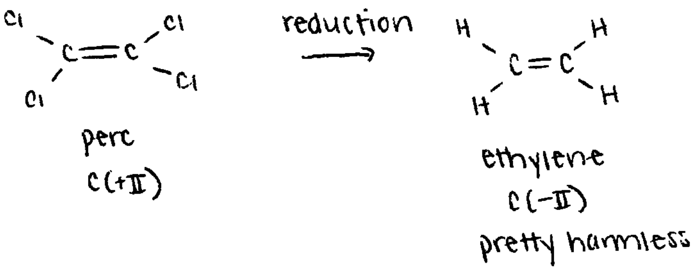
energy is once-through; these are closed loops

doesn't turn over quickly

also species-specific (predator-prey) interactions

Redox Chemistry this is how most energy transfer (after solar radiation) occurs

for example (assigning oxidation states)



add reducing equiv. to groundwater to deal with perc pollution

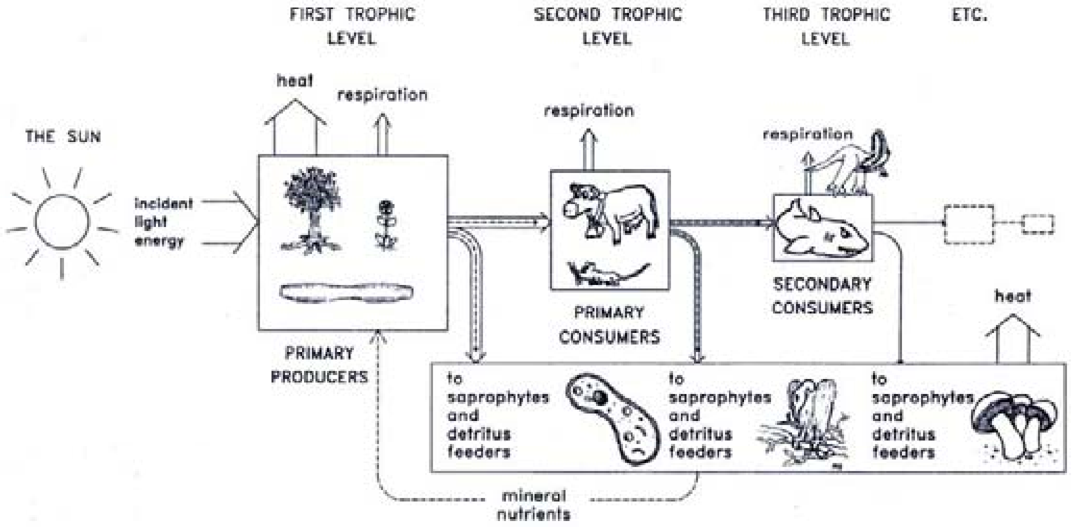


FIGURE 2-17 A simple energy flow diagram, or food chain, for an ecosystem. Energy input to the system comes from sunlight, of which only a fairly small fraction is captured as chemical energy in the biomass of the primary producers. Organisms at the second trophic level (herbivores, or primary consumers) typically utilize only a small portion of this chemical energy; a large portion goes directly to saprophytic microorganisms and detritus-feeding animals as dead organic matter (detritus). The amount of chemical energy available per unit time to the third trophic level (carnivores, or secondary consumers) is lower still, due to energy loss via the respiration of the herbivores and due to the large fraction of herbivore biomass that goes directly to saprophytes and detritus feeders.

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment*, 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

$\frac{1}{4}CH_2O + \frac{1}{4}O_2 \rightarrow H_2O +$ stuff $\quad \Delta G^\circ = -29.85$ kcal/mol

$\frac{1}{4}CH_2O + \frac{1}{5}NO_3^- \rightarrow \frac{1}{10}N_2 \quad -30.26$ kcal/mol

also $Fe(OH)_3$ -24 kcal/mol

SO_4^{2-} -7.4

CO_2 -5.5

$\Delta G = \Delta G^\circ + RT\ln Q$

we have N_2 atmosphere, so Q is large and ΔG less negative

this is ecological redox sequence

actual reaction is $\frac{1}{4}CH_2O \rightarrow \frac{1}{8}CO_2 + \frac{1}{8}CH_4$

methanogenesis

(all others are respiration)

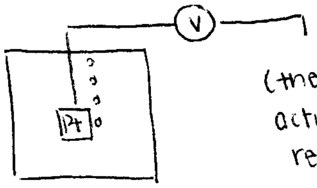
sequence can be seen in both time + space (ex. sediments)

C oxidation state doesn't change – this is fermentation rxn.

10/14/04

pe is analogous to pH "master variable"

reference: $H^+ + e^- \rightarrow \frac{1}{2}H_2 \quad \Delta G^\circ = 0$

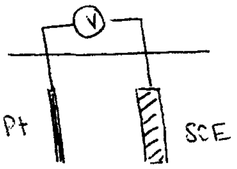


(the other actual half-reaction)

pe = 16.9 Eh (Eh in volts)

– just a Nernst eqn. conversion

ORP is related but not the same:



rxn. of interest happens on Pt

use of equil. model isn't quite accurate (think about this)

pe° is like pKa (w/ everything at standard state, the pe at which [ox] = [red])

pe-pH diagrams

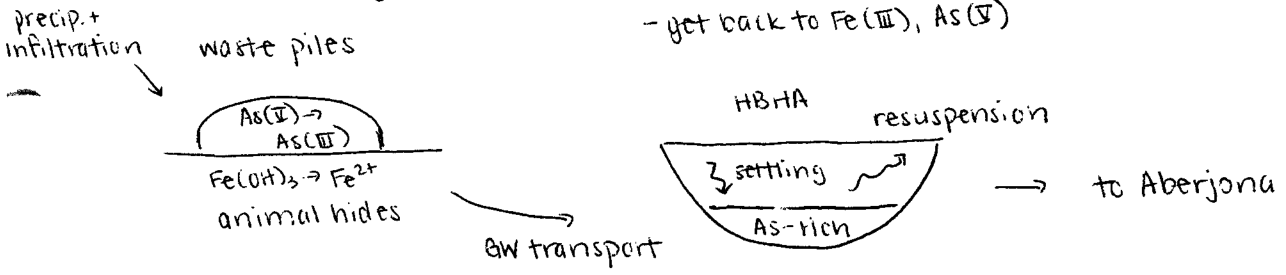
"ate" – more oxidized

"ite" – less oxidized

Halls Brook/Aberjona

precip. + oxidation (?)

– get back to Fe(III), As(V)



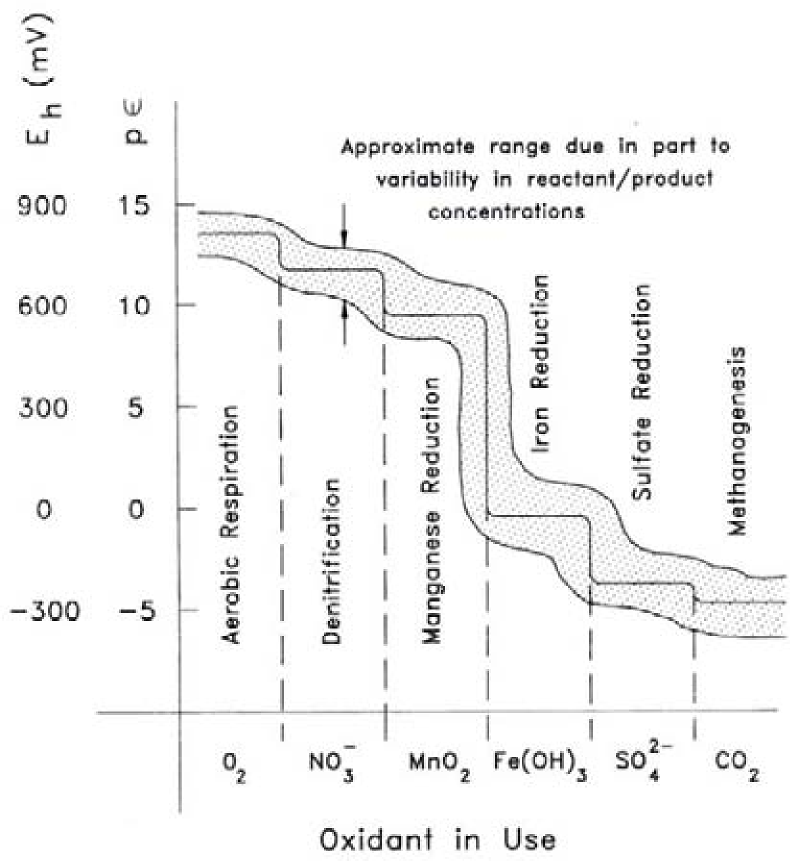


FIGURE 2-21 The ecological redox sequence. In an organic-rich environment that becomes isolated from the atmosphere, bacteria, after first consuming any available oxygen, utilize alternative oxidants in the sequence shown from left to right. As each oxidant is being utilized, the pϵ and E_h of the system lie in the approximate ranges shown on the vertical axis. The broad and indefinite ranges of pϵ and E_h associated with each oxidant are intended to reflect both variation in the oxidant and reductant concentrations and the fact that while pϵ and E_h are calculated on the basis of equilibrium, natural redox systems are usually not at equilibrium.

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment*, 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

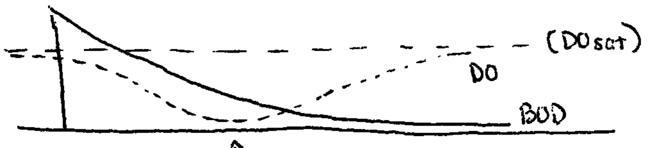
BOD - a main concern of wastewater treatment (made up of DOC)

model as first-order

$$\frac{d(BOD)}{dt} = -\underset{\substack{\uparrow \\ \text{typically} \\ 0.1-0.2\ \text{day}^{-1}}}{k_{BOD}} \cdot BOD = \frac{d[O_2]}{dt}$$

reaeration also happening

$J = -k([DO]_{sat} - [DO])$



↑ at this point, O_2 consumption by BOD equals O_2 supply from re-aeration

Streeter-Phelps:
- location of max. DO sag
- intensity of sag

wastewater issues: pathogens, DO, nutrients, maybe contaminants like endocrine disruptors

how biodegradable is a compound?

oxidation state

substitution (inertness, ex. CFC's - also fewer bugs have the enzymes)

branched or aromatic also tend to go slower

size - large molecules may need to be broken first

empirical measurement, like BOD

first-order works if population growth isn't stimulated (ex. cometabolism)

2 elements to model:

Michaelis-Menten enzyme kinetics (single chemical, steady pop.?)

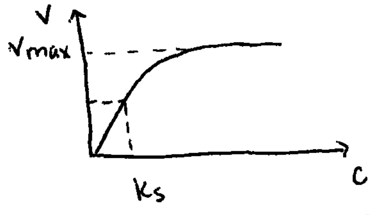
uptake rate → Monod growth model

10/19/04

1) example of cometabolism: methanotrophs degrading chlorinated pollutant
   - in this case, first-order might be appropriate

2) other situation: energy-yielding

Michaelis-Menten:



(where $v = \frac{1}{2} v_{max}$)

$v = \frac{mol}{cell \cdot sec}$

assumes population is growing (?)

$\frac{dc}{dt} = -vx$ x: $\frac{\text{cells}}{L}$ how substrate consumption relates to growth

$\frac{dx}{dt} = vxy$ y is cell yield, $\frac{\text{cells}}{\text{mol substrate}}$

can express as first-order: $\frac{dx}{dt} = \mu x$ ($\mu = vy$)

higher-level organisms: role in concentrating chemicals, rather than direct metabolism
- partitioning
- pharmacokinetic (model fish as a system - transport, rates etc.)

liver is mostly oxidative

partitioning: model fish as oil/fat + water

Kow (and solubility) used as predictor

DDT in osprey - concentrated through diet, not partitioning

metals also wouldn't follow this passive model (enzyme uptake instead)

Mercury:

$Hg(0)$ can partition air ↔ water
Hg^{2+}
$(CH_3)_2Hg$, CH_3Hg
} microbial transformations

↘ ↓

partitions very strongly into fish (and very toxic)

Abiotic Sinks

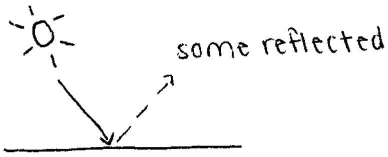
direct sunlight.

~3000 $\frac{\mu E}{m^2 \cdot sec}$ (Einstein = mol photons)

quanta

~700 W/m^2 ($W = J/s$)
energy
conversion depends on λ

$$E = h\nu = \frac{hc}{\lambda}$$



attenuated w/ depth

$I = I_0 e^{-nz}$

n: extinction coeff. (depends on what's dissolved)

then needs to be absorbed - more likely for aromatic/conjugated systems

Possibilities:

$A \xrightarrow{h\nu} A^* \rightarrow A + \text{heat}$

$\rightarrow A + \text{light}$ (fluorescence, short half-life)

$\rightarrow {}^3A \rightarrow A + \text{light}$ (phosphorescence, longer half-life)

intersystem crossing

$\rightarrow A^+ + e^-$

direct photolysis: $AB + h\nu \rightarrow AB^* \rightarrow A + B$

can also get reaction w/o direct photolysis:

- photosensitization

  $UPC \xrightarrow{h\nu} UPC^*$ unknown photoreactive chromophore

  $UPC^* + A \rightarrow UPC + \text{product}$

  humics are important UPC's in freshwater

  ex. $\text{humic} + O_2 \xrightarrow{h\nu} \text{humic} + HO_2^\bullet$ (superoxide)

- indirect photolysis w/ reactive oxygen species, ex. $\cdot OH$

10/26/04

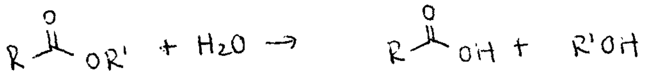
indirect photolysis can be diffusion-limited:

$\cdot OH + X \rightarrow$

governed not by equil. $[\cdot OH]$ but how fast $\cdot OH$ is produced

Hydrolysis

ester - subst. carboxylic acid



$$RC(=O)OR' + H_2O \rightarrow RC(=O)OH + R'OH$$

alcohol + carboxylic acids - good microbial food

can also be acid- or base-catalyzed

$$\frac{dc}{dt} = -k_N c - k_a[H^+]c - k_b[OH^-]c$$

reaction won't change pH → pseudo 1st-order

$$\frac{dc}{dt} = -(k_N + k_a' + k_b')c$$ where $k_a' = k_a[H^+]$, $k_b' = k_B[OH^-]$

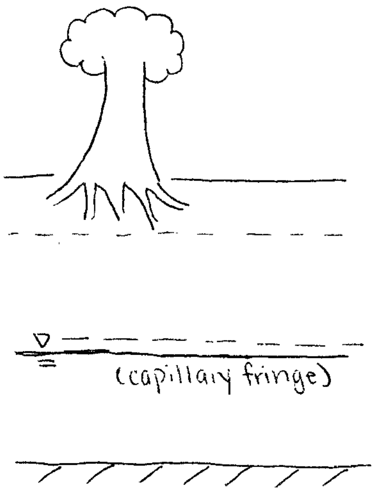
these constants are tabulated

ex. design of pesticides - can plan for a certain rate constant (half-life)

Subsurface

fate + transport perspective: care about drinking water quality

economic damage + health threat (ex. leaking underground storage tank)



soil – biologically active

unsaturated | vadose zone – water + air in pores

saturated zone – only water in pores

other sources of contaminants: waste pits (As in Aberjona, U byproducts in Concord), landfills, septic tanks

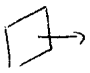
DNAPL (dense) → sink to bottom → into cracks in bedrock, hard to recover (though still potential for exposure – drill well into bedrock, or water that re-enters aquifer)

Bangladesh: redox geochemistry leaches As from rocks

hard to measure velocity directly

Darcy's Law $q = -K\frac{dh}{dx}$ (1-D)

↑ hydraulic cond. (property of aquifer) [L/T] also

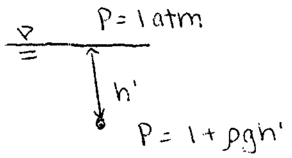


q through "window" of porous medium

$\frac{m^3/s}{m^2} \rightarrow m/s$

head: $h = z + \frac{P}{\rho g} + \cancel{\frac{v^2}{2g}}$ → neglect in GW

(elevation + pressure head)



under hydrostatic conditions, head is constant w/ depth

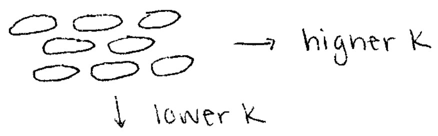
3-D: $\vec{q} = -K\vec{\nabla}h$

holds if K is isotropic (+ homogeneous)

scale of measuring K vs. scale at which it's applied

K depends on size and how well sorted (large, uniform particles → large K)

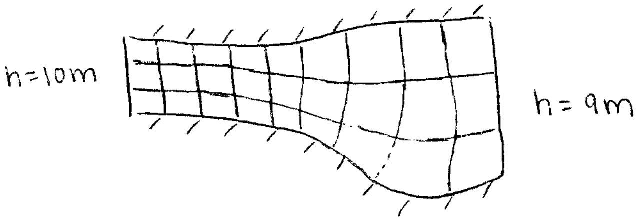
example of anisotropy:



seepage velocity $v = \frac{q}{n}$ v tells us how fast a chemical (i.e. a particular parcel of water) moves

10/28

flow nets - useful as descriptive and analytical tool



head is constant w/depth (into the page)

top view

think of each streamtube as a pipe (constant flow rate)

if width constant → q is constant → head lines equally spaced

as streamtube gets wider, q decreases (to maintain const. Q) so dh/dx ↓ also → head lines farther apart

streamlines and head lines must be ⊥, or else flow will cross streamtubes

completed flow net → calculate flow

know $\frac{dh}{dx}$ → get q → Q from dimensions

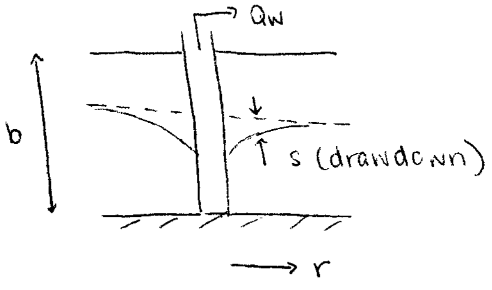
limitations: 2-D, assumes isotropic + homogeneous K

works for steady flow (if time-varying, then there can be storage)

classic example - flow under a dam

estimate travel time - seepage velocity in each square

another tool - effect of well



using radial symmetry

mass balance in cylinder of radius r:

$$Q_w = q_r \underset{\uparrow \atop \text{area}}{(2\pi r b)} = 2\pi r b \cdot K \frac{ds}{dr}$$

$$\boxed{\frac{ds}{dr} = \frac{Q_w}{2\pi r b K}}$$

to find s(r), need to integrate - bounded by R (radius of influence), where s=0

result: $s(r) = \frac{Q_w}{2\pi b K} \ln\left(\frac{R}{r}\right)$

(Theim equation)

assumptions used:

- $s \ll b$
- steady-state

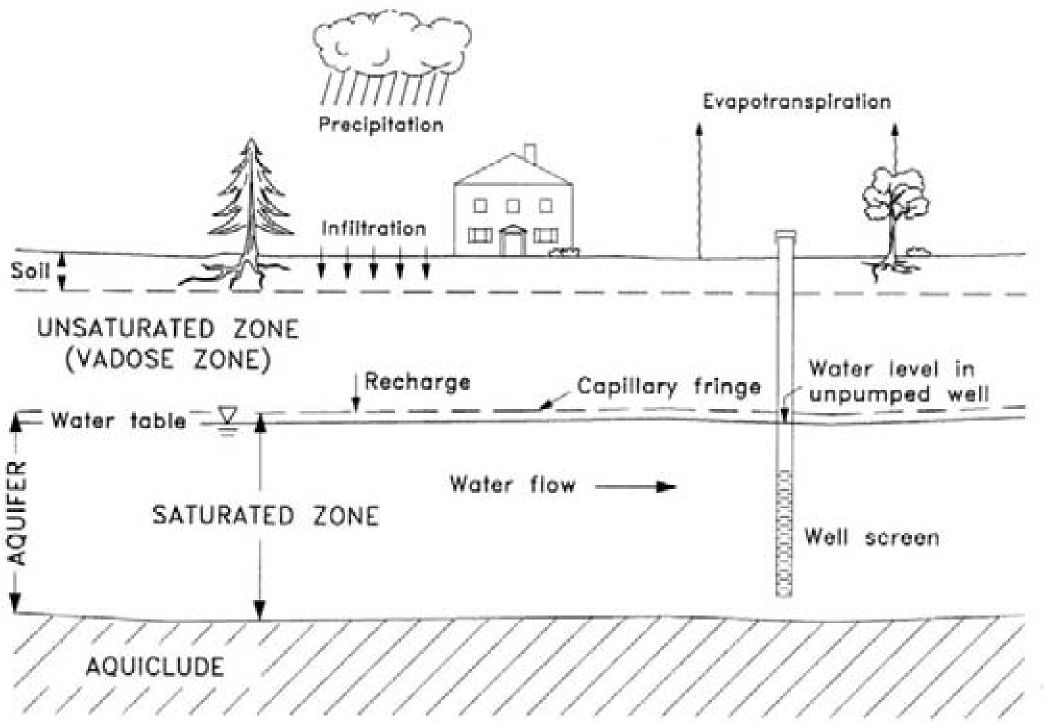


FIGURE 3-1 A representative subsurface environment, showing an upper unsaturated zone and a lower saturated zone with an aquiclude beneath. An aquiclude is nearly impermeable to water. The saturated zone above the aquiclude is a water table aquifer. A well is used to withdraw water from the aquifer.

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment*, 2^{nd} Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

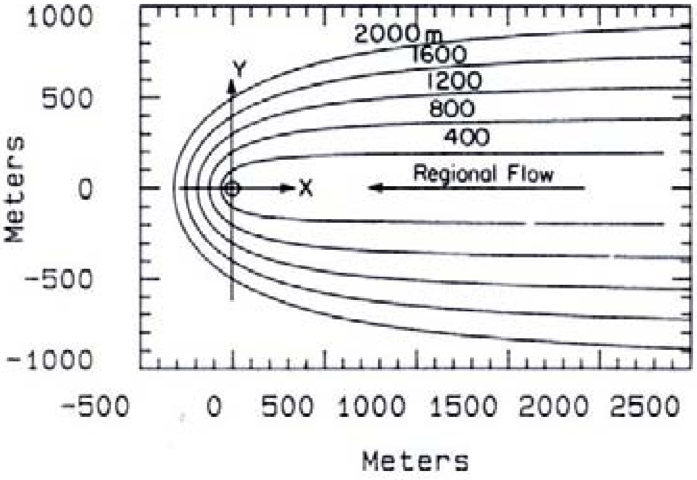


FIGURE 3-13 Type curves for the capture zone of a single pumping well located at the point (0,0), for several values of Q_w/bq_a. In the absence of dispersion, all water lying within the capture zone, along with any contaminants it may be carrying, will eventually end up in the well. Note that these curves do *not* form a flow net (adapted from Javandel and Tsang, 1986).

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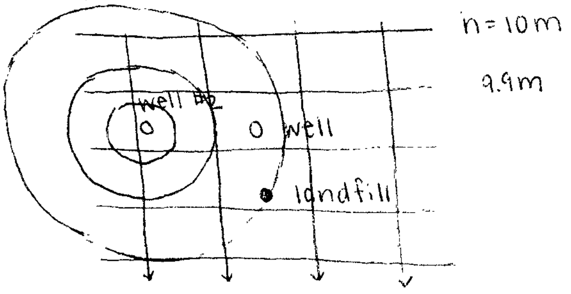
linearity (s<<b, so water table thickness ≈ constant) allows superposition

plan view of aquifer:

isopotentials for well



compare background slope ($\frac{dh}{dx}$)
and drawdown from well

balanced where $\frac{dh}{dx} = \frac{Q_w}{2\pi r T}$ (T=Kb)

well #2 – more difficult case

superposition (head at various points = $h_{backgr.} + h_{well}$) → can draw flow net

gives capture curve (limit of what goes into well, at various Q_w and background flow)

design to avoid or maximize capture

11/2/04

capture curves – derived from flow nets

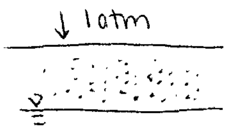
Transient Well Hydraulics: when storage is changing

storativity $S = \frac{\Delta \text{volume}/\text{area}}{\Delta \text{head}}$ (dimensionless)

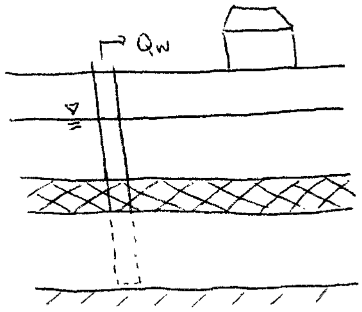
swimming pool: S=1

aquifer: S<1, S≈n (porosity)

there are other mechanisms of storage, also



phreatic



confining layer

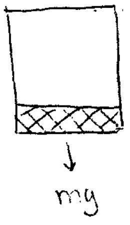
confined

elastic storage

$S = S_s \cdot b$ "elastic storativity"

like spring constant

like getting water out of a sponge



↑P, σ' (mechanics – each grain pressing against others)

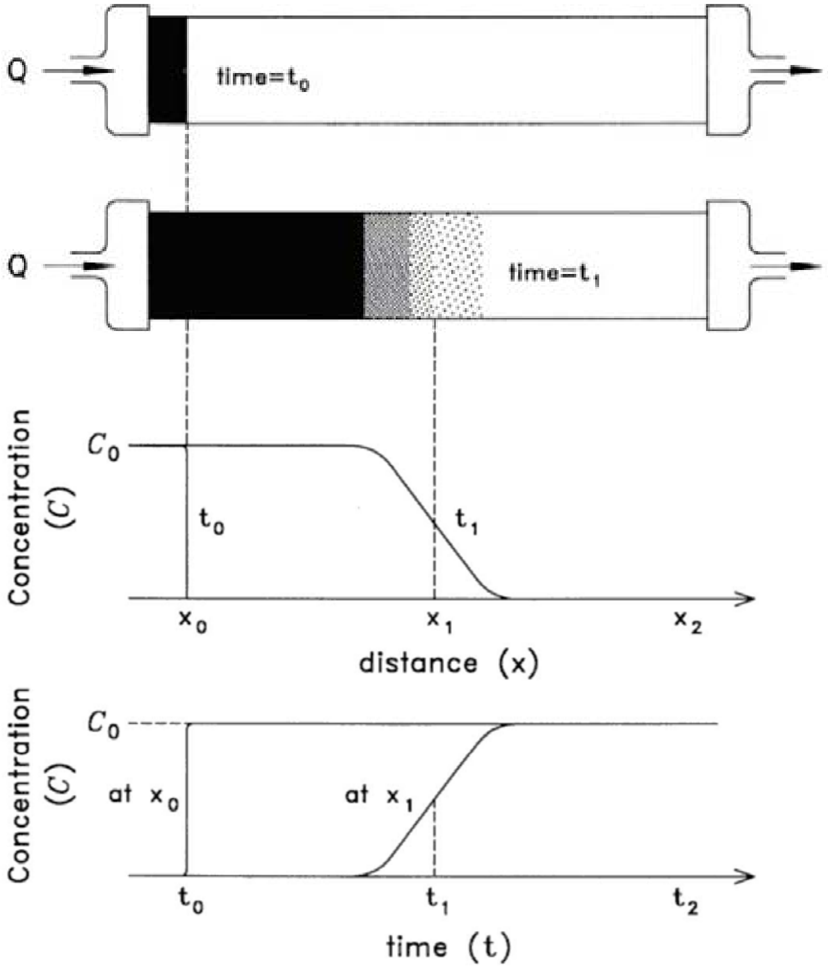


FIGURE 3-18 Dispersion of a *continuous* tracer injection in a sand column experiment. The behavior of a *front* of the tracer is shown in the next to last panel; tracer concentration is presented as a function of distance at fixed times t_0 and t_1. A *breakthrough curve,* a plot of concentration as a function of time at a fixed point, is shown in the bottom panel. (Compare with Fig. 3-28, which shows breakthrough curves for pulse inputs.)

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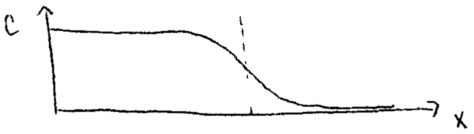
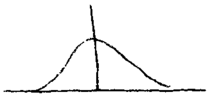
continuous input (rather than pulse) is more likely

front moves forward and spreads



$c(x,t) = \frac{C_0}{2}\,\text{erfc}\left(\frac{x-vt}{\sqrt{4D_x t}}\right)$

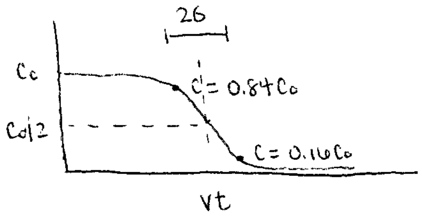


$\frac{1}{\sqrt{2\pi}} e^{-x^2}$

$\text{erf} = \int_0^x \frac{1}{\sqrt{2\pi}} e^{-x^2}$ (so -1 to 1)

$\text{erfc} = 1 - \text{erf}$ (2 to 0)

a better sketch:



corresponding to 68% between 2σ

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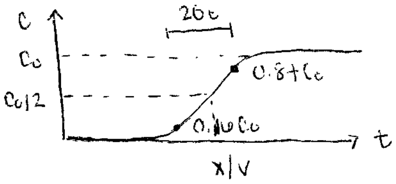
at a fixed position:



$\sigma_t \cdot v = \sigma_x$

"breakthrough curve"

applies to single flow tube

more realistically, c(t) at some well:

summation of various flowtubes
(different travel times)
also due to heterogeneity (of composition, K)

note: in phreatic aquifer, superposition is good approx. if $s \ll b$

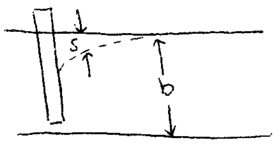


chart in book: pulse/continuous, 1-D/2-D/3-D
steady-state flow with time-varying c

sorption → retardation factor

$$K_d = \frac{\text{conc. in solid}}{\text{conc. in water}}$$

$$R = \frac{\Sigma \text{ all species}}{\Sigma \text{ all mobile species}} = \frac{C_w \cdot n + C_s \rho_s (1-n)}{C_w \cdot n} = \frac{C_w \cdot n + C_w K_d \rho_s (1-n)}{C_w \cdot n}$$

$$= 1 + \frac{K_d \rho_s (1-n)}{n}$$

assumes local, instantaneous equil.

also that isotherm is linear ($C_s \propto C_w$)

finally, back to transport models.

$D_{eff} = D/R$, $v_{eff} = v/R$

can also express as $R = 1 + \frac{K_d \rho_b}{n}$ ρ_b: bulk density

(these refer to saturated case - if there are bubbles, n must be adjusted)

* note: might be useful to derive R for bubbles case *

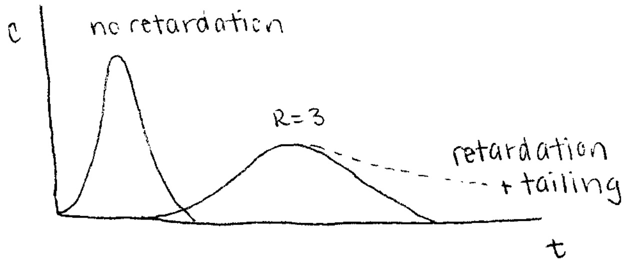
$K_d = K_{oc} \cdot f_{oc}$ use empirical K_{oc}/K_{ow} relationships

with inorganics, surface complexation instead - harder to model

-generally determine K_d empirically

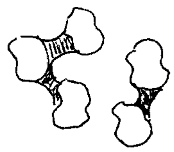
what if local, instantaneous equil. doesn't hold?

(kinetics - reaction takes time)



(indicates it's kinetics-limited)

Unsaturated zone



$P_{water} < 1$ atm (meniscus towards water)

ψ is water potential (bars)

remove water → meniscus curves more → P_{water} ↓

hydraulic conductivity is lowered also — discontinuous

all related: porewater pressure, water content, conductivity

- furthermore, hysteresis effect (drying vs. wetting)

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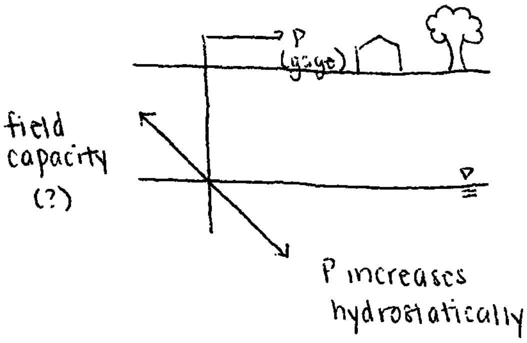
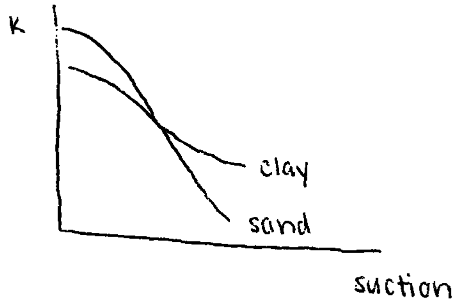
unsaturated zone, continued

$P < 1$ atm



if water content > field capacity, then recharge to water table



how do plants get water?

with a given suction, clay loses less water → greater continuity, higher K

Ψ_{soil} (water potential)

$= P + \rho g h$

$\uparrow$ less than atm.

$\Psi_{plant} = P - mRT$ ← osmotic (m: molar conc.)

$\uparrow$ high enough to keep plant up

$\Psi_{air} = \frac{RT}{V_{molar}} \ln \frac{e_a}{e_{sat}}$ ← partial pressure of water vapor in air

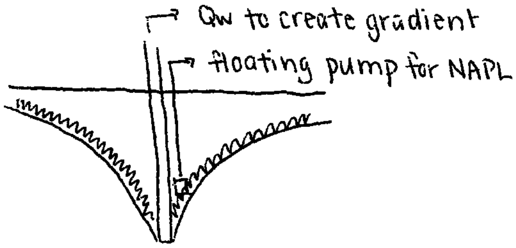
$\Psi_{soil} > \Psi_{plant} > \Psi_{air}$

NAPL

pure NAPL: $K = \frac{\overset{\text{char. of aquifer}}{k}\rho g}{\underset{\text{viscosity}}{\mu}}$

more viscous ↔ move more slowly

multiphase (NAPL, water) is harder to deal with - NAPL becomes discontinuous
pumping air (NAPL partitions into air) could work, or some other liquid
or have microbes degrade - energetically favorable



works until discontinuity sets in

Biodegradation in GW

① Modeling Equations.

Michaelis-Menten (and Monod)

I. $V = V_{max}\frac{C}{C+K_s}$ (uptake rate) $\frac{mol}{time\text{-}cell}$

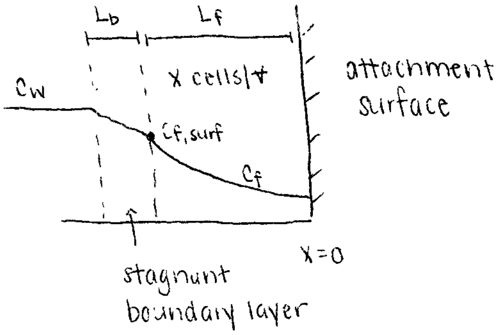
II. $\frac{dC}{dt} = -VX$ X: cell density, $\frac{cells}{\forall}$

III. $\mu = V \cdot Y$ μ: growth rate, Y: cell yield, $\frac{cells}{mol}$

IV. $\frac{dX}{dt} = (\mu - d)X$ d: death rate

μ and d: both $time^{-1}$

Biofilms – attachment can be an advantage, rather than depending on diffusion



Governing equation in biofilm:

$$\frac{d}{dx}\left(D_f \frac{dC_f}{dx}\right) = \frac{V_{max} C_f}{C_f + K_s} \cdot X \leftarrow \text{cell density}$$

solve to get $C_f(x)$

$$D_f \frac{dC_f}{dx}\Big|_{surf} = \int_0^{L_f} VX\,dx = D_B \frac{(C_w - C_{f,surf})}{L_b}$$

amount that enters film (surface of film)

$$\frac{dC_f}{dx}\Big|_{x=0} = 0$$

$$\boxed{C_{min} = K_s \frac{d}{V_{max}Y - d}}$$

steady-state result

② Enhanced Biodegradation:

redox – add oxidant (O_2 gas, water saturated w/ O_2, NO_3^-)

each has difficulties. flow of O_2 gas, saturation limit of water, role of NO_3^- in eutrophication

degrade oxidized contaminants (ex. perchlorate, ClO_4^- in explosives)

w/ reductant such as CH_2O (ex. molasses) – reductive dehalogenation

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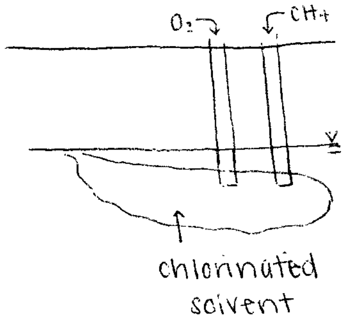
changing redox state also useful for metals:

U(VI) → U(IV)

mobile   complexed

Co-metabolism:



if methanotrophs can grow here, MMO will also oxidize the solvent (w/o gaining energy from it) -- need conditions that allow methanotrophs to grow, i.e. presence of CH_4 and O_2

Atmospheric

Differences between atmosphere and surface water:

- scale and boundaries
- advective and dispersive timescales ↓
- relationship between height|temp.|density

    water: $P = \rho g z$

    atmosphere: $P = P_0 e^{-(1.2 \times 10^{-6}\ cm^{-1})h}$ b/c compressible
- degradation: light-driven reactions are major sink
  (subsurface dominated by biodegradation, b/c lots of surface area)
  ↑ attachment of biofilms

Background chemistry:

air is ~78% N_2, 21% O_2, almost 1% Ar

inert trace gases (Ne, He, Kr, Xe)

reactive trace gases: CO_2, CH_4, H_2, N_2O, O_3, H_2O

CO, NO_2, NH_3, SO_2, H_2S

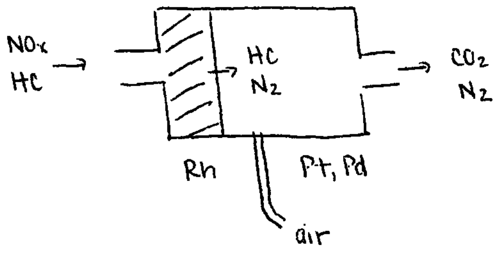
contaminants - especially concerned about particulates

VOC's, NO_x, SO_x, PM esp. from combustion

soot (an example of PIC, products of incomplete combustion) can have health effects by being particulate, or as carriers of PAH's

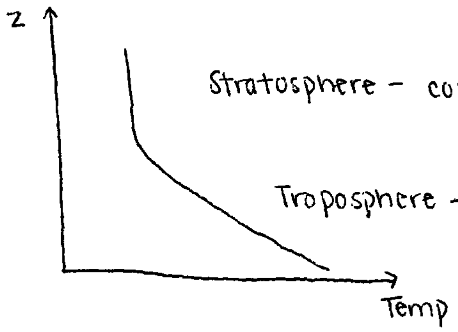
NO_x, SO_x from impurities - may be gaseous first, then condense

↳ also from high temperature (rxn. of N_2, O_2 in atmosphere) catalytic converter - same concept as redox, but catalytic surface + high T rather than engine



(b/c NO_x produced at very high T, this is kept cooler)

Structure of Atmosphere:

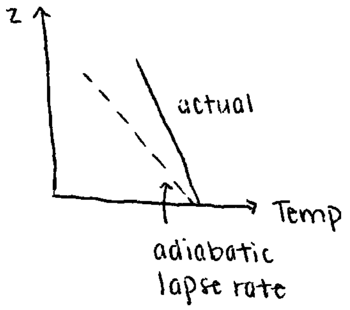


Stratosphere - constant T keeps it stable (compare to lake, warm water above cold - different T|P relationship)

Troposphere - atmospheric chemistry, public health effects

Adiabatic Lapse Rate - about 10°c|1000m

parcel of air rises and expands (lower P) - does P-V work on surroundings - lose internal energy, so T falls



stable (inhibit mixing)

if actual is counterclockwise of adiabatic → favor mixing

* check this *

<u>11|18|04</u>

~ microns: size at which particles begin to settle (stokes)

dry lapse rate - water vapor is present, but doesn't condense

if water condenses, heat will be released, so parcel of air cools more slowly (no longer just P-V work)

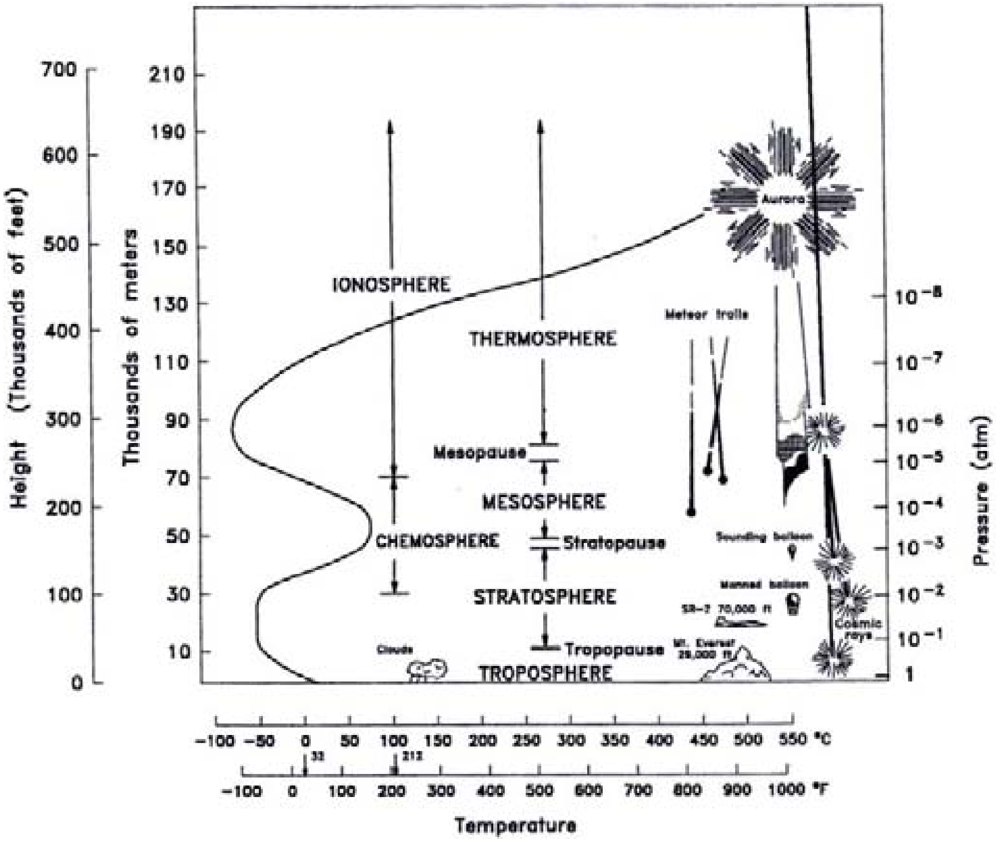


FIGURE 4-1 Vertical structure of the atmosphere. Weather phenomena are confined almost entirely to the troposphere, as are most air pollutants, which are removed by various processes before they can mix into the stratosphere. Certain long-lived pollutants, however, such as the chlorofluorocarbons (CFCs), do mix into the stratosphere, and other pollutants can be injected physically to stratospheric altitudes by processes such as volcanic eruptions or nuclear explosions. Note that more than one term may refer to a given layer of the atmosphere (adapted from *Introduction to Meteorology*, by F. W. Cole. Copyright © 1970, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.).

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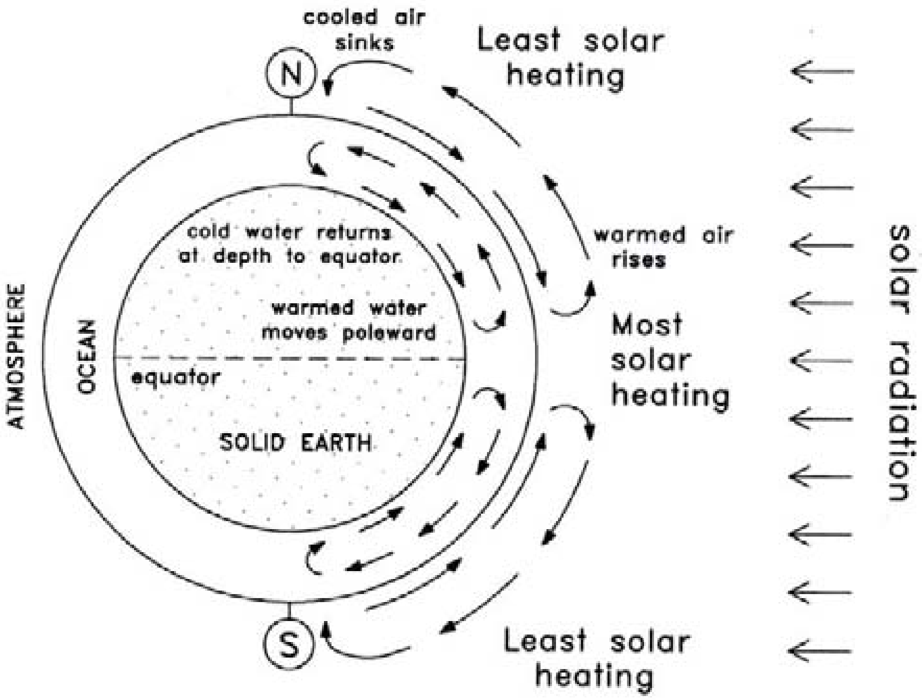

FIGURE 4-11 Global-scale tropospheric circulation as it would be if Earth did not rotate. Heat is transported from the equatorial area to the cold polar regions by both atmospheric and oceanic currents in each hemisphere.

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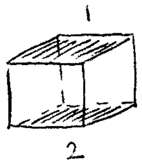


$\downarrow q_1 = -K\frac{dh}{dy}\Big|_1$

$\downarrow q_2 = -K\frac{dh}{dy}\Big|_2$

if $\frac{dh}{dy}$ is same at each face, then no storage →
it's 2^{nd} deriv. that matters

$$S\frac{dh}{dt} = Kb\left(\frac{d^2h}{dy^2} + \frac{d^2h}{dx^2}\right)$$

compare to transport equation ($Kb \leftrightarrow D$)

solution: $s(r,t) = \frac{Q_w}{4\pi \underbrace{Kb}_{T}} W(u)$

$W(u)$: well function

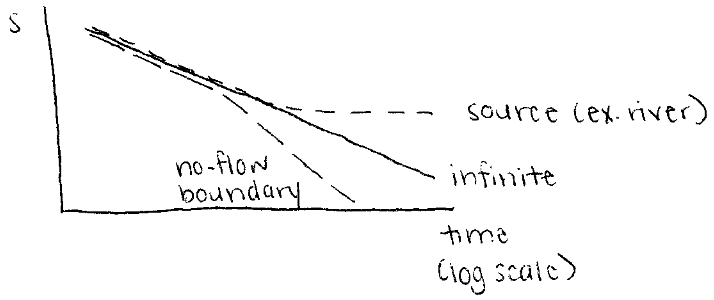
$u = \frac{r^2 S}{4Tt}$

approximation
(in book)
needs $\ominus$ sign

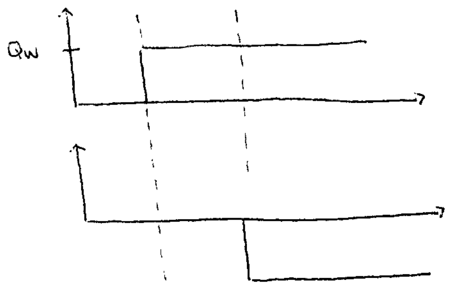
for $u < 10^{-2}$, can use $s(r,t) = 0.183\frac{Q_w}{T}\log\left(\frac{2.25tT}{r^2S}\right)$

boundary condition:
assume we're pumping in an infinite aquifer

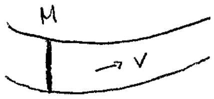
drawdown curves can tell us about boundaries



pump schedule – superposition



1-D transport, porous media:

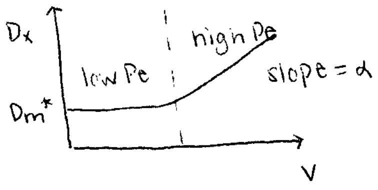


$v = q/n$

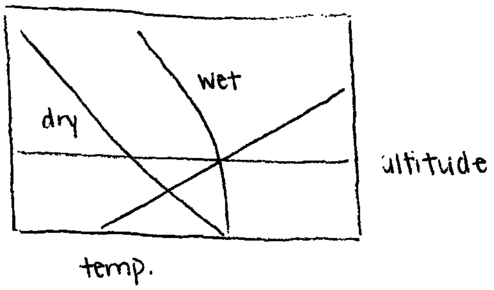
$$c(x,t) = \frac{M}{n\sqrt{4\pi D_x t}}e^{-\frac{(x-vt)^2}{4D_x t}}$$

$D_x = D_m^* + \alpha v$
↑ mechanical dispersivity
≈ diameter [L]

$D_m^* = D_{mol} \cdot n^2$



$Pe = \frac{\alpha v}{D_m^*}$ apparently skew T | log P



at low temp. there is little moisture – dry + wet lapse rates are similar

heated air will rise + cool, reaches dew point → switch to wet lapse rate
conditional stability – shift from stable to unstable when dew point is reached

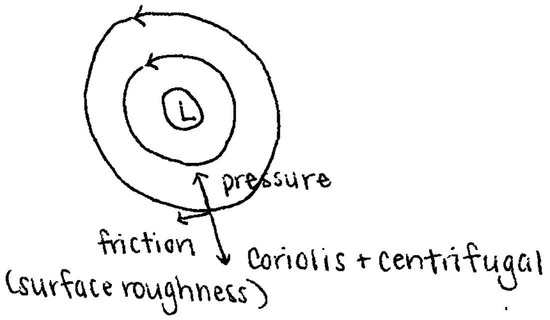
Circulation Patterns:

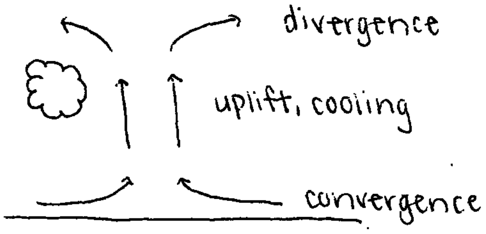
1) heated at equator, cooled at poles – basic circulation cells
2) Coriolis b/c earth's rotation
   divides into 3 cells (why?) in each hemisphere → probably strength of Coriolis
   rises at equator (moist) and sinks at 30° latitude (deserts)

Synoptic scale:

both fronts involve cold + warm air
   cold front – cold air overtakes warm, moves faster, more intense
   warm front – warm air displaces, moves slower, more diffuse
      both involve uplift, precipitation

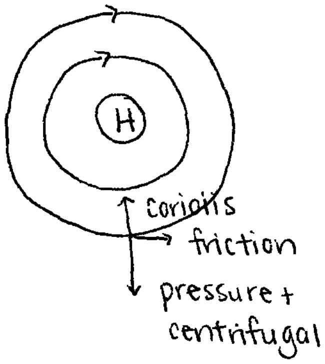
cyclones – N. Hemisphere

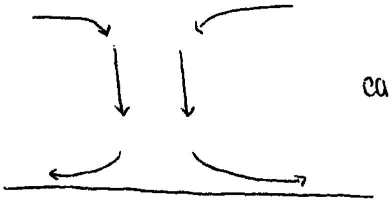




in N. Hemisphere,
Coriolis to the right

– energy can be enhanced by instability (condensation)
→ kinetic E → storms





can lead to inversion

colder easterlies meet warmer westerlies

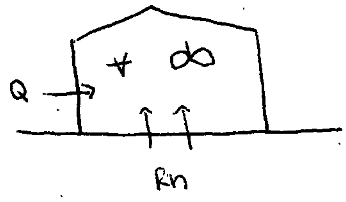
cold ←
→ warm   shear leads to eddies → cold front tends to overtake warm front

local effects – orographic (mountain, rain shadow)

rises on wet adiabat, descends on dry adiabat

11/23/04

indoor air pollution – box model



$\frac{Q}{V} = ACH$

pulse input: $C = C_0 e^{-ACH \cdot t}$ (like stirred reactor)

continuous: $\dot{M} = C_{ss} Q$

can apply this to urban scale

air pollution is most of a problem when inversion is strong and wind speeds are low, and in this case the box model works well

Plume Model – urban scale, generally applicable   Pasquill-Gifford

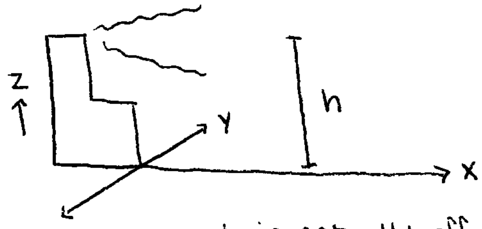
$C(x,y,z)$ only need to consider steady-state (at wind speed ~ 1 m/s, steady-state is reached quickly)

vs. groundwater, where transient phase is important

changes w/turbulence – time-avg. over several eddies

conventions are different.

instead of D_x, D_y, D_z we have $\sigma_x, \sigma_y, \sigma_z$ (σ_x overshadowed by advection)



h is actually effective stack height

$$C = \frac{\overset{\text{mass/time}}{Q}}{u} \frac{g_1 g_2}{2\pi \sigma_y \sigma_z}$$

$\sigma^2 = 2Dt$, substitute → looks like lake model

$$g_1 = e^{-0.5y^2/\sigma_y^2}$$

$$g_2 = e^{-0.5\frac{(z-h)^2}{\sigma_z^2}} + e^{-0.5\frac{(z+h)^2}{\sigma_z^2}}$$

FIGURE 4-22c The rain shadow effect. Moist air, shown here as coming off the ocean, is forced to rise by the presence of a mountain range (orographic lifting). As it rises, it cools according to the dry adiabatic lapse rate, until the dew point is reached. Precipitation then can occur as the air continues to rise along the windward side of the mountain range, its further cooling corresponding to a wet adiabatic lapse rate. The air loses much of its original moisture to precipitation, and as it descends on the leeward side of the mountains, it warms according to the dry adiabatic lapse rate. Thus, when the air has descended on the leeward side to its original altitude (sea level in this example), it is drier and warmer than it was on the windward side. The result is a drier, warmer climate and a dearth of precipitation on the leeward side.

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment,* 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

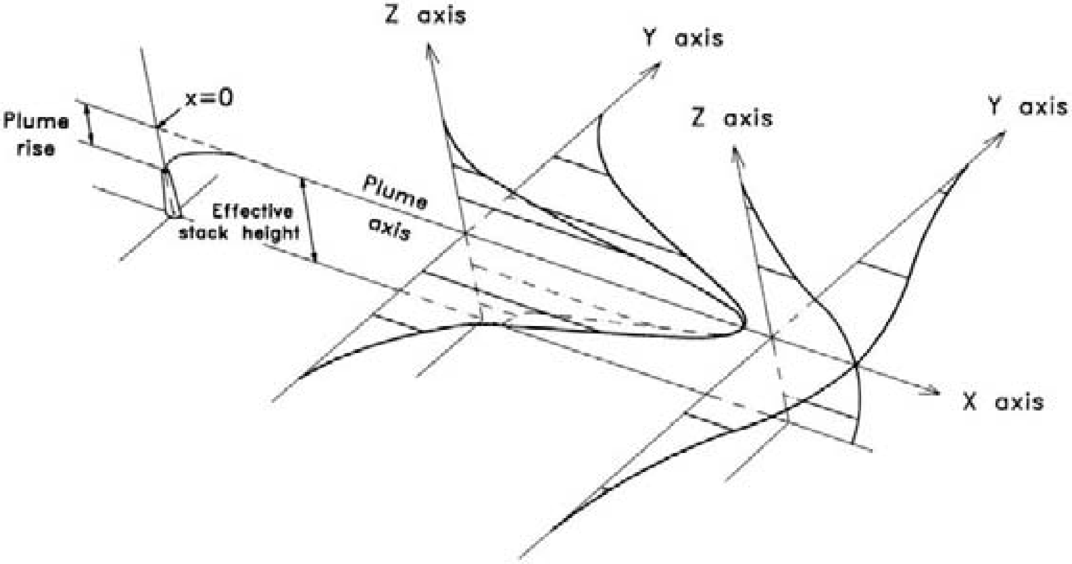
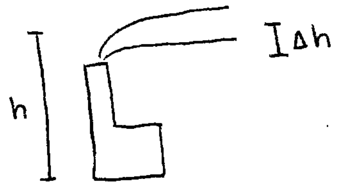


FIGURE 4-24 Cross sections of pollutant concentrations at two locations downwind of a smokestack. Note that physical height of the stack is typically less than the effective height of the stack, which takes plume rise into account. The total flux of pollutant is identical at each downwind location, although concentration decreases as the plume widens. The shape of each concentration versus distance plot is a normal, or Gaussian, curve; hence, this is often called a Gaussian plume (adapted from Boubel *et al.*, 1994).

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment*, 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

h includes plume rise – buoyancy and upward momentum



$\Delta h = \frac{1.6 F_b^{1/3} x^{2/3}}{u}$ where $F_b = \frac{g d^2 V}{4}\left(\frac{T_s - T_a}{T_s}\right)$

T_s: source temp.
T_a: ambient temp.

2nd term of g_z: image source to account for no-flux boundary at ground (reflects off ground)

σ_y and σ_z depend on wind speed and atmospheric stability

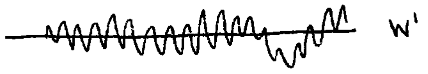
Briggs formulas: "open country" vs. "urban" to account for roughness

least stable during periods of intense insolation → unstable b/c buoyancy

higher wind speed → shorter travel time so less mixing (per distance) counters the effect of increased turbulence

graphs of σ vs. x show how D increases w/scale – larger eddies involved

can measure turbulence more directly:



turbulence intensity

$i_y = \frac{\sigma_y}{u}$ (statistical σ_y, not Pasquill-Gifford σ_y)

and then

$\sigma_z = i_z \cdot f_z \cdot x$

↳ empirical formulae (urban/rural, stability categories?)

regional scale – ex. SO_2 effects on acid rain

very different timescales, response over many km, averaged over ~ years

numerical modeling: transport + reaction (sinks)

↓

how do power plants in Midwest affect lakes in Adirondacks? (for example)

relate emissions to conc. (long-term average)

11|30|04

large-scale transport: ~days or more (ex. chernobyl)

convection at equator can bring stuff up to stratosphere

model as 2 boxes:

for troposphere, $\frac{dC_T}{dt} = -.07C_T$ $t_{1/2} \sim 10$ years

stratosphere $\frac{dC_S}{dt} = -0.3C_S$ $t_{1/2} \sim$ years

physical (mixing) and chemical sinks

what if ρ is much different from that of air?

- can Gaussian, Pasquill-Gifford models be used?
  not really b/c density dominates transport (rather than advection, diffusion)

ex. tanker carrying liquified natural gas

Atmospheric Sinks - Deposition

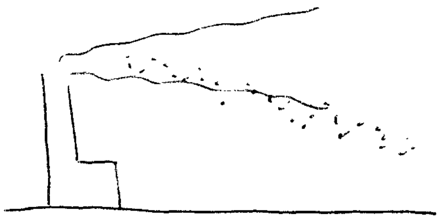
	dry	wet
gases	- absorption (dep. velocity)	- partitioning (washout ratio) - scavenging
particles	- Stokes settling - impaction	- rainout - washout

Stokes settling

$$W_s = \frac{2}{9}\frac{gr^2\Delta\rho}{\mu}$$

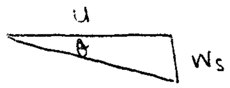
$\mu(\text{air}) = 1.8\times10^{-4}$ g/cm·s (poise)

50-100μm particles or larger



significant "fall velocity"

correct P-G model with angle:



non-spherical particles - use some effective aerodynamic diameter

smaller particles - settling is negligible

impaction: mass of insect vs. tight turn of streamline around car

(macro-example) ↘ inertia, can't follow streamline

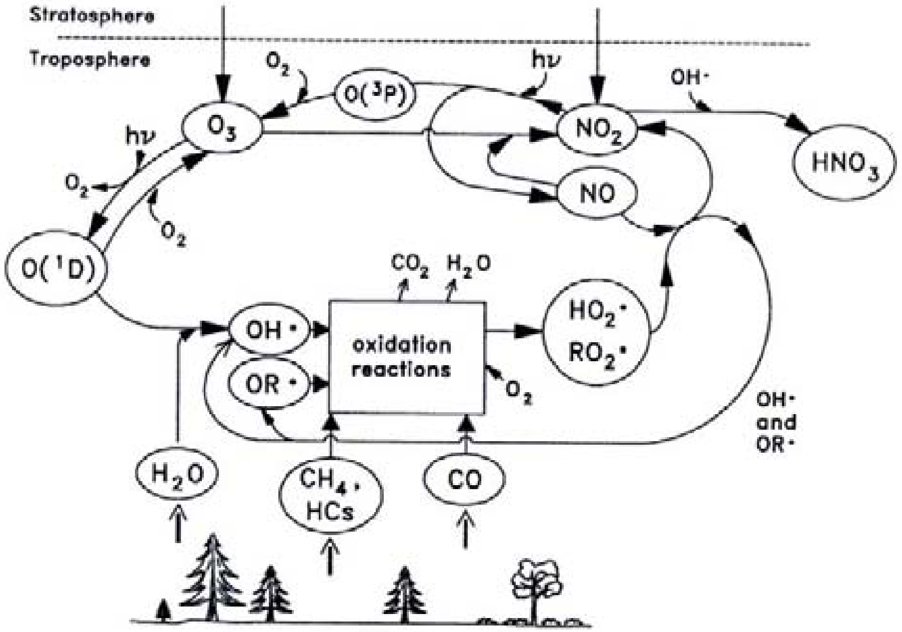


FIGURE 4-34 A simplified diagram of the tropospheric chemical system. One of the net effects of this system is the oxidation of reduced gases (methane and hydrocarbons) emitted by biota and human activities. Some of the oxidized species such as nitrate (in the form of nitric acid, HNO_3) may be deposited to the surface. Note the O_3-NO_x cycle in the top of the diagram (this is later shown in more detail in Fig. 4-35) and the routes for formation of the highly reactive OH· radical. [The atomic oxygen species $O(^1D)$ and $O(^3P)$ are singlet and triplet, respectively (see Section 2.7.1), with D and P referring to the angular momentum of the species.]

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment,* 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

ex. flow over forest is very complex, so deposition velocity (empirical)

$V_d = o(0.1-1\ cm/s)$

$J = V_d \cdot C$

absorption of gases - ex. on surface of leaf

diffusion through boundary layer $J = \frac{D}{\delta} C$ like thin-film model

D/δ is "piston velocity"

also consider plant characteristics - stomata

(let in CO_2 for photosynthesis - diurnal cycle)

wet processes (rain/snow)

C_a for flux, need rainfall intensity

$C_w = \frac{C_a}{H} = C_a$ (washout ratio) if equil. is fast relative to residence time

particles: rainout - particle is nucleus of condensation

washout - particle collides w/ already-existing raindrop

modeled using empirical 1st-order scavenging coeff.

$C = C_0 e^{-\lambda t}$ $\lambda = 4\times10^{-5} \rightarrow 3\times10^{-3}\ s^{-1}$

this approach can be used for gases also (ex. SO_2)

$\lambda = 10^{-4} I^{0.53}$ ↳ irreversible so equil. not the best

$\uparrow$ intensity of rainfall, mm/hr

Chemical sources/sinks

oxidation reactions with some reactive oxygen species

$\cdot OH$ and $\cdot OR$

NO_2/ozone cycle - can't have more O_3 than NO_2 originally present

but other ways of oxidizing NO back to NO_2 (other than using up O_3 in back-reaction) - $HO_2^{\cdot}$ and $RO_2^{\cdot}$ can do this

$HO_2^{\cdot}/RO_2^{\cdot}$ formed from hydrocarbons, attacked by $\cdot OH$ and reacts with O_2

process regenerates $\cdot OH$, also produces NO_2

Where does $\cdot OH$ come from?

$O_3 \rightarrow O_2 + O$

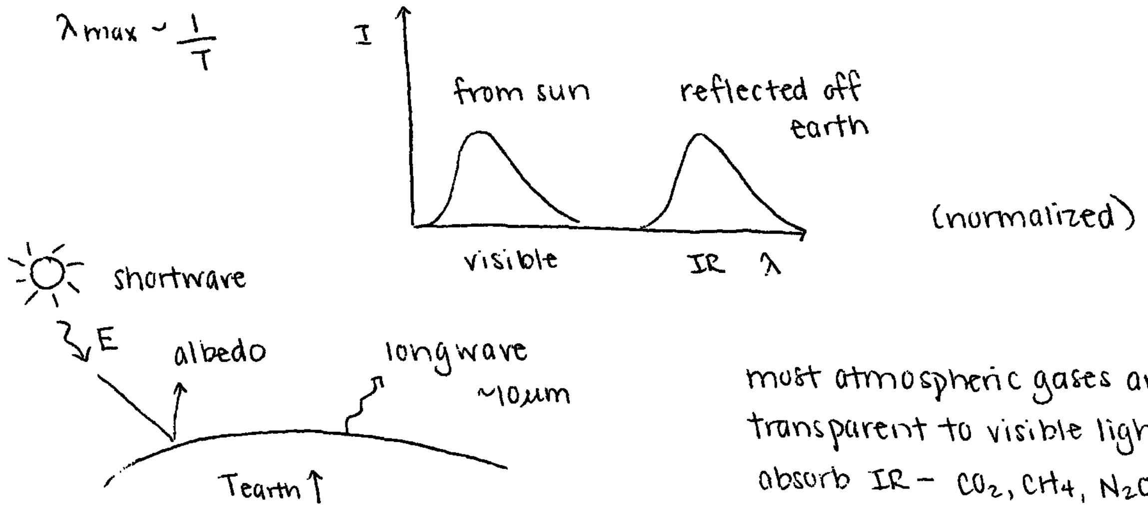
$H_2O + O \rightarrow 2\ \cdot OH$

how can we control air quality? NO_x and HC's (can't really affect sunlight or ozone...)

that cycle is throughout stratosphere - what about Antarctic ozone hole?

polar stratospheric clouds (ice) - reservoir compounds release Cl_2 when sun comes out in spring

$\lambda_{max} \sim \frac{1}{T}$



most atmospheric gases are transparent to visible light, but absorb IR - CO_2, CH_4, N_2O etc.

steady-state: not all longwave gets back to space → increase Tearth to increase flux

transmission vs. wave # - water vapor is important

CO_2, CH_4 particularly important b/c nothing else absorbs there (esp. CH_4)

mass balances are hard to close, esp. ecosystem (deforestation)

CH_4 increasing ≈ 1%/year

methane hydrates (phase diagram)

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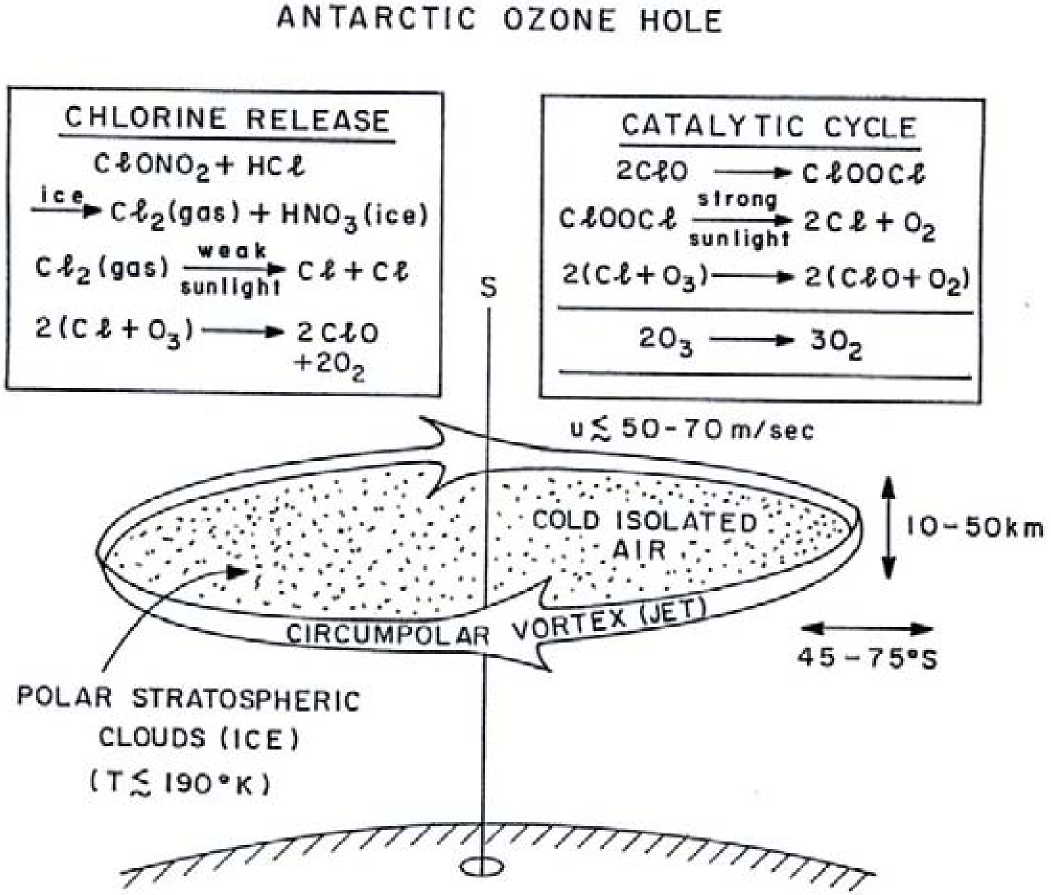

FIGURE 4-41 Key chemical processes of the Antarctic ozone hole. Of particular importance are the polar stratospheric clouds, which catalyze the release of ozone-destroying chlorine from chlorine nitrate and hydrogen chloride (Prinn and Hartley, 1992).

Image Courtesy of Academic Press, *Chemical Fate and Transport in the Environment*, 2nd Edition 2002, Hemond, H.F. and Fechner-Levy, Elizabeth J.

acid deposition

$NO_x \rightarrow HNO_3$ $SO_x \rightarrow H_2SO_4$

12/2/04

$[\cdot OH] \approx 10^6$ molec/cm³

reactions are essentially diffusion-limited $k = 3\times10^{-13} \frac{cm^3}{molec\cdot sec}$ for many chemicals

acid deposition → surface water chemistry

2-bucket system – estimates impaction/dry poorly b/c geometry-dependent

effects: C_T fixed by pCO_2

Alk affected by HNO_3/H_2SO_4 ⇒ adjusted pH

things that may change:

- mineral weathering (soft water – aluminosilicates weather to silica + cations which contribute to Alk, and clays)
  may resist effects of acid dep.

biological uptake includes NO_3^-, removal of NO_3^- increases Alk

watershed chart: input/output of major ions

Stratosphere

cutoff for sunlight ~ 290 nm (Earth's surface)

in stratosphere, $\lambda < 290$ nm → all sorts of different photochemistry

ex. photolysis of oxygen $O_2 \rightarrow 2O$

$O + O_2 \rightarrow O_3$ direct formation of ozone

ozone in Dobson Units – 10μm thick at STP over Earth's surface

destruction of stratospheric ozone:

CFC's ex. F-12 CCl_2F_2 refrigerants, AC's
(thermo. properties, inert)
Cl's make stable to oxidation

tropospheric $t_{1/2}$ is long → diffuse to stratosphere → photolyzed

chemicals released: Cl_2, HCl, $ClONO_3$
↓
photodissociates easily

$O_3 + Cl \rightarrow O_2 + ClO$

$ClO + ClO \rightarrow O_2 + Cl_2$