The equation describing the concentration of any tracer in an elongated reactor is known as the advection-dispersion equation and may be written as:

\[ \frac{D^2}{Dx^2}c = 0 \]

Schematic of a mixed flow reactor
(both advection and dispersion must be accounted for)

The system is defined to be coincident with the reactor. Therefore concentrations at \( c_{n-1} \) and \( c_{n+1} \) which arise when writing mass balances on each segment are outside the defined system. These are obtained using boundary conditions.

**NOTES**

The concentrations computed in this document are at the interfaces between segments. These locations are referred to in this document as "nodes".
Define the "system" to be coincident with the reactor. Break the system into some number "n" of segments or slices, each with a thickness $\Delta x$.

We will write a mass balance on a substance, "s" on each segment having a finite length, $\Delta x$.

In words: accumulation within segment = advection in - advection out - dispersion in + dispersion out - decay within segment

We will use Fick’s first Law to describe dispersive flux: 

$$J_{\text{dispersive}} = -D \frac{\partial c}{\partial x}$$

The negative is used so that a positive dispersive flux will occur in the direction of decreasing concentration.

$$V \frac{\Delta c}{\Delta t} = Q \cdot c(x) - Q \left[ c(x) + \frac{\partial}{\partial x} c(x) \right] \Delta x - \left( D A_c \frac{\partial}{\partial x} c(x) \right) + D A_c \left( \frac{\partial}{\partial x} c(x) + \frac{\partial}{\partial x^2} c(x) \Delta x \right) - k V \cdot c$$

Now, if we combine terms we get:

$$V \frac{\Delta c}{\Delta t} = -Q \left( \frac{\partial}{\partial x} c(x) \right) \Delta x + D A_c \frac{\partial^2}{\partial x^2} c \cdot \Delta x - k V \cdot c$$

divide thru by the volume $V = A_c \cdot \Delta x$

$$\frac{\Delta c}{\Delta t} = \frac{-Q}{A_c \cdot \Delta x} \left( \frac{\partial}{\partial x} c(x) \right) \Delta x + \frac{D A_c}{A_c \cdot \Delta x} \frac{\partial^2}{\partial x^2} c \cdot \Delta x - k \cdot c$$

Now cancel terms and let $\Delta x$ and $\Delta x$ shrink to zero, note that $U = \frac{Q}{A_c}$

$$\frac{\partial}{\partial t} c = -U \frac{\partial}{\partial x} c(x) + D \frac{\partial^2}{\partial x^2} c - k \cdot c$$

Now assume the system is operating at steady state so the left side of the equation equals zero. This results in a 2nd order, ordinary, differential equation

$$0 = -U \frac{d}{dx} c(x) + D \frac{d^2}{dx^2} c - k \cdot c$$
BOUNDARY CONDITIONS:

Inlet boundary condition: In this problem the contaminant enters the tank through a pipe and we assume dispersion is negligible. Thus the mass of contaminant entering the tank per time via advection must equal the mass carried away by advection and dispersion.

\[ Q \cdot c_{in} = Q \cdot c_{o} - D \cdot A_c \frac{dc}{dx} \]

Outlet boundary condition: We specify that the concentration of the chemical does not change as it crosses the exit boundary at L. In equation form:

\[ \frac{dc}{dx}(L, t) = 0 \]

NUMERICAL SOLUTION TECHNIQUE - finite difference approach - divide the reactor into a number of segments, write a mass balance on each segment. Treat derivative terms as finite difference approximations. In this document we will use a centered difference approximation for both derivative terms. Other possible approximations are a forward difference and backward difference scheme.

\[ 0 = D \left( \frac{c_{i+1} - 2 \cdot c_{i} + c_{i-1}}{\Delta x^2} \right) - U \left( \frac{c_{i+1} - c_{i-1}}{2 \cdot \Delta x} \right) - k \cdot c_{i} \]

We can write an equation of this form for each segment. Now separate variables and rewrite the equation with separate terms for each internal node \( c_i \), \( c_{i-1} \) and \( c_{i+1} \)

\[ - \left( \frac{D}{u \cdot \Delta x} + \frac{1}{2} \right) \cdot c_{i-1} + \left( \frac{2 \cdot D}{U \cdot \Delta x} + \frac{k \cdot \Delta x}{U} \right) \cdot c_{i} - \left( \frac{D}{U \cdot \Delta x} - \frac{1}{2} \right) \cdot c_{i+1} = 0 \]

Notice that each internal node equation contains 3 unknowns, \( c_{i-1} \), \( c_{i} \), \( c_{i+1} \). If we divide the reactor into n segments we will have n+2 unknowns \( c_0 \) through \( c_n \). If we write an equation for each internal node plus one for each “boundary node” that will give n equations. Because each unknown can appear in as many as 3 equations we will need to solve the entire system at once using matrix algebra techniques (or do some hellaceous algebra !)
**Inlet boundary equation**: If we write a standard node equation for the inlet concentration, \( c_0 \), we will end up with an equation containing an unknown not in the system, \( c_{-1} \)

\[
-\left( \frac{D}{u \Delta x} + \frac{1}{2} \right) c_{-1} + \left( \frac{2 D}{U \Delta x} + \frac{k \Delta x}{U} \right) c_0 - \left( \frac{D}{U \Delta x} - \frac{1}{2} \right) c_1 = 0
\]

We can eliminate this unknown by making use of the inlet boundary condition:

\[
Q c_{\text{in}} = Q c_0 - D A_c \frac{d}{dx} c_0
\]

Note: \( \frac{d}{dx} c_0 \) may be viewed as \( \frac{d}{dx} c \) evaluated at \( c_0 \)

Now use a centered difference approximation of the derivative term to write

\[
Q c_{\text{in}} = Q c_0 - D A_c \frac{c_1 - c_{-1}}{2 \Delta x}
\]

Solving for \( c_{-1} \) we get:

\[
 c_{-1} = c_1 + \frac{2 \Delta x U}{D} c_{\text{in}} - \frac{2 \Delta x U}{D} c_0
\]

Substitute the expression for \( c_{-1} \) into the standard node equation to obtain an equation at the inlet in terms of unknowns inside the system and \( c_{\text{in}} \) which is known.

\[
\left( \frac{2 D}{U \Delta x} + \frac{k \Delta x}{U} + 2 + \frac{\Delta x U}{D} \right) c_0 - \left( \frac{D}{U \Delta x} \right) c_1 = \left( 2 + \frac{\Delta x U}{D} \right) c_{\text{in}}
\]

where \( c_{\text{in}} \), the concentration entering the reactor, is assumed known.

**Outlet boundary condition**

If we write a standard node equation for the \( n^{\text{th}} \) node we incur an unknown, \( c_{n-1} \), not within the system. In a fashion similar to the inlet we will handle this using the downstream boundary condition.

\[
-\left( \frac{D}{u \Delta x} + \frac{1}{2} \right) c_{n-1} + \left( \frac{2 D}{U \Delta x} + \frac{k \Delta x}{U} \right) c_n - \left( \frac{D}{U \Delta x} - \frac{1}{2} \right) c_{n-1} = 0
\]
Recall the outlet boundary condition: \( \frac{d}{dx} c(L, t) = 0 \). In words this says that the concentration across the reactor exit does not change, thus \( c_{n-1} = c_{n+1} \). If we make this substitution into our standard node equation we get:

\[
\left( \frac{D}{U \cdot \Delta x} \right) c_{n-1} + \left( \frac{2 D}{U \cdot \Delta x} + \frac{k \cdot \Delta x}{U} \right) c_n = 0
\]

**Summary so far:**

O.K. we break our reactor (could be a river) into some number, \( n \), of segments.

Using the advection-dispersion equation (really just a mass balance) as the governing PDE we write a mass balance on each segment.

Because we are doing a numerical solution we employ a finite difference approximation of the governing PDE. We choose a centered difference approximation for the first and second derivatives in the PDE.

We develop physically realistic boundary conditions which are employed to obtain equations for the concentration at the inlet and outlet of the reactor.

At this point we can write an equation for the inlet, one for each segment, and one for the outlet.

\[
\left( \frac{2 D}{U \cdot \Delta x} + \frac{k \cdot \Delta x}{U} + 2 \right) c_0 - \left( \frac{D}{U \cdot \Delta x} \right) c_1 = \left( 2 - \frac{\Delta x U}{D} \right) c_{in} \quad \text{.....inlet equation, 1}
\]

\[
- \left( \frac{D}{U \cdot \Delta x} \right) c_{i-1} + \left( \frac{2 D}{U \cdot \Delta x} + \frac{k \cdot \Delta x}{U} \right) c_i - \left( \frac{D}{U \cdot \Delta x} - \frac{1}{2} \right) c_{i+1} = 0 \quad \text{..... node equation, 1 for each segment}
\]

\[
- \left( \frac{D}{U \cdot \Delta x} \right) c_{n-1} + \left( \frac{2 D}{U \cdot \Delta x} + \frac{k \cdot \Delta x}{U} \right) c_n = 0 \quad \text{..... outlet equation, 1}
\]

An examination of the equations above indicates that if the system properties, \( \Delta x \), \( D \), \( U \) and \( k \) are constant throughout the reactor then we have a set of \( n \) linear equations with \( n \) unknowns. The coefficients for each equation for the internal equations are the same. These can be solved using matrix techniques.
An example:

\[ Q := 0.001 \times 10^6 \text{gal/day} \quad H := 10 \text{ ft} \quad B := 10 \text{ ft} \quad n := 8 \quad k := 0.01 \text{ day}^{-1} \]

\[ D := 0.0002 \text{ ft}^2 / \text{sec} \quad U := \frac{Q}{HB} \quad \text{Length} := 100 \text{ ft} \quad \Delta x := \frac{\text{Length}}{n} \quad c_{in} := 100 \text{ mg/liter} \]

\[
\text{segments} := \frac{\text{Length}}{\Delta x} \quad \text{segments} = 8
\]

\[ a := \left( \frac{2D}{U \Delta x} + \frac{k \Delta x}{U} + 2 + \frac{\Delta x \cdot U}{D} \right), \quad b := \frac{D}{U \Delta x}, \quad \text{and} \quad d := \left( 2 + \frac{\Delta x \cdot U}{D} \right) \]

\[ \text{......inlet equation coefficients} \]

\[ e := \left( \frac{D}{U \Delta x} + \frac{1}{2} \right), \quad f := \frac{2D}{U \Delta x} + \frac{k \Delta x}{U}, \quad \text{and} \quad g := \frac{D}{U \Delta x} - \frac{1}{2} \]

\[ h := \left( \frac{D}{U \Delta x} \right), \quad j := \left( \frac{2D}{U \Delta x} + \frac{k \Delta x}{U} \right) \]

\[ \text{......outlet equation coefficients} \]

\[ U \cdot \Delta x \quad D = 0.967 \]

Compute stability parameter for chosen parameters.
If greater than 2.0 system will become unstable.

Now, arrange the equations in matrix format. Note that the coefficient matrix is tridiagonal

\[
[\text{coefficient matrix}] \cdot [\text{unknown vector}] = [\text{external loadings vector}]
\]
While there are a variety of ways to solve a set of linear equations we will do it by inverting the coefficient matrix.

\[
\begin{pmatrix}
a & b & 0 & 0 & 0 & 0 & 0 & 0 \\
e & f & g & 0 & 0 & 0 & 0 & 0 \\
0 & e & f & g & 0 & 0 & 0 & 0 \\
0 & 0 & e & f & g & 0 & 0 & 0 \\
0 & 0 & 0 & e & f & g & 0 & 0 \\
0 & 0 & 0 & 0 & e & f & g & 0 \\
0 & 0 & 0 & 0 & 0 & e & f & g \\
0 & 0 & 0 & 0 & 0 & 0 & h & j \\
\end{pmatrix}
\begin{pmatrix}
c_0 \\
c_1 \\
c_2 \\
c_3 \\
c_4 \\
c_5 \\
c_6 \\
c_7 \\
c_8 \\
\end{pmatrix}
= 
\begin{pmatrix}
d \\
c_{\text{in}} \\
\end{pmatrix}
\]

concentration at the interface between segments

\[
c = \begin{pmatrix}
51.46 \\
31.696 \\
19.523 \\
12.025 \\
7.406 \\
4.564 \\
2.8 \\
1.777 \\
0.85 \\
\end{pmatrix}
\text{mg liter^{-1}}
\]
$i := 0..\text{segments}$

$x_j := i \cdot \Delta x$  \text{distance from reactor inlet for each computed concentration}$