1 Molecular Diffusion

- Notion of concentration
- Molecular diffusion, Fick’s Law
- Mass balance
- Transport analogies; salt-gradient solar ponds
- Simple solutions
- Random walk analogy to diffusion
- Examples of sources and sinks
Motivation

- Molecular diffusion is often negligible in environmental problems
- Exceptions: near interfaces, boundaries
- Responsible for removing gradients at smallest scales
- Analytical framework for turbulent and dispersive transport
Concentration

- Contaminant => mixture
  - Carrier fluid (B) and contaminant/tracer (A)
  - If dissolved, then solvent and solute
  - If suspended, then continuous and dispersed phase

- Concentration \((c \text{ or } \rho_A)\) commonly based on mass/volume (e.g. mg/l); also
  - mol/vol (chemical reactions)
  - Mass fraction (salinity): \(\rho_A/\rho\)

- Note: 1 mg/l ~ 1 mg/kg (water) = 1 ppm
Molecular Diffusion

One-way flux (M/L²-T)

\[ = \rho_A w_A \]

Net flux

\[ = w_A (\rho_{A1} - \rho_{A2}) \]

\[ = -w_A \ell_m \frac{\partial \rho_A}{\partial z} \]

\[ \mathbf{J}_A = -D_{AB} \nabla \rho_A \]
Ficks Law and Diffusivities

\[ \vec{J}_A = -D_{AB} \nabla \rho_A \]

\[ \nabla() = \frac{\partial}{\partial x}() \vec{i} + \frac{\partial}{\partial y}() \vec{j} + \frac{\partial}{\partial z}() \vec{k} \]

\( D_{AB} \) is isotropic and essentially uniform (temperature dependent), but depends on A, B

Table 1.1 summarizes some values of \( D_{AB} \)

Roughly: \( D_{\text{air}} \sim 10^{-1} \text{ cm}^2/\text{s}; \ D_{\text{water}} \sim 10^{-5} \text{ cm}^2/\text{s} \)
Diffusivities, cont’d

Diffusivities often expressed through Schmidt no.

\[ \text{Sc} = \frac{\nu}{D} \]

Roughly: \( \nu_{\text{air}} \sim 10^{-1} \text{ cm}^2/\text{s} \); \( \nu_{\text{water}} \sim 10^{-2} \text{ cm}^2/\text{s} \)

\( \text{Sc}_{\text{air}} \sim 1 \)

\( \text{Sc}_{\text{water}} \sim 10^{3} \)

Also: Prandlt no. \( \text{Pr} = \frac{\nu}{\kappa} \) (\( \kappa \) = thermal cond.)

Add advection; total flux of \( A \) is:

\[ \vec{N}_A = \rho_A \vec{q} - D_{AB} \nabla \rho_A \]

macroscopic velocity vector
Conservation of Mass

Like a bank account except expressed as rates:

(rate of) change in account = (rate of) (inflow – out) +/- (rate of) prod/consumption

Example for x-direction

\[
in = (N_A)_x \Delta y \Delta z
\]

\[
out = (N_A)_{x+\Delta x} \Delta y \Delta z = \left[ (N_A)_x + \left( \frac{\partial N_A}{\partial x} \right) \Delta x \right] \Delta y \Delta z
\]

\[
net\ in = \left[ -\left( \frac{\partial N_A}{\partial x} \right) \Delta x \right] \Delta y \Delta z
\]
Conservation of Mass, cont’d

Account balance

\[ = \rho_A \Delta x \Delta y \Delta z \]

Rate of change of account balance

\[ = \frac{\partial}{\partial t} (\rho_A) \Delta x \Delta y \Delta z \]

Rate of production

\[ = r_A \Delta x \Delta y \Delta z \]
Conservation of Mass, cont’d

Sum all terms (incl. advection in 3D)

\[
\frac{\partial \rho_A}{\partial t} + \frac{\partial}{\partial x} (N_A)_x + \frac{\partial}{\partial y} (N_A)_y + \frac{\partial}{\partial z} (N_A)_z
\]

\[
\frac{\partial \rho_A}{\partial t} + \nabla \cdot \vec{N}_A = r_A
\]

Flux divergence (dot product of two vectors is scalar)

For carrier fluid B

\[
\frac{\partial \rho_B}{\partial t} + \nabla \cdot \vec{N}_B = r_B
\]
Conservation of Mass, mixture

\[ r_A = -r_B \]
\[ \vec{N}_A + \vec{N}_B = \rho \vec{q} \]
\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{q}) = 0 \]
\[ \frac{\partial \rho}{\partial t} \approx \nabla \rho \approx 0 \]
\[ \nabla \cdot \vec{q} = 0 \]

Conservation of total mass
\[ \rho_A + \rho_B = \rho \]

Liquids are nearly incompressible

Divergence = 0; Continuity
Conservation of Mass, contaminant

\[ \rho_A = c \]

\[ \frac{\partial c}{\partial t} + \nabla \cdot (c \vec{q}) = \nabla \cdot (D \nabla c) + r \]

Conservative form of mass cons.

\[ \frac{\partial c}{\partial t} + c \nabla \cdot \vec{q} + \vec{q} \cdot \nabla c = D \nabla^2 c + (\nabla D)(\nabla c) + r \]

N.C. form

\[ \frac{\partial c}{\partial t} + \vec{q} \cdot \nabla c = D \nabla^2 c \nabla + r \]

If \( \vec{q} = r = 0 \) => Fick's Law of Diffusion
Heuristic interpretation of Advection and diffusion

Advection
Flux ~ negative gradient

Diffusion
Difference in fluxes (divergence) ~ curvature
Analogs

\[ \frac{\partial c}{\partial t} = D \nabla^2 c \]

Ficks Law (mass transfer)

\[ \frac{\partial T}{\partial t} = \kappa \nabla^2 T \]

Fourier’s Law (heat transfer)

\[ \frac{\partial \vec{q}}{\partial t} + (\vec{q} \cdot \nabla) \vec{q} = \nu \nabla^2 \vec{q} + \frac{\vec{r}_m}{\rho} \]

Newton’s Law (mom. Transfer)

Air

\[
\begin{align*}
\nu/D & \quad \text{Sc} & \sim 1 \\
\nu/\kappa & \quad \text{Pr} & \sim 0.7 \\
\end{align*}
\]

Water

\[
\begin{align*}
\sim 10^3 \\
\sim 8 \\
\end{align*}
\]

\[ D \sim \kappa \sim \nu \]

\[ D << \kappa << \nu \]
Example: Salt Gradient Solar Ponds (WE 1-1)
like El Paso Solar Pond

~3m

dense brine
Solar Pond, diffusive salt flux to UCZ

\[ c = \rho S \]

\[ c_{UCZ} = (1033 \text{ Kg/m}^3)(50 \times 10^{-3} \text{ Kg/Kg}) = 52 \text{ Kg/m}^3 \]

\[ c_{BCZ} = (1165 \text{ Kg/m}^3)(250 \times 10^{-3} \text{ Kg/Kg}) = 291 \text{ Kg/m}^3 \]

\[ J_s = \frac{Ddc}{dz} \]

\[ = (2 \times 10^{-9})(239 \text{ Kg/m}^3)/1.2m = 4.0 \times 10^{-7} \text{ Kg/m}^2 \cdot \text{s} \]

\[ = 344 \text{ Kg/day} \]
Solar Pond: diffusive thermal flux to UCZ

$\phi_{sn} = 250 \text{ W/m}^2$

$T_1 = 30^\circ\text{C}$

$T_2 = 80^\circ\text{C}$

$\beta = \text{fraction of } \phi_{sn} \text{ absorbed at surface}$

$\eta = \text{extinction coefficient}$

$C_p = \text{heat capacity (4180 J/Kg}^\circ\text{C);}$

$\kappa = \text{thermal diffusivity (1.5x10}^{-7} \text{ m}^2/\text{s)}$}

$\phi^* = \eta(1-\beta)\phi_{sn} / \rho C_p \kappa$

$c_1, c_2 \text{ from } T=T_1 \text{ at } z_1, \ T=T_2 \text{ at } z_2$
Solar Pond: thermal flux

\[ \phi_{sn} = 250 \text{ W/m}^2 \]

\[ T_1 = 30^\circ C \]

\[ \phi_s(z) = \phi_{sn}(1-\beta)e^{-\eta z} \]

\[ T_2 = 80^\circ C \]

\[ J_t = \rho C_p \kappa \left( \frac{dT}{dz} \right)_{z=z_2} \]

\[ = \rho C_p \kappa \frac{T_2 - T_1}{z_2 - z_1} + (1 - \beta)\phi_{sn} \left[ e^{-\eta z_2} + \frac{(e^{-\eta z_2} - e^{-\eta z_1})}{\eta(z_2 - z_1)} \right] \]

\[ z_1 = 0.3 \text{ m}; \ z_2 = 1.5 \text{ m}, \ \beta=0.5, \ \eta = 0.6 \implies J_t = 7 \text{ W/m}^2 \]

Compare with \((1-0.5)(250)\exp(-0.6\times1.5) = 51 \text{ W/m}^2\)

reaching BCZ (\(~13\% \text{ lost})\)
Solar Pond: total energy extraction

\[ \phi_{sn} = 250 \text{ W/m}^2 \]

\[ T_1 = 30^\circ \text{C} \]

\[ \phi_s(z) = \phi_{sn}(1-\beta)e^{-\eta z} \]

\[ T_2 = 80^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Energy Flux at surface</th>
<th>250 W/m²</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Flux reaching BCZ</td>
<td>51</td>
<td>20</td>
</tr>
<tr>
<td>Energy Flux extracted</td>
<td>34</td>
<td>14</td>
</tr>
<tr>
<td>Electricity extracted (theoretical)</td>
<td>4.8</td>
<td>2</td>
</tr>
<tr>
<td>Electricity extracted (net actual)</td>
<td>2.4</td>
<td>1</td>
</tr>
</tbody>
</table>

Carnot efficiency
\[ \eta_c = \frac{\left(T_2-T_1\right)}{T_2+273} \]

[24 KWe for 1 ha]
Simple Solutions

Inst. injection of mass $M$

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}
\]

**bc:** $c = 0$ at $x = \pm \infty$

**ic:** $c = \frac{M}{A} \delta(x)$ at $t = 0_+$

$r = \frac{M}{A} \delta(x) \delta(t)$ with $c = 0$ at $t = 0$

(alternative)
Simple Solutions, cont’d

Inst. injection of mass $M$

Solution by similarity transform (Crank, 1975) or inspection

\[ c = \frac{B}{t^{1/2}} e^{-\frac{x^2}{4Dt}} \]

\[ A \int_{-\infty}^{\infty} c \, dx = M \]

\[ M = 2AB\sqrt{\pi D} \]

\[ c(x,t) = \frac{M}{2A\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \]

Add a current

\[ c(x,t) = \frac{M}{2A\sqrt{\pi Dt}} e^{-\frac{(x-ut)^2}{4Dt}} \]
Gaussian Solution
Spatial Moments

\[ m_o = \int_{-\infty}^{\infty} c(x,t) dx \]

\[ M = m_o A \]

Mass; indep of t

\[ m_1 = \int_{-\infty}^{\infty} cx \, dx \]

\[ x_c = \frac{m_1}{m_o} = ut \]

Center of mass

\[ m_2 = \int_{-\infty}^{\infty} cx^2 \, dx \]

\[ \sigma_x^2 = \frac{m_2}{m_o} - \left( \frac{m_1}{m_2} \right)^2 = 2Dt \]

Plume variance
Spatial Moments, cont’d

Relationship of moments to equation parameters

\[ m_2 = \int_{-\infty}^{\infty} \frac{M}{2A\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} x^2 dt \]

\[ = 2 \frac{M}{A} Dt \]

\[ \sigma_x^2 = \frac{m_2}{m_0} = \frac{2MDt / A}{M / A} = 2Dt \]

Without current, odd moments are 0
Spatial Moments, cont’d

Rewrite in terms of $\sigma$

$$c(x, t) = \frac{M}{2A\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}}$$

$$= \frac{M}{A\sqrt{2\pi \sigma_x}} e^{-\frac{x^2}{2\sigma_x^2}}$$

or in 3-D (isotropic)

$$c(x, t) = \frac{M}{8(\pi D t)^{3/2}} e^{-\frac{(x^2+y^2+z^2)}{4Dt}}$$

$$= \frac{M}{(2\pi)^{3/2} \sigma^3} e^{-\frac{(x^2+y^2+z^2)}{2\sigma^2}}$$

Plume dilutes by spreading:

In 1-D, $c \sim t^{1/2} \sim \sigma_x^{-1}$

In 3-D, $c \sim t^{3/2} \sim \sigma^{-3}$
Moment generating equation

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}
\]

\[
m_i = \int_{-\infty}^{\infty} x^i c \, dx
\]

Approach 1: moments of \( c(x,t) \) => \( \sigma^2 = \frac{m^2}{m_0} = 2Dt \)

Approach 2: moments of \( ge \) => moment generation eq.

\[
\int_{-\infty}^{\infty} x^i (each \ term) \, dx
\]
Moment generating eq., cont’d

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

\[ m_i = \int_{-\infty}^{\infty} x^i c dx \]

0th moment

\[ \int_{-\infty}^{\infty} \frac{\partial c}{\partial t} dx = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} c dx = \frac{dm_0}{dt} \]

\[ \int_{-\infty}^{\infty} D \frac{\partial^2 c}{\partial x^2} dx = D \left( \frac{\partial c}{\partial x} \right)_{-\infty}^{\infty} = 0 \]

2nd moment

\[ \int_{-\infty}^{\infty} x^2 \frac{\partial c}{\partial t} dx = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} x^2 c dx = \frac{dm_2}{dt} \]

\[ \int_{-\infty}^{\infty} Dx^2 \frac{\partial^2 c}{\partial x^2} dx = Dx^2 \left( \frac{\partial c}{\partial x} \right)_{-\infty}^{\infty} - 2 \int_{-\infty}^{\infty} xD \frac{\partial c}{\partial x} dx = -2xD(c)_{-\infty}^{\infty} + 2 \int_{-\infty}^{\infty} Dc dx = 2Dm_0 \]
Moment generating eq., cont’d

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

\[ m_i = \int_{-\infty}^{\infty} x^i c \, dx \]

0th moment

\[ \frac{dm_0}{dt} = 0 \]

\[ \Rightarrow m_0 = \text{const} = M/A \]

2nd moment

\[ \frac{dm_2}{dt} = 2Dm_o \]

\[ \Rightarrow \frac{d\sigma^2}{dt} = 2D \text{ or } \sigma^2 = 2Dt \]
How fast is molecular diffusion?

Creating linear salinity distribution from initial step profile

Assume 80 cm tank; 40 2cm steps

Time to diffuse: \( \sigma^2 = 2Dt \)

\[
t = \frac{\sigma^2}{2D} \approx \frac{(2\text{cm})^2}{(2)(1.3\times10^{-5}\text{ cm}^2/\text{s})}
\]

\[
= 1.5\times10^5\text{s} \sim 2\text{ days}
\]

If thermal diffusion (100 x faster), \( t < 1 \text{ hr} \)
Spatially distributed sources

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

"bc" \( c = 0 \) at \( x = \infty \)

"ic" \( c = c_o \) for \( x < 0 \) at \( t = 0 \)

\( c = c_o/2 \) at \( x = 0 \)

\( c = 0 \) for \( x > 0 \) at \( t = 0 \)
Spatially distributed sources

\[ dc(\xi, t) = \frac{dM}{2A\sqrt{\pi Dt}} e^{-\frac{\xi^2}{4Dt}} = \frac{c_o d\xi}{2\sqrt{\pi Dt}} e^{-\frac{\xi^2}{4Dt}} \]

\[ c(x, t) = \int_x^\infty \frac{c_o d\xi}{2\sqrt{\pi Dt}} e^{-\frac{\xi^2}{4Dt}} = \frac{c_o}{2} \left[ 1 - \operatorname{erf}\left( \frac{x}{2\sqrt{Dt}} \right) \right] = \frac{c_o}{2} \operatorname{erfc}\left( \frac{x}{2\sqrt{Dt}} \right) \]
Error Function

\[ \text{erf}(\omega) = \frac{2}{\sqrt{\pi}} \int_{0}^{\omega} e^{-\alpha^2} d\alpha \]

\[ \text{erfc}(\omega) = \frac{2}{\sqrt{\pi}} \int_{\omega}^{\infty} e^{-\alpha^2} d\alpha \]

\[ \text{erf}(0) = 0 \]
\[ \text{erf}(\infty) = 1 \]
\[ \text{erfc}(x) = 1 - \text{erf}(x) \]
Example: DO in Fish aquarium (WE 1-4)

\[ c(z,t) = c_1 + \frac{1}{2} 2(c_2 - c_1) \text{erfc} \left( \frac{z}{2\sqrt{Dt}} \right) \]

\[ \frac{c - c_1}{c_2 - c_1} = \text{erfc} \left( \frac{z}{2\sqrt{Dt}} \right) \]

Evaluate at \( z = 15 \text{ cm} \), \( D = 2 \times 10^{-5} \text{ cm}^2/\text{s} \) (Table 1-1)

<table>
<thead>
<tr>
<th>t</th>
<th>( \frac{z}{(4Dt)^{0.5}} )</th>
<th>( \text{erfc}[(z/ (4Dt)^{0.5})] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1hr</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>1d</td>
<td>5.7</td>
<td>( 10^{-15} )</td>
</tr>
<tr>
<td>1 mo</td>
<td>1.0</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Again, very slow!
Diffusion as correlated movements

\[ x(t) = \int_0^t u(t') dt' \]

Analogy between \( p(x) \) and \( c(x) \); ergotic assumption

For many particles, both distributions become Normal (Gaussian) through Central Limit Theorem
Statistics of velocity

\[ \bar{u} = 0 \quad \text{mean velocity} \]

\[ u^2 = \text{const.} \quad \text{variance} \]

\[ u(t)u(t-\tau) = u(0)u(\tau) = u(-\tau)u(0) \quad \text{auto co-variance} \]

\[ \frac{u(t)u(t-\tau)}{u(t)^2} = R(\tau) \quad \text{auto correlation} \]
Statistics of position

\[ x(t) = \int_{0}^{t} u(t') dt' \]

\[ \bar{x} = \int_{0}^{t} u(t') dt' = \int_{0}^{t} \bar{u}(t) dt = 0 \]

\[ x^2(t) \] increases with time, as follows

\[ \frac{d x^2(t)}{d t} = 2 x(t) \frac{d x}{d t} = 2 \left[ \int_{0}^{t} u(t') dt' \right] u(t) = 2 \int_{0}^{t} u(t) u(t') dt' \]

\[ \frac{d x^2(t)}{d t} = 2 u^2(t) \int_{0}^{t} R(t-t') dt' = 2 u^2(t) \int_{0}^{t} R(\tau) d\tau \]

\[ D = \frac{d x^2}{2 d t} = \frac{d \sigma^2}{2 d t} = \bar{u}^2 \int_{0}^{t} R(\tau) d\tau \quad \text{Taylor's Theorem (1921); classic} \]

\[ [D] = [V^2 T] \]

Earlier, \( D = \omega_A \ell_m \ [VL] \) or \( D = \frac{\sigma^2}{2t} \ [L^2/T] \)
Random Walk (WE 1-3)

Special case: \( u(t) = U \) or \( -U \)  

direction changes randomly after \( \Delta t \)

Walker’s position at time \( t = N\Delta t \)

Probability distribution:

\[
p(\chi, N) = \frac{N!}{\left( \frac{N + \chi}{2} \right)! \left( \frac{N - \chi}{2} \right)!} \left( \frac{1}{2^N} \right)
\]

\( \chi = x / Ut \)

Bernoulli Distribution

Approaches Gaussian for large \( N \)

Example for \( N = 3 \)
Statistics of position

\[ \bar{x}(t) = \sum_{i=1}^{N} \bar{u}(t) = 0 \]

\[ \sigma^2 = \left( \sum_{i=1}^{N} u \Delta t \right)^2 = \Delta t^2 \left[ (u_1 + u_2 + \ldots + u_i + \ldots u_N)(u_1 + u_2 + \ldots u_N) \right] \]

\[ = N \Delta t^2 U^2 = t U^2 \Delta t = t \Delta x^2 / \Delta t \]

\[ D = \frac{\sigma^2}{2t} = \frac{U^2 \Delta t}{2} = \frac{\Delta x^2}{2 \Delta t} \quad \text{[L}^2/\text{T]} \]

Alternatively, derive D from Taylor’s Theorem
Examples of Sources and Sinks (r terms)

- 1\textsuperscript{st} order
- 0\textsuperscript{th} order
- 2\textsuperscript{nd} order
- Coupled reactions
- Mixed order
Example: radioactive decay

\[ \frac{dc}{dt} = -kc \]

\[ c / c_o = e^{-kt} \]

Linearity \(\Rightarrow\) 1st O decay multiplies simple sol’n by \(e^{-kt}\); e.g.

Also very convenient in particle tracking models

\[ c = \frac{M}{2A\sqrt{\pi Dt}} e^{-kt} \]
0th Order

Example: silica uptake by diatoms (high diatom conc)

\[ \frac{dS}{dt} = -B \]

\[ S = S_o - Bt \]

S = substrate (silica) concentration

B = rate (depends on diatom population, but assume large)
2nd Order

Example: particle-particle collisions/reactions; flocculant settling)

\[
\frac{dc}{dt} = -Bc^2
\]

\[
c = \frac{1}{c_0 + Btc_o}
\]

Behavior depends on \(c_o\); slower than \(e^{-kt}\).

Can be confused with multiple species undergoing 1st order removal
Coupled Reactions

Example: Nitrogen oxidation

\[
\frac{dN_1}{dt} = -K_{12}N_1 \quad \text{N}_1 = \text{NH}_3\text{-N}
\]

\[
\frac{dN_2}{dt} = K_{12}N_1 - K_{23}N_2 \quad \text{N}_2 = \text{NO}_2\text{-N}
\]

\[
\frac{dN_3}{dt} = K_{23}N_2 \quad \text{N}_3 = \text{NO}_3\text{-N}
\]

If N’s are measured as molar quantities, or atomic mass, then successive K’s are equal and opposite
Mixed Order—Saturation Kinetics
(Menod kinetics)

Example: algal uptake of nutrients—focus on algae

\[
\frac{dc}{dt} = \frac{kS}{S + S_o}
\]

\(c = \) algal concentration
\(S = \) substrate concentration
\(S_o = \) half-saturation const

\(S \ll S_o \implies \frac{dc}{dt} \approx \frac{kS}{S_o} = k'S\) \hspace{1cm} (1st Order)

\(S \gg S_o \implies \frac{dc}{dt} \approx k\) \hspace{1cm} (0th Order)
1 Wrap-up

Molecular diffusivities

\[ D = \frac{d\sigma^2}{2\ell m} \]  
Molecular motion; Eulerian frame

\[ D = \frac{d\sigma^2}{2dt^2} \]  
Method of moments

\[ D = u^2 \int_0^\infty R(\tau) d\tau \]  
Molecular motion; Lagrangian frame

D is “small” ~ 1x10^{-5} cm²/s for water

Inst. point source solutions are Gaussian; other solutions built from

- Spatial and temporal integration, coordinate translation, linear source/sink terms