Appendix 1B

Derivation of the Relaxation Method Algorithm

I. Diffusion/reaction of a single species (e.g., O_2)

The sediment is divided into vertical layers, or boxes. Within a given box, steady state is defined as the condition where the sum of the fluxes sum to zero; the important fluxes are diffusion and reaction. We define a few units of currency:

$$inv\left[\frac{\text{mol}}{\text{cm}^2}\right] = conc\left[\frac{\text{mol}}{\text{l pw}}\right] \cdot \Delta z \cdot \Phi \cdot 10^{-3} \qquad \text{(A1.b.1)}$$

where *inv* is the inventory of a solute within a box, per unit area on the sediment surface, and *conc*, its pore-water concentration.

Derivation of the diffusion expression. Using the currency of the solute inventory, the diffusive and reaction fluxes into and out of the box at level "i" are,

$$0 = D\frac{F_{i-1} + F_i}{2}\frac{2}{\Delta z_{i-1} + \Delta z_i}(conc_{i-1} - conc_i) \cdot 10^{-3}$$

$$- D\frac{F_i + F_{i+1}}{2}\frac{2}{\Delta z_i + \Delta z_{i+1}}(conc_i - conc_{i+1}) \cdot 10^{-3}$$

$$+ J\left[\frac{\text{mol}}{\text{l tot s}}\right] \cdot 10^{-3} \cdot \Delta z \qquad \text{(A1.b.2)}$$

where the subscript "i-1" indicates the box above and i+1 the box below. F is the formation factor (see chapter 2), Δz is the thickness of the box [cm], and J is the reaction rate, in moles/liter total/second. When the sum of these fluxes for each box i equals zero, as above, then the system is in steady state.

The expression converted to the currency of concentrations [moles/l pore water]:

$$0 = D\frac{F_{i-1} + F_i}{2}\frac{2}{(\Delta z_{i-1} + \Delta z_i)\,\Delta z_i}\frac{1}{\Phi}(conc_{i-1} - conc_i)$$

$$- D\frac{F_i + F_{i+1}}{2}\frac{2}{(\Delta z_i + \Delta z_{i+1})\,\Delta z_i}\frac{1}{\Phi}(conc_i - conc_{i+1})$$

$$+\frac{j}{\Phi} \qquad \text{(A1.b.3)}$$

which is obtained by substituting (A1.b.1) into (A1.b.2).

To simplify the notation, I define

$$D_- = D\frac{F_{i-1} + F_i}{2}\frac{2}{(\Delta z_{i-1} + \Delta z_i)\,Dzi}\frac{1}{\Phi} \qquad \text{(A1.b.4)}$$

$$D_+ = D\frac{F_i + F_{i+1}}{2}\frac{2}{(\Delta z_i + \Delta z_{i+1})\,\Delta z_i}\frac{1}{\Phi} \qquad \text{(A1.b.5)}$$

$$x_i = conc_i \qquad \text{(A1.b.6)}$$

Then equation (A1.b.3) becomes,

$$0 = D_-\,(x_{i-1} - x_i) - D_+\,(x_i - x_{i+1}) + \frac{J}{\Phi} \qquad \text{(A1.b.7)}$$

Iteration to a solution. Since the first guess for the steady state concentrations, x_i, to the diffusion/reaction equation is usually incorrect, we define

$$R_i = D_-\,(x_{i-1} - x_i) - D_+\,(x_i - x_{i+1}) + \frac{J}{\Phi} \neq 0 \qquad \text{(A1.b.8)}$$

where the residual term R_i is defined for all boxes, i.

The solution is found by iteration, using a procedure analogous to Newton's method for finding the solution to

$$f(x) = 0 \qquad \text{(A1.b.9)}$$

on an interval. Each successive guess ($x + \Delta x$) for the value of x to satisfy this expression is determined using the last guess (x), by finding the y intercept of the tangent to the curve f(x), so that Δx satisfies

$$\left.\frac{\partial f}{\partial x}\right|_{x_1} \cdot \Delta x + f(x_1) = 0 \qquad \text{(A1.b.10)}$$

For the system of solute concentrations in a vertical stack of n boxes in the sediment, there is a system of n equations with n unknown Δx_i values. Each concentration (x_i) appears in three equations, the ones describing the fluxes for the box itself, plus above and below (Δx_i, Δx_{i-1}, Δx_{i+1}). A generalized equation is

$$\frac{\partial R_i}{\partial x_{i-1}} \Delta x_{i-1} + \frac{\partial R_i}{\partial x_i} \Delta x_i + \frac{\partial R_i}{\partial x_{i+1}} \Delta x_{i+1} = - R_i \qquad \text{(A1.b.11)}$$

Boundary conditions. At the sediment surface, the solute concentration is fixed at the bottom water value

$$x_1 = x_{bw}. \qquad \text{(A1.b.12)}$$

During the iteration, the concentration at i=1 remains constant, so that,

$$\Delta x_1 = 0. \qquad \text{(A1.b.13)}$$

Accordingly, the expression for i=2 analogous to expression (A1.b.11) is,

$$\frac{\partial R_2}{\partial x_2}\Delta x_2 + \frac{\partial R_2}{\partial x_3}\Delta x_3 = -R_2. \qquad \text{(A1.b.14)}$$

At the bottom boundary (i = n), the imposed condition is that the diffusive flux equals zero; that is

$$x_{n+1} = x_n \qquad \text{(A1.b.15)}$$

and, during the iteration,

$$\Delta x_{n+1} = \Delta x_n. \qquad \text{(A1.b.16)}$$

Therefore, the constraining equation from the bottom box (i = n) is,

$$\frac{\partial R_n}{\partial x_{n-1}}\Delta x_{n-1} + \left(\frac{\partial R_n}{\partial x_n} + \frac{\partial R_n}{\partial x_{n+1}}\right)\Delta x_n = -R_n. \qquad \text{(A1.b.17)}$$

The n equations for the n unknowns $\Delta x_{(1 \to n)}$ are solved simultaneously using Gauss-Jordan elimination (Press et al., 1986). For a simple system consisting of only 4 depth levels, the matrices are constructed as follows:

$$\begin{vmatrix} \frac{\partial R_2}{\partial x_2} & \frac{\partial R_2}{\partial x_3} & 0 & 0 \\ \frac{\partial R_3}{\partial x_2} & \frac{\partial R_3}{\partial x_3} & \frac{\partial R_3}{\partial x_4} & 0 \\ 0 & \frac{\partial R_4}{\partial x_3} & \frac{\partial R_4}{\partial x_4} & \frac{\partial R_4}{\partial x_5} \\ 0 & 0 & \frac{\partial R_5}{\partial x_4} & \frac{\partial R_5}{\partial x_5}+\frac{\partial R_5}{\partial x_6} \end{vmatrix} \begin{vmatrix} \Delta x_2 \\ \Delta x_3 \\ \Delta x_4 \\ \Delta x_5 \end{vmatrix} = \begin{vmatrix} -R_2 \\ -R_3 \\ -R_4 \\ -R_5 \end{vmatrix}$$

(A1.b.18)

II. pH-Coupled Carbonate System

In contrast to the equation describing the distribution of O_2 in sediment pore water (described above) the equations describing CO_2, HCO_3^-, and $CO_3^=$ are coupled together by the carbonate buffer system. Three constraints are used to define the state of the system within each box: the ΣCO_2 balance, the alkalinity balance, and the requirement of pH equilibrium. Thus, there are three equations for each box, and three unknowns, representing the Δx's for the three species.

As for the treatment of O_2, above, subscripts following a variable indicate the box number or depth level. Superscripts following a variable denote the species, as,

$$x^1 = CO_2$$

$$x^2 = HCO_3^-$$

$$x^3 = CO_3^=$$

Superscripts leading a variable indicate that the variable is associated with one of the three constraints described above, so that

$${}^1R_i,$$

for example, is the residual of the ΣCO_2 equation, described below.

k = 1: ΣCO_2 balance. In steady state, the diffusion of all three species should equal the sum of the inputs of carbon by organic carbon oxidation and calcite dissolution:

$$^1R_i = \sum_{j=1}^{3} D^j_- (x^j_{i-1} - x^j_i) - D^j_+ (x^j_i - x^j_{i+1}) + \frac{J^1}{\Phi} + \frac{J^3}{\Phi} \qquad \text{(A1.b.19)}$$

k = 2: alkalinity balance. The alkalinity balance in the code is normalized to units of calcite dissolution, so that the quantity conserved is twice the alkalinity:

$$^2R_i = \frac{1}{2}\left[D^2_- (x^2_{i-1} - x^2_i) - D^2_+ (x^2_i - x^2_{i+1})\right] + D^3_- (x^3_{i-1} - x^3_i) - D^3_+ (x^3_i - x^3_{i+1}) + \frac{j^3}{\Phi} \qquad \text{(A1.b.20)}$$

k = 3: pH equilibrium. The three species are required to be in pH balance in each box:

$$^3R_i = \frac{x^1_i \cdot x^3_i}{(x^2_i)^2} - \frac{K'_1}{K'_2} \qquad \text{(A1.b.21)}$$

where the denominator in the first term is squared (an abundance of superscripts!).

Solution by iteration. The system of equations is solved by iteration similarly to the case of a single species, above. The general equation is:

$$^kR_i = \sum_{j=1}^{3} \left[\frac{\partial^k R_i}{\partial x^j_{i-1}} \Delta x^j_{i-1} + \frac{\partial^k R_i}{\partial x^j_i} \Delta x^j_i + \frac{\partial^k R_i}{\partial x^j_{i+1}} \Delta x^j_{i+1}\right]. \qquad \text{(A1.b.22)}$$

When the summation term is expanded, there are nine terms, constraining nine unknown Δx's.

In order to simplify the notation, the following abbreviation will be used in the text and in the code.

$$\text{define: } \frac{\partial^k R_i}{\partial x_l^j} \equiv DR(K,J,L,I) \qquad (A1.b.24)$$

k = equation number: 1 = ΣCO_2
2 = alkalinity
3 = pH equilibrium

j = species number: 1 = CO_2
2 = HCO_3^-
3 = $CO_3^=$

l = level offset: 1 → i-1 (level above)
2 → i
3 → i+1 (level below)

i = depth level

Using this notation, for example, the FORTRAN term for the derivative of the residual of the ΣCO_2 equation at depth level number 7, with respect to changes in the bicarbonate concentration in box number 7, is

$$\frac{\partial\ ^{\Sigma CO_2}R_7}{\partial\ HCO3\ (7)} \equiv DR(1,2,2,7)$$

A sample of the matrix construction for the simultaneous solution of these equations can be presented by further shortening the notation to:

$$1227 \equiv DR(1,2,2,7).$$

The matrix appropriate to a system four boxes deep (including i=1 for bottom water) would be given by:

$$\left|\begin{array}{ccccccccc} 1122 & 1222 & 1322 & 1132 & 1232 & 1332 & 0 & 0 & 0 \\ 2122 & 2222 & 2322 & 2132 & 2232 & 2332 & 0 & 0 & 0 \\ 3122 & 3222 & 3322 & 3132 & 3232 & 3332 & 0 & 0 & 0 \\ 1113 & 1213 & 1313 & 1123 & 1223 & 1323 & 1133 & 1233 & 1333 \\ 2113 & 2213 & 2313 & 2123 & 2223 & 2323 & 2133 & 2233 & 2333 \\ 3113 & 3213 & 3313 & 3123 & 3223 & 3323 & 3133 & 3233 & 3333 \\ 0 & 0 & 0 & 1114 & 1214 & 1314 & \begin{array}{c}1124\\+1134\end{array} & \begin{array}{c}1224\\+1234\end{array} & \begin{array}{c}1324\\+1334\end{array} \\ 0 & 0 & 0 & 2114 & 2214 & 2314 & \begin{array}{c}2124\\+2134\end{array} & \begin{array}{c}2224\\+2234\end{array} & \begin{array}{c}2324\\+2334\end{array} \\ 0 & 0 & 0 & 3114 & 3214 & 3314 & \begin{array}{c}3124\\+3134\end{array} & \begin{array}{c}3124\\+3234\end{array} & \begin{array}{c}3324\\+3334\end{array} \end{array}\right| \left|\begin{array}{c} \Delta x_2^1 \\ \Delta x_2^2 \\ \Delta x_2^3 \\ \Delta x_3^1 \\ \Delta x_3^2 \\ \Delta x_3^3 \\ \Delta x_4^1 \\ \Delta x_4^2 \\ \Delta x_4^3 \end{array}\right| = \left|\begin{array}{c} {}^1R_2 \\ {}^2R_2 \\ {}^3R_2 \\ {}^1R_3 \\ {}^2R_3 \\ {}^3R_3 \\ {}^1R_4 \\ {}^2R_4 \\ {}^3R_4 \end{array}\right|$$

(A1.b.25)