V.4

FORMS OF THE ADVECTION-DIFFUSION EQUATION AND THEIR SOLUTIONS

From the derivation presented in Harleman's notes, the basic advection-diffusion equation (ADE) for a non-turbulent fluid is:

$$\frac{dC_A}{dt} = D_{AB}\nabla^2 C_A + \frac{r_A}{\rho} \qquad (1)$$

The last term accounts for production or decay of dissolved component *A*. Rate r_A is expressed in density units, hence the division by the bulk density ρ. Eq.1 fits the general form of the Reynold Transport Theorem for a differential control volume that moves with the fluid:

$$\frac{d\Phi_{sys}}{dt} = [Flux\ of\ \Phi]_{cv}^{out} - [Flux\ of\ \Phi]_{cv}^{in} + [Rate\ of\ Change\ of\ \Phi\ in\ CV] \qquad (2)$$

The net flux through a CV moving with the flow is due to diffusion and is expressed for the differential CV as the gradient of diffusive flux, which for a constant D_{AB} is proportional to the second-order gradient of concentration. Expand the substantial derivative on the LHS of Eq.1 to obtain the useful form:

$$\frac{\partial C_A}{\partial t} + \tilde{u}\cdot\nabla C_A = D_{AB}\nabla^2 C_A + \frac{r_A}{\rho} \qquad (3)$$

Harleman provides us with Eq.3 in full Cartesian notation as well as in cylindrical coordinates. We can also imagine that spherical coordinates might be handy, and a number of texts provide the equation in that form.

Before moving on, note that Harleman (without specifically stating so) invokes the assumption of incompressibility ($\nabla u = 0$) in order to eliminate terms that contain ∇u. If we are working in atmospheric systems for which incompressibility cannot be reasonably invoked, a more complex form of the A-D equation results. This complex form is not amenable to any analytical solution. Largely for this reason, air pollution modelers developed alternate approaches based on gaussian statistical distributions of pollutants. These are known as "gaussian plume models", and it is shown in Ch.2 of Harleman's notes that there is a direct connection between gaussian models and the more conventional A-D models. We will limit ourselves to incompressible fluids. However, even in that domain, we will find use for gaussian distributions in calibrating model parameters.

At this point, Harleman begins to discuss simple solution techniques for the ADE. However, we are sufficiently well versed in turbulent phenomena to go ahead and discuss the turbulent form of the ADE, and then address all the solution methods together. Without much fuss we can adapt Eq.1 for the turbulent case using a Reynolds time-averaging approach. As with the Navier-Stokes equations, the time-averaged form of the ADE ends up the same as the instantaneous form of ADE except that time-averaged variables for velocity and concentration are substituted for the instantaneous variables, and, one extra block of turbulent transport terms appear:

$$\frac{d\overline{C}_A}{dt} = -\nabla[Turb.\ Flux\ of\ A] + D_{AB}\nabla^2\overline{C}_A + \frac{r_A}{\rho} \qquad (4)$$

which, with our knowledge of the general form of time-averaged eddy transport, we can rewrite as:

$$\frac{d\overline{C}_A}{dt} = -\nabla[\overline{u_i' C_A'}] + D_{AB}\nabla^2\overline{C}_A + \frac{r_A}{\rho} \qquad (5)$$

where u_i' is either u', v', or w', as appropriate.

As with momentum, we can describe eddy transport of A via the Fickian Analogy for each of the three coordinate directions:

$$\overline{u'C_A'} = -K_{Ax}[\partial\overline{C}_A/\partial x]$$
$$\overline{v'C_A'} = -K_{Ay}[\partial\overline{C}_A/\partial y]$$
$$\overline{w'C_A'} = -K_{Az}[\partial\overline{C}_A/\partial z]$$

In general, $K_{Ax} \neq K_{Ay} \neq K_{Az}$, because turbulence is anisotropic. As with any turbulent diffusivity, we expect K_{Ai} to vary with space in all three directions, and with time if the system is unsteady. This rather unwieldy, since it is unlikely we would ever have enough information about a natural water to completely specify all of these functional relationships. Many an engineer and many a graduate student has been kept busy devising new ways to model these parameters. In this course we will discuss a few of the methods for estimating these parameters from field experiments. Otherwise, we will focus more on the fundamental aspects of the problems without spending too much time on parameterization, which in any case tends to be very system-specific.

Recognizing that the K_{Ai} coefficients are, in general, functions of x, y, and z, we cannot extract them from the gradient terms the way we did for the true constant D_{AB}. Thus we must write:

$$\frac{d\overline{C}_A}{dt} = \nabla[K_{Ai}\cdot\nabla\overline{C}_A] + D_{AB}\nabla^2\overline{C}_A + \frac{r_A}{\rho} \qquad (6)$$

If the substantial derivative is expanded and the compact notation expanded into full cartesian form, you get Eq.1-30 in Harleman's notes (in which Harleman uses the notation E instead of K for eddy diffusivity).

To begin the process of finding solutions for this rather ungainly looking equation (which occupy the entirety of Crank's book on the subject) we solve the simple one-dimensional diffusion equation, and then build up more complex solutions through the principle of superposition.

Solution of the Diffusion Equation

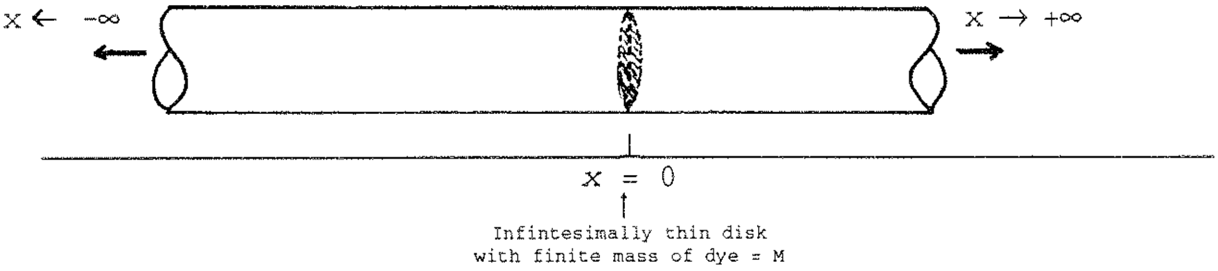
Begin with diffusion only. The governing equation is

$$\frac{\partial C_A}{\partial t} = D_{AB}\nabla^2 C_A \tag{7}$$

This equation is second order but it is *linear*. Linear differential equations allow us a great simplification. If we can define a complex system as a sum of very simple components, then the solution to the complex system is simply a linear combination (a summation) of the solutions of the equations that represent the simpe components. This is known as the Principle of Superposition. Let us see how this works.

Imagine the simplest possible system of Fickian diffusion: a single "slug" of a conservative tracer, concentrated at a single point, in a purely one-dimensional system. We could envision such a system as an infinite pipe filled with stagnant fluid in which we have placed an infinitesimally thin disk of dye tracer:

Figure 1.



After the dye disk is "released", it will begin to spontaneously diffuse outward in both directions. A gradient of concentration will develop in the *x* direction. We assume the disk is uniform, so ther are no initial gradients of concentration in the *x* or *y* directions, and because there is no fluid motion, no such lateral gradients can ever develop in this ideal system. Thus, this system is strictly 1-D and the governing equation reduces to simply

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{8}$$

(We have dropped the subscripts for simplicity). There are several approaches to solving this problem. One of the most direct is as follows. First, define the initial and boundary conditions:

a) Initial: $C \to \infty$ for $x \to 0$
(t = 0) $C = 0$ for $x \neq 0$

b) Boundary: $C \to 0$ for $|x| \to \infty$
(for all t)

For these conditions we can use the Laplace transform to solve Eq.8, which yields

$$C = \frac{B}{\sqrt{t}} \exp - \left[\frac{x^2}{4Dt}\right] \tag{9}$$

where B is a constant that we must evaluate. Try the obvious step of using the boundary and initial conditions. Note that setting $t = 0$ or $C = 0$, or $|x| \to \infty$ does not yield any useful values of B. The only other condition defined for the system is the total mass of dye, M. Use the conservation of this mass to solve for B.

First, relate the mass of dye to the concentration distribution of dye at any time:

$$M = \int_{-\infty}^{+\infty} \rho C A \, dx = \rho A \int_{-\infty}^{+\infty} C \, dx \tag{10}$$

Substitute Eq.9 into Eq.10 to obtain

$$M = \rho A \int_{-\infty}^{+\infty} \frac{B}{\sqrt{t}} \exp - \left[\frac{x^2}{4Dt}\right] dx \tag{11}$$

At this point, if you are a calculus wizard, or if you pore over a table of integral substitutions , you will find that there is a general substitution of the form

$$\int_{-\infty}^{+\infty} e^{-a^2x^2} dx = \frac{\sqrt{\pi}}{a} \tag{12}$$

If we let $a = 1/\sqrt{4Dt}$ we can dramatically simplify Eq.11 and write

$$M = \rho A\left[\frac{\sqrt{\pi}}{1/\sqrt{4Dt}}\right] = \rho AB\frac{\sqrt{4\pi Dt}}{\sqrt{t}} = \rho AB\sqrt{4\pi D} \tag{13}$$

which means that M is time-invariant, as we know it must be. So, rearrange to get

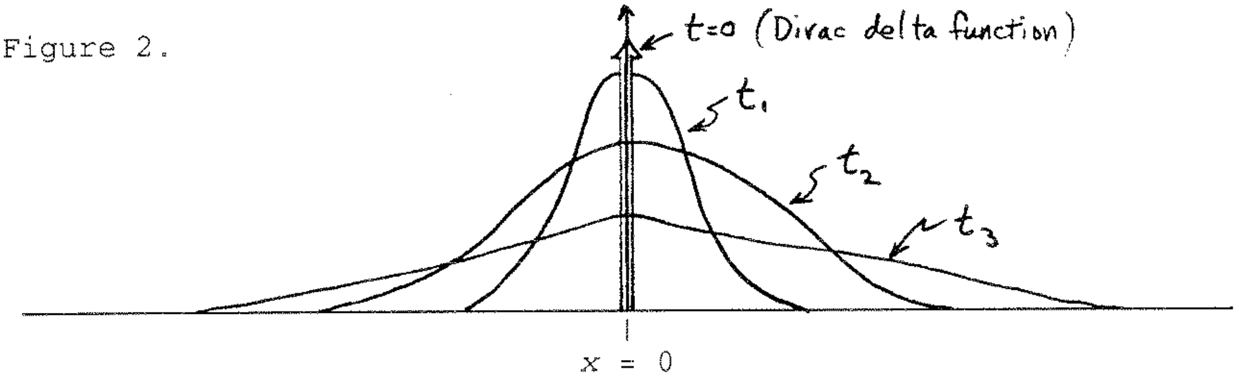
$$B = \frac{M}{\rho A\sqrt{4\pi D}} \tag{14}$$

and substitute Eq.14 into Eq.9

$$C(x,t) = \frac{M}{\rho A\sqrt{4\pi Dt}} \exp-\left[\frac{x^2}{4Dt}\right] \tag{15}$$

Interestingly enough, Eq.15 is a form of the Gaussian (or normal) distribution function. It means that at any time $t > 0$, the mass of dye in the tube is characterized by a Gaussian distribution. This should not surprise us, given that diffusion is a random redistribution of mass. For example, if we plot the concentration of dye as a function of x in the tube at three time-points after the release, we observe something like:

Figure 2.



The area beneath each curve is identical and is proportional to the total mass M.

Admittedly, the instantaneous release of a conservative substance into a 1-D tube of stagnant fluid is not a very exciting system to study. But this system has a nice solution, and is the fundamental component for building up more complex systems via superposition.

Consider for example a somewhat more realistic case in which we place a partition at $x = 0$ in our infinite cylinder. On one side of the partition the cylinder is filled with pure water. On the other side it is filled with dyed water containing dye at concentration $c = c_0$. We wish to describe the diffusion of dye after we remove the partition at $t = 0$.

Again we have a 1-D diffusion problem, but now the initial conditions are

$c = c_0$ for $t \leq 0$, $x < 0$

$c = 0$ for $t \leq 0$, $x \geq 0$

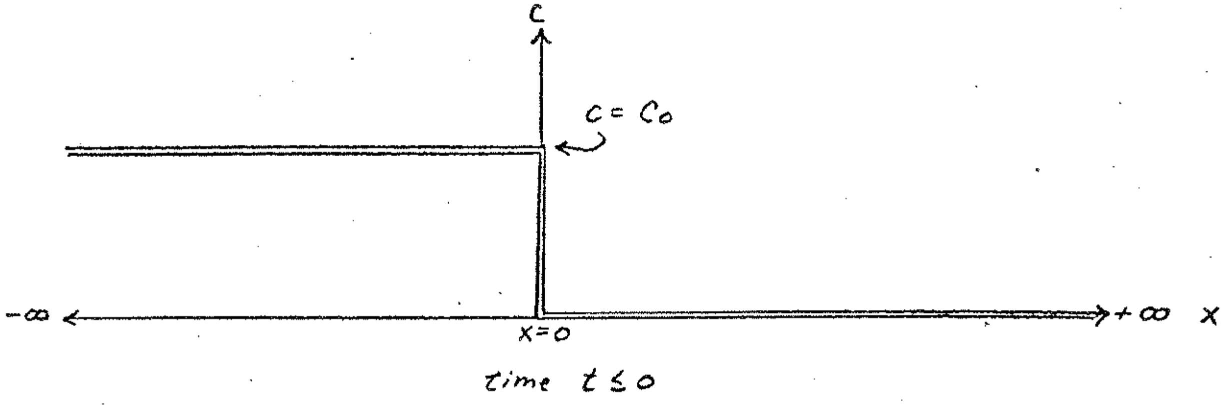


Figure 3

and we require that

$$c \to c_o \quad \text{as } x \to -\infty \quad \text{for all } t$$

$$c \to 0 \quad \text{as } x \to +\infty \quad \text{for all } t$$

The problem can be solved by considering the situation shown in Figure 3 to be made up of a series of instantaneous sources in the half-plane $x < 0$.

Consider the finite element of width $d\xi$ located a distance ξ from an arbitrary point x as shown in Figure 4 below:

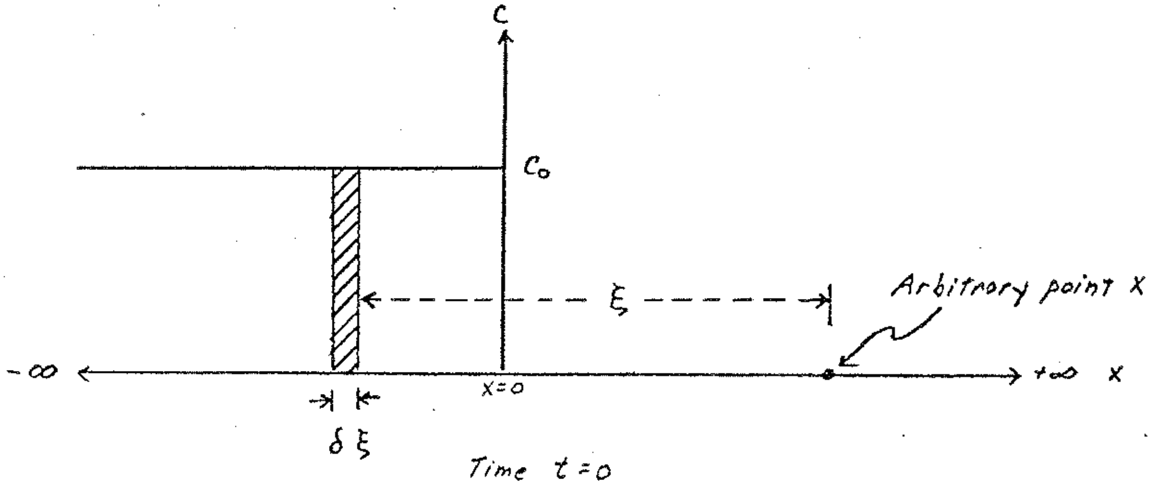


Figure 4

The mass of dye in the finite element is given by

$$\delta M = \rho c_o \,\delta\xi\, A \quad (\text{'A' is the area of our cylinder}).$$

If this finite element of dyed water starts diffusing at time $t = 0$, then Equation (15) tells us that the concentration of dye from this element at the arbitrary point x is given by

$$c = \frac{\delta M}{\rho A \sqrt{4\Pi Dt}} \, e^{-\frac{\xi^2}{4Dt}}$$

or

$$c = \frac{c_o}{\sqrt{4\Pi Dt}} \, e^{-\frac{\xi^2}{4Dt}} \,\delta\xi$$

It is seen that the solution to the situation shown in Figure 4 is given by summing the above expression over all the finite elements of dyed water from $x = 0$ to $x = -\infty$. In terms of our variable ξ, we see that ξ will then go from $\xi = x$ (since this is the distance from x to the closest finite element) to $\xi = +\infty$, so that we have

$$c = \int_x^\infty \frac{c_o}{\sqrt{4\Pi Dt}} \, e^{-\frac{\xi^2}{4Dt}} \, d\xi \quad .$$

By making the change of variable

$$\eta = \frac{\xi}{\sqrt{4Dt}}$$

the above integral becomes

$$c = \frac{c_o}{\sqrt{\Pi}} \int_{\frac{x}{\sqrt{4Dt}}}^{\infty} e^{-\eta^2}\, d\eta \qquad (16)$$

The above integral does not have an analytical solution, but can be solved by using the error function. The error function (erf) is an extensively tabulated integral (see, for instance, your CRC math tables) defined by

$$\mathrm{erf}(\omega) = \frac{2}{\sqrt{\Pi}} \int_{0}^{\omega} e^{-\alpha^2} d\alpha$$

with the properties:

$$\mathrm{erf}(-\omega) = -\mathrm{erf}(\omega) \;\; ; \;\; \mathrm{erf}(0) = 0 \;\; ; \;\; \mathrm{erf}(\infty) = 1 \, .$$

Thus,

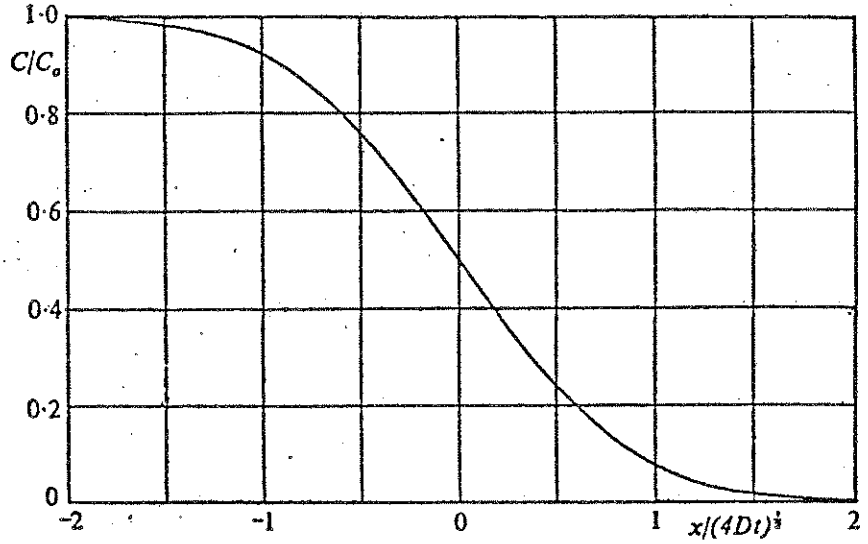
$$\int_{\frac{x}{\sqrt{4Dt}}}^{\infty} e^{-\eta^2} d\eta = \int_{0}^{\infty} e^{-\eta^2}\, d\eta - \int_{0}^{\frac{x}{\sqrt{4Dt}}} e^{-\eta^2} d\eta = \frac{\sqrt{\Pi}}{2} - \frac{\sqrt{\Pi}}{2}\, \mathrm{erf}\left[\frac{x}{\sqrt{4Dt}}\right]$$

$$= \frac{\sqrt{\Pi}}{2}\left\{1 - \mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right)\right\} .$$

1 - erf is referred to as the complementary error function, erfc. Substituting the above into Equation (16), we then have our final result

$$c = \frac{c_o}{2}\, \mathrm{erfc}\left[\frac{x}{\sqrt{4Dt}}\right] .$$

If $\frac{c}{c_o}$ is plotted as a function of $\frac{x}{\sqrt{4Dt}}$, the following graph is obtained (Crank, 1956):



Concentration-distance curve for an extended source of infinite extent.

Figure 6

The above example illustrates an important fact: by using the principle of superpositioning (you knew it was there, didn't you?) it is possible to build, from simple solutions to simple problems, more complex solutions to more complex problems, without the necessity of solving mathematically difficult partial differential equations.

The Error Function and its Derivative

x x	$\frac{2}{\sqrt{\pi}} e^{-x^2}$ $\frac{2}{\sqrt{\pi}} e^{-x^2}$	erf x erf x
0.00	1.12837 91671	0.00000 00000
0.01	1.12826 63348	0.01128 34156
0.02	1.12792 79057	0.02256 45747
0.03	1.12736 40827	0.03384 12223
0.04	1.12657 52040	0.04511 11061
0.05	1.12556 17424	0.05637 19778
0.06	1.12432 43052	0.06762 15944
0.07	1.12236 36333	0.07885 77198
0.08	1.12118 06004	0.09007 81258
0.09	1.11927 62126	0.10128 05939
0.10	1.11715 16068	0.11246 29160
0.11	1.11480 80500	0.12362 28962
0.12	1.11224 69379	0.13475 83518
0.13	1.10946 97934	0.14586 71148
0.14	1.10647 82654	0.15694 70331
0.15	1.10327 41267	0.16799 59714
0.16	1.09985 92726	0.17901 18132
0.17	1.09623 57192	0.18999 24612
0.18	1.09240 56008	0.20093 58390
0.19	1.08837 11683	0.21183 98922
0.20	1.08413 47871	0.22270 25892
0.21	1.07969 89342	0.23352 19230
0.22	1.07506 61963	0.24429 59116
0.23	1.07023 92672	0.25502 25996
0.24	1.06522 09449	0.26570 00590
0.25	1.06001 41294	0.27632 63902
0.26	1.05462 18194	0.28689 97232
0.27	1.04904 71096	0.29741 82185
0.28	1.04329 31885	0.30788 00680
0.29	1.03736 33334	0.31828 34959
0.30	1.03126 09096	0.32862 67595
0.31	1.02498 93657	0.33890 81503
0.32	1.01855 22310	0.34912 59948
0.33	1.01195 31119	0.35927 86550
0.34	1.00519 56887	0.36936 45293
0.35	0.99828 37121	0.37938 20536
0.36	0.99122 10001	0.38932 97011
0.37	0.98401 14337	0.39920 59840
0.38	0.97665 89542	0.40900 94534
0.39	0.96916 75592	0.41873 87001
0.40	0.96154 12988	0.42839 23550
0.41	0.95378 42727	0.43796 90902
0.42	0.94590 06256	0.44746 76184
0.43	0.93789 45443	0.45688 66945
0.44	0.92977 02537	0.46622 51153
0.45	0.92153 20130	0.47548 17198
0.46	0.91318 41122	0.48465 53900
0.47	0.90473 08685	0.49374 50509
0.48	0.89617 66223	0.50274 96707
0.49	0.88752 57337	0.51166 82612
0.50	0.87878 25789	0.52049 98778
	$\left[{(-5)3 \atop 5}\right]$	$\left[{(-5)1 \atop 5}\right]$

x x	$\frac{2}{\sqrt{\pi}} e^{-x^2}$	erf x erf x
0.50	0.87878 25789	0.52049 98778
0.51	0.86995 15467	0.52924 36198
0.52	0.86103 70343	0.53789 86305
0.53	0.85204 34444	0.54646 40969
0.54	0.84297 51813	0.55493 92505
0.55	0.83383 66473	0.56332 33663
0.56	0.82463 22395	0.57161 57638
0.57	0.81536 63431	0.57981 58062
0.58	0.80604 33431	0.58792 29004
0.59	0.79666 75911	0.59593 64972
0.60	0.78724 34317	0.60385 60908
0.61	0.77777 51846	0.61168 12189
0.62	0.76826 71442	0.61941 14619
0.63	0.75872 35764	0.62704 64433
0.64	0.74914 87161	0.63458 58291
0.65	0.73954 67634	0.64202 93274
0.66	0.72992 18814	0.64937 65889
0.67	0.72027 81930	0.65662 77023
0.68	0.71061 97784	0.66378 22027
0.69	0.70095 06721	0.67084 00622
0.70	0.69127 42604	0.67780 11938
0.71	0.68159 62792	0.68466 55502
0.72	0.67191 88112	0.69143 31231
0.73	0.66224 62838	0.69810 39429
0.74	0.65258 24665	0.70467 80779
0.75	0.64293 10692	0.71115 56337
0.76	0.63329 57399	0.71753 67528
0.77	0.62368 00626	0.72382 16140
0.78	0.61408 75556	0.73001 04313
0.79	0.60452 16696	0.73610 34538
0.80	0.59498 57863	0.74210 09647
0.81	0.58548 32161	0.74800 32806
0.82	0.57601 71973	0.75381 07509
0.83	0.56659 08944	0.75952 37569
0.84	0.55720 73967	0.76514 27115
0.85	0.54786 97173	0.77066 80576
0.86	0.53858 07918	0.77610 02683
0.87	0.52934 34773	0.78143 98455
0.88	0.52016 05514	0.78668 73192
0.89	0.51103 47116	0.79184 32468
0.90	0.50196 85742	0.79690 82124
0.91	0.49296 46742	0.80188 28258
0.92	0.48402 54639	0.80676 77215
0.93	0.47515 33132	0.81156 35586
0.94	0.46635 05090	0.81627 10190
0.95	0.45761 92546	0.82089 08073
0.96	0.44896 16700	0.82542 36496
0.97	0.44037 97913	0.82987 02930
0.98	0.43187 55710	0.83423 15043
0.99	0.42345 08779	0.83850 80696
1.00	0.41510 74974	0.84270 07929
	$\left[{(-5)1 \atop 5}\right]$	$\left[{(-5)1 \atop 5}\right]$

See Example 1.

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \qquad \frac{\sqrt{\pi}}{2} = 0.88622\ 69255$$

x	$\frac{2}{\sqrt{\pi}}e^{-x^2}$	erf x	x	$\frac{2}{\sqrt{\pi}}e^{-x^2}$	erf x erf x
1.00	0.41510 74974	0.84270 07929	1.50	0.11893 02892	0.96610 51465
1.01	0.40684 71315	0.84681 04962	1.51	0.11540 38270	0.96727 67481
1.02	0.39867 13992	0.85083 80177	1.52	0.11195 95356	0.96841 34969
1.03	0.39058 18368	0.85478 42115	1.53	0.10859 63195	0.96951 62091
1.04	0.38257 98936	0.85864 99465	1.54	0.10531 30683	0.97058 56899
1.05	0.37466 69570	0.86243 61061	1.55	0.10210 86576	0.97162 27333
1.06	0.36684 43034	0.86614 35866	1.56	0.09898 19506	0.97262 81220
1.07	0.35911 31488	0.86977 32972	1.57	0.09593 17995	0.97360 26275
1.08	0.35147 46245	0.87332 61584	1.58	0.09295 70461	0.97454 70093
1.09	0.34392 97827	0.87680 31019	1.59	0.09005 65239	0.97546 20158
1.10	0.33647 95978	0.88020 50696	1.60	0.08722 90586	0.97634 83833
1.11	0.32912 49667	0.88353 30124	1.61	0.08447 34697	0.97720 68366
1.12	0.32186 67103	0.88678 78902	1.62	0.08178 85711	0.97803 80884
1.13	0.31470 55742	0.88997 06704	1.63	0.07917 31730	0.97884 28397
1.14	0.30764 22299	0.89308 23276	1.64	0.07662 60821	0.97962 17795
1.15	0.30067 72759	0.89612 38429	1.65	0.07414 61034	0.98037 55850
1.16	0.29381 12389	0.89909 62029	1.66	0.07173 20405	0.98110 49213
1.17	0.28704 45748	0.90200 03990	1.67	0.06938 26972	0.98181 04416
1.18	0.28037 76702	0.90483 74269	1.68	0.06709 68781	0.98249 27870
1.19	0.27381 08437	0.90760 82860	1.69	0.06487 33895	0.98315 25869
1.20	0.26734 43470	0.91031 39782	1.70	0.06271 10405	0.98379 04586
1.21	0.26097 83664	0.91295 55080	1.71	0.06060 86436	0.98440 70075
1.22	0.25471 30243	0.91553 38810	1.72	0.05856 50157	0.98500 28274
1.23	0.24854 83805	0.91805 01041	1.73	0.05657 89788	0.98557 84998
1.24	0.24248 44335	0.92050 51843	1.74	0.05464 93607	0.98613 45950
1.25	0.23652 11224	0.92290 01283	1.75	0.05277 49959	0.98667 16712
1.26	0.23065 83281	0.92523 59418	1.76	0.05095 47262	0.98719 02752
1.27	0.22489 58748	0.92751 36293	1.77	0.04918 74012	0.98769 09422
1.28	0.21923 35317	0.92973 41930	1.78	0.04747 18791	0.98817 41959
1.29	0.21367 10145	0.93189 86327	1.79	0.04580 70274	0.98864 05487
1.30	0.20820 79868	0.93400 79449	1.80	0.04419 17233	0.98909 05016
1.31	0.20284 40621	0.93606 31228	1.81	0.04262 48543	0.98952 45446
1.32	0.19757 88048	0.93806 51551	1.82	0.04110 53185	0.98994 31565
1.33	0.19241 17326	0.94001 50262	1.83	0.03963 20255	0.99034 68051
1.34	0.18734 23172	0.94191 37153	1.84	0.03820 38966	0.99073 59476
1.35	0.18236 99865	0.94376 21961	1.85	0.03681 92653	0.99111 10301
1.36	0.17749 41262	0.94556 14366	1.86	0.03547 88774	0.99147 24883
1.37	0.17271 40811	0.94731 23980	1.87	0.03417 98920	0.99182 07476
1.38	0.16802 91568	0.94901 60353	1.88	0.03292 18811	0.99215 62228
1.39	0.16343 86216	0.95067 32958	1.89	0.03170 38307	0.99247 93184
1.40	0.15894 17077	0.95228 51198	1.90	0.03052 47404	0.99279 04292
1.41	0.15453 76130	0.95385 24394	1.91	0.02938 36241	0.99308 99398
1.42	0.15022 55027	0.95537 61786	1.92	0.02827 95101	0.99337 82251
1.43	0.14600 45107	0.95685 72531	1.93	0.02721 14412	0.99365 56502
1.44	0.14187 37413	0.95829 65696	1.94	0.02617 84752	0.99392 25709
1.45	0.13783 22708	0.95969 50256	1.95	0.02517 96849	0.99417 93336
1.46	0.13387 91486	0.96105 35095	1.96	0.02421 41583	0.99442 62755
1.47	0.13001 33993	0.96237 28999	1.97	0.02328 09986	0.99466 37246
1.48	0.12623 40239	0.96365 40654	1.98	0.02237 93244	0.99489 20004
1.49	0.12254 00011	0.96489 78648	1.99	0.02150 82701	0.99511 14132
1.50	0.11893 02892	0.96610 51465	2.00	0.02066 69854	0.99532 22650
	$\left[{(-5)1 \atop 5}\right]$	$\left[{(-5)1 \atop 5}\right]$		$\left[{(-5)1 \atop 5}\right]$	$\left[{(-6)4 \atop 5}\right]$

$\frac{\sqrt{\pi}}{2}=0.88622\ 69255$

for large x : $\text{erf}\, x \simeq 1 - \frac{1}{\sqrt{\pi}}\frac{e^{-x^2}}{x}$

INITIAL AND BOUNDARY CONDITIONS FOR SOLUTIONS OF THE A.D.E.

For simple systems, or for systems in which only an approximate answer is needed, it is appropriate to simplify the governing ADEs. An important simplification is to reduce the dimensionality of the problem by integrating in one direction and assuming a uniform distribution of contaminant in that direction (e.g., depth-average, and then model variations only in the x and y directions). Other important simplification center on the anisotropy and functionality of the diffusivity coefficients. For example, one can assume isotropic turbulence. Or one can assume that diffusivity does not significantly vary with respect to space or time. We will explore some of these simplifications soon.

But regardless of the simplifications taken, no system is properly posed mathematically unless a suitable number of independent governing equations have been defined, and the requisite initial and boundary conditions specified.

Indeed, in much "real-world" work, posing the ADE in a suitable form is a comparatively straightforward exercise: the real work often is the proper specification of boundary conditions and finding solutions that satisfy those conditions. This point should be absolutely clear: There is no such thing as a solution to the ADE. What you solve is the ADE <u>and</u> the constraints of a particular set of initial and boundary conditions. If you change a boundary condition, you also change the solution, sometimes rather dramatically. At this point we will review a range of typical initial and boundary conditions, and see how they qualitatively affect the form of the ADE. Subsequently, we will look at some specific examples and look at the effects on the solutions.

How Many Governing Equations?

Before anything else, you must have a determinate system: the number of equations must equal the number of unknown variables. For a binary system we have two unknowns C_A and C_B, but we always have a mass balance equation that relates these two variables: $C_A + C_B = 1$. (Go back and look at the definition of dimensionless concentrations if to see why this is so). Thus, for a binary system we need one other independent equation. The logical choice is the ADE for constituent A. If we have a n-component system, we have n-1 binary pairs, so we need n-1 ADEs, typically one for each of the minor constituents because the major component (the solvent fluid) is in great excess of all the rest, and we track its transport through the equations of motion.

Initial/Boundary Conditions

The No-Flux Condition: This is analogous to the no-slip condition for the equations of motion. If a solid surface or an interface between two fluids (e.g., air/water) is impervious to flow and is chemically/biologically unreactive (neither a source nor a sink of A) then we can (indeed must) specify that, right at the surface, there is no flux of A in the direction normal to that surface:

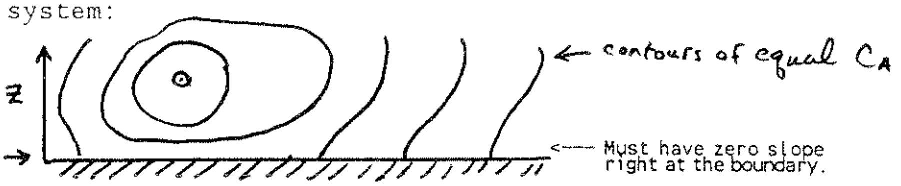
$$J_{surf} = 0$$

A most important corollary of the no-flux condition, when we use the Fickian description of fluxes, is that

$$\nabla C_A = 0 \quad \{\forall(x,y,z) \mid (x,y,z) = \text{no-flux surf.}\}$$

This says simply that if the normal flux goes to zero at the surface, and the molecular diffusivity is always nonzero, then the gradient of concentration must equal zero for all coordinates located at the surface. Visualize this for a geometrically simple, 2-D system:

$$\frac{\partial C_A}{\partial z} = 0 \quad \text{at } z = 0 \rightarrow$$

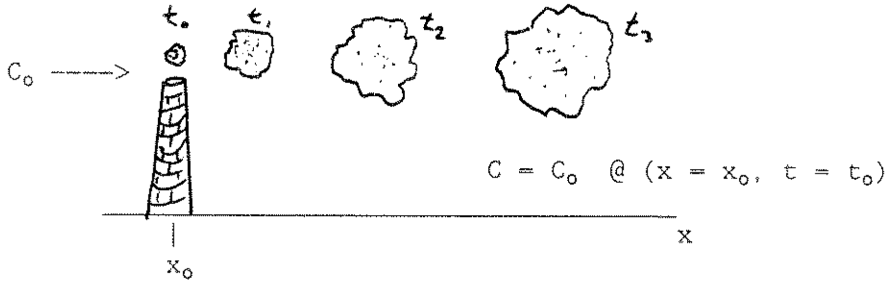


While this is analogous to a no-slip condition for velocity, notice an important difference: there we said $u = 0$ at the boundary, but because momentum flows across the boundary (as shear stress) $du/dz \neq 0$ at the surface, and a gradient of velocity is typically observed at the boundary.

Specified-Concentration Condition: Often it is convenient or realistic to specify a concentration at a point, at a series of points, or along a line segment or a plane segment.

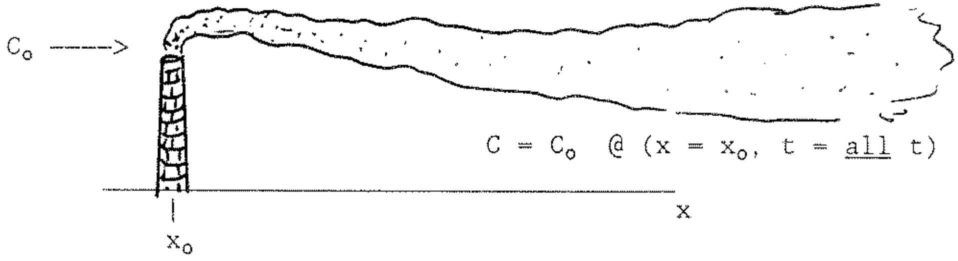
$$C = C_o \quad \text{at} \quad (x,y,z) = (x_o,y_o,z_o)$$

This is commonly used as a "source condition". For example, suppose we have a smokestack that emits a puff of contaminant at $t = t_o$. We can model this as an instantaneous release of specified concentration:



$$C = C_o \quad @ \ (x = x_o, \ t = t_o)$$

Or, for a continuous release of contaminant at x_o:



$$C = C_o \quad @ \ (x = x_o, \ t = \underline{\text{all}} \ t)$$

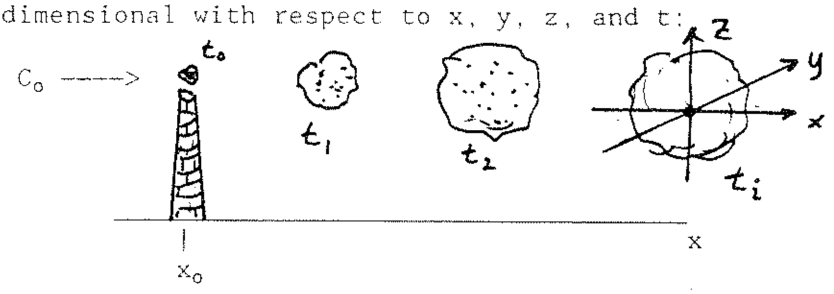
Note that a boundary source is not the same thing, either mathematically or physically as an "internal" source or sink term as defined by r_A. We will discuss the r_A term and its role in a moment.

Relationship Between Boundary Source Dimensionality and Governing Equations:

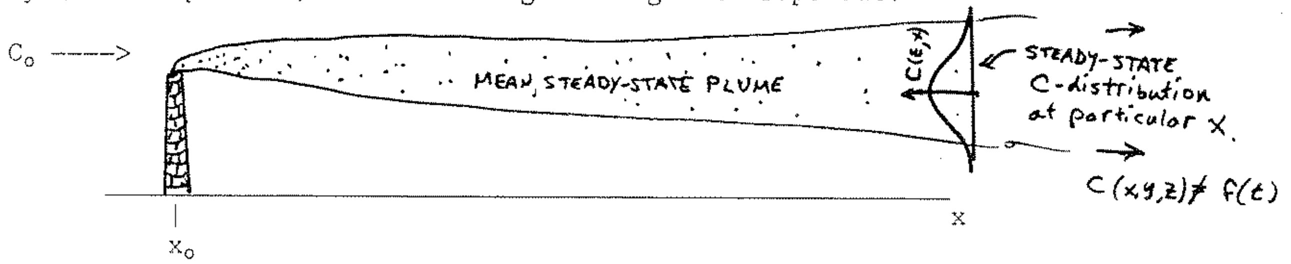
As we delve into some particular cases, we will find that there is a close linkage between the dimensionality of a source boundary condition and the dimensionality of the overall problem. Interestingly, the relationship between the two is inverse.

> The dimensionality of the requisite ADE that governs a system is <u>inversely</u> proportional to the dimensionality of the boundary source of the constituent of interest.

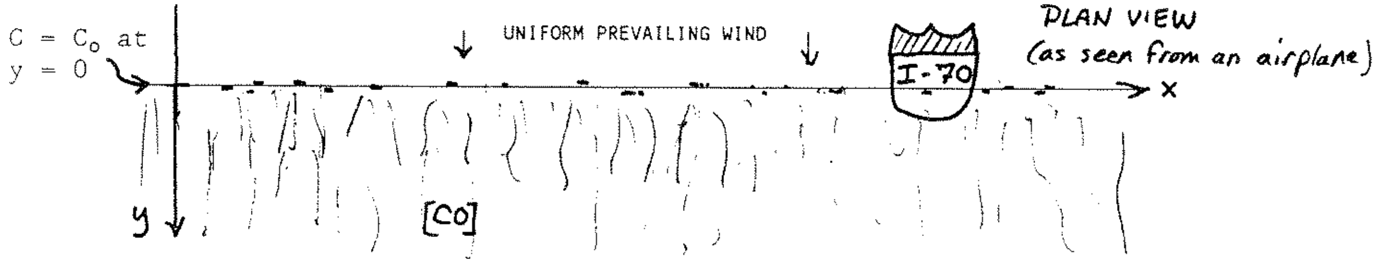
For example, choose a source condition that has the lowest possible dimensionality: an instantaneous release at a point (like the puff above). This source is zero-dimensional with respect to x, y, z, and t:



After release, the concentrations in the system vary in all three directions and with time, so the governing ADE must be a full three-dimensional, unsteady form of the equation. If we increase the time-dimension of the source, and make it continuous as we did above, then the system can reach a steady state and the unsteady (time-dependent) term of the governing ADE drops out:



Suppose we increase one of the spatial dimensions of the source? For example, instead of a continuous point source, we have a source that can be modeled as a continuous line of essentially infinite extent. What would this be? How about the average emissions of carbon monoxide from Interstate 70 as it crosses the flat wheat-fields of Kansas:



For this system, no variation in the x-direction is possible and at steady state the governing equation is a steady, 2-D form of the ADE.

Likewise, for an infinite plane (2-D) source, the governing equation reduces to one-dimensional in the longitudinal direction. Some of these boundary conditions may seem far-fetched to you now, but we will find that because of a modeling phenomenon known as "source images", it is more realistic than you might imagine to have sources that act as if they are infinite extent. We will explore this soon.

SOURCE AND SINK TERMS: OVERVIEW

The term designated r_A accounts for the production or loss of A within the system. This terms is sometimes referred to as a source or sink term, but it is quite different in form and function from a source or sink boundary condition. In most models, the initial source of a component A is handled as an initial or boundary condition, as in the examples above. Once A enters the system of interest, it may behave conservatively, meaning it does not decay nor is it removed from the system by any sort of uptake onto solids or into organisms, nor does it move across a boundary (e.g., volatilize from water into air. For a conservative component, $r_A = 0$ and all boundaries except the source(s) are no-flux boundaries. If a component is removed, either by chemical or biological decay, by adsorption or precipitation, or by transfer into another phase, we must account for this removal of mass. If the removal mechanism occurs throughout the fluid (either heterogeneously or homogeneously) the loss is accounted for by some functional form of r_A. If the removal occurs only at boundaries, then the loss is typically accounted for by suitable boundary conditions. Examples are given below. The arguments above also hold for sources. If some process produces A throughout the fluid, then an r_A production term is used, if processes at boundaries generate A, then source boundary conditions are most often used.

Homogeneous r_A: This means that r_A is not intrinsically a function of location in the flow (x, y, or z). The magnitude of r_A may vary with location, but only because it depends on some other variable that changes with location. For example, the loss of A typically depends in some way on the concentration of A which varies with location, but if r_A is homogeneous, there is no explicit dependence of r_A on spatial variables. Many common processes can be modeled, or at least approximated by a homogeneous r_A function.

- Purely chemical reactions where the components that react with A are uniformly distributed throughout the fluid. Examples for water are: acid-base reactions, complexation reactions involving ubiquitous components (e.g., natural organic matter or chloride), surface reactions on uniformly distributed suspended particles. For air: reactions with oxygen, surface reactions on uniformly distributed suspended particles.

- Bacterial degradation when the "inoculum" of active bacteria is uniformly distributed, and the growth conditions (temperature, minor nutrients, etc.) are also uniform.

- Photochemical reactions in the troposphere, where light intensity is essentially uniform in space. Examples are many of the reactions leading to smog formation. Note that this uniformity is not true in water which absorbs light over shallow depths.

Typical Forms of Homogeneous Reaction Terms: Most common is $r_A = f(C_A)$. The easiest to work with computationally are so called zeroth-order or first-order reaction. The order of a reaction is defined as the value of the exponent applied to C_A:

$r_A = kC_A^0 = k$ —— Zeroth Order (constant w/r/t to C_A)

$r_A = kC_A^1 = kC_A$ —— First Order (linear w/r/t to C_A)

$r_A = kC_A^2 =$ —— Second Order (rate proportional to C_A^2)

$r_A = kC_A^{1.7} =$ —— Non-integer Order (occurs with complex mechanisms)

$r_A = kC_A^2 + k'C_A$ —— Mixed Order (again, due to particular mechanism)

Note that, unless the dimensionless concentration C_A is used, the units on k are different in each case. If common density or molarity units are used, the units on k must match both the units of C_A and the exponent on C_A to produce the proper units on r_A (= mass/volume/time or moles/volume/time). For such formulas, when we say the process is spatially homogenous, we mean that $k \neq f(x,y,z)$.

When a biological process governs the rate of production or decay, a model of enzyme-mediated kinetics is often the most realistic. The simplest and most widely used formula for enzyme kinetics is the Monod Equation (the name is that French biologist Jacques Monod and is pronounced Mon-Oh):

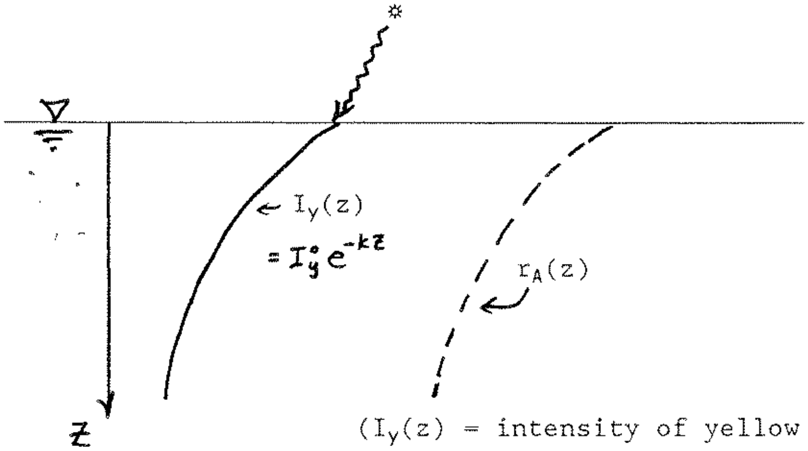
$$r_A = \frac{X}{Y}\mu_{max}\frac{C_A}{k_{1/2} + C_A}$$

where X is cell density, Y is the yield (= mass of cells per mass of A consumed) and $k_{1/2}$ is the half-saturation constant (= the value of C_A that produces removal at one-half of the maximum (saturation) removal rate). Those unfamiliar with the biochemistry underlying this equation can find explanations in any number of applied or theoretical texts on the subjects.

We will come back to the details of some of the popular kinetic formulations later in these notes. For now, note that the zeroth-order formulation is the simplest, because the rate is constant and is independent of C_A. Unfortunately, not too many interesting processes have such simple kinetics. First order decay is very popular because it is linear and the solution of the rate expression is a simple exponential decay of C_A. Higher-order kinetics are much more difficult to incorporate into the ADE, and therefore have been largely avoided until recently. Monod kinetics are described by a hyperbolic function that can be especially unpleasant to work with, but some important water-quality models include this essential biological equation in the governing ADEs.

I also note in passing that there is a depressing lack of kinetic data for aquatic processes, so use of many of the latest aquatic ADE models are limited by the available data. Reaction kinetics of air pollutants have been studied in much greater detail, and some surprisingly sophisticated kinetic-transport models have been developed and realistically parameterized. The work done on photochemical smog in the Los Angeles basin is notable in this respect.

Heterogeneous r_A: This means that r_A intrinsically varies as a function of location in the flow (x, y, or z). That is $r_A = f(x,y,z)$ in general, and at the least $r_A = f(x)$ or some other direction. For the common rate expressions given above, this is equivalent to saying that $k = f(x,y,z)$. Heterogeneity in the reaction term comes about when some factor or component not explicitly modeled varies with respect to location. For example, suppose we are modeling the aqueous transport of a pesticide that is photochemically degraded by visible light in the yellow wavelength region. The rate of photolysis of this pesticide will be a function of depth (as well as of time of day):



($I_y(z)$ = intensity of yellow light)

Use of a Lambert-Beer Law formulation for $r_A(z)$ would be appropriate, with an intensity factor that depends on the solar angle (latitude, season, time of day). Such models have been developed by the U.S. EPA for pesticide degradation.

Another example: suppose a contaminant is subject to bacterial decay. Bacterial enzyme activity is a function of temperature, so if the water column is thermal stratified, the parameters in the Monod equation will change with depth. If the water quality model is comprehensive and includes a thermal energy balance/buoyancy routine, the calculated water temperature can be passed from that routine to the ADE for the biodegrading contaminant. Temperature correction factors in the r_A term can then account for the implicit depth variation in the rate. If, as is more often the case, the transport of the contaminant is modeled by itself, its accuracy can be improved by incorporating some assumed or measured temperature profile into a temperature corrected form of r_A. An analogous situation might occur in an estuary in which vertical or lateral variations in salinity affect the viability or activity of bacteria.

Boundary Sources or Sinks: One can find abundant examples of both homogeneous and heterogeneous loss or production of components at boundaries. Volatile organic compounds leave or enter the water at the air-water interface. Carbon dioxide is removed from the atmosphere by plants at the earth's surface. Oxygen is removed from lakes by bacterial respiration in the sediments. Nutrients are taken out of estuaries by rooted macrophytes in intertidal flats, although sometimes macrophytes reverse the process and pump nutrients from the sediments to the water. Phosphorus and heavy metals are released to lake waters by redox processes in the sediments.

Because these processes are fixed at boundaries, it is generally easiest to treat them as boundary conditions rather than as spatially heterogenous r_A terms. There are innumerable ways of dealing with these boundary processes, but most fall into two categories.

1. Specified Concentration at a Boundary. If a removal mechanism is extremely fast with respect to transport rates (more about this later) and is not subject to saturation over the time scales of interest, then a convenient boundary condition is to specify that $C_A^{bound.} = 0$. For example, for most eutrophic lakes it is appropriate to specify that the dissolved oxygen concentration at the sediment-water interface is zero. Conversely, if an interface supplies a constituent at a very fast rate, but the maximum possible concentration is fixed by some chemical saturation limit, a fixed, non-zero $C_A^{bound.}$ can be specified. For example, in a lake or the ocean, it may be appropriate to specify that the dissolved oxygen directly at the surface is always at the saturation value. For sediments or an aquifer matrix containing a large amount of a relatively insoluble mineral, the concentrations of the mineral components right at the interface may be constant and fixed by the solubility product.

2. Specified Boundary Flux. If the rate of removal is fairly constant, or can be specified as a function of time, then the flux at the boundary can be specified at some non-zero value. For example, macrophytes may pump out (or in) nutrients at a fairly steady rate. Or, the nutrient flux may be a time-dependent function of sunlight (i.e., photosynthetic activity). A more sophisticated example is the means by which gas exchange across the air water interface is sometimes handled. The transfer of oxygen or carbon dioxide or volatile compounds can be limited by the local mixing right at the interface. In some models, a subroutine calculates the flux across the interface as a function of wind shear or some other forcing function, and then this flux becomes a boundary condition for the transport model within the water column.