8 Surface Processes

Mass Exchange Volatilization Reaeration Momentum Transfer Oil spills Surface Heat Transfer Lake temperature models

Air water exchange

Equilibrium: Henry's Law





Typical units for [H]:

atm-m³/mol (K_H) or dimensionless (K_H ')

For air $K_H' \sim 42 K_H$

Two-film theory

Ex: liquid side

H





$$k_{l}(c_{l} - c_{le}) = k_{g}(c_{ge} - c_{e}) = k(c_{l} - c_{g}/H)$$

 $=\frac{c_{ge}}{c_{e}}$ 3 eqns, 3 unknows (c_{le}, c_{ge}, k)

Two-film theory



Resistances in series:

 $k_l << Hk_g => 1$ dominates (liquid side controlled) $k_l >> Hk_g => 2$ dominates (gas side controlled)

Medium with lower equilibrium concentration controls

Typical values for air and water

"Typical" values for air (as gas) $D_a \sim 0.1 \text{ cm}^2/\text{s}, \ 0.1 < z_a < 1 \text{ cm}$ $= k_a = D_a/z_a = 0.1$ to 1 cm/s "Typical" values for water (as liquid) $D_1 \sim 2 \times 10^{-5} \text{ cm}^2/\text{s}$, $0.002 < z_1 < 0.02 \text{ cm}$ = k₁ = D₁/z₁ = 10⁻³ to 10⁻² cm/s

 $K_g \sim 100 k_l$ so if H >> 0.01 then water side controlled (think DO); if H << 0.01 then air side controlled (think evaporation)

Example of liquid side control



Liquid side control, cont'd



If we double k_l (halve z_l), (c_e - c_g) doubles, both gradients ~ double => twice the mass flux; red line

If we double k_g (halve z_g), (c_e - c_g) is halved, both gradients ~ const => similar mass flux; green line

Therefore mass flux controlled by liquid side

Surface Renewal Theory

Described previously for streamreaeration formulae (Chapter 7) \mathbf{z}_{I} (or \mathbf{z}_{w} or δ) not stagnant, but timedependent ~ $[Dt]^{1/2}$, where t is reciprocal of a renewal rate, depending on bottom generated turbulence. Thus k_i (hence k) = $D_i/z_i \sim D^{1/2}$

Measurement of gas exchange

 Gas-evasion experiment: introduce chemically conservative gas (e.g., CO₂, propane, radon) at c > saturation, and watch c decline with distance due to volatilization

In open water bodies (or rivers where you don't know flow rate) introduce a second, non-volatile tracer such as salt.

Sometimes use tracer of opportunity



Gasses other than oxygen

 $K_a \sim D$ (stagnant film), $D^{1/2}$ (surface) renewal), $D^{2/3}$ (split the difference) \bullet From Chapter 1, Sc = v/D ~ MW^b (b ~ 0.35 to 0.4) $K_{a}/K \sim (D_{02}/D)^{2/3} \sim (32/MW)^{-1/4}$ $Example: Propane C_3H_8, MW = 44$ • $K_a/K = (32/44)^{-1/4} = 1.08$ Calibrations actually shows K_a/K ~1.39

How far downstream must one go?

 O'Connor-Dobbins at 20°C: K_a = 3.9u ^{0.5}/h^{1.5}

u = 0.3 m/s, h = 1 m, K_a = 2.1 d⁻¹

x~ u/K_a = (0.3 m/s)(86400s/d)/(2.1d⁻¹) ~ 12 km

Application to open waters

h = water depth orX thermocline depth $c_{nv} = \frac{\dot{m}_{nv}}{\sqrt{2\pi\sigma uh}} e^{-y^2/2\sigma^2}$ \dot{m}_{ν} (propane) \dot{m}_{nv} (salt) $c_{v} = \frac{\dot{m}_{v}}{\sqrt{2\pi\sigma uh}} e^{-y^{2}/2\sigma^{2}} e^{-k_{l}x/hu}$ $\frac{c_v}{c_{nv}}\frac{\dot{m}_{nv}}{\dot{m}_v}\mathbf{1}$ $\frac{c_v}{c_{nv}} = \frac{\dot{m}_v}{\dot{m}_{nv}} e^{-k_l x/hu}$ 0 e⁻¹ 0 X 0 hu/k

Mass transfer in lakes and oceans

- Most contaminants of concern are water side controlled (e.g., DO, VOC)
- In rivers, source of turbulence is bottom roughness
- In deep water bodies (lakes, oceans) it is wind stress => u_{w^*} (water-side friction velocity) which affects z_l
- Contaminants that are air side controlled also affected by wind (through z_q)

k_l vs u_{w*}



 u_{w^*} because transfer is water side controlled and u_{w^*} is indicator of turbulence; yet u_{w^*} not easily measured



k_{I} (or z_{I}) vs u_{10}



Example film coefficients

$k_l = 0.0004 + 0.00004 u_{10}^2$

$k_g = 0.3 + 0.2u_{10}$

 k_l and k_g in cm/s; u_{10} in m/s [Schwarzenbach et al, 1993] Note that both depend on u_{10}

Examples

Above eqns:

 $u_{10} = 5 \text{ m/s} => k_1 = 1.4 \times 10^{-3} \text{ cm/s}$ (green dot);

 $k_{q} = 1.3 \text{ cm/s}$

Figure 8.8:

 $z_{l} = \delta = 120 \ \mu m = 1.2 \times 10^{-2} \ cm.$

For DO, D = $2x10^{-5}$ cm²/s

 $k_1 = D/z_1 = 2x10^{-5}/1.2x10^{-3} = 1.7x10^{-3}$ cm/s (red dot)

k_{I} (or z_{I}) vs u_{10}



Yu and Hamrick (1984)

Emerson (1075)

Volatile Halogenated Organic Compound (VHOC) Experiment

 CH₃Cl₃ and other one carbon VOCs (THMs) and two carbon VOCs (solvents) discharged with waste water.

- Used to
 - compute volatilization (assuming known residence time) or
 - compute residence time (with known volatilization)

TCE data in Boston Harbor



Kossik, Gschwend & Adams, 1987

TCE Experiment, cont'd

Nominal residence time (w/o volatilization; excluding presumed outlier)



TCE Experiment, cont'd

With volatilization



For CH_3Cl_3 H = 1.13 (dimensionless) >> 1 => ws control D = $1.0x10^{-5}$ cm²/s

TCE Experiment, cont'd

From Figure 8.8 and $u_{10} = 5 \text{ m/s}$, $\delta = 1.2 \text{x} 10^{-2} \text{ cm}$

 $\label{eq:k} \begin{array}{l} k = D/\delta = (1.0 x 10^{-5})/(1.2 x 10^{-2}) = 0.00083 \ \text{cm/s} = 3 \\ \text{cm/hr} = 0.72 \ \text{m/d} \end{array}$

 $1/t^* = 1/t + k/h$

 $1/t = 1/t^* - k/h = (1/5.6d) - (0.72 m/d)/6m$

 $=0.18 - 0.12 = 0.06d^{-1} => \tau = 17 d$

Estimated τ is too high; reason is likely extraneous or under-accounted sources of CH₃Cl₃

Momentum Exchange

Chapters 2, 3 discussed surface shear stress for eddy diffusivity and hydrodynamic modeling

Previous section discussed stress as source of turbulence governing mass exchange

Also of interest in transporting floating material, specifically spilled hydrocarbons

Oil Spills

Composition
Fate
Transport (spreading, advection)
Clean-up



Marine Sources (10³ MT/yr)

	N. America	Global
Natural Seeps	160	600
Petroleum Extraction	3	38
Petroleum Transport	9	150
Petroleum Consumption	84	480
Total	260	1300

About half is anthropogenic

(Oil in the Sea III, NRC, 2003)

Composition

- Crude and Refined Oils
- Always multiple constituents
- Characterized by Boiling Point (or distillation cut)

Fate





Transport Models

Spreading and Advection
Pre-planning (evaluate risk)
Real-time (assist clean-up; needs to be quick and dirty)
Hind-cast (who is responsible, damage

assessment)

Simple advection model



Ekman Model

Linearized equations of motion; constant viscosity



Ekman Model, cont'd

X

$$w = \frac{\tau_{sy}}{\rho_w \sqrt{E\Omega}} \exp\left\{\sqrt{\frac{\Omega}{2E}}(1+i)z + \frac{i\pi}{4}\right\}$$

Surface drift 45° to right;







Other effects of wind: Coastal Upwelling/Downwelling



Other effects of wind: Langmuir Circulation





Figure by MIT OCW.


Idealized spreading, cont'd



Comments

Theory applies down to slick thickness of about 0.1 mm

Additional spreading due to

- Time-varying spillage
- Wind, waves and non-uniform currents
- Dispersion of submerged (slower moving) oil droplets

Field experiments show oil often very nonuniform (90% of volume in 10% of area)

Oil Transport Models

- Slick advected with underlying surface current plus 3% of wind speed (~10% deflection to right)
- (3-D) models simulate transport of subsurface dispersed oil.
- Currents can be observed or predicted (sophistication depends on application available time)
- Fate processes often computed independently from transport

Model Simulations



NOAA's 3D GNOME; ANS Crude off Coast of Florida

Mechanical Clean-up

Oil Containment Boom



Chemical Dispersion

Surfactants that reduce interfacial tension Create dispersed droplets Subsurface/bottom impacts vs surface/shoreline ♦ Air (large spills) or boat application Window of opportunity

Chemical Dispersion, cont'd



In situ Burning

- Considered secondary option (like chemical dispersants)
- Most appropriate for offshore spills (reduced AQ impacts)



Surface Heat Transfer and Temperature Modeling

Surface heat fluxes
Linearized surface heat transfer
Cooling ponds
Natural lakes and reservoirs

Importance of Temperature

- Important WQ parameter
 - Thermal pollution
 - Species preference (fish habitat)
- Affects rate constants
 - K=K₂₀θ^{T-20}
- Produces density stratification
 - ρ = ρ(T)
- Important tracer (e.g., E_z)

Surface Heat Transfer (W-m⁻²)



 $\phi_n = \phi_{sn} + \phi_{an} - \phi_{br} - \phi_e - \phi_c$

Solar Radiation

 \bullet Short wave length (< 3µm) Direct plus diffuse (scattered, reflected) Absorbed & re-radiated (> 3μ m) by clouds Measured by pyranometer Incident clear sky radiation calculated from latitude, date and time of day Corrections for cloud cover and reflection

Net Solar Radiation (cont'd)



$\phi_{sn} = \phi_s - \phi_{sr} \cong 0.94 \phi_{sc} \left(1 - 0.65 C^2 \right)$

C = fractional cloud cover

Depth-variation of solar radiation

Measured with
Secchi disk or *in-situ* pyranometer

$$\phi_z = (1 - \beta)\phi_{sn}e^{-\eta z}$$
$$\eta = \frac{1.7}{d_D}$$
$$\beta \sim 0.5$$



Atmospheric Radiation

Long wave length (> 3μm)
Re-radiated from atmosphere
Measured by pyrgeometer
Incident clear sky radiation calculated from absolute air temperature, vapor pressure
Corrections for cloud cover and reflection

Incident Radiation Formulae

$$\phi_{ac} = \varepsilon \sigma (T_a + 273)^4$$

 σ = Stefan-Boltzman const (5.7x10⁻⁸ W/m²-°K⁴)

 ϵ = emissivity (dimensionless)

 $\varepsilon = 0.92 x 10^{-5} (T_a + 273)^2$ Swinbank (1963)

 $\varepsilon = \left\{ 1.0 - 0.26 / \exp[7.77 x 10^{-5} (T_a)^2] \right\}$ [Itso-Jackson (1969)

 $\varepsilon = 1.24 \left(\frac{e}{(T_a + 273)} \right)^{\frac{1}{7}}$ e = vapor pressure, mbar Brutsaert (1975)

Net Atmospheric radiation

 $\phi_{an} = 0.97 \varepsilon \sigma (T_a + 273)^4 (1.0 + 0.17C^2)$

C = fractional cloud cover

~3% reflection

Back Radiation

Water surface is nearly a black body (ε ~ 0.97)

$\phi_{br} = 0.97\sigma(T_s + 273)^4 = 5.5x10^{-8}(T_s + 273)^4$

Evaporative Heat Flux



Evaporative Heat Flux (cont'd)

Mass transfer => heat transfer using latent heat of vaporization

 $L_v = (2493. - 2.26T_s) \times 10^3$ J/Kg

$$\phi_e = L_v E = f(W_z)(e_s - e_a)$$

 $\phi_e = 3.72W_2(e_s - e_2)$ "Lake Hefner", Marciano and Harbeck (1954)

 $(W/m^2; W_2 \text{ in m/s}; e_s, e_2 \text{ in mb})$

 $\phi_e = 5.1A^{-0.05}W_2(e_s - e_2)$ "Fetch-dependence" Harbeck, (1962)

(A in ha)

ez W_{7} es e_z and W_z vary vertically (height above water) and horizontally (above water or on-shore)

7

Ζ

Evaporation from non-natural water bodies

 e_7

 $\phi_{e} = f(W_{z}) (e_{s} - e_{z})$



decreased evaporation

e_s decreases with pressure

Conductive Heat Flux

 Computed from evaporative flux using Bowen Ratio

$$\phi_c = R_b \phi_e$$

$$R_b = C_b \frac{(T_s - T_z)}{(e_s - e_z)}$$

C_b =0.61 mb/°C;

Summary



functions of T_s

functions of external factors (met and astronomical conditions)

Strategies for computation: table look up

Self regulation: errors in calculations compensate

Linear Heat Transfer



K ~ 20-50 W/m²°C

Example: Periodic Heat Loss



Periodic Heat Loss (cont'd)





Examples

 $K/\rho c = 1m/d^*$; h = 10m, k=K/\rho ch = 0.1d⁻¹



* K ~ 48 W/m²°C

Cooling Lakes and Ponds

Used to cool electric power plants Shallow (vertically well-mixed) Erected with dikes T = T(x,y) + T(t)Deep reservoirs Damming of reservoirs Cooling capacity • $r = KA_p / \rho cQ_o$



Example: shallow-longitudinal



Jirka et al. (1978)

Stratification in Lakes & Reservoirs

Factors causing vertical stratification
Differential absorbtion
Reduced vertical mixing
Factors causing horizontal stratification
Strong through flow
Strong wind

Differential absorbtion

Reservoir classification based on horizontal through flow (Orlob, 1969)

Through flow velocity = L/(V/Q) $Int' wave speed ~ (q \Delta \rho / \rho h)^{0.5} ~ Nh$ • N = buoyancy freq = $[(g/\rho)(d\rho/dz)]^{0.5}$ L = length; Q = flow; h = depth; V = vol $F_r = LQ/VNh$ F_r << 1 vertically stratified</p> F_r >> 1 vertically mixed

1-D Reservoir Modeling


Surface Layer

Well mixed layer

 Convective mixing
 Wind mixing

 Wind mixing algorithm for surface

 Oceans (Kraus-Turner)
 1-D model below

WM

1-D

Surface Layer (cont'd)



Many variants

Lake stability

Stability index (PE of water body with equivalent mass and heat content but uniform density – PE of stratified body)

$$SI = \int_{0}^{h} [\overline{\rho} - \rho(z)][z - z_{c}]gA(z)dz$$

$$\overline{\rho} = \int_{0}^{h} \rho(z)A(z)dz / \int_{0}^{h} A(z)dz$$
 Average density
$$z_{c} = \int_{0}^{h} \rho(z)A(z)zdz / \int_{0}^{h} \rho(z)A(z)dz$$
 Center of mass