Modeling Pollution

Transport and transfer processes.

Solvent phase (soil, air, water) that contains the solute (pollutant).

The amount of solute suspended, dissolved or otherwise contained in the solvent is usually expressed as a concentration.

Concentrations are expressed in a variety of units.

(1) Volumetric mass/volume (mg/L)
(2) massic mass/mass (ppm)
(3) Molarity (Volumetric; moles/volume)
(4) Molality (massic: moles/mass)
(5) Mole fraction (massic: moles/moles)
(6) Equivalents (mole * valence/volume)
(7) Activity (disintegrations per second/volume or /mass)

Most common in environmental flow and transport models are volumetric and massic. The others are also used and in most cases are easily interchangeable

Non-reactive pollutants

Non-reactive pollutants are pollutants that <u>do</u> <u>not</u> undergo changes, exchanges, or reactions while traversing the region of interest.

Solutes are constituents that are soluble in the solvent or larger aggregates that do not constitute a distinct mobile phase from the transporting or host medium

Examples are chemicals dissolved in water, solids suspended in water (liquid-solid emulsion), oil dispersed in water (liquid-liquid emulsion), water dispersed in air (liquid-gas emulsion), nitrogen dissolved in air (mixture).

Examples of systems that are not strictly solvent-solute pairs is oil-water system where each liquid has a distinct phase (oil slick in an estuary). Such a system is called a two-phase (multi-phase) system.

Transport mechanisms

Advection is the transport of solutes by motion of the host fluid.

If the host fluid is "driven" by density gradients the motion is called natural convection.

If the host fluid is "driven" by pressure gradients the motion is called forced convection.

Diffusion is the mixing of solutes by Brownian motion processes. Net transport is proportional to concentration gradients.

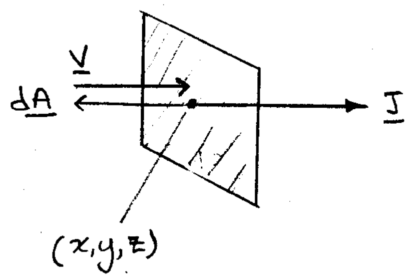
Dispersion is the mixing of solutes by small and large scale variations in the velocity field caused by shear flow, turbulent fluctuations, and braided flow paths. Net transport is usually proportional to concentration gradients.

Shear induced dispersion (open channel & pipe flow)

turbulent diffusion (open flows)

hydrodynamic dispersion (porous media)

Flux is the amount of a quantity (mass, momentum, energy) that passes a point in space per unit area per unit time



$\underline{J}$ flux vector
$\underline{V}$ velocity vector
$\underline{dA}$ area vector
φ quantity per unit volume of interest

Usually mass flows are of greatest interest

mass flux is mass per unit time per unit area that passes the point (x, y, z)

advective flux: $\dfrac{c\,\underline{V}\cdot\underline{dA}}{\underline{dA}} = \underline{J}$ $\quad J = \varphi U$ (mass flux)
$\quad = cU$ (contaminant flux)

diffusive flux: Usually Fick's first law of diffusion is assumed to apply

diffusive flux: $\underline{J} = -D\left(\frac{\partial c}{\partial x}\underline{i}, \frac{\partial c}{\partial y}\underline{j}, \frac{\partial c}{\partial z}\underline{k}\right) = -D\nabla c$

dispersive flux: Most models of dispersion use a Fickian-type flux law

$$\underline{J} = -\underline{D}_h \left(\frac{\partial c}{\partial x} \underline{i}, \frac{\partial c}{\partial y} \underline{j}, \frac{\partial c}{\partial z} \underline{k} \right) = -\underline{D}_h \bullet \nabla c$$

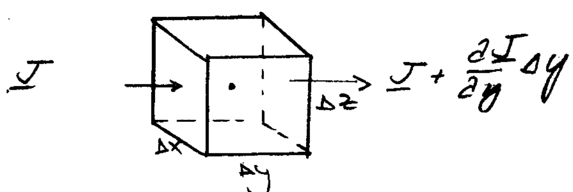
Usually the diffusive flux and dispersive flux are combined as

$$\underline{J} = -\underline{D} \bullet \nabla c$$

$$\underline{D} = \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \longleftarrow$$ Dispersion matrix and the individual elements are dispersion coefficients

Advection

Now consider an element in space, and apply the transport theorem assuming the only mechanism is advection.



$$0 = \frac{\partial}{\partial t} \int_{CV} c \, d\forall + \int_{C.S.} c \, (\underline{V} \cdot d\underline{A})$$

Observe that $\int_{C.S.} c(\underline{V} \cdot d\underline{A})$ is identical to $\int_{C.S.} \underline{J} \cdot d\underline{A}$

$$0 = \frac{\partial c}{\partial t} \Delta x \Delta y \Delta z + \left(\frac{\partial J}{\partial x} + \frac{\partial J}{\partial y} + \frac{\partial J}{\partial z} \right) \Delta x \Delta y \Delta z$$

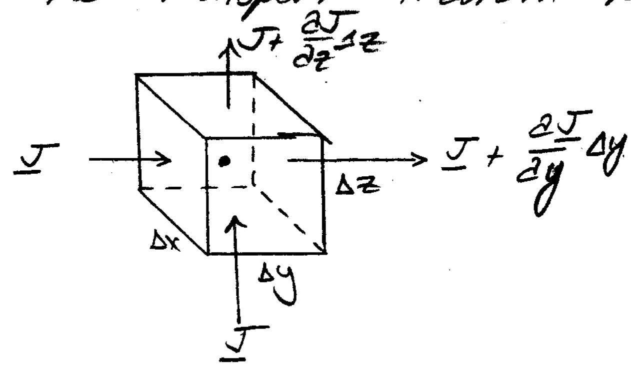
This principle is fundamental to linking the Reynold's Transport theorem to pollutant transport.

$$\therefore \quad \frac{\partial c}{\partial t} = -\nabla \cdot (c\underline{V})$$

OR $$\underline{\underline{0 = \frac{\partial c}{\partial t} + \nabla \cdot c\underline{V}}} \longleftarrow$$ Fundamental equation of advective transport

Diffusion

Similar to advection one can study an element in space and apply the transport theorem to the flux term



$$0 = \frac{d}{dt}\int_{CV} c\,d\forall + \int_{C.S.} \underline{J}\cdot d\underline{A}$$

$$0 = \frac{\partial c}{\partial t}\Delta x\Delta y\Delta z + \left(\frac{\partial J}{\partial x} + \frac{\partial J}{\partial y} + \frac{\partial J}{\partial z}\right)\Delta x\Delta y\Delta z$$

$$0 = \frac{\partial c}{\partial t} + \nabla\cdot\underline{J} = \frac{\partial c}{\partial t} + \underbrace{\nabla\cdot(-D\,\nabla c)}$$

in one-dimension to illustrate the structure we have

$$\frac{\partial}{\partial x}\left(-D\frac{\partial c}{\partial x}\right)$$

Typically the diffusion coefficient is independent of position so we write $-D\frac{\partial^2 c}{\partial x^2}$

$\therefore$

$$0 = \frac{\partial c}{\partial t} - \nabla\cdot(D\nabla c) \longleftarrow \text{Fundamental equation of diffusion.}$$

Diffusion is typically assumed to be an isotropic process so the 3-D diffusion equation is

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right)$$

Advection-Dispersion

When several processes are combined, a net flux term is used:

$$\underline{J} = c\underline{V} - D \cdot \nabla c$$

and the mass balance is

$$0 = \frac{\partial}{\partial t}\int_{CV} c\, d\forall + \int_{C.S.} \underline{J} \cdot d\underline{A}$$

$$0 = \frac{\partial c}{\partial t}\Delta x \Delta y \Delta z + \nabla \cdot \left(c\underline{V} - \underline{D} \cdot \nabla c \right) \Delta x \Delta y \Delta z$$

In an isotropic case the 3D result is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_{xx}\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_{yy}\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_{zz}\frac{\partial c}{\partial z}\right) - \frac{\partial}{\partial x}(cu) - \frac{\partial}{\partial y}(cv) - \frac{\partial}{\partial z}(cw).$$

Now why all the fluid mechanics? The dispersion coefficients usually are related to the velocity field

$$J_{shear} = -\underbrace{\varepsilon_{shear}}_{\text{velocity dependent}}\frac{\partial \bar{c}}{\partial x} \qquad J_{turbulent} = -\underbrace{\varepsilon_{turb}}_{\text{velocity dependent}}\frac{\partial c}{\partial x}$$

$$J_{hydrodynamic} = -\underbrace{\varepsilon_{hydro}}_{= \underbrace{\alpha_L}_{\text{dispersivity}} U}\frac{\partial c}{\partial x}$$

∴ Solution of advection-dispersion equations requires detailed knowledge of velocity field ⇒ requires ability to solve models of <u>flow</u>

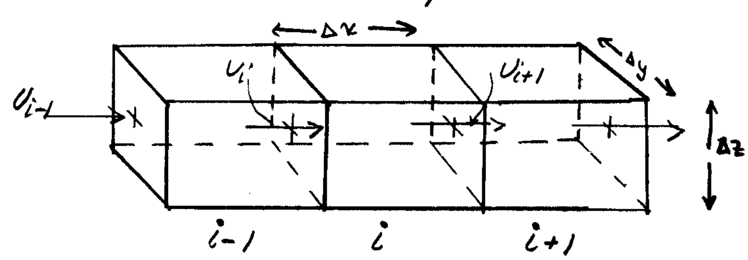
Cell Balance Method

An alternative to Reynold's transport theorem is the cell balance method – fundamentally it is identical.

The cell balance method is more intuitaive, and has the advantage of directly producing difference equations that are necessary for obtaining numerical solutions to flow and transport problems.

Cell balance method assumes that the region of interest can be represented by interconnected cells. The quantities of interest are assumed to have uniform properties in the cell (complete mixing) and enter and leave the cell across the cell face.

Use advection as an example



In cell balance models the equivalent to Reynold's Transport theorem is a material balance

Mass stored in a cell: $C_i \Delta x \Delta y \Delta z$

Rate of change of mass stored in a cell: $\frac{\Delta C_i}{\Delta t} \Delta x \Delta y \Delta z$

Rate of mass entering cell: $C_{i-1} U_i \Delta y \Delta z$

Rate of mass leaving cell: $C_i U_{i+1} \Delta y \Delta z$

Cell balance

$$0 = \frac{\Delta c_i}{\Delta t}\Delta x \Delta y \Delta z - c_i U_{i+1}\Delta y \Delta z + c_{i-1} U_i \Delta y \Delta z$$

Divide by cell volume and rearrange

$$\frac{\Delta c_i}{\Delta t} = \frac{c_{i-1}U_i - c_i U_{i+1}}{\Delta x}$$

Now take the limit as $\Delta t \to 0$ and $\Delta x \to 0$;

$$\frac{\partial c_i}{\partial t} = -\frac{\partial cU}{\partial x}$$ (Which is the same result using Reynold's transport theorem)

So what? Look at the equation just before the limiting process. It is a difference equation that provides a recipie to predict the time variation of c, in terms of flow characteristics. It is actually an upwind finite-difference approximation for the PDE that describes advective transport.

We could write these difference equations for all cells in the region of interest and have a model to predict behavior; for example

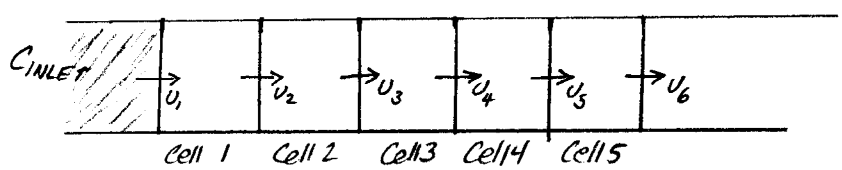
$$c_i(t+\Delta t) = c_i(t) + \frac{\Delta c_i}{\Delta t}\cdot \Delta t = c_i^t + \frac{\Delta t}{\Delta x}\left(c_{i-1}^t U_i^t - c_i^t U_{i+1}^t\right)$$

These concepts are the basis of most flow and transport models currently in use.

To complete the cell balance model one needs to specify boundary conditions (how does the region of interest behave at its inlet and outlet) and initial conditions (how does the region of interest look when we start).

If the velocity field is unknown, then a similar approach using fluid mechanics principles is used to determine values of U_i^t.

To complete the simple example here we will assume the upstream boundary is $C = C_{INLET}$, and the downstream boundary is a zero reflection boundary. A 5-cell model could be written as follows



$$C_1^{t+\Delta t} = C_1^t + \frac{\Delta t}{\Delta x}\left(\underline{C_{INLET}}\,U_1 - C_1^t U_2\right)$$
$$C_2^{t+\Delta t} = C_2^t + \frac{\Delta t}{\Delta x}\left(C_1^t U_2 - C_2^t U_3\right)$$
$$C_3^{t+\Delta t} = C_3^t + \frac{\Delta t}{\Delta x}\left(C_2^t U_3 - C_3^t U_4\right)$$
$$C_4^{t+\Delta t} = C_4^t + \frac{\Delta t}{\Delta x}\left(C_3^t U_4 - C_4^t U_5\right)$$
$$C_5^{t+\Delta t} = C_5^t + \frac{\Delta t}{\Delta x}\left(C_4^t U_5 - C_5^t \underline{U_6}\right)$$

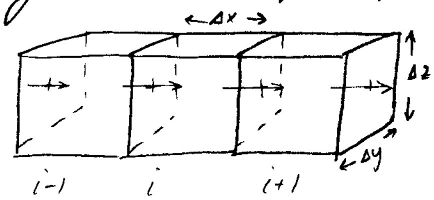
Downstream B.C. $U_5 = U_6$

This model is easily programmed into a computer spreadsheet or computer program.

Cell Balance Method – Diffusion

In the advection example of the cell balance method we wrote a balance for concentration in the cell and related it to the flux of concentration into/out of the cell.

We can apply the same principle to diffusion



Mass in cell $\quad C_i \Delta x \Delta y \Delta z$; Rate of change of mass in cell $\quad \frac{\Delta C_i}{\Delta t} \Delta x \Delta y \Delta z$

Mass entering cell

$$D\left(\frac{C_{i-1} - C_i}{\Delta x}\right) \Delta y \Delta z \quad \text{(Fick's first law)}$$

Mass leaving cell $\quad D\left(\frac{C_i - C_{i+1}}{\Delta x}\right) \Delta y \Delta z$

Cell Balance: $\quad 0 = \frac{\Delta C_i}{\Delta t} \Delta x \Delta y \Delta z + D \frac{C_{i-1} - C_i}{\Delta x} \Delta y \Delta z - D \frac{C_i - C_{i+1}}{\Delta x} \Delta y \Delta z$

divide by $\Delta x \Delta y \Delta z$, rearrange

$$\frac{\Delta C_i}{\Delta t} = \underbrace{D\left(\frac{C_{i-1} - 2C_i + C_{i+1}}{\Delta x^2}\right)}$$

In $\lim \Delta t \to 0, \Delta x \to 0$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

(Same result as Reynold's transport theorem)

If D varies in space, various averaging schemes are used (we will make use of spatial variation in groundwater flow – a diffusion equation!)

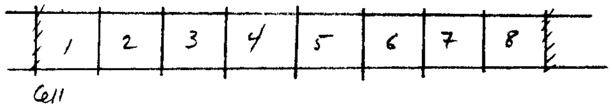
Written as an explicit update

$$C_i^{t+\Delta t} = C_i^t + D\frac{\Delta t}{\Delta x^2}\left(C_{i-1}^t - 2C_i^t + C_{i+1}^t\right)$$

implicit:

$$C_i^{t+\Delta t} - D\frac{\Delta t}{\Delta x^2}\left(C_{i-1}^{t+\Delta t} - 2C_i^{t+\Delta t} + C_{i+1}^{t+\Delta t}\right) = C_i^t$$

Now to complete the model, we simply write balances for all cells. For example consider 8 cells



$$c_1^{t+\Delta t} = c_1^t + D\frac{\Delta t}{\Delta x^2}(c_0 - 2c_1 + c_2)$$
$$c_2^{t+\Delta t} = c_2^t + D\frac{\Delta t}{\Delta x^2}(c_1 - 2c_2 + c_3)$$
$$c_3^{t+\Delta t} = c_3^t + D\frac{\Delta t}{\Delta x^2}(c_2 - 2c_3 + c_4)$$
$$c_4^{t+\Delta t} = c_4^t + D\frac{\Delta t}{\Delta x^2}(c_3 - 2c_4 + c_5)$$
$$c_5^{t+\Delta t} = c_5^t + D\frac{\Delta t}{\Delta x^2}(c_4 - 2c_5 + c_6)$$
$$c_6^{t+\Delta t} = c_6^t + D\frac{\Delta t}{\Delta x^2}(c_5 - 2c_6 + c_7)$$
$$c_7^{t+\Delta t} = c_7^t + D\frac{\Delta t}{\Delta x^2}(c_6 - 2c_7 + c_8)$$
$$c_8^{t+\Delta t} = c_8^t + D\frac{\Delta t}{\Delta x^2}(c_7 - 2c_8 + c_9)$$

c_0 & c_9 are unknown, boundary conditions

c_0 = known value (Dirchlet boundary condition

$c_9 = c_8$ (no-flux boundary condition)

Easily programmed into a spreadsheet.

Stability – experimentation will show that if $D\frac{\Delta t}{\Delta x^2} \le \frac{1}{2}$ then the numerical solution will be stable and convergent (converges to corresponding PDE). If this requirement is violated solution will be unstable.

An implicit formulation is unconditionally stable but requires solution of a system of linear equations,

$$c_1^{t+\Delta t} - D\frac{\Delta t}{\Delta x^2}(c_0^{t+\Delta t} - 2c_1^{t+\Delta t} + c_2^{t+\Delta t}) = c_1^t$$
$$c_2^{t+\Delta t} - D\frac{\Delta t}{\Delta x^2}(c_1^{t+\Delta t} - 2c_2^{t+\Delta t} + c_3^{t+\Delta t}) = c_2^t$$
$$c_3^{t+\Delta t} - D\frac{\Delta t}{\Delta x^2}(c_2^{t+\Delta t} - 2c_3^{t+\Delta t} + c_4^{t+\Delta t}) = c_3^t$$
$$c_4^{t+\Delta t} - D\frac{\Delta t}{\Delta x^2}(c_3^{t+\Delta t} - 2c_4^{t+\Delta t} + c_5^{t+\Delta t}) = c_4^t$$
$$c_5^{t+\Delta t} - D\frac{\Delta t}{\Delta x^2}(c_4^{t+\Delta t} - 2c_5^{t+\Delta t} + c_6^{t+\Delta t}) = c_5^t$$
$$c_6^{t+\Delta t} - D\frac{\Delta t}{\Delta x^2}(c_5^{t+\Delta t} - 2c_6^{t+\Delta t} + c_7^{t+\Delta t}) = c_6^t$$
$$c_7^{t+\Delta t} - D\frac{\Delta t}{\Delta x^2}(c_6^{t+\Delta t} - 2c_7^{t+\Delta t} + c_8^{t+\Delta t}) = c_7^t$$
$$c_8^{t+\Delta t} - D\frac{\Delta t}{\Delta x^2}(c_7^{t+\Delta t} - 2c_8^{t+\Delta t} + c_9^{t+\Delta t}) = c_8^t$$

A third stable formulation is called the Crank-Nicolson scheme. It is obtained by a weighted average in time of the right hand side of the difference equation

$$\frac{\Delta C_i}{\Delta t} = \alpha D \left(\frac{C_{i-1}^{t+\Delta t} - 2C_i^{t+\Delta t} + C_{i+1}^{t+\Delta t}}{\Delta x^2} \right) + (1-\alpha) D \left(\frac{C_{i-1}^{t} - 2C_i^{t} + C_{i+1}^{t}}{\Delta x^2} \right)$$

After rearrangement

$$C_i^{t+\Delta t} - \alpha D \frac{\Delta t}{\Delta x^2} \left(C_{i-1}^{t+\Delta t} - 2C_i^{t+\Delta t} + C_{i+1}^{t+\Delta t} \right) = C_i^t + (1-\alpha) D \left(C_{i-1}^t - 2C_i^t + C_{i+1}^t \right)$$

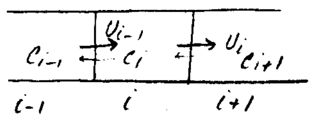
$\alpha = 0$ explicit
$\alpha = 1$ implicit
$\alpha = 1/2$ Crank-Nicolson

For parabolic (diffusion) equations the CN scheme is unconditionally stable, convergent, and relatively accurate

Spreadsheet construction –

Advection + Dispersion

Cell Balance Method For Advection (modified for arbitrary flow direction)



Cell mass : $\frac{\Delta C_i}{\Delta t} \Delta x \Delta y \Delta z$

Advective Cell flux : $\frac{1}{2} U_{i-1} \left[\left(1 + \frac{U_{i-1}}{|U_{i-1}|}\right) C_{i-1} + \left(1 - \frac{U_{i-1}}{|U_{i-1}|}\right) C_i \right] \Delta y \Delta z \; -$

$\frac{1}{2} U_i \left[\left(1 + \frac{U_i}{|U_i|}\right) C_i + \left(1 - \frac{U_i}{|U_i|}\right) C_{i+1} \right] \Delta y \Delta z$

Dispersive Cell flux : $D \left(\frac{C_{i-1} - 2C_i + C_{i+1}}{\Delta x} \right) \Delta y \Delta z$

Combine to obtain

$$\frac{\Delta C_i}{\Delta t} \Delta x \Delta y \Delta z = D \left(\frac{C_{i-1} - 2C_i + C_{i+1}}{\Delta x} \right) \Delta y \Delta z + \frac{1}{2} U_{i-1} \left[\left(1 + \frac{U_{i-1}}{|U_{i-1}|}\right) C_{i-1} + \left(1 - \frac{U_{i-1}}{|U_{i-1}|}\right) C_i \right] \Delta y \Delta z$$

$$- \frac{1}{2} U_i \left[\left(1 + \frac{U_i}{|U_i|}\right) C_i + \left(1 - \frac{U_{i+}}{|U_i|}\right) C_{i+1} \right] \Delta y \Delta t$$

Divide by $\Delta x \Delta y \Delta z$

$$\frac{\Delta C_i}{\Delta t} = \underbrace{\frac{D}{\Delta x^2}\left(C_{i-1} - 2C_i + C_{i+1}\right)}_{\text{Dispersion}} + \underbrace{\frac{1}{2\Delta x}\left(U_{i-1}\left[\left(1 + \frac{U_{i-1}}{|U_{i-1}|}\right) C_{i-1} + \left(1 - \frac{U_{i-1}}{|U_{i-1}|}\right) C_i \right] - U_i \left[\left(1 + \frac{U_i}{|U_i|}\right) C_i + \left(1 - \frac{U_i}{|U_i|}\right) C_{i+1} \right] \right)}_{\text{Advection}}$$

↳ If dispersion varies spatially this term is modified as

$$\frac{D_{i-1} + D_i}{2\Delta x}\left(\frac{C_{i-1} - C_i}{\Delta x}\right) - \frac{D_i + D_{i+1}}{2\Delta x}\left(\frac{C_i - C_{i+1}}{\Delta x}\right)$$