2 MATHEMATICAL BASIS

In this section, we are to give governing equations, initial conditions, and boundary conditions for simulating water flow and chemical and sediment transport in watershed systems.

2.1 Water Flow in One-Dimensional River/Stream/Canal Network

The governing equations of water flow in one-dimensional river/stream/canal can be derived based on the conservation law of water mass and linear momentum (Singh, 1996), and can be written as follows.

The continuity equation:

$$\frac{\partial A}{\partial t}+\frac{\partial Q}{\partial x}=S_S+S_R-S_E+S_I+S_1+S_2 \qquad \textbf{(2.1.1)}$$

where t is time [t]; x is the axis along the river/stream/canal direction [L]; A is cross-sectional area of the river/stream [L^2]; Q is flow rate of the river/stream/canal [L^3/t]; S_S is the man-induced source [L^3/t/L]; S_R is the source due to rainfall [L^3/t/L]; S_E is the sink due to evapotranspiration [L^3/t/L]; S_I is the source due to exfiltration from the subsurface media [L^3//t/L]; S_1 and S_2 are the source terms contributed from overland flow [L^3/t/L].

The momentum equation:

$$\frac{\partial Q}{\partial t}+\frac{\partial VQ}{\partial x}=-gA\frac{\partial\left(Z_O+h\right)}{\partial x}-\frac{gAh}{c\rho}\frac{\partial\Delta\rho}{\partial x}-\frac{\partial F_x}{\partial x}+\left(M_S+M_R-M_E+M_I+M_1+M_2\right)+\frac{B\tau^S-P\tau^b}{\rho} \qquad \textbf{(2.1.2)}$$

where h is water depth [L]; V is river/stream/canal velocity [L/t]; g is gravity [L/t^2]; Z_o is bottom elevation [L]; $\Delta\rho=\rho-\rho_o$ is the density deviation [M/L^3] from the reference density (ρ_o), which is a function of temperature and salinity as well as other chemical concentrations; c is the shape factor of the cross-sectional area; F_x is the momentum flux due to eddy viscosity [L^4/t^2]; M_S is the external momentum-impulse from artificial sources/sinks [L^3/t^2]; M_R is the momentum-impulse gained from rainfall [L^3/t^2]; M_E is the momentum-impulse lost to evapotranspiration [L^3/t^2]; M_I is the momentum-impulse gained from the subsurface due to exfiltration [L^3/t^2]; M_1 and M_2 are the momentum-impulse gained from the overland flow [L^3/t^2]; ρ is the water density [M/L^3]; B is the top width of the cross-section [L]; τ^s is the surface shear stress [$M/t^2/L$]; P is the wet perimeter [L]; and τ^b is the bottom shear stress [$M/t^2/L$], which can be assumed proportional to the flow rate as $\tau^b/\rho=\boldsymbol{\kappa V}^2$ where $\kappa=gn^2/R^{1/3}$ and R is the hydraulic radius (L) and n is the Manning's roughness.

2.1.1 Fully Dynamic Wave Approaches

Equations (2.1.1) and (2.1.2) written in the conservative form are the governing equations for one-dimensional flow in river/stream/canals. Depending on the simplification of the momentum equation, one can have three approaches: fully dynamic wave, diffusive wave, and kinematic wave. For the fully dynamic wave approach, all terms in Eq. (2.1.2) are retained. Under such circumstances, the conservative form of the governing equations may be used or they may be cast in the advection form or in the characteristic form. In this report the characteristic form of the fully dynamic approach will be used as the main option because it is the most natural way and amenable to the advective numerical methods, e.g., the upstream approximation or the Lagrangian-Eulerian method.

For a non-prismatic river/stream/canal network, the cross-sectional area is a function not only of the water depth but also of the river distance, i.e.,

$$A(x,t) = A^{\#}\left(h(x,t),x\right) \tag{2.1.3}$$

where $A^{\#}$ is a function of the water depth $h(x,t)$ and the axis along the river/stream/canal direction x. Differentiating Eq. (2.1.3) with respect to x and t, respectively, we have

$$\frac{\partial A}{\partial t} = \frac{\partial A^{\#}}{\partial h}\frac{\partial h}{\partial t} + \frac{\partial A^{\#}}{\partial x}\frac{\partial x}{\partial t} = \frac{\partial A^{\#}}{\partial h}\frac{\partial h}{\partial t} = B\frac{\partial h}{\partial t} \tag{2.1.4}$$

and

$$\frac{\partial A}{\partial x} = \frac{\partial A^{\#}}{\partial h}\frac{\partial h}{\partial x} + \frac{\partial A^{\#}}{\partial x}\frac{\partial x}{\partial x} = \frac{\partial A^{\#}}{\partial h}\frac{\partial h}{\partial x} + \frac{\partial A^{\#}}{\partial x} = B\frac{\partial h}{\partial x} + \frac{\partial A^{\#}}{\partial x} \tag{2.1.5}$$

where $B(x,t) = B^{\#}(h,x) = \partial A^{\#}/\partial h$ is the top width of the cross-section, [L].

Substituting $Q = VA$ and Eqs. (2.1.4) and (2.1.5) into Eqs. (2.1.1) and (2.1.2), we obtain

$$\frac{\partial h}{\partial t} + V\frac{\partial h}{\partial x} + \frac{A}{B}\frac{\partial V}{\partial x} = \frac{1}{B}\left(S_S + S_R - S_E + S_I + S_1 + S_2\right) - \frac{V}{B}\frac{\partial A^{\#}}{\partial x} \tag{2.1.6}$$

$$\frac{\partial V}{\partial t} + V\frac{\partial V}{\partial x} + g\frac{\partial h}{\partial x} = -\frac{1}{A}\frac{\partial F_x}{\partial x} - g\frac{\partial Z_o}{\partial x} - \frac{gh}{c\rho}\frac{\partial \Delta\rho}{\partial x} + \frac{1}{A}\left[\begin{array}{l} -V\left(S_S + S_R - S_E + S_I + S_1 + S_2\right) + \\ \left(M_S + M_R - M_E + M_I + M_1 + M_2\right) + \dfrac{B\tau^S - P\tau^b}{\rho} \end{array}\right] \tag{2.1.7}$$

Equations (2.1.6) and (2.1.7) can be written in matrix form as

$$\frac{\partial \mathbf{E}}{\partial \mathrm{t}} + \mathbf{A}\frac{\partial \mathbf{E}}{\partial \mathrm{x}} = \mathbf{R} + \mathbf{D} \tag{2.1.8}$$

where

$$\mathbf{E} = \{h \quad V\}^T; \qquad \mathbf{A} = \begin{bmatrix} V & \frac{A}{B} \\ g & V \end{bmatrix}; \qquad \mathbf{R} = \{R_1 \quad R_2\}^T; \qquad \mathbf{D} = \{0 \quad D\}^T \tag{2.1.9}$$

in which

$$R_1 = \frac{1}{B}\left(S_S + S_R - S_E + S_I + S_1 + S_2\right) - \frac{V}{B}\frac{\partial A^{\#}}{\partial x} \tag{2.1.10}$$

$$R_2 = -g\frac{\partial Z_0}{\partial x} - \frac{gh}{c\rho}\frac{\partial(\Delta\rho)}{\partial x} + \frac{1}{A}\begin{bmatrix} -V\left(S_S + S_R - S_E + S_I + S_1 + S_2\right) + \\ \left(M_S + M_R - M_E + M_I + M_1 + M_2\right) + \dfrac{B\tau^s - P\tau^b}{\rho} \end{bmatrix} \tag{2.1.11}$$

$$D = -\frac{1}{A}\frac{\partial F_x}{\partial x} = \frac{1}{A}\frac{\partial}{\partial x}\left(A\varepsilon\frac{\partial V}{\partial x}\right) \qquad \textit{in which} \quad F_x = -A\varepsilon\frac{\partial V}{\partial x} \quad \textit{has been assumed} \tag{2.1.12}$$

where ε is the eddy viscosity.

The eigenvalues and eigenvectors of **A** are

$$\lambda_1 = V + \sqrt{\frac{gA}{B}} \qquad \mathbf{e_1} = \left\{\frac{1}{2}\sqrt{\frac{A}{gB}} \quad \frac{1}{2}\right\}^T \tag{2.1.13}$$

$$\lambda_2 = V - \sqrt{\frac{gA}{B}} \qquad \mathbf{e_2} = \left\{-\frac{1}{2}\sqrt{\frac{A}{gB}} \quad \frac{1}{2}\right\}^T \tag{2.1.14}$$

Denoting $c = \sqrt{\frac{gA}{B}}$, we define

$$\mathbf{L} = \begin{bmatrix} \frac{c}{2g} & -\frac{c}{2g} \\ \frac{1}{2} & \frac{1}{2} \end{bmatrix} \quad \textit{which gives} \quad \mathbf{L^{-1}} = \begin{bmatrix} \frac{g}{c} & 1 \\ -\frac{g}{c} & 1 \end{bmatrix} \tag{2.1.15}$$

where **L** and $\mathbf{L}^{-1}$, respectively, are the right and left eigenmatrices, respectively, of the matrix **A**. Set

$$\partial\mathbf{W} = \mathbf{L}^{-1}\partial\mathbf{E} = \begin{bmatrix} \frac{g}{c} & 1 \\ -\frac{g}{c} & 1 \end{bmatrix}\begin{Bmatrix} \partial h \\ \partial V \end{Bmatrix} \tag{2.1.16}$$

where **W** is a characteristic wave variable. Equation (2.1.16) transforms the primitive variable $\mathbf{E} = \{h, V\}^T$ to the characteristic variable $\mathbf{W} = \{W_1, W_2\}^T$.

Multiplying both side of Eq. (2.1.8) by $\mathbf{L^{-1}}$ yields

$$\mathbf{L^{-1}}\frac{\partial \mathbf{E}}{\partial \mathbf{t}} + \mathbf{L^{-1}A\,L\,L^{-1}}\frac{\partial \mathbf{E}}{\partial \mathrm{x}} = \mathbf{L^{-1}R} + \mathbf{L^{-1}D} \qquad \textbf{(2.1.17)}$$

Since by definition $\partial\mathbf{W} = \mathbf{L^{-1}}\partial\mathbf{E}$ and $\mathbf{L^{-1}AL}$ is a diagonal matrix whose entries are the eigenvalues of **A**, we have

$$\frac{\partial \mathbf{W}}{\partial \mathrm{t}} + \begin{bmatrix} V+c & 0 \\ 0 & V-c \end{bmatrix}\frac{\partial \mathbf{W}}{\partial \mathrm{x}} = \mathbf{L^{-1}R} + \mathbf{L^{-1}D} \qquad or \qquad \frac{D\mathbf{W}}{Dt} = \mathbf{L^{-1}R} + \mathbf{L^{-1}D} \qquad \textbf{(2.1.18)}$$

Substituting $\mathbf{L^{-1}}$ ($\mathbf{L^{-1}}$ is defined by Eq. (2.1.15)) into the right hand side of Eq. (2.1.18) and making an integral transformation so that $(g/c)\partial h = \partial\omega$, we obtain

$$\frac{D_{V+c}(V+\omega)}{D\tau} \equiv \frac{\partial(V+\omega)}{\partial t} + (V+c)\frac{\partial(V+\omega)}{\partial x} = \frac{g}{c}R_1 + R_2 + D \qquad \textbf{(2.1.19)}$$

$$\frac{D_{V-c}(V-\omega)}{D\tau} \equiv \frac{\partial(V-\omega)}{\partial t} + (V-c)\frac{\partial(V-\omega)}{\partial x} = -\frac{g}{c}R_1 + R_2 + D \qquad \textbf{(2.1.20)}$$

in which

$$c = \sqrt{\frac{gA}{B}}; \quad \omega = \int_0^h \frac{g}{c(s)}ds \qquad \textbf{(2.1.21)}$$

where c is the wave speed and ω is the transformed wave speed. Equation (2.1.19) simply states that the positive gravity wave ($V+\omega$) is advected by the speed ($V+c$) while Equation (2.1.20) states that the negative gravity wave ($V-\omega$) is advected by the speed ($V-c$).

For transient simulations, the water depth (or water stage) and the cross-sectionally averaged velocity must be given as the initial condition. In addition, appropriate boundary conditions need to be specified to match the corresponding physical system.

The system of Eqs. (2.1.19) and (2.1.20) are identical to the system of Eqs. (2.1.1) and (2.1.2) on the differential level. They offer advantages in their amenability to innovative advective numerical methods such as the upstream finite difference, upwind finite element, or semi-Lagrangian scheme. Furthermore, the implementation of boundary conditions is very straightforward. Only when the wave is coming into the region of interest, the boundary condition is required. For the wave that is going out of the region of interest, there is no need to specify a boundary condition.

Open upstream boundary condition:

The boundary condition at an upstream point depends on flow conditions. If the flow is supercritical, both waves are transported into the region and two boundary conditions are needed. The water depth and velocity at the boundary are determined entirely by the flow condition that prevails at the upstream. The governing equations for this case can be set up based on the continuity of mass as well as momentum between the boundary and the upstream as follows

$$VA = V_{up}A_{up} = Q_{up} \quad and \quad \rho VAV + \rho g h_c A = \rho V_{up}A_{up}V_{up} + \rho g h_{upc}A_{up} = M_{up} \quad \textbf{(2.1.22)}$$

where V_{up} is the cross-sectional averaged velocity from the incoming upstream fluid, A_{up} is the cross-sectional area in the upstream, Q_{up} is the flow rate of the incoming fluid from the upstream, h_c is the water depth to the centroid of the cross-sectional area of the boundary, h_{upc} is the water depth to the centroid of the upstream cross-sectional area, and M_{up} is the momentum-impulse of the incoming fluid from the upstream. It should be noted that both the water depth and velocity in the upstream must be measured to provide values of Q_{up} and M_{up}. If the flow is critical, the positive wave is transported into the region from upstream and the negative wave is immobile. The water depth and velocity at the boundary are determined by the flow conditions prevail at the upstream and by the condition of critical flow. The governing equations for this case may be set up based on the continuity of mass and the requirement of critical flow condition as

$$VA = Q_{up} \qquad and \qquad \frac{BQ^2}{gA^3} = 1 \qquad \textbf{(2.1.23)}$$

If the flow is subcritical, while the positive wave is transported into the region, the negative wave is transported out of the region. The water depth and velocity are determined by the flow condition prevail at upstream and by flow dynamics in the region. The governing equations are set up based on the continuity of mass between the boundary and the upstream, and on flow dynamics in the region

$$VA = Q_{up} \qquad and \qquad F_{-}(V,h) = 0 \qquad \textbf{(2.1.24)}$$

where $F_{-}(V, h)$, a function of velocity and water depth, is the negative wave boundary function.

In summary, the boundary condition at an open upstream boundary point is given by Eqs. (2.1.22), (2.1.23), and (2.1.24), respectively, for the case of supercritical, critical, and subcritical flows, respectively.

Open downstream boundary condition:

If the flow is supercritical on an open downstream boundary point, both waves are transported out of region. Under such circumstances, no boundary conditions are needed. The water depth and velocity on the boundary are determined by flow dynamics in the region. The governing equations for V and h are

$$F_{+}(V,h) = 0 \qquad and \qquad F_{-}(V,h) = 0 \qquad \textbf{(2.1.25)}$$

where $F_{+}(V, h)$, a function of V and h, is the positive wave boundary function. If the flow is critical, the water depth and velocity at the boundary are determined by flow dynamics in the region and by the condition of critical flow. Thus, the governing equations for critical flow are given by

$$F_{+}(V,h) = 0 \qquad and \qquad \frac{BQ^2}{gA^3} = 1 \qquad \textbf{(2.1.26)}$$

If the flow is subcritical, while the positive wave is transported out of the region, the negative wave is transported into the region. The water depth and velocity are determined by flow dynamics in the region and by what is the control on the boundary. The governing equations may be given by

$$F_+(V,h)=0 \quad and \quad VA=Q_{dn}(h) \qquad or \qquad F_+(V,h)=0 \quad and \quad h=h_{dn}(t) \qquad \textbf{(2.1.27)}$$

where $Q_{dn}(h)$, a function of h, is the rating curve function for the downstream boundary and $h_{dn}(t)$, a function of t, is the water depth at the downstream boundary. The adaptation of Eq. (2.1.27) depends on the physical configuration at the boundary.

In summary, the boundary condition at an open downstream boundary is given by Eqs. (2.1.25), (2.1.26), and (2.1.27), respectively, for the case of supercritical flow, critical flow, and subcritical flows, respectively.

Closed upstream boundary condition:

At the closed upstream boundary, physically all flow conditions can occur. When the supercritical flow happens, both positive and negative waves are transported into the region. Two boundary condition equations are needed. Because the boundary is closed, it is impermeable. The governing equations can be obtained by simply substituting $Q_{up} = 0$ and $M_{up} = 0$ into Eq. (2.1.22) to yield

$$VA=0 \qquad and \qquad \rho VAV+\rho g h_c A=0 \qquad \textbf{(2.1.28)}$$

The solutions for Eq. (2.1.28) are not unique. One possible solution is $V = 0$ and $h = 0$.

For the critical flow, the velocity is equal to the wave speed, $V = c$, the negative wave is immobile. On the other hand, the positive wave is transported into the region of interest, one boundary-condition equation is needed. Because the closed boundary is impermeable, the governing equations may be set up by imposing zero flow rate and the condition of critical flow as

$$VA=0 \qquad and \qquad \frac{BQ^2}{gA^3}=1 \qquad \textbf{(2.1.29)}$$

When the flow is subcritical, the positive wave is transported into the region of interest while the negative wave is transported out of the region of interest. Only the boundary condition for the positive wave is needed. Since no fluid from the outside world is transported into the region via the boundary, the boundary condition for the positive wave can be stated with $Q = VA = 0$. The governing equations for V and h are thus given by

$$VA=0 \qquad and \qquad F_-(V,h)=0 \qquad \textbf{(2.1.30)}$$

In summary, the boundary condition at a closed upstream point is given by Eqs. (2.1.28), (2.1.29), and (2.1.30), respectively, for the case of supercritical flow, critical flow, and subcritical flows, respectively.

Closed downstream boundary condition:

At the closed downstream boundary, physical condition dictates that the velocity at the boundary is zero. Since the velocity is zero, supercritical flow cannot occur at the closed boundary point because the water depth is greater or equal to zero. Therefore, the flow can only be either critical or subcritical. For critical flow, $c = V = 0$, which is very unlikely. Therefore, it is highly unlikely that critical flow will occur at the closed downstream boundary.

For the subcritical flow, the positive wave is transported out of the region and no boundary condition is needed for this wave. On the other hand, the negative wave is transported into the region of interest. The governing equations for V and h are

$$F_+(V,h) = 0 \qquad and \qquad V = 0 \tag{2.1.31}$$

which is based on the physics that $V = 0$ and the water depth is governed by internal flow dynamics.

In summary, supercritical flow cannot occur at a closed downstream point. The boundary condition at a closed downstream boundary point is either V = 0 and h = 0 for critical flow or is given by Eq. (2.1.31) for subcritical flow.

Natural internal boundary condition at junctions:

For the junction node J (Figure 2.1-1), we have one unknown: the water surface elevation or the stage, H_J. The governing equation for this junction is obtained as

$$\frac{d\forall_J}{dh_J}\frac{dh_J}{dt} = \sum_I^{N_J} Q_{IJ} = \sum_I^{N_J} V_{IJ} A_{IJ} \tag{2.1.32}$$

for the case when the storage effect of the junction is accounted for, or

$$\sum_I^{N_J} Q_{IJ} = \sum_I^{N_J} V_{IJ} A_{IJ} = 0 \tag{2.1.33}$$

for the case when the storage effect of the junction is not included.

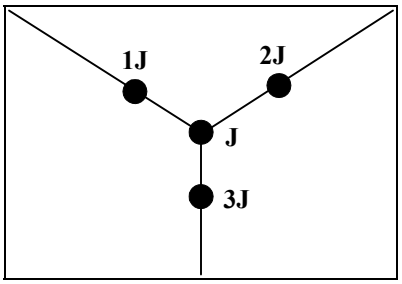


Fig. 2.1-1. Schematic of a Junction

In Eqs. (2.1.32) and (2.1.33), $\forall_J$ is the volume of the junction J; h_J is the water depth of the junction J; Q_{IJ} is the flow rate of the I^{th} reach to the J^{th} junction; I is the identification number of

river/stream/canal reach; N_J is the total number of river/stream/canal reaches that are connected to the junction J (it is 3 in the case shown); V_{IJ} and A_{IJ} are the velocity and cross sectional area, respectively, of the I^{th} reach at the location entering the J^{th} junction.

The node IJ located at the boundary between the I^{th} reach and the J^{th} junction is termed the natural internal boundary of reach I. The governing equations for the internal boundary node IJ depend on whether this node is a downstream or an upstream node in reference to the reach I. Let us say that node IJ is a downstream point if the flow is from the reach I toward the junction J. On the other hand, we say that the node IJ is an upstream point if the flow is from the junction J toward the reach I. With this definition, we can generate equations for any internal boundary node IJ, which will be stated in the following.

If IJ is a downstream internal boundary, we have three cases to consider: subcritical flow, critical flow, and supercritical flow. For the case of subcritical flow, the positive wave is going out of the reach and no boundary condition for this wave is needed. On the other hand, the negative wave is going into the region and its boundary condition is obtained by the assumption that no loss in energy between the junction and node IJ. The governing equations for node IJ are given as

$$F_+\left(V_{IJ}, h_{IJ}\right) = 0 \qquad and \qquad E_{IJ} = \frac{V_{IJ}^2}{2g} + h_{IJ} + Z_{oIJ} = H_J \tag{2.1.34}$$

where $F_+(V_{IJ},h_{IJ})$, a function of the velocity V_{IJ} (velocity at node IJ) and h_{IJ} (water depth at node IJ), is the positive wave boundary function; E_{IJ} is the energy line at node IJ, Z_{oIJ} is the bottom elevation at node IJ; and H_J is the water surface elevation of the junction J. The second equation of Eq. (2.1.34) is obtained from the assumption that the total energy is constant from the junction to the node IJ. In the case of critical flow, the positive wave is going out of the reach and there is no need of a boundary condition for this wave. The negative wave is immobile and its boundary condition is given by the condition of critical flow. The governing equations for node IJ under critical flow are given by

$$F_+\left(V_{IJ}, h_{IJ}\right) = 0 \qquad and \qquad \frac{Q_{IJ}^2 B_{IJ}}{g A_{IJ}^3} = 1 \tag{2.1.35}$$

where B_{IJ} is the top width of the cross-section of the I-th reach at node IJ and A_{IJ} is the cross-section area of the I-th reach at node IJ. In the case of supercritical flow, both positive and negative waves are going out of the reach, therefore no boundary conditions are needed and the governing equations for node IJ under supercritical flow are given by

$$F_+\left(V_{IJ}, h_{IJ}\right) = 0 \qquad and \qquad F_-\left(V_{IJ}, h_{IJ}\right) = 0 \tag{2.1.36}$$

where $F_-\left(V_{IJ}, h_{IJ}\right)$, a function of the velocity V_{IJ} and h_{IJ}, is the negative wave boundary function.

If IJ is an upstream point, we have also three cases to consider: subcritical, critical, and supercritical flows. For the case of subcritical flow, the positive wave is going into the reach and its boundary condition is obtained with the assumption that the specific energy is constant between the junction J and the node IJ. With this assumption, the governing equations for node IJ are given by

$$H_J = \frac{V_{IJ}^2}{2g} + h_{IJ} + Z_{oIJ} \qquad \text{and} \qquad F_{-}(V_{IJ}, h_{IJ}) = 0 \qquad \textbf{(2.1.37)}$$

In the case of critical flow, the positive wave is going into the reach from the junction and its boundary condition is obtained with the assumption of constant energy line between the junction and the node *IJ*, and the negative wave is immobile and its boundary condition is obtained from the condition of critical flow. The governing equations for node *IJ* under critical flow are given by

$$H_J = \frac{V_{IJ}^2}{2g} + h_{IJ} + Z_{oIJ} \qquad \text{and} \qquad \frac{Q_{IJ}^2 B_{IJ}}{g A_{IJ}^3} = 1 \qquad \textbf{(2.1.38)}$$

In the case of supercritical flow, both positive and negative waves are going into the region from the junction *J* to the reach *I*. Two boundary conditions are required for this case. One of the boundary conditions is obtained with the assumption of constant energy line between the junction *J* and the node *IJ*. The other boundary condition is obtained with the assumption that the supercritical flow at node *IJ* will become a critical flow in a very short distance (so short that it can be conceptually considered to locate at *IJ*). With these assumptions the governing equations for node *IJ* under supercritical flow is given by Eq. (2.1.38).

In summary, the governing equations at a natural internal boundary node of a reach connecting to junctions are given by one of Eq. (2.1.34) through (2.1.38) depending on whether the node IJ is a downstream or an upstream point and whether the flow is supercritical, critical, or subcritical.

Controlled internal boundary condition at control structures:

For any structure, *S* (which may be a weir, a gate, or a culvert), there are two river/stream/canal reaches connecting to the structure. The node *1S* located at the upstream of the structure is termed the controlled-internal boundary of the first reach while the Node *2S* located at the downstream of the structure is called the controlled-internal boundary of the second reach (Fig. 2.1-2). The specification of boundary conditions for the internal boundaries separated by a structure requires elaboration.

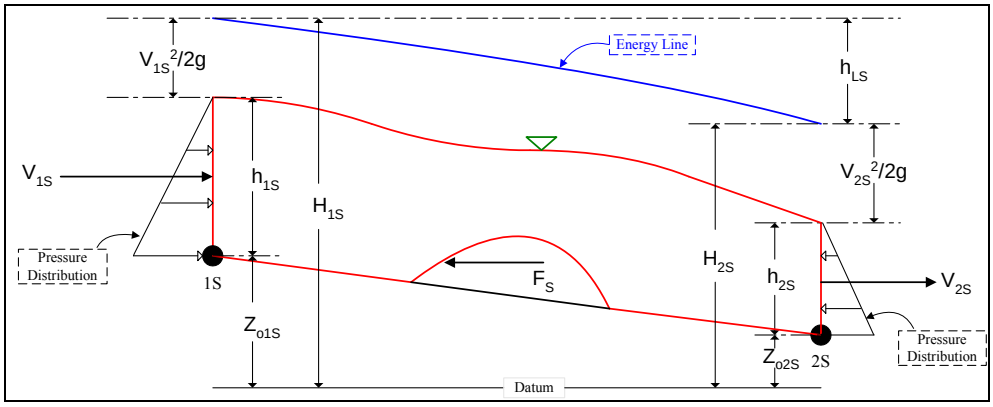


Fig. 2.1-2. The control volume (red outline) between Nodes 1S and 2S

The flow configuration around a structure and its surrounding reaches may be very dynamic under transient flows. Governing equations of flow at Nodes *1S* and *2S* depend on the changing dynamics of water stages around the structure. When both stages are below the height of the structure, the two reaches connecting the structure are decoupled. When at least one of the stages is above the structure, two reaches are either sequentially coupled or fully coupled via the structure. Here for sake of simplicity of discussions, we assume that the flow direction is from Reach *1* to Reach *2*. In other words, Reach *1* is an upstream reach and Reach *2* is a downstream reach. If the flow direction is reversed, we can have the boundary condition similarly prescribed.

There are five unknowns, V_{1S} (velocity of the upstream reach Node *1S*), h_{1S} (the water depth of the upstream Node *1S*), Q (the flow rate through the internal-boundary complex), V_{2S} (the velocity of the downstream reach Node *2S*), and h_{2S} (the water depth of the downstream Node *2S*); five equations must be set up for this internal-boundary complex consisting of a upstream reach node, a structure, and a downstream node. The governing equations for these five unknowns can be obtained depending on the flow conditions at the upstream and downstream reaches separated by the internal boundary structure. The flow condition can be supercritical, critical, or subcritical at Node *1S* and Node *2S*.

Node *1S* is a downstream point relative to the first reach or is the upstream point relative to the structure. The positive wave is transported out of *Reach 1* over the structure to *Reach 2*, and there is no need of a boundary condition for this wave. As for the negative wave, if the flow is supercritical, it is transported out of the reach, and there is no need to prescribe a boundary condition for this wave. Thus, the governing equations for Node *1S* under supercritical flow are given by

$$F_+(V_{1S}, h_{1S}) = 0, \qquad F_-(V_{1S}, h_{1S}) = 0, \qquad \textit{and} \quad Q = V_{1S} A_{1S} \tag{2.1.39}$$

where $F_+(V_{1S},h_{1S})$, a function of V_{1S} and h_{1S}, is the positive wave boundary function; and $F_-(V_{1S},h_{1S})$, a function of V_{1S} and h_{1S}, is the negative wave boundary function.

If the flow is critical, the negative wave is immobile and its governing equation must satisfy the condition of critical flow. Thus, the two governing equations for Node *1S* under critical flow are given by

$$F_+(V_{1S}, h_{1S}) = 0, \qquad \frac{Q^2 B_{1S}}{g A_{1S}^3} = 1, \qquad \textit{and} \quad Q = V_{1S} A_{1S} \tag{2.1.40}$$

where B_{1S} and A_{1S}, respectively, are the top width and the area, respectively, of the cross-section at Node *1S*.

If the flow is subcritical, the negative wave is transported into the reach from the downstream reach via the structure, and its boundary condition is obtained by equating the flow rates at Nodes *1S* and *2S*. Thus the governing equations for Node *1S* under subcritical flow are given by

$$F_+(V_{1S}, h_{1S}) = 0, \qquad V_{1S} A_{1S} = V_{2S} A_{2S}, \qquad \textit{and} \quad Q = V_{1S} A_{1S} \tag{2.1.41}$$

A comment is in order here. When the flow at Note *1S* is supercritical or critical, the flow in the

upstream reach is decouple from the flow in the downstream reach. Under such conditions, Eq. (2.1.39) or (2.1.40) is used to solve to the values of V_{1S} and h_{1S}, which then yield the flow rate Q, the energy level H_{1S} at Node *1S*, or the momentum-impulse M_{1S} at Node *1S*. These quantities (Q, H_{1S}, and M_{1S}) may serve as the boundary conditions for Node *2S*. As to which of these quantities is needed for the internal boundary Node *2S* depends on the flow condition at Node *2S*. This point will be taken up when the boundary conditions for Node *2S* are addressed. When the flow at Node *1S* is subcritical, then the flows in the upstream and downstream reaches are coupled via the second equation in Eq. (2.1.41).

On the other hand, Node *2S* is an upstream point relative to the second reach or a downstream point relative to the structure. If the flow is supercritical at Node *2S*, both the positive and the negative waves are coming into the reach from the upstream reach via the structure, and two boundary conditions are needed. These two boundary conditions can be obtained by the principle of mass continuity and the principle of momentum/impulse or the Bernoulli's equation between Nodes *1S* and *2S*. The structure between Nodes *1S* and *2S* will exert reaction force, F_S, on the fluid between two nodes or it induces energy loss, h_{LS}, between two nodes (Fig. 2.1-2). Thus, the governing equations for Node *2S* are

$$Q = V_{1S}A_{1S}, \qquad V_{2S}A_{2S} = V_{1S}A_{1S}, \qquad \textit{and} \qquad \begin{matrix} H_{2S} + h_{LS} = H_{1S} \\ \textit{or} \\ M_{2S} + F_S = M_{1S} \end{matrix} \tag{2.1.42}$$

where F_S is the force exerted by the structure on the fluid; h_{LS} is the energy loss between Nodes *1* and *2*; H_{2S} and H_{1S} (defined in Fig. 2.1-2), respectively, are the energy level at Nodes *2S* and *1S*, respectively; and M_{2S} ($=\rho V_{2S}A_{2S}V_{2S}+\rho g\, h_{2Sc}A_{2S}$) and M_{1S} ($=\rho V_{1S}A_{1S}V_{1S}+\rho g\, h_{1Sc}A_{1S}$), respectively, are the momentum-impulse at Nodes *2S* and *1S*, respectively (where ρ is the fluid density, g is the gravity constant, h_{2Sc} is the water depth to the centroid of the cross-sectional area at Node *2*, and h_{1Sc} is the water depth to the centroid of the cross-sectional area at Node *1*).

If the flow at Node *2S* is critical, one of the two boundary equations is obtained by the requirement of critical conditions while the other is obtained by the principle of mass continuity and the principle of momentum/impulse or the Bernoulli's equation between Nodes *1S* and *2S*. Thus, the governing conditions for Node *2S* are given as follows

$$\begin{matrix} \dfrac{Q^2 B_{2S}}{gA_{2S}^3} = 1, \qquad V_{2S}A_{2S} = V_{1S}A_{1S}, \qquad Q = V_{1S}A_{1S} \\ \textit{or} \\ \dfrac{Q^2 B_{2S}}{gA_{2S}^3} = 1, \qquad V_{2S}A_{2S} = V_{1S}A_{1S}, \qquad Q = V_{1S}A_{1S}, \quad \textit{and} \end{matrix} \qquad \begin{matrix} H_{2S} + h_{LS} = H_{1S} \\ \textit{or} \\ M_{2S} + F_{1S} = M_{1S} \end{matrix} \tag{2.1.43}$$

If the flow at Node *2S* is subcritical, the positive wave is transported into the reach from the upstream reach via the structure while the negative wave is transport out of the reach. The boundary condition for the positive wave is obtained by the principle of mass continuity and the principle of

momentum/impulse or the Bernoulli's equation between Nodes *1S* and *2S*. Thus the two governing equations for Node *2S* under subcritical flow are given as follows

$$F_{-}(V_{2S}, h_{2S}) = 0, \qquad V_{2S}A_{2S} = V_{1S}A_{1S}, \qquad Q = V_{1S}A_{1S}$$

or

$$F_{-}(V_{2S}, h_{2S}) = 0, \quad V_{2S}A_{2S} = V_{1S}A_{1S}, \quad Q = V_{1S}A_{1S}, \quad \textit{and} \quad \begin{matrix} H_{2S} + h_{LS} = H_{1S} \\ \textit{or} \\ M_{2S} + F_{1S} = M_{1S} \end{matrix} \qquad \textbf{(2.1.44)}$$

In summary, the governing equations for internal boundary nodes separated by a structure are given by any combination of Eq. (2.1.39), (2.1.40), or (2.1.41) and Eq. (2.1.42), (2.1.43), or (2.1.44). All combinations provide five governing equations for five unknowns (V_{1S}, h_{1S}, Q, V_{2S}, and h_{2S}), except for one combination.

The combination of Eq. (2.1.41) and Eq. (2.1.42) only generates four equations; one more equation is needed. This combination represents the situation that flow in the upstream reach is subcritical and in the downstream reach is supercritical. For this situation to occur, flow must under go a transitional state of critical flow over the structure, and the critical flow condition on the structure must be satisfied. Thus, the following additional governing equations can be set up by applying the principle of mass continuity and the principle of momentum-impulse or the Bernoulli equation to a control volume between Node 1S and the structure (Fig. 2.1-3) as

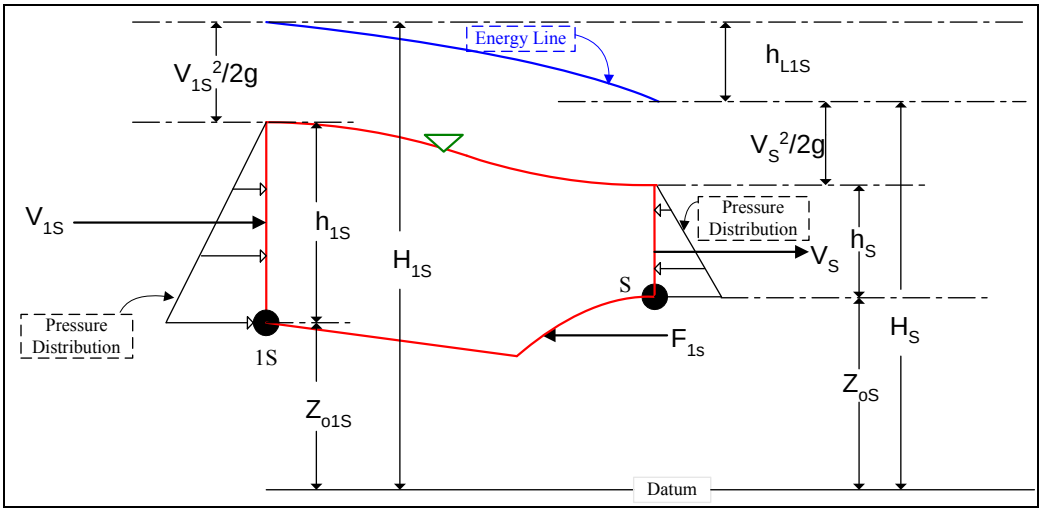


Fig. 2.1-3. The control volume (red outline) between Node 1S and structure.

$$\frac{Q^2 B_S}{gA_S^3} = 1, \qquad V_S A_S = V_{1S}A_{1S}, \qquad Q = V_{1S}A_{1S}, \quad \textit{and} \quad \begin{matrix} H_S + h_{L1S} = H_{1S} \\ \textit{or} \\ M_S + F_{1S} = M_{1S} \end{matrix} \qquad \textbf{(2.1.45)}$$

where A_S, B_S, and V_S, are the area, top width, and velocity of the cross-sectional area over the

structure; h_{L1S} is head loss between Node 1S and the structure; F_{1S} is the force the structure exerts on the fluid between Node 1S and the structure, H_S is the total head over the structure (Fig. 2.1-3); and M_S (= $\rho V_S A_S V_S$ + g $h_{Sc} A_S$) is the momentum-impulse at the structure (where h_{Sc} is the water depth to the centroid of the cross-sectional area at the structure). Now, Eq. (2.1.41), (2.1.42), and (2.1.45) give seven equations for seven unknowns (V_{1S}, h_{1S}, Q, V_{2S}, h_{2S}, V_S, and h_S).

The theoretical presentation about the governing equations for the internal-boundary complex is valid for any structure including weirs, gates, and culverts. The differences among various structures are characterized by the formulation of the head loss functions, $h_{LS}(Q, h_{1S}, h_{2S})$ and h_{L1S} (Q, h_{1S}, h_S), which depend on the flow rate Q and the water depth h_{1S}, and h_{2S}.

2.1.2 Diffusive Wave Approaches

In a diffusive approach, the inertia terms in the momentum equation is assumed negligible when compared with the other terms. By further assuming negligible eddy viscosity and $M_S = M_R = M_E = M_I = M_1 = M_2 = 0$, we approximate the river/stream/canal velocity with the following equation (Hergarten and Neugebauer, 1995).

$$V = \frac{-a}{n}\left[\frac{R}{1+\left(\frac{\partial Z_o}{\partial x}\right)^2}\right]^{2/3} \frac{1}{\sqrt{\left|-\frac{\partial H}{\partial x} - \frac{h}{c\rho}\frac{\partial \Delta\rho}{\partial x} + \frac{B\tau^S}{Ag\rho}\right|}}\left(\frac{\partial H}{\partial x} + \frac{h}{c\rho}\frac{\partial \Delta\rho}{\partial x} - \frac{B\tau^S}{Ag\rho}\right) \qquad \textbf{(2.1.46)}$$

where n is Manning's roughness [$tL^{-1/3}$], a is a unit-dependent factor ($a = 1$ for SI units and $a = 1.49$ for U.S. Customary units) to make the Manning's roughness unit-independent, R is the hydraulic radius [L], and $H = h + Z_o$ is the water stage.

Using the definition $Q = VA$ and substituting Eq. (2.1.46) into Eq. (2.1.1), we obtain

$$B\frac{\partial H}{\partial t} - \frac{\partial}{\partial x}\left(K\left[\frac{\partial H}{\partial x} + \frac{h}{c\rho}\frac{\partial \Delta\rho}{\partial x} - \frac{B\tau^S}{Ag\rho}\right]\right) = S_S + S_R - S_E + S_I + S_1 + S_2 \qquad \textbf{(2.1.47)}$$

in which

$$K = \frac{a\,A\,R^{2/3}}{n}\frac{1}{\left[1+\left(\frac{\partial Z_o}{\partial x}\right)^2\right]^{2/3}}\frac{1}{\sqrt{\left|-\frac{\partial H}{\partial x} - \frac{h}{c\rho}\frac{\partial \Delta\rho}{\partial x} + \frac{B\tau^S}{Ag\rho}\right|}} \qquad \textbf{(2.1.48)}$$

To achieve transient simulations, either water depth or stage must be given as the initial condition. In addition, appropriate boundary conditions need to be specified to match the corresponding physical system. In our model, four types of boundary conditions may be specified depending on physical configurations of the boundary. These boundary conditions are addressed below.

Dirichlet boundary condition: prescribed water depth or stage

On a Dirichlet boundary, either the water depth or stage can be prescribed as a function of time.

This boundary condition can be expressed as

$$h = h_d(t) \qquad or \qquad H = h + Z_o = H_d, \quad on \quad B_d \tag{2.1.49}$$

where $h_d(t)$ is a prescribed time-dependent water depth on the Dirichlet boundary [L], $H_d(t)$ is a prescribed time-dependent water stage [L], and B_d is the Dirichlet boundary point. A Dirichlet boundary point can locate at the upstream or down stream point, control structures, or even interior point.

Flux boundary condition: prescribed flow rate

On a flux boundary, a time-dependent flow rate is prescribed as a function of time as

$$-K\left(\frac{\partial H}{\partial x} + \frac{h}{c\rho}\frac{\partial \Delta\rho}{\partial x} - \frac{B\tau^S}{Ag\rho}\right) = Q_f(t) \quad on \quad B_f \tag{2.1.50}$$

where $Q_f(t)$ a prescribed time-dependent flow rate [L^3/t] and B_f is a flux boundary point. Mathematically, a flux boundary condition can be applied to an upstream or downstream point. However, in practice, it is often applied to an upstream boundary point.

Water depth-dependent boundary condition: prescribed rating curve

This condition is often used to describe the flow rate at a downstream river/stream boundary at which the flow rate is a function of water depth. It can be written as

$$-K\left(\frac{\partial H}{\partial x} + \frac{h}{c\rho}\frac{\partial \Delta\rho}{\partial x} - \frac{B\tau^S}{Ag\rho}\right) = Q_r(h(x_r, t)) \quad on \quad B_r \tag{2.1.51}$$

where $Q_r(h(x_r,t))$ is a water depth-dependent flow rate [L^3/t], x_r is the x-coordinate on the boundary B_r, and B_r is a boundary point on which the prescribed rating curve is applied.

Junction boundary condition:

This condition is applied to a boundary of a river/stream/canal reach that is connected to a junction (Fig. 2.1-1). For the junction complex consisting of N_J river/stream/canal reaches (e.g., in Fig. 2.1-1, $N_J = 3$) and one junction (say J), we have ($N_J + 1$) unknowns, which are flow rates, Q_{IJ} (Q_{IJ} is the flow rate from the I-th reach to junction J), and water stage at junction J, H_J. Therefore, we need to set up ($N_J + 1$) equations. The first equation is obtained by applying the continuity of mass at the junction to result in Eq. (2.1.35) for the case when the storage effect of the junction must be accounted for or Eq. (2.1.36) when this effect is negligible. The other N_J equations can be obtained by assuming the energy loss from any reach to the junction is negligible to result in

$$\frac{1}{2g}\left(\frac{Q_{IJ}}{A_{IJ}}\right)^2 + H_{IJ} = H_J, \quad I \in N_J \quad where \quad Q_{IJ} = -K\left(\frac{\partial H}{\partial x} + \frac{h}{c\rho}\frac{\partial \Delta\rho}{\partial x} - \frac{B\tau^S}{Ag\rho}\right)\Bigg|_{IJ} \tag{2.1.52}$$

where H_{IJ} is the water stage the internal boundary Node IJ of the I-th reach connecting to junction J.

Equations (2.1.32) or (2.1.33) along with Eq. (2.1.52) provide ($N_J + 1$) equations to solve for ($N_J + 1$) unknowns.

Weir boundary condition:

For any weir (*W*), there are two river/stream/canal reaches connecting to it. Node *1W* located just upstream of the weir is termed the controlled-internal boundary of the upstream reach while Node *2W* located just downstream of the weir is called the controlled-internal boundary of the downstream reach (Figure 2.1-4). The specification of boundary conditions for the internal boundaries for the diffusive wave approach is given as

$$-\mathbf{n}\cdot\mathrm{K}\left(\nabla H+\frac{h}{c\rho}\nabla(\Delta\rho)-\frac{B\tau^{S}}{Ag\rho}\right)\Big|_{1\mathrm{W}}=Q_{W}\left(h_{up},h_{dn}\right)\qquad \textit{and}$$
$$-\mathbf{n}\cdot\mathrm{K}\left(\nabla H+\frac{h}{c\rho}\nabla(\Delta\rho)-\frac{B\tau^{S}}{Ag\rho}\right)=Q_{W}\left(h_{up},h_{dn}\right) \qquad \textbf{(2.1.53)}$$

where Q_w is the weir discharge rate, which is a given function of the water depths h_{up} at Node *1W* and h_{dn} at Node *2W* (Fig. 2.1-5).

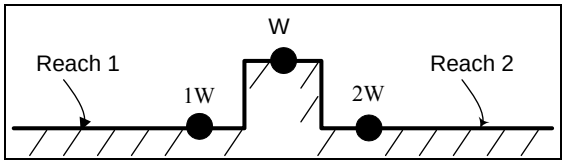


Fig. 2.1-4. Schematic of weir.

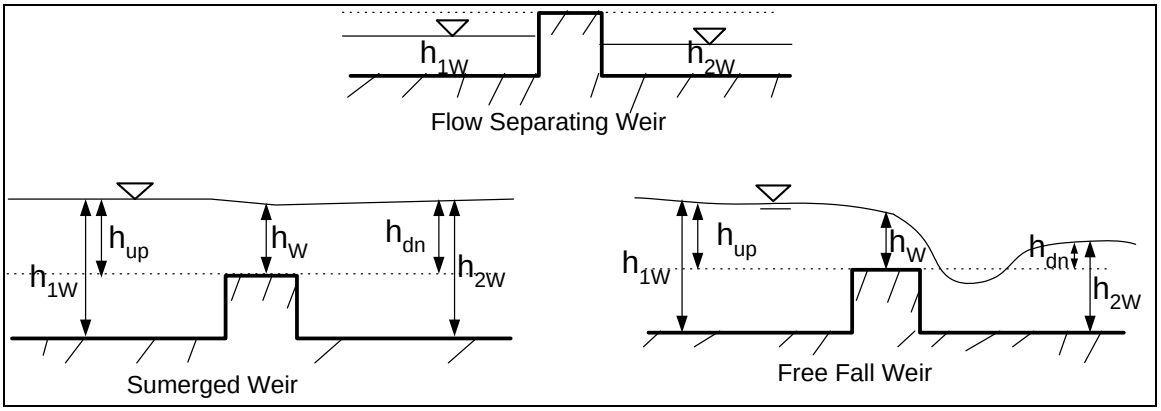


Fig. 2.1-5. Flow configurations around a weir.

The flow configuration around the weir and its surrounding reaches may be very dynamic under transient flows. Both of the water stages at Nodes *1W* and *2W* may be below the weir, both may be above the weir, or one below the weir while the other is above the weir (Fig. 2.1-5). When both stages are below the height of the weir, the two reaches connecting the weir are decoupled. When at least one of the stages is above the weir, two reaches are coupled via the weir. The weir discharge, Q_w, can be obtained by solving the continuity equation and the Bernoulli equation between Nodes *1W* and *2W*. The weir formulae under various stage conditions are given as

(1) For submerged flow

$$Q_W = C_W h_{dn} L_W \sqrt{2g\left(h_{up} - h_{dn}\right)} \quad if \quad h_{dn} \geq \frac{2}{3} h_{up} \quad and \quad h_{dn} < h_{up} \tag{2.1.54}$$

(2) For free fall flow

$$Q_W = \frac{2}{3\sqrt{3}} C_W h_{up} L \sqrt{2g h_{up}} \quad if \quad h_{dn} < \frac{2}{3} h_{up} \tag{2.1.55}$$

(3) For decoupled flow

$$Q_W = 0 \tag{2.1.56}$$

where C_w is the weir coefficient and L_w is the weir length. It should be noted that the above formulae are valid for broad weir. For other types of weirs, different weir discharge formulae may be used and they can easily be incorporated into the computer code.

Gate boundary condition:

For any gate (G), there are two river/stream/canal reaches connecting to it. Node *1G* located just upstream of the gate G is termed the controlled-internal boundary of the upstream reach while Node *2G* located just downstream of the gate G is called the controlled-internal boundary of the downstream reach (Fig. 2.1-6). The specification of boundary conditions for the internal boundaries separated by a gate can be made similar to that of a weir as follows.

$$\begin{aligned} -\mathbf{n}\cdot\mathbf{K}\left(\nabla H + \frac{h}{c\rho}\nabla(\Delta\rho) - \frac{B\tau^S}{Ag\rho}\right)\Big|_{1G} &= Q_g\left(h_{up}, h_{dn}\right) \quad and \\ -\mathbf{n}\cdot\mathbf{K}\left(\nabla H + \frac{h}{c\rho}\nabla(\Delta\rho) - \frac{B\tau^S}{Ag\rho}\right)\Big|_{2G} &= Q_g\left(h_{up}, h_{dn}\right) \end{aligned} \tag{2.1.57}$$

where Q_g is the gate discharge rate, which is a given function of the water depths h_{up} at *1G* and h_{dn} at *2G* (Fig. 2.1-7).

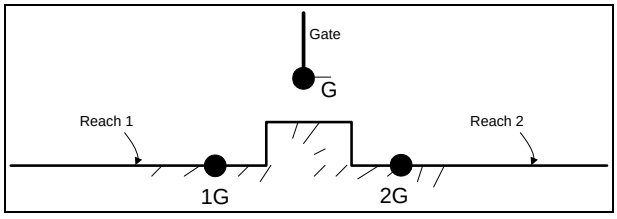


Fig. 2.1-6. Schematic of Gate.

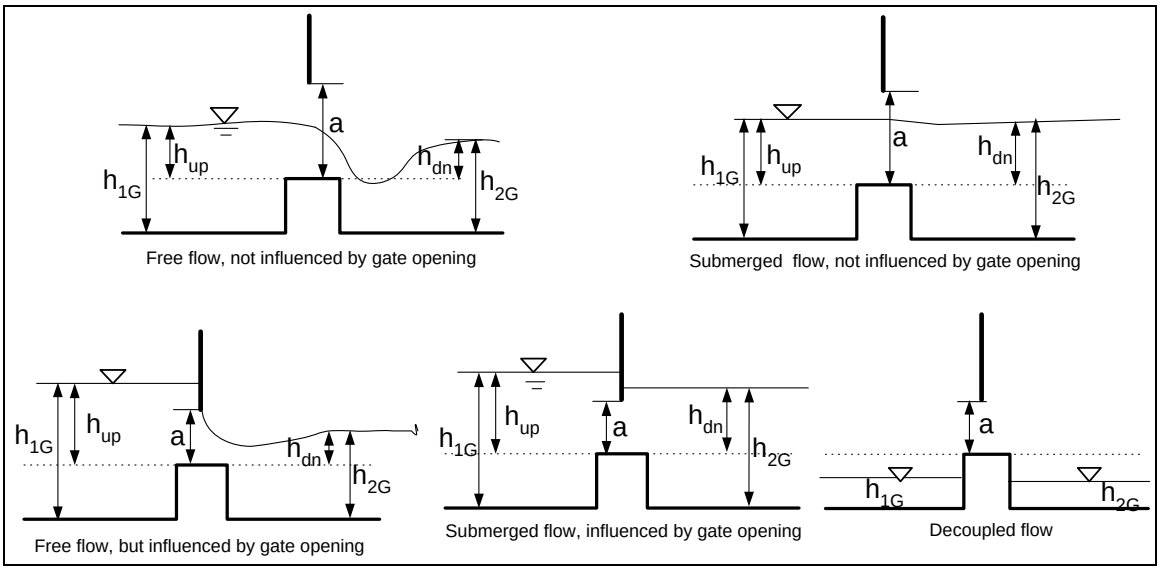


Fig. 2.1-7. Flow configurations around a gate.

The flow configuration around the gate and its surrounding reaches may be very dynamic under transient flows. Depending on the water stages at Nodes *1G* and *2G* (H_{1G} and H_{2G}), we have several configurations (Fig. 2.1-7). The gate discharge, Q_g, can be obtained by solving the continuity equation and the Bernoulli equation between Nodes *1G* and *2G*. The gate formulae under various stage conditions are given as

(1) For free fall flow and not influenced by the gate opening

$$Q_g = \frac{2}{3\sqrt{3}} C_g h_{up} L_g \sqrt{2gh_{up}} \quad if \quad h_{dn} < \frac{2}{3} h_{up} \quad and \quad a > \frac{2}{3} h_{up} \tag{2.1.58}$$

(2) For submerged flow and not influenced by the gate opening

$$Q_g = C_g h_{dn} L_g \sqrt{2g\left(h_{up} - h_{dn}\right)} \quad if \quad h_{dn} \geq \frac{2}{3} h_{up}, h_{dn} < h_{up}, \quad and \quad a > \frac{2}{3} h_{up} \tag{2.1.59}$$

(3) For free flow and influenced by the gate opening

$$Q_g = \frac{2}{3\sqrt{3}} C_g a L_g \sqrt{2gh_{up}} \quad if \quad h_{dn} < \frac{2}{3} h_{up} \quad and \quad a < \frac{2}{3} h_{up} \tag{2.1.60}$$

(4) For submerged flow and influenced by the gate opening

$$Q_g = C_g a L_g \sqrt{2g\left(h_{up} - h_{dn}\right)} \quad if \quad h_{dn} \geq \frac{2}{3} h_{up}, h_{dn} < h_{up}, \quad and \quad a < \frac{2}{3} h_{up} \tag{2.1.61}$$

(5) For decoupled flow

$$Q_g = 0 \tag{2.1.62}$$

where C_g is the gate coefficient, a is the gate opening, and L_g is the weir length.

Culvert boundary condition:

Similar to weirs and gates, the boundary conditions for the culvert can be stated as

$$\begin{aligned} -\mathbf{n}\cdot\mathbf{K}\left(\nabla H+\frac{h}{c\rho}\nabla(\Delta\rho)-\frac{B\tau^S}{Ag\rho}\right)\Big|_{1C}&=Q_C\left(h_{up},h_{dn}\right)\quad and\\ -\mathbf{n}\cdot\mathbf{K}\left(\nabla H+\frac{h}{c\rho}\nabla(\Delta\rho)-\frac{B\tau^S}{Ag\rho}\right)\Big|_{2C}&=Q_C\left(h_{up},h_{dn}\right)\end{aligned} \tag{2.1.63}$$

where Q_c is the discharge through the culvert or culverts, Node *1C* is the point upstream of the culvert and *2C* is the point downstream of the culvert, h_{up} is the water stage above the culvert at Node *1C*, and h_{dn} is the water stage above the culvert at Node *2C*. A wide range of culvert discharge formulae can be used and they can be easily incorporated in the computer code.

2.1.3 Kinematic Wave Approaches

In a kinematic approach, all the assumptions for the diffusive approach are hold. However, the velocity is given by modifying Eq. (2.1.46) with $\partial Z_o/\partial x$ replacing $\partial H/\partial x$ as follows

$$V=\frac{-a}{n}\left[\frac{R}{1+\left(\frac{\partial Z_0}{\partial x}\right)^2}\right]^{2/3}\frac{1}{\sqrt{\left|-\frac{\partial Z_o}{\partial x}-\frac{h}{c\rho}\frac{\partial\Delta\rho}{\partial x}+\frac{B\tau^S}{Ag\rho}\right|}}\left(\frac{\partial Z_o}{\partial x}+\frac{h}{c\rho}\frac{\partial\Delta\rho}{\partial x}-\frac{B\tau^S}{Ag\rho}\right) \tag{2.1.64}$$

Substituting Eq. (2.1.64) into Eq. (2.1.1) and using the definition $Q = VA$, we obtain

$$\frac{\partial A}{\partial t}+\frac{\partial VA}{\partial x}=S_S+S_R-S_E+S_I+S_1+S_2 \tag{2.1.65}$$

It is noted that Eq. (2.1.65) represents the advective transport of the cross-sectional area, A. It is an ideal equation amenable for numerically innovative advective transport algorithm.

To achieve transient simulations, either water depth or stage must be given as the initial condition. In addition, appropriate boundary conditions need to be specified to match the corresponding physical configuration. In a kinematic wave approach, boundary conditions are required only at upstream boundaries. An upstream boundary point can be an open boundary or a closed boundary. On an open upstream boundary, either the cross-sectional area (equivalent to water depth or water stage) or the flow rate can be specified as

$$A=A_{up}\quad or\quad \mathbf{n}\cdot\mathrm{VA}=\mathrm{Q_{up}}\quad on\quad B_{up} \tag{2.1.66}$$

where H_{up} is the water stage of the incoming upstream flow, Q_{up} is the flow rate of the incoming

upstream flow, and B_{up} is the open upstream boundary point. The flow rate through a closed upstream boundary point is by default equal to zero.

2.1.4 Thermal Transport

The thermal transport equation is derived based on the conservation principle of energy as:

$$\frac{\partial(\rho_W C_W AT)}{\partial t}+\frac{\partial(\rho_W C_W QT)}{\partial x}-\frac{\partial}{\partial x}\left(D^H A\frac{\partial T}{\partial x}\right) = S_h^a + S_h^r + S_h^n - S_h^b - S_h^e - S_h^s + S_h^i + S_h^{o1} + S_h^{o2} + S_h^c \quad \textbf{(2.1.67)}$$

where ρ_w is the water density [M/L^3]; C_w is the heat capacity of water [L^2/t^2/T]; T is the temperature [T]; D^H is the apparent thermal conductivity including the effect of dispersion, diffusion, and conduction [E/t/L/T = ML/t^3/T, where E is the unit of energy]; S_h^a is the heat source due to artificial injection/withdraw including rainfall [E/t/L = ML/t^3]; S_h^r is the heat source due to rainfall [E/t/L=ML/t^3]; S_h^n is the heat source due to net radiation [E/t/L = ML/t^3]; S_h^b is the heat sink due to back radiation from water surface to the atmosphere [E/t/L = ML/t^3]; S_h^e is the heat sink due to evaporation [E/t/L = ML/t^3]; S_h^s is the heat sink due to sensible heat flux [E/t/L = ML/t^3]; S_h^i is the heat source due to exfiltration from subsurface [E/t/L = ML/t^3]; S_h^{o1} is the heat source from overland flow via Bank *1* [E/t/L = ML/t^3]; S_h^{o2} is the heat source from overland flow via Bank *2* [E/t/L = ML/t^3]; and S_h^c is the heat source due to chemical reaction [E/t/L = ML/t^3]. In Eq. (2.1.67), S_h^r, S_h^i, S_h^{o1}, and S_h^{o2} are given by

$$S_h^r = C_W \rho_W S_R T^r; \qquad S_h^i = \begin{cases} C_W \rho_W S_I T^i & if \quad S_I \geq 0 \\ C_W \rho_W S_I T & if \quad S_I < 0 \end{cases} \quad \textbf{(2.1.68)}$$

and

$$S_h^{o1} = \begin{cases} C_W \rho_W S_1 T^{o1} & if \quad S_1 \geq 0 \\ C_W \rho_W S_1 T & if \quad S_1 < 0 \end{cases}; \qquad S_h^{o2} = \begin{cases} C_W \rho_W S_2 T^{o2} & if \quad S_2 \geq 0 \\ C_W \rho_W S_2 T & if \quad S_2 < 0 \end{cases} \quad \textbf{(2.1.69)}$$

where T^r is the temperature of the rainwater [T], T^i is the temperature of the exfiltration water from the subsurface flow [T], T^{o1} is the temperature of the water from overland flow via river Bank *1* [T], and T^{o2} is the temperature of the water from overland flow via river Bank *2* [T].

The heat source due to net radiation, S_h^n, heat sink due to back radiation, S_h^b, heat sink due to evaporation, S_h^e, and heat sink due to sensible heat, S_h^s, are given by their respective heat fluxes as follows

$$S_h^n = BH_n; \quad S_h^b = BH_b; \quad S_h^e = BH_e; \quad S_h^s = BH_s \quad \textbf{(2.1.70)}$$

where H_n, H_b, H_e, and H_s are the net radiation flux, back radiation flux, latent heat flux, and sensible heat flux, respectively. These fluxes depend on only meteorological condition and water temperature. They may be computed from follow equations (Yeh, 1969; Yeh et al., 1973; McCuen, 1989; Song and Li. 2000; and Jennifer et al., 2002).

Net radiation H_n

$$H_n = (1 - a_s)H_{so} + (1 - a_\ell)H_{\ell o} \qquad \textbf{(2.1.71)}$$

in which

$$H_{so} = H_o \cdot (0.61s + 0.35) \quad Btu / ft^2 / day \qquad \textbf{(2.1.72)}$$

and

$$H_{\ell o} = \varepsilon\sigma(T_a + 460)^4 \left[C + 0.031(e_a)^{1/2}\right] \qquad Btu / ft^2 / day \qquad \textbf{(2.1.73)}$$

where a_s and a_ℓ are the albedos of the water surface for short- and long-wave radiation respectively; H_{so} and $H_{\ell o}$ are the solar short- and long-wave radiation respectively; H_o is the solar constant, s is the percentage of possible sunshine; ε **= 0.97** is emissivity of water surface**;** $\sigma = 4.15 \times 10^{-8}$ Btu/ft^2/day/R^4 is the Stenfan-Boltzmann constant; T_a is air temperature in ^oF; C is the brunt coefficient; and e_a is the air vapor pressure in millimeter of mercury.

Back radiation H_b

$$H_b = \varepsilon\sigma(T_a + 460)^4 \quad Btu / ft^2 / day \qquad \textbf{(2.1.74)}$$

Sensible heat flux H_s

$$H_s = 0.26(73 + 7.3W)(T - T_a) \cdot (p / 760) \quad Btu / ft^2 / day \qquad \textbf{(2.1.75)}$$

where W is the wind speed in miles per hour and p is the atmospheric pressure in millimeter of mercury.

Latent heat flux of evaporation H_e

$$H_e = 0.26(73 + 7.3W)(e_w - e_a) \quad Btu / ft^2 / day \qquad \textbf{(2.1.76)}$$

where e_w is the saturated vapor pressure in millimeter of mercury at the water temperature T.

In addition to the initial boundary condition, boundary conditions must be specified for the temperature. Four types of global boundary conditions are provided in this report as follows.

Dirichlet boundary condition:

This condition is applied when the temperature is prescribed as a function of time on the boundaries:

$$T = T_{db}(x_b, t) \quad on \quad B_d \qquad \textbf{(2.1.77)}$$

where $T_{db}(x_b,t)$ is a time-dependent temperature on the Dirichlet boundary B_d [T].

Variable boundary condition:

This boundary condition is employed when the flow direction would change with time during simulations. Two cases are considered, regarding to the flow direction on the boundary.

< Case 1 > Flow is coming in from outside:

$$\rho_w C_w Q T - D^H A \frac{\partial T}{\partial x} = \rho_w C_w Q T_{vb}(x_b, t) \quad on \quad B_v \tag{2.1.78}$$

< Case 2 > Flow is going out from inside:

$$- D^H A \frac{\partial T}{\partial x} = 0 \quad on \quad B_v \tag{2.1.79}$$

where $T_{vb}(x_b,t)$ is a time-dependent temperature [T] through the variable boundary B_v, which is associated with the incoming flow.

Cauchy boundary condition:

This boundary condition is employed when the total heat-flow rate is given at the river/stream boundary. Usually, this boundary is an upstream boundary node. The conditions can be expressed as

$$\rho_w C_w Q T - D^H A \frac{\partial T}{\partial x} = \Phi_{cb}(x_b, t) \tag{2.1.80}$$

where $\Phi_{cb}(x_b,t)$ is total heat-flow rate (E/t = ML^2/t^3, where E denotes the unit of energy) through the Cauchy boundary, which takes a positive value if it is going out of the region and a negative value if it is coming into the region.

Neumann boundary condition:

This boundary condition is used when the conductive heat-flow rate is known at the river/stream boundary node. It can be written as

$$- D^H A \frac{\partial T}{\partial x} = \Phi_{nb}(x_b, t) \tag{2.1.81}$$

where $\Phi_{nb}(x_b,t)$ is the heat flux through the Neumann boundary.

In addition to the above four types of global boundary conditions, two types of internal boundary conditions are implemented: internal boundary nodes connecting to natural junctions and two internal boundary nodes for every control structures. These internal boundary conditions are mathematically stated similar to fluid flow of diffusive wave approaches.

Internal boundary condition at junctions:

If Node *IJ* is the internal node from Reach *I* connecting to Junction *J* (Fig. 2.1-1), the boundary conditions at Node *IJ* is given as

$$\left(\rho_w C_w QT - D^H A\frac{\partial T}{\partial x}\right)\Big|_{IJ} = \rho_w C_w \frac{1}{2} Q_{IJ}\left[(1+sign(Q_{IJ}))T_{IJ} + (1-sign(Q_{IJ}))T_J\right] \qquad \textbf{(2.1.82)}$$

where $sign(Q_{IJ})$ is equal 1.0 if the flow is from Reach I into Junction J, -1.0 if flow is from Junction J into Reach I; T_{IJ} is the temperature at Node IJ; and T_J is the temperature at Junction J which is given by

$$\sum_i \rho_w C_w \frac{1}{2} Q_{iJ}\left[(1+sign(Q_{iJ}))T_{iJ} + (1-sign(Q_{ij}))T_J\right] = 0 \qquad \textbf{(2.1.83)}$$

if the storage effect of Junction J is negligible or

$$\frac{d(\rho_w C_w V_J T_J)}{dt} = \sum_i \rho_w C_w \frac{1}{2} Q_{iJ}\left[(1+sign(Q_{iJ}))T_{iJ} + (1-sign(Q_{iJ}))T_J\right] \qquad \textbf{(2.1.84)}$$

if the storage effect of Junction J is significant.

Internal boundary condition at control structure:

If Nodes *1S* and *2S* are two internal boundary nodes connecting to Structure S (Fig. 2.1-2), the boundary conditions at Nodes *1S* and *2S* are given

$$\begin{aligned}\left(\rho_w C_w QT - D^H A\frac{\partial T}{\partial x}\right)\Big|_{1S} &= \left(\rho_w C_w QT - D^H A\frac{\partial T}{\partial x}\right)\Big|_{2S} \\ &= \rho_w C_w \frac{1}{2} Q_S\left[(1+sign(Q_S))T_{1S} + (1-sign(Q_S))T_{2S}\right]\end{aligned} \qquad \textbf{(2.1.85)}$$

where $sign(Q)$ is equal 1.0 if the flow is from Node *1S* to Node *2S*, -1.0 if flow is from Node *2S* to Node *1S*; T_{1S} is the temperature at Node *1S*; and T_{2S} is the temperature at Node *2S*.

2.1.5 Salinity Transport

$$\frac{\partial(AS)}{\partial t} + \frac{\partial(QS)}{\partial x} - \frac{\partial}{\partial x}\left(D^S A\frac{\partial S}{\partial x}\right) = M_s^{\,a} + M_s^{\,r} - M_s^{\,e} + M_s^{\,i} + M_s^{\,ol} + M_s^{\,o2} \qquad \textbf{(2.1.86)}$$

where S is the salinity [M/L^3]; D^S is the longitudinal dispersion coefficient for salinity [L^2/t]; $M_s^{\,a}$ is the artificial source of the salt [M/t/L]; $M_s^{\,r}$ is the salt source from rainfall [M/t/L]; $M_s^{\,e}$ is the salt sink from evaporation, which most likely would be zero [M/t/L]; $M_s^{\,i}$ is the salt source from subsurface [M/t/L]; $M_s^{\,o1}$ is the salt source from overland via River Bank *1* [M/t/L]; and $M_s^{\,o2}$ is the salt source from overland source viz River Bank *2* [M/L/t]. In Eq. (2.1.86), $M_s^{\,e}$ is likely to be zero and $M_s^{\,r}$, $M_s^{\,i}$, $M_s^{\,o1}$, and $M_s^{\,o2}$ are given by

$$M_s^{\,r} = S_R S^r; \qquad M_s^{\,i} = \begin{cases} S_I S^i & if \quad S_I \ge 0 \\ S_I S & if \quad S_I < 0 \end{cases} \qquad \textbf{(2.1.87)}$$

and

$$M_s^{ol} = \begin{cases} S_1 S^{ol} & if \quad S_1 \geq 0 \\ S_1 S & if \quad S_1 < 0 \end{cases}; \qquad M_s^{o2} = \begin{cases} S_2 S^{o2} & if \quad S_2 \geq 0 \\ S_2 S & if \quad S_2 < 0 \end{cases} \tag{2.1.88}$$

where S^r is the salinity of the rainwater [M/L^3], S^i is the salinity of the exfiltration water from the subsurface flow [M/L^3], S^{o1} is the salinity of the water from overland flow via River Bank *1* [M/L^3], and S^{o2} is the salinity of the water from overland flow via River Bank *2* [M/L^3].

As in thermal transport, four types of global boundary conditions for salinity transport are provided in this report as follows:

Dirichlet boundary condition:

This condition is applied when the salinity is prescribed as a function of time on the boundaries:

$$S = S_{db}\left(x_b, t\right) \tag{2.1.89}$$

where $S_{db}\left(x_b, t\right)$ is a time-dependent salinity on the Dirichlet boundary [M/L^3].

Variable boundary condition:

This boundary condition is employed when the flow direction would change with time during simulations. Two cases are considered, regarding to the flow direction on the boundary.

< Case 1 > Flow is coming in from outside:

$$QS - D^S A \frac{\partial S}{\partial x} = QS_{vb}\left(x_b, t\right) \tag{2.1.90}$$

< Case 2 > Flow is going out from inside:

$$-D^S A \frac{\partial S\left(x_b, t\right)}{\partial x} = 0 \tag{2.1.91}$$

where $S_{vb}\left(x_b, t\right)$ is a time-dependent salinity on the variable boundary [M/L^3], which is associated with the incoming flow.

Cauchy boundary condition:

This boundary condition is employed when the total salt-flow rate is given at the river/stream boundary. Usually, this boundary is an upstream boundary node. The conditions are expressed as

$$QS - D^S A \frac{\partial S}{\partial x} = \Phi_{cb}\left(x_b, t\right) \tag{2.1.92}$$

where $\Phi_{cb}\left(x_b, t\right)$ is total salt-flow rate on the Cauchy boundary [M/t], which takes a positive value if it is going out of the region and a negative value if it is coming into the region.

Neumann boundary condition:

This boundary condition is used when the dispersive salt-flow rate is known at the river/stream boundary node. It can be written as

$$-D^S A\frac{\partial S}{\partial x} = \Phi_{nb}\left(x_b, t\right) \tag{2.1.93}$$

where $\Phi_{nb}\left(x_b, t\right)$ is the salt rate due to salt concentration through the Neumann boundary [M/L].

The internal boundary conditions at junctions and control structures for salinity transport are stated similarly to those for thermal transport as follows.

Internal boundary condition at junctions:

If Node *IJ* is the internal node from Reach *I* connecting to Junction *J* (Fig. 2.1-1), the boundary condition at Node *IJ* is given as

$$\left(QS - D^S A\frac{\partial S}{\partial x}\right)\Big|_{IJ} = \frac{1}{2}Q_{IJ}\left[\left(1+sign\left(Q_{IJ}\right)\right)S_{IJ} + \left(1-sign\left(Q_{IJ}\right)\right)S_J\right] \tag{2.1.94}$$

where S_{IJ} is the salinity at Node *IJ* and S_J is the salinity at Junction *J*, which is governed by

$$\sum_i \frac{1}{2}Q_{IJ}\left[\left(1+sign\left(Q_{iJ}\right)\right)S_{iJ} + \left(1-sign\left(Q_{iJ}\right)\right)S_J\right] = 0 \tag{2.1.95}$$

if the storage effect of Junction *J* is negligible or

$$\frac{d\left(V_J S_J\right)}{dt} = \sum_i \frac{1}{2}Q_{iJ}\left[\left(1+sign\left(Q_{iJ}\right)\right)S_{iJ} + \left(1-sign\left(Q_{iJ}\right)\right)S_J\right] \tag{2.1.96}$$

if the storage effect of Junction *J* is significant.

Internal boundary condition at control structure:

If Nodes *1S* and *2S* are two internal boundary nodes connecting to Structure *S* (Fig. 2.1-2), the boundary conditions at nodes 1S and 2S are given

$$\left(QS - D^S A\frac{\partial S}{\partial x}\right)\Big|_{1S} = \left(QS - D^S A\frac{\partial S}{\partial x}\right)\Big|_{2S} = \frac{1}{2}Q_S\left[\left(1+sign\left(Q_S\right)\right)S_{1S} + \left(1-sign\left(Q_S\right)\right)S_{2S}\right] \tag{2.1.97}$$

where S_{1S} is the salinity at Node *1S* and S_{2S} is the salinity at Node *2S*.

2.2 Water Flow in Two-Dimensional Overland Regime

The governing equations for two-dimensional overland flow can be derived based on the conservation law of water mass and linear momentum [Wang and Connor, 1975]. The governing equations of a dynamic wave model in conservative form can be written as follows.

The continuity equation:

$$\frac{\partial h}{\partial t}+\frac{\partial (uh)}{\partial x}+\frac{\partial (vh)}{\partial y}=S+R-E+I \qquad \textbf{(2.2.1)}$$

where h is the water depth [L]; u is the velocity component in the x-direction [L/t]; v is the velocity component in the y-velocity [L/t]; S_S is the man-induced source [$L^3/t/L^2$]; S_R is the source due to rainfall [$L^3/t/L^2$]; S_E is the sink due to evapotranspiration [$L^3/t/L^2$]; and S_I is the source from subsurface media due to exfiltration [L/t]. It should be noted that $uh = q_x$ is the flux the x-direction [$L^3/t/L^2$] and $vh = q_y$ is the flux in the y-direction [$L^3/t/L^2$].

The x-momentum equation:

$$\frac{\partial (uh)}{\partial t}+\frac{\partial u(uh)}{\partial x}+\frac{\partial v(uh)}{\partial y}=-gh\frac{\partial (Z_o+h)}{\partial x}-\frac{gh^2}{2\rho}\frac{\partial \Delta\rho}{\partial x}-\frac{\partial F_{xx}}{\partial x}-\frac{\partial F_{yx}}{\partial y}+$$
$$\left(M_X{}^S+M_X{}^R-M_X{}^E+M_X{}^I\right)+\frac{\tau_x^s-\tau_x^b}{\rho} \qquad \textbf{(2.2.2)}$$

where Z_o is the bottom elevation of overland [L];]; $\Delta\rho = \rho - \rho_o$ is the density deviation [M/L^3] from the reference density (ρ_o), which is a function of temperature and salinity as well as other chemical concentrations; $M_X{}^S$ is the x-component of momentum-impulse from artificial sources/sinks [L^2/t^2]; $M_X{}^R$ is the x-component of momentum-impulse gained from rainfall [L^2/t^2]; $M_X{}^E$ is the x-component of momentum-impulse lost to evapotranspiration [L^2/t^2]; $M_X{}^I$ is the x-component of momentum-impulse gained from the subsurface media due to exfiltration [L^2/t^2]; F_{xx} and F_{yx} are the water fluxes due to eddy viscosity along the x-direction [L^3/t^2]; τ_x^s is the component of surface shear stress along the x-direction over unit horizontal overland area [$M/L/t^2$]; τ_x^b is the component of bottom shear stress along the x-direction over unit horizontal overland area [$M/L/t^2$], which can be assumed proportional to the x-component flow rate, i.e., $\tau_x^b/\rho = \kappa|\mathbf{V}|u$.

The y-momentum equation:

$$\frac{\partial (vh)}{\partial t}+\frac{\partial u(vh)}{\partial y}+\frac{\partial v(vh)}{\partial y}=-gh\frac{\partial (Z_o+h)}{\partial y}-gh\frac{gh^2}{2\rho}\frac{\partial \Delta\rho}{\partial y}-\frac{\partial F_{xy}}{\partial x}-\frac{\partial F_{yy}}{\partial y}+$$
$$\left(M_y{}^S+M_y{}^R-M_y^E+M_y{}^I\right)+\frac{\tau_y^s-\tau_y^b}{\rho} \qquad \textbf{(2.2.3)}$$

where M_y^S is the y-component of momentum-impulse from artificial sources/sinks [L^2/t^2]; M_y^R is the y-component of momentum-impulse gained from rainfall [L^2/t^2]; M_y^E is the y-component of momentum-impulse lost to evapotranspiration L^2/t^2]; M_y^I is the y-component of momentum-impulse gained from the subsurface media due to exfiltration [L^2/t^2]; F_{xy} and F_{yy} are the water fluxes due to eddy viscosity along the y-direction [L^3/t^2]; τ_y^s is the component of surface shear stress along the y-direction over unit horizontal overland area [M/L/t^2]; τ_y^b is the component of bottom shear stress along the y-direction over unit horizontal overland area [M/L/t^2], which can be assumed proportional to the y-component flow rate, i.e., $\tau_y^b/\rho = \kappa|\mathbf{V}|v$.

2.2.1 Fully Dynamic Wave Approaches

Eqs. (2.2.1) through (2.1.3) written in conservative form are the governing equations for two-dimensional flow in overland. Depending on the simplification of the momentum equation, one can have three approaches: fully dynamic wave, diffusive wave, and kinematic wave. For the fully dynamic wave approach, all terms in Eqs. (2.2.1) and (2.2.3) are retained. Under such circumstances, the conservative form of the governing equations may be used or they may be cast in the advection form or in the characteristic form. In this report, while the conservative form of fully dynamic wave equation is used as an option, the characteristic form of the fully dynamic approach will be used as a primary option. The characteristic form is the most natural way to deal with hyperbolic-dominant equations and amenable to the advective numerical methods, for example the upstream approximation or the Lagrangian-Eulerian method.

With an adequate mathematical manipulation, Eqs. (2.2.1) through (2.2.3) can be written in advective form as follows

$$\frac{\partial h}{\partial t} + u\frac{\partial h}{\partial x} + h\frac{\partial u}{\partial x} + v\frac{\partial h}{\partial y} + h\frac{\partial v}{\partial y} = \left(S + R - E + I\right) \tag{2.2.4}$$

$$\begin{aligned}\frac{\partial u}{\partial t} + g\frac{\partial h}{\partial x} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} &= -g\frac{\partial Z_o}{\partial x} - \frac{1}{h}\left[\frac{\partial F_{xx}}{\partial x} + \frac{\partial F_{yx}}{\partial y}\right] \\ &- \frac{u\left(S + R - E + I\right) - \left(M_X^S + M_X^R - M_x^E + M_X^I\right)}{h} + \frac{\tau_x^s - \tau_x^b}{\rho h}\end{aligned} \tag{2.2.5}$$

$$\begin{aligned}\frac{\partial v}{\partial t} + g\frac{\partial h}{\partial x} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} &= -g\frac{\partial Z_o}{\partial y} - \frac{gh^2}{2\rho}\frac{\partial \Delta\rho}{\partial y} - \frac{1}{h}\left[\frac{\partial F_{xy}}{\partial x} + \frac{\partial F_{yy}}{\partial y}\right] \\ &- \frac{v\left(S + R - E + I\right) - \left(M_y^S + M_y^R - M_y^E + M_y^I\right)}{h} + \frac{\tau_y^s - \tau_y^b}{\rho h}\end{aligned} \tag{2.2.6}$$

which can be written in matrix form as

$$\frac{\partial \mathbf{E}}{\partial t} + \mathbf{A}_x\frac{\partial \mathbf{E}}{\partial x} + \mathbf{A}_y\frac{\partial \mathbf{E}}{\partial y} = \mathbf{R} + \mathbf{D} \tag{2.2.7}$$

where

$$\mathbf{E} = \{\mathrm{h} \quad \mathrm{u} \quad \mathrm{v}\}^T; \quad \mathbf{A_x} = \begin{bmatrix} u & h & 0 \\ g & u & 0 \\ 0 & 0 & u \end{bmatrix}; \quad \mathbf{A_y} = \begin{bmatrix} v & 0 & h \\ 0 & v & 0 \\ g & 0 & v \end{bmatrix} \tag{2.2.8}$$

$$\mathbf{R} = \begin{Bmatrix} R_1 \\ R_2 \\ R_3 \end{Bmatrix} = \begin{Bmatrix} S + R - E + I \\ -g\dfrac{\partial Z_o}{\partial x} - \dfrac{gh^2}{2\rho}\dfrac{\partial \Delta\rho}{\partial x} - \dfrac{u\left(S_S + S_R - S_E + S_I\right) - \left(M_X{}^S + M_X{}^R - M_x{}^E + M_X{}^I\right)}{h} + \dfrac{\tau_x^s - \tau_x^b}{\rho h} \\ -g\dfrac{\partial Z_o}{\partial y} - \dfrac{gh^2}{2\rho}\dfrac{\partial \Delta\rho}{\partial y} - \dfrac{v\left(S_S + S_R - S_E + S_I\right) - \left(M_y{}^S + M_y{}^R - M_y{}^E + M_y{}^I\right)}{h} + \dfrac{\tau_y^s - \tau_y^b}{\rho h} \end{Bmatrix} \tag{2.2.9}$$

$$\mathbf{D} = \begin{Bmatrix} 0 \\ \mathrm{D_x} \\ D_y \end{Bmatrix} = \begin{Bmatrix} 0 \\ -\dfrac{1}{h}\left[\dfrac{\partial F_{xx}}{\partial x} + \dfrac{\partial F_{yx}}{\partial y}\right] \\ -\dfrac{1}{h}\left[\dfrac{\partial F_{xy}}{\partial x} + \dfrac{\partial F_{yy}}{\partial y}\right] \end{Bmatrix} = \begin{Bmatrix} 0 \\ \dfrac{1}{h}\left[\dfrac{\partial}{\partial x}\left(h\varepsilon_{xx}\dfrac{\partial u}{\partial x}\right) + \dfrac{\partial}{\partial y}\left(h\varepsilon_{xy}\dfrac{\partial u}{\partial y} + h\varepsilon_{yx}\dfrac{\partial v}{\partial x}\right)\right] \\ \dfrac{1}{h}\left[\dfrac{\partial}{\partial x}\left(h\varepsilon_{xy}\dfrac{\partial u}{\partial y} + h\varepsilon_{yx}\dfrac{\partial v}{\partial x}\right) + \dfrac{\partial v}{\partial y}\left(h\varepsilon_{yy}\dfrac{\partial v}{\partial y}\right)\right] \end{Bmatrix} \tag{2.2.10}$$

Let the matrix **B** be the linear combination of the matrices $\mathbf{A_x}$ and $\mathbf{A_y}$ as follows

$$\mathbf{B} = \mathbf{A} \cdot \mathbf{k} = \mathbf{A_x} k_x + \mathbf{A_y} k_y = \begin{bmatrix} uk_x + vk_y & hk_x & hk_y \\ gk_x & uk_x + vk_y & 0 \\ gk_y & 0 & uk_x + vk_y \end{bmatrix} \tag{2.2.11}$$

where **A** is a third rank vector with the matrices $\mathbf{A_x}$ and $\mathbf{A_y}$ as its components and **k** is a unit vector. The eigenvalues and eigenvectors of the defined matrix **B** are

$$\lambda_1 = uk_x + vk_y \qquad \mathbf{e_1} = \{0 \quad k_y \quad -k_x\}^T \tag{2.2.12}$$

$$\lambda_2 = uk_x + vk_y + \sqrt{gh} \qquad \mathbf{e_2} = \left\{\frac{\sqrt{gh}}{2} \quad \frac{gk_x}{2} \quad \frac{gk_y}{2}\right\}^T \tag{2.2.13}$$

$$\lambda_3 = uk_x + vk_y - \sqrt{gh} \qquad \mathbf{e_3} = \left\{-\frac{\sqrt{gh}}{2} \quad \frac{gk_x}{2} \quad \frac{gk_y}{2}\right\}^T \tag{2.2.14}$$

where k_x and k_y are the *x*- and *y*-component of the unit vector **k**.

Now we compose an eigenmatrix and its inverse from the eigenvectors of **B** as

$$\mathbf{L} = \begin{bmatrix} 0 & \frac{\sqrt{gh}}{2} & -\frac{\sqrt{gh}}{2} \\ k_y & \frac{gk_x}{2} & \frac{gk_x}{2} \\ -k_x & \frac{gk_y}{2} & \frac{gk_y}{2} \end{bmatrix} \quad and \quad \mathbf{L}^{-1} = \begin{bmatrix} 0 & k_y & -k_x \\ \frac{1}{\sqrt{gh}} & \frac{k_x}{g} & \frac{k_y}{g} \\ -\frac{1}{\sqrt{gh}} & \frac{k_x}{g} & \frac{k_y}{g} \end{bmatrix} \tag{2.2.15}$$

Let us define a characteristic vector **W** by

$$\partial\mathbf{W} = \mathbf{L}^{-1}\partial\mathbf{E} = \begin{bmatrix} 0 & k_y & -k_x \\ \frac{1}{\sqrt{gh}} & \frac{k_x}{g} & \frac{k_y}{g} \\ -\frac{1}{\sqrt{gh}} & \frac{k_x}{g} & \frac{k_y}{g} \end{bmatrix} \begin{Bmatrix} \partial h \\ \partial u \\ \partial v \end{Bmatrix} \quad in\ which \quad \mathbf{W} = \begin{Bmatrix} W_1 \\ W_2 \\ W_3 \end{Bmatrix}^T \tag{2.2.16}$$

where the first characteristic variable W_1 is a vorticity or shear wave. The second and third components, W_2 and W_3, are the amplitudes of the two gravity waves. The multiplication of Eq. (2.2.7) by $\mathbf{L}^{-1}$ yields

$$\mathbf{L}^{-1}\frac{\partial \mathbf{E}}{\partial \mathrm{t}} + \mathbf{L}^{-1}\mathbf{A}_\mathrm{x}\mathbf{L}\mathbf{L}^{-1}\frac{\partial \mathbf{E}}{\partial \mathrm{x}} + \mathbf{L}^{-1}\mathbf{A}_\mathrm{y}\mathbf{L}\mathbf{L}^{-1}\frac{\partial \mathbf{E}}{\partial \mathrm{y}} = \mathbf{L}^{-1}\mathbf{R} + \mathbf{L}^{-1}\mathbf{D} \tag{2.2.17}$$

or, with the transformation between **E** and **W** given by $\mathbf{L}^{-1}\partial\mathbf{E} = \partial\mathbf{W}$,

$$\frac{\partial \mathbf{W}}{\partial t} + \mathbf{L}^{-1}\mathbf{A}_\mathrm{x}\mathbf{L}\frac{\partial \mathbf{W}}{\partial x} + \mathbf{L}^{-1}\mathbf{A}_\mathrm{y}\mathbf{L}\frac{\partial \mathbf{W}}{\partial y} = \mathbf{L}^{-1}\mathbf{R} + \mathbf{L}^{-1}\mathbf{D} \tag{2.2.18}$$

Substituting $\mathbf{A}_\mathrm{x}$ and $\mathbf{A}_\mathrm{y}$ in Eq. (2.2.8) and $\mathbf{L}^{-1}$ and **L** in Eq. (2.2.15) into Eq. (2.2.18), and performing matrix multiplication, we obtain

$$\frac{\partial \mathbf{W}}{\partial t} + \begin{bmatrix} u & \frac{gck_y}{2} & -\frac{gck_y}{2} \\ \frac{hk_y}{c} & u+ck_x & 0 \\ \frac{hk_y}{c} & 0 & u-ck_x \end{bmatrix} \frac{\partial \mathbf{W}}{\partial x} + \begin{bmatrix} v & -\frac{gck_x}{2} & \frac{gck_x}{2} \\ -\frac{hk_x}{c} & v+ck_y & 0 \\ \frac{hk_x}{c} & 0 & v-ck_y \end{bmatrix} \frac{\partial \mathbf{W}}{\partial y} = \mathbf{L}^{-1}\mathbf{R} + \mathbf{L}^{-1}\mathbf{D} \tag{2.2.19}$$

where

$$\mathrm{c} = \sqrt{\mathrm{gh}} \tag{2.2.20}$$

It is noted that the coefficient matrices $\mathbf{L}^{-1}\mathbf{A}_x\mathbf{L}$ and $\mathbf{L}^{-1}\mathbf{A}_y\mathbf{L}$, respectively, of $(\partial\mathbf{W}/\partial x)$ and $(\partial\mathbf{W}/\partial y)$, respectively, are not diagonal matrices because $\mathbf{L}^{-1}$ is not an eigenmatrix of $\mathbf{A}_x$ nor of $\mathbf{A}_y$. Rearranging Eq. (2.2.19), we obtain

$$\frac{\partial \mathbf{W}}{\partial t}+\begin{bmatrix} u & 0 & 0 \\ 0 & u+ck_x & 0 \\ 0 & 0 & u-ck_x \end{bmatrix}\frac{\partial \mathbf{W}}{\partial x}+\begin{bmatrix} v & 0 & 0 \\ 0 & v+ck_y & 0 \\ 0 & 0 & v-ck_y \end{bmatrix}\frac{\partial \mathbf{W}}{\partial y}+\begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix}=\mathbf{L}^{-1}\left(\mathbf{R}+\mathbf{D}\right) \qquad \textbf{(2.2.21)}$$

where

$$\begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix}=\begin{Bmatrix} g\left(k_y\dfrac{\partial h}{\partial x}-k_x\dfrac{\partial h}{\partial y}\right) \\ \dfrac{h}{c}\left[k_yk_y\dfrac{\partial u}{\partial x}+k_xk_x\dfrac{\partial v}{\partial y}-k_xk_y\left(\dfrac{\partial u}{\partial y}+\dfrac{\partial v}{\partial x}\right)\right] \\ \dfrac{-h}{c}\left[k_yk_y\dfrac{\partial u}{\partial x}+k_xk_x^{(2)}\dfrac{\partial v}{\partial y}-k_xk_y\left(\dfrac{\partial u}{\partial y}+\dfrac{\partial v}{\partial x}\right)\right] \end{Bmatrix} \qquad \textbf{(2.2.22)}$$

For a general consideration, we define a new $\mathbf{L}^{*-1}$ (and its inverse $\mathbf{L}^*$) which plays the following transformation.

$$\partial\mathbf{W}=\mathbf{L}^{*-1}\,\partial\mathbf{E}=\begin{bmatrix} 0 & k_y^{(1)} & -k_x^{(1)} \\ \dfrac{1}{c} & \dfrac{k_x^{(2)}}{g} & \dfrac{k_y^{(2)}}{g} \\ -\dfrac{1}{c} & \dfrac{k_x^{(2)}}{g} & \dfrac{k_y^{(2)}}{g} \end{bmatrix}\begin{Bmatrix} \partial h \\ \partial u \\ \partial v \end{Bmatrix};\quad \mathbf{L}^*=\begin{bmatrix} 0 & \dfrac{c}{2} & -\dfrac{c}{2} \\ \dfrac{k_y^{(2)}}{k} & \dfrac{gk_x^{(2)}}{2k} & \dfrac{gk_x^{(2)}}{2k} \\ -\dfrac{k_x^{(2)}}{k} & \dfrac{gk_y^{(2)}}{2k} & \dfrac{gk_y^{(2)}}{2k} \end{bmatrix} \qquad \textbf{(2.2.23)}$$

where $k = \mathbf{k}^{(1)}\cdot\mathbf{k}^{(2)}$ is the inner product of $\mathbf{k}^{(1)}$ and $\mathbf{k}^{(2)}$. It should be noted that two unit wave directions $\mathbf{k}^{(1)}$ and $\mathbf{k}^{(2)}$ should not be orthogonal so that the transformation will not be singular. Multiplying both side of Eq. (2.2.7) by this new $\mathbf{L}^{*-1}$ and repeating mathematical manipulations involved in Eqs. (2.2.19) and (2.2.21), we have

$$\frac{\partial \mathbf{W}}{\partial t}+\begin{bmatrix} u & 0 & 0 \\ 0 & u+ck_x^{(2)} & 0 \\ 0 & 0 & u-ck_x^{(2)} \end{bmatrix}\frac{\partial \mathbf{W}}{\partial x}+\begin{bmatrix} v & 0 & 0 \\ 0 & v+ck_y^{(2)} & 0 \\ 0 & 0 & v-ck_y^{(2)} \end{bmatrix}\frac{\partial \mathbf{W}}{\partial y}+\begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix}=\mathbf{L}^{*-1}\left(\mathbf{R}+\mathbf{D}\right) \qquad \textbf{(2.2.24)}$$

where

$$\begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix} = \begin{Bmatrix} g\left(k_y^{(1)} \frac{\partial h}{\partial x} - k_x^{(1)} \frac{\partial h}{\partial y} \right) \\ \frac{h}{c}\left[k_y^{(2)} k_y^{(2)} \frac{\partial u}{\partial x} + k_x^{(2)} k_x^{(2)} \frac{\partial v}{\partial y} - k_x^{(2)} k_y^{(2)} \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right] \\ \frac{-h}{c}\left[k_y^{(2)} k_y^{(2)} \frac{\partial u}{\partial x} + k_x^{(2)} k_x^{(2)} \frac{\partial v}{\partial y} - k_x^{(2)} k_y^{(2)} \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right] \end{Bmatrix} \qquad \textbf{(2.2.25)}$$

Substituting $\mathbf{L}^{*-1}$ defined in Eq. (2.2.23) into the right hand side of Eq. (2.2.24), we obtain

$$\begin{Bmatrix} \frac{\partial W_1}{\partial t} + u\frac{\partial W_1}{\partial x} + v\frac{\partial W_1}{\partial y} \\ \frac{\partial W_2}{\partial t} + \left(u + ck_x^{(2)}\right)\frac{\partial W_2}{\partial x} + \left(v + ck_y^{(2)}\right)\frac{\partial W_2}{\partial y} \\ \frac{\partial W_3}{\partial t} + \left(u - ck_x^{(2)}\right)\frac{\partial W_3}{\partial x} + \left(v - ck_y^{(2)}\right)\frac{\partial W_3}{\partial y} \end{Bmatrix} + \begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix} = \begin{Bmatrix} A_1 \\ A_2 \\ A_3 \end{Bmatrix} + \begin{Bmatrix} B_1 \\ B_2 \\ B_3 \end{Bmatrix} \qquad \textbf{(2.2.26)}$$

where

$$\begin{Bmatrix} A_1 \\ A_2 \\ A_3 \end{Bmatrix} = \begin{Bmatrix} k_y^{(1)} R_2 - k_x^{(1)} R_3 \\ \frac{1}{c} R_1 + \frac{k_x^{(2)}}{g} R_2 + \frac{k_y^{(2)}}{g} R_3 \\ \frac{-1}{c} R_1 + \frac{k_x^{(2)}}{g} R_2 + \frac{k_y^{(2)}}{g} R_3 \end{Bmatrix} \quad \textit{and} \quad \begin{Bmatrix} B_1 \\ B_2 \\ B_3 \end{Bmatrix} = \begin{Bmatrix} k_y^{(1)} D_x - k_x^{(1)} D_y \\ \frac{k_x^{(2)}}{g} D_x + \frac{k_y^{(2)}}{g} D_y \\ \frac{k_x^{(2)}}{g} D_x + \frac{k_y^{(2)}}{g} D_y \end{Bmatrix} \qquad \textbf{(2.2.27)}$$

Writing out Eq. (2.2.26) in its three components, we have the following three equations for three unknowns W_1, W_2, and W_3

$$\frac{\partial W_1}{\partial t} + u\frac{\partial W_1}{\partial x} + v\frac{\partial W_1}{\partial y} + S_1 = A_1 + B_1 \qquad \textbf{(2.2.28)}$$

$$\frac{\partial W_2}{\partial t} + \left(u + ck_x^{(2)}\right)\frac{\partial W_2}{\partial x} + \left(v + ck_y^{(2)}\right)\frac{\partial W_2}{\partial y} + S_2 = A_2 + B_2 \qquad \textbf{(2.2.29)}$$

$$\frac{\partial W_3}{\partial t} + \left(u - ck_x^{(2)}\right)\frac{\partial W_3}{\partial x} + \left(v - ck_y^{(2)}\right)\frac{\partial W_3}{\partial y} + S_3 = A_3 + B_3 \qquad \textbf{(2.2.30)}$$

Equations (2.2.28), (2.29), and (2.230) indicate that the vorticity wave is advected by the velocity **V**, the positive gravity wave by $\mathbf{V} + c\mathbf{k}^{(2)}$, and the negative gravity wave by $\mathbf{V} - c\mathbf{k}^{(2)}$, where $\mathbf{k}^{(2)}$ is a unit vector.

We can write Eq. (2.2.26) in Lagrangian form as

$$\begin{Bmatrix} \frac{D_V W_1}{D\tau} \\ \frac{D_{V+ck^{(2)}} W_2}{D\tau} \\ \frac{D_{V-ck^{(2)}} W_3}{D\tau} \end{Bmatrix} + \begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix} = \begin{Bmatrix} A_1 \\ A_2 \\ A_3 \end{Bmatrix} + \begin{Bmatrix} B_1 \\ B_2 \\ B_3 \end{Bmatrix} \qquad \textbf{(2.2.31)}$$

where **V** is the transporting velocity of the vorticity wave W_1, (**V** + c**k**$^{(2)}$) is the transporting velocity of positive gravity wave W_2, and (**V** - c**k**$^{(2)}$) is the transporting velocity of negative gravity wave W_3. Substituting the definition of the characteristic variable **W** in Eq. (2.2.23) into Eq. (2.2.31), we have the following three equations for the three waves

$$k_y^{(1)} \frac{D_V u}{D\tau} - k_x^{(1)} \frac{D_V v}{D\tau} + S_1 = A_1 + B_1 \qquad \textbf{(2.2.32)}$$

$$\frac{2}{g} \frac{D_{V+ck^{(2)}} c}{D\tau} + \frac{k_x^{(2)}}{g} \frac{D_{V+ck^{(2)}} u}{D\tau} + \frac{k_y^{(2)}}{g} \frac{D_{V+ck(2)} v}{D\tau} + S_2 = A_2 + B_2 \qquad \textbf{(2.2.33)}$$

$$-\frac{2}{g} \frac{D_{V-ck^{(2)}} c}{D\tau} + \frac{k_x^{(2)}}{g} \frac{D_{V-ck^{(2)}} u}{D\tau} + \frac{k_y^{(2)}}{g} \frac{D_{V-ck^{(2)}} v}{D\tau} + S_3 = A_3 + B_3 \qquad \textbf{(2.2.34)}$$

It is noted that a diagonalization can be achieved with special selections of $k_x^{(1)}$, $k_y^{(1)}$, $k_x^{(2)}$, and $k_y^{(2)}$ to make S_1, S_2, and S_3 zeros.

In solving Eqs. (2.2.28) through (2.2.30) or Eqs. (2.2.32) through (2.2.34), the water depth h, and the velocity components, u and v, must be given initially or they can be obtained by simulating the steady-state version of Eqs. (2.2.28) through (2.2.30). In addition, appropriate boundary conditions need to be specified to match the corresponding physical system. The characteristics form of the governing equation offers great advantages over the primitive form in adapting appropriate numerical algorithms and in defining boundary conditions. Innovative hyperbolic numerical algorithms can be employed to approximate the system because each of the three equations is a decoupled advective transport equation of a wave. The specification of boundary conditions is made easy pending the wave direction. We demonstrate how boundary conditions are specified in the following. An overland boundary segment can be either open or closed. In the former case, the boundary condition for any wave is needed only when it is transported into the region of interest. When a wave is transported out of the region, there is no need to specify the boundary condition because internal flow dynamics due to this wave affects the boundary values of u, v, and h. In the later case, the flow rate on the boundary is zero.

Open upstream boundary condition:

At an open upstream boundary segment, the vorticity is always transported into the region from upstream. If the flow is supercritical, then both gravity waves also transported into the region from

upstream; thus three boundary conditions are needed. The water depth and velocity components at the boundary are determined entirely by the flow condition that prevails at the upstream. The governing equations for this case can be set up based on the continuity of mass as well as momentums between the upstream and boundary as

$$\mathbf{n}\cdot\mathbf{V}h = q_n^{(up)}(\mathbf{x}_b,t);\ \mathbf{n}\cdot\mathbf{V}uh + n_x\frac{gh^2}{2} = M_x^{up}(\mathbf{x}_b,t);\ and\ \mathbf{n}\cdot\mathbf{V}vh + n_y\frac{gh^2}{2} = M_y^{up}(\mathbf{x}_b,t) \quad \textbf{(2.2.35)}$$

where **n** is the outward unit vector of the boundary segment; $q_n^{up}(\mathbf{x}_b,t)$, a function of time *t*, is flow rate normal to the boundary from the upstream; $\mathbf{x}_b$ is the coordinate on the boundary; n_x is the *x*-component of **n**; $M_x^{up}(\mathbf{x}_b,t)$ is the *x*-momentum/impulse from the upstream; n_y is the *y*-component of **n**; and $M_y^{up}(\mathbf{x}_b,t)$ is the *y*-momentum/impulse from the upstream. It is noted that *u*, *v*, and *h* from the upstream must be given to provide q_n^{up}, M_x^{up} and M_y^{up}.

In the case of subcritical flow, one of the two gravity waves is transported into the region while the other is transported out of the region. The water depth and velocity are determined with the upstream flow condition and internal flow dynamics. The governing equations are set up based on the continuity of mass between the boundary and the upstream and on the flow dynamics in the region as

$$\begin{aligned}&\mathbf{n}\cdot\mathbf{V}h = q_n^{(up)}(\mathbf{x}_b,t)\ \ or\ \ h+Z_o = H_{up}(\mathbf{x}_b,t);\ \ell\cdot\mathbf{V}h = q_\ell^{(up)}(\mathbf{x}_b,t);\ and\ F_+(u,v,h)=0\\ &\qquad\qquad or\\ &\mathbf{n}\cdot\mathbf{V}h = q_n^{(up)}(\mathbf{x}_b,t)\ \ or\ h+Z_o = H_{up}(\mathbf{x}_b,t);\ \ell\cdot\mathbf{V}h = q_\ell^{(up)}(\mathbf{x}_b,t);\ and\ F_-(u,v,h)=0\end{aligned} \quad \textbf{(2.2.36)}$$

where ℓ is the unit vector parallel to the boundary segment; $H_{up}(\mathbf{x}_b,t)$, a function of time *t*, is the water stage in the incoming fluid from the upstream; $q_\ell^{up}(\mathbf{x}_b,t)$, a function of time *t*, is the flow rate parallel to the boundary.

Open downstream boundary condition:

At an open downstream boundary segment, the vorticity is always transported out of the region into downstream. If the flow is supercritical, then both gravity waves also transported out of the region into downstream; thus three is no need to specify the boundary conditions. The water depth and velocity components at the boundary are determined entirely by internal flow dynamics. The governing equations for this case are given by

$$F_\otimes(u,v,h)=0;\quad F_+(u,v,h)=0;\quad and\quad F_-(u,v,h)=0 \quad \textbf{(2.2.37)}$$

where $F_\otimes(u,v,h)$, a function of velocity and water depth, is the vorticity wave boundary function.

In the case of subcritical flow, one of the two gravity waves is transported into the region from downstream while the other is transported out of the region into downstream. The water depth and

velocity are determined by the internal flow dynamics and the control of the downstream boundary segment

$$\begin{aligned} &F_{\otimes}(u,v,h)=0;\quad F_{+}(u,v,h)=0;\ and\ h=h_{dn}(\mathbf{x}_b,t)\ or\ \mathbf{n}\cdot\mathbf{V}h=q_n^{dn}(h) \\ &\qquad\qquad or \\ &F_{\otimes}(u,v,h)=0;\quad F_{-}(u,v,h)=0;\ and\ \ h=h_{dn}(\mathbf{x}_b,t)\ or\ \mathbf{n}\cdot\mathbf{V}h=q_n^{dn}(h) \end{aligned} \qquad \textbf{(2.2.38)}$$

where $h^{dn}(t)$, a function of time t, is the water depth of the downstream boundary an $q_n^{dn}(h)$, a function of water depth h, is the rating curve of the downstream boundary.

Closed upstream boundary condition:

At the closed upstream boundary, physically all flow conditions can occur. The vorticity wave is always transported from the outside of the boundary into the region. When the supercritical flow happens, both gravity waves are also transported into the region. Thus, three boundary condition equations are needed. Because the boundary is closed, it is impermeable. The governing equations can be obtained by simply substituting $q_n^{up}=0$, $M_x^{up}=0$, and $M_y^{up}=0$ into Eq. (2.2.35) to yield

$$\mathbf{n}\cdot\mathbf{V}h=0;\quad \mathbf{n}\cdot\mathbf{V}uh+n_x\frac{gh^2}{2}=0;\quad and\quad \mathbf{n}\cdot\mathbf{V}vh+n_y\frac{gh^2}{2}=0 \qquad \textbf{(2.2.39)}$$

The solutions for Eq. (2.2.39) are not unique. One of the possible solution is $u=0$, $v=0$, and $h=0$.

When the flow is subcritical, one of the two gravity waves is transported from the outside of the boundary into the region while the other is transported from inside the boundary to the outside The boundary conditions are needed only for the incoming waves. Since no fluid from the outside world is transported into the region via the closed boundary, one of the two boundary condition equations can be stated with $\mathbf{n}\cdot\mathbf{V}=0$. The other boundary equation can be obtained by assuming no slip condition on the boundary. Thus, three governing equations are given as

$$\mathbf{n}\cdot\mathbf{V}h=0;\ \ell\cdot\mathbf{V}h=0;\ and\ F_{+}(u,v,h)=0\quad or\quad \mathbf{n}\cdot\mathbf{V}h=0;\ \ell\cdot\mathbf{V}h=0;\ and\ F_{-}(u,v,h)=0 \qquad \textbf{(2.2.40)}$$

depending on which wave is transported out of the region.

Closed downstream boundary condition:

At the closed downstream boundary, physical condition dictates that normal flow rate at the boundary is zero. The vorticity wave is always transported out of the region. If the flow is supercritical, both gravity waves are also transported out of the region. The velocity and water depth on the boundary is determined entirely by internal flow dynamics and no boundary condition is needed. The governing equations are given by the wave boundary functions subject to the constraint that fluid flux is zero as follows:

$$F_{\otimes}(u,v,h)=0;\ \ F_{+}(u,v,h)=0;\quad and\quad F_{-}(u,v,h)=0\quad subject\ to\quad \mathbf{n}\cdot\mathbf{V}=0 \qquad \textbf{(2.2.41)}$$

The only feasible solution of Eq. (2.1.31) is $u=0$, $v=0$, and $h=0$. Therefore, supercritical flow

cannot occur at a closed downstream segment.

In the case of subcritical flow, one of the two gravity waves is transported into the region while the other is transported out of the region. The water depth and velocity are determined with the internal flow dynamics and the condition of zero normal flux as

$$F_{\otimes}(u,v,h)=0;\ F_{+}(u,v,h)=0;\ and\ \mathbf{n}\cdot\mathbf{V}h=0\ \ or\ \ F_{\otimes}(u,v,h)=0;\ F_{-}(u,v,h)=0;\ and\ \mathbf{n}\cdot\mathbf{V}h=0 \qquad \textbf{(2.2.42)}$$

Overland-river interface boundary condition:

At the overland-river interface, the flux must be continuous as

$$(\mathbf{n}\bullet\mathbf{V})h\Big|_{Bank\,1}=S_1 \qquad and \qquad (\mathbf{n}\bullet\mathbf{V})h\Big|_{Bank\,2}=S_2 \qquad \textbf{(2.2.43)}$$

where S_1 and S_2 are sources of water which appear in Eq. (2.1.1)

2.2.2 Diffusive Wave Approaches

For diffusion wave models, the inertia terms in Eqs. (2.2.2) and (2.2.3) are assumed not important when compared to the others. With the further assumption that eddy viscosity is insignificant and $M_x^S=M_x^R=M_x^E=M_x^I=M_y^S=M_y^R=M_y^E=M_y^I=0$, we approximate the velocity $\mathbf{V}=(u,v)$ as follows

$$\mathbf{V}=\frac{-a}{n}\left[\frac{h}{1+(\nabla Z_o)^2}\right]^{2/3}\frac{1}{\sqrt{\left|-\nabla H-\frac{h}{2\rho}\nabla(\Delta\rho)+\frac{\tau^s}{\rho gh}\right|}}\left(\nabla H+\frac{h}{2\rho}\nabla(\Delta\rho)-\frac{\tau^s}{\rho gh}\right) \qquad \textbf{(2.2.44)}$$

Using the definition $\mathbf{q}=\mathbf{V}h$ and substituting Eq. (2.2.44) into Eq. (2.2.1), we obtain

$$\frac{\partial H}{\partial t}-\nabla\cdot\left[K\left(\nabla H+\frac{h}{2\rho}\nabla(\Delta\rho)-\frac{\boldsymbol{\tau}^s}{\rho gh}\right)\right]=S_S+S_R-S_E+S_I \qquad \textbf{(2.2.45)}$$

in which

$$K=\frac{a\,h^{5/3}}{n}\frac{1}{\left[1+(\nabla Z_o)^2\right]^{2/3}}\frac{1}{\sqrt{\left|-\nabla H-\frac{h}{2\rho}\nabla(\Delta\rho)+\frac{\tau^s}{\rho gh}\right|}} \qquad \textbf{(2.2.46)}$$

To achieve transient simulations, either water depth or stage must be given as the initial condition. In addition, appropriate boundary conditions need to be specified to match the corresponding physical system. In our model, four types of boundary conditions may be specified depending on physical configurations of the boundary. These boundary conditions are addressed below.

Dirichlet boundary condition: prescribed water depth or stage

On a Dirichlet boundary, either the water depth or stage can be prescribed as a function of time. This boundary condition can be expressed as

$$h = h_d\left(\mathbf{x}_b, t\right) \quad or \quad H = h + Z_0 = H_d(\mathbf{x}_b, t), \quad on \quad B_d \tag{2.2.47}$$

where $h_d\left(\mathbf{x}_b, t\right)$ is a prescribed time-dependent water depth on the Dirichlet boundary [L], $H_d(\mathbf{x}_b, t)$ is a prescribed time-dependent water stage [L], and B_d is the Dirichlet boundary segment. A Dirichlet boundary segment can locate at the up-streams or down-streams, control structures, or even interior points.

Flux boundary condition: prescribed flow rate

On a flux boundary, a time-dependent flow rate is prescribed as a function of time as

$$-\mathbf{n}\cdot K\left(\nabla H + \frac{h}{2\rho}\nabla\left(\Delta\rho\right) - \frac{\boldsymbol{\tau}^s}{\rho g h}\right) = q_f\left(\mathbf{x}_b, t\right) \quad on \quad B_f \tag{2.2.48}$$

where **n** is an outward unit vector at the flux boundary point, $q_f\left(\mathbf{x}_b, t\right)$ a prescribed time-dependent flow rate [L^3/t/L], and B_f is a flux boundary segment. Mathematically, a flux boundary condition can be applied to an upstream or downstream segment. However, in practice, it is often applied to an upstream boundary segment.

Water depth-dependent boundary condition: prescribed rating curve

This condition is often used to describe the flow rate at a downstream boundary at which the flow rate is a function of water depth. It can be written as

$$-\mathbf{n}\cdot K\left(\nabla H + \frac{h}{2\rho}\nabla\left(\Delta\rho\right) - \frac{\boldsymbol{\tau}^s}{\rho g h}\right) = q_r\left(h\left(x_r, t\right)\right) \quad on \quad B_r \tag{2.2.49}$$

where $q_r(h(x_r,t))$ is a water depth-dependent flow rate [L^3/t/L], $\mathbf{x}_r$ is the *x*-coordinate on the boundary B_r, and B_r is a boundary segment on which the prescribed rating curve is applied.

Overland-river interface boundary condition:

At the overland-river interface, the flux must be continuous as

$$\begin{aligned} -\mathbf{n}\cdot K\left(\nabla H + \frac{h}{2\rho}\nabla\left(\Delta\rho\right) - \frac{\boldsymbol{\tau}^s}{\rho g h}\right)\Big|_{Bank\,1} &= S_1 \quad and \\ -\mathbf{n}\cdot K\left(\nabla H + \frac{h}{2\rho}\nabla\left(\Delta\rho\right) - \frac{\boldsymbol{\tau}^s}{\rho g h}\right)\Big|_{Bank\,2} &= S_2 \end{aligned} \tag{2.2.50}$$

where S_1 and S_2 are sources of water which appear in Eq. (2.1.1)

2.2.3 Kinematic Wave Approaches

In a kinematic approach, all the assumptions for the diffusive approach are hold. However, the velocity is given by modifying Eq. (2.2.44) with ∇Z_0 replacing ∇H as follows

$$\mathbf{V} = \frac{-a}{n}\left[\frac{h}{1+\left(\nabla Z_o\right)^2}\right]^{2/3} \frac{1}{\sqrt{\left|-\nabla Z_o - \frac{h}{2\rho}\nabla\left(\Delta\rho\right)+\frac{\tau^s}{\rho g h}\right|}}\left(\nabla z_o + \frac{h}{2\rho}\nabla\left(\Delta\rho\right) - \frac{\tau^s}{\rho g h}\right) \qquad \textbf{(2.2.51)}$$

Substituting Eq. (2.2.51) into Eq. (2.2.1) and using the definition **q** = **V***h*, we obtain

$$\frac{\partial h}{\partial t} + \nabla\cdot\left(\mathbf{V}h\right) = S_S + S_R - S_E + S_I \qquad \textbf{(2.2.52)}$$

It is noted that Eq. (2.2.52) represents the advective transport of the water depth, *h*. It is an ideal equation amenable for numerically innovative advective transport algorithm.

To achieve transient simulations, either water depth or stage must be given as the initial condition. In addition, appropriate boundary conditions need to be specified to match the corresponding physical configuration. In a kinematic wave approach, boundary conditions are required only at upstream boundaries. An upstream boundary segment can be an open boundary or a closed boundary. On an open upstream boundary, either the water depth or the flow rate can be specified as

$$h = h_{up}\left(\mathbf{x}_{up}, t\right) \quad or \quad \mathbf{n}\cdot\mathbf{V}h = q_{up}\left(\mathbf{x}_{up}, t\right) \quad on \quad B_{up} \qquad \textbf{(2.2.53)}$$

where $h_{up}\left(\mathbf{x}_{up}, t\right)$ is the water depth of the incoming upstream flow, $q_{up}\left(\mathbf{x}_{up}, t\right)$ is the flow rate of the incoming upstream flow, $\mathbf{x}_{up}$ is the coordinate on the upstream boundary, and B_{up} is the open upstream boundary segment. The flow rate through a closed upstream boundary segment is by default equal to zero.

2.2.4 Thermal Transport

The thermal transport equation is derived based on the conservation principle of energy as:

$$\begin{aligned}\frac{\partial\left(\rho_w C_w h T\right)}{\partial t} + \nabla\cdot\left(\rho_w C_w \mathbf{q}\mathrm{T}\right) - \nabla\cdot\left(\mathbf{D}^{\mathrm{H}} h\cdot\nabla T\right) \\ = H_a + H_r + H_n - H_b - H_e - H_s + H_i + H_c\end{aligned} \qquad \textbf{(2.2.54)}$$

where ρ_w is the water density [M/L^3]; C_w is the heat capacity of water [L^2/t^2/T]; T is the temperature [T]; $\mathbf{D}^{\mathrm{H}}$ is the apparent thermal conductivity tensor including the effect of dispersion, diffusion, and

conduction [E/L/t/T = ML/t^3/T, where E is the unit of energy]; H_a is the heat source due to artificial injection/withdraw including rainfall [E/t/L^2 = M/t^3]; H_r is the heat source due to rainfall [E/t/L^2 = M/t^3]; H_n is the heat source due to net radiation [E/t/L^2 = M/t^3]; H_b is the heat sink due to back radiation from water surface to the atmosphere [E/t/L^2 = M/t^3]; H_e is the heat sink due to evaporation [E/t/L^2 = M/t^3]; H_s is the heat sink due to sensible heat flux [E/t/L^2 = M/t^3]; H_i is the heat source due to exfiltration from subsurface [E/t/L^2 = M/t^3]; and H_c is the heat source due to chemical reaction [E/t/L^2 = M/t^3]. In Eq. (2.2.54), H_r and H_i are given by

$$H_r = C_w \rho_w R T^r; \qquad H_i = \begin{cases} C_w \rho_w I T^i & if \quad I \geq 0 \\ C_w \rho_w I T & if \quad I < 0 \end{cases} \tag{2.2.55}$$

where R is the rainfall rate [L/t], T^r is the temperature of the rainwater [T], I is the exfiltration rate [L/t], and T^i is the temperature of the exfiltration water from the subsurface flow [T]. H_n, H_b, H_e, and H_s are the net radiation flux, back radiation flux, latent heat flux, and sensible heat flux, respectively. These fluxes depend on only meteorological condition and water temperature. The formulation of these heat/energy fluxes were presented in Section 2.1.

In addition to the initial boundary condition, boundary conditions must be specified for the temperature. Four types of global boundary conditions are provided in this report as follows.

Dirichlet boundary condition:

This condition is applied when the temperature is prescribed as a function of time on the boundaries:

$$T = T_{db}\left(\mathbf{x}_b, t\right) \qquad on \qquad B_d \tag{2.2.56}$$

where $T_{db}\left(\mathbf{x}_b, t\right)$ is a time-dependent temperature on the Dirichlet boundary B_d [T].

Variable boundary condition:

This boundary condition is employed when the flow direction would change with time during simulations. Two cases are considered, regarding to the flow direction on the boundary.

< Case 1 > Flow is coming in from outside:

$$\mathbf{n} \cdot \left(\rho_w C_w \mathbf{q} T - \mathbf{D}^{\mathbf{H}} h \cdot \nabla T \right) = \mathbf{n} \cdot \rho_w C_w \mathbf{q} T_{vb}\left(\mathbf{x}_b, t\right) \qquad on \qquad B_v \tag{2.2.57}$$

< Case 2 > Flow is going out from inside:

$$-\mathbf{n} \cdot \mathbf{D}^{\mathbf{H}} h \cdot \nabla T = 0 \qquad on \qquad B_v \tag{2.2.58}$$

where $T_{vb}\left(\mathbf{x}_b, t\right)$ is a time-dependent temperature on the variable boundary B_v [T], which is associated with the incoming flow.

Cauchy boundary condition:

This boundary condition is employed when the total heat-flow rate is given at the boundary. Usually, this boundary is a flow-in boundary. The conditions can be expressed as

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{q}T - \mathbf{D}^{\mathbf{H}}h\cdot\nabla T\right) = \Phi_{cb}(t) \quad on \quad B_c \tag{2.2.59}$$

where $\Phi_{cb}(t)$ is total heat flux on the Cauchy boundary B_c [E/L/t = ML/t^3, where E denotes the unit of energy], which takes a positive value if it is going out of the region and a negative value if it is coming into the region.

Neumann boundary condition:

This boundary condition is used when the conductive heat-flow rate is known at the boundary. It can be written as

$$-\mathbf{n}\cdot\mathbf{D}^{\mathbf{H}}h\cdot\nabla T = \Phi_{nb}(\mathbf{x}_b, t) \quad on \quad B_n \tag{2.2.60}$$

where $\Phi_{nb}(\mathbf{x}_b, t)$ is the heat flux on the Neumann boundary B_n [E/L/t].

In addition to the four types of global boundary conditions, an internal boundary condition may be specified for the exchange of energy/heat flux between the overland and river/stream network. Mathematically, this boundary condition is described below.

Overland-river interface boundary condition:

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{q}T - \mathbf{D}^{\mathbf{H}}h\cdot\nabla T\right)\Big|_{Bank\,1} = S_h^{o1} \quad and \quad \mathbf{n}\cdot\left(\rho_w C_w \mathbf{q}T - \mathbf{D}^{\mathbf{H}}h\cdot\nabla T\right)\Big|_{Bank\,2} = S_h^{o2} \tag{2.2.61}$$

where S_h^{o1} and S_h^{o2} are the heat sources, which appeared in Eq. (2.1.67). These heat sources can be calculated using Eq. (2.1.69) if the temperatures in the overland water and river water are discontinuous at the interfaces. If the temperatures are continuous, then these heat sources should be formulated by imposing the continuity of the temperatures in the overland water and river water at the interface.

2.2.5 Salinity Transport

$$\frac{\partial(hS)}{\partial ts} + \nabla\cdot(\mathbf{q}S) - \nabla\cdot\left(h\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right) = M_s^{as} + M_s^{rs} - M_s^{es} + M_s^{is} \tag{2.2.62}$$

where S is the salinity [M/L^3]; $\mathbf{D}^{\mathbf{S}}$ is the longitudinal dispersion coefficient for salt [L^2/t]; M_s^{as} is the artificial source of the salt [M/t//L^2]; M_s^{rs} is the salt source from rainfall [M/t/L^2; M_s^{es} is the salt sink from evaporation [M/t/L^2]; M_s^{is} is the salt source from subsurface [M/t/L^2]. In Eq. (2.2.62), M_s^{es} is likely to be zero and M_s^{rs} and M_s^{is} are given by

$$M_s^{rs} = RS^r; \quad M_s^{is} = \begin{Bmatrix} IS^i & if\ I \ge 0 \\ IS & if\ I < 0 \end{Bmatrix} \tag{2.2.63}$$

where R is the rainfall rate [L/t], S^r is the salinity of the rainwater [M/L^3], I is the exfiltration rate [L/t], and S^i is the salinity of the exfiltration water from the subsurface flow [M/L^3].

As in thermal transport, four types of global boundary conditions for salinity transport are provided in this report as follows.

Dirichlet boundary condition:

This condition is applied when the salinity is prescribed as a function of time on the boundaries:

$$S = S_{db}\left(\mathbf{x}_b, t\right) \quad on \quad B_d \tag{2.2.64}$$

where $S_{db}\left(\mathbf{x}_b, t\right)$ is a time-dependent salinity on the Dirichlet boundary B_d [M/L^3].

Variable boundary condition:

This boundary condition is employed when the flow direction would change with time during simulations. Two cases are considered, regarding to the flow direction on the boundary.

< Case 1 > Flow is coming in from outside:

$$\mathbf{n}\cdot\left(\mathbf{q}S - h\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right) = \mathbf{n}\cdot\mathbf{q}S_{vb}\left(\mathbf{x}_b, t\right) \quad on \quad B_v \tag{2.2.65}$$

< Case 2 > Flow is going out from inside:

$$-\mathbf{n}\cdot h\mathbf{D}^{\mathbf{S}}\cdot\nabla S = 0 \quad on \quad B_v \tag{2.2.66}$$

where $S_{vb}\left(\mathbf{x}_b, t\right)$ is a time-dependent salinity on the variable boundary B_v [M/L^3], which is associated with the incoming flow.

Cauchy boundary condition:

This boundary condition is employed when the total salt-flow rate is given at the boundary. Usually, this boundary is a flow-in boundary. The conditions are expressed as

$$\mathbf{n}\cdot\left(\mathbf{q}S - h\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right) = S_{cb}\left(\mathbf{x}_b, t\right) \quad on \quad B_c \tag{2.2.67}$$

where $S_{cb}\left(\mathbf{x}_b, t\right)$ is total salt-flow rate on the Cauchy boundary B_c [M/L/t], which takes a positive value if it is going out of the region and a negative value if it is coming into the region.

Neumann boundary condition:

This boundary condition is used when the dispersive salt-flow rate is known at the boundary. t can be written as

$$-\mathbf{n}\cdot h\mathbf{D}^{\mathbf{S}}\cdot\nabla S = S_{nb}(t) \quad on \quad B_n \tag{2.2.68}$$

where $S_{nb}(t)$ is the salt flux on the Neumann boundary [M/L/t].

As in thermal transport, in addition to the four types of global boundary conditions, an internal boundary condition may be specified for the exchange of salt between the overland and river/stream network. Mathematically, this boundary condition is described below.

River-overland interface boundary condition:

$$\mathbf{n}\cdot\left(\mathbf{q}S-\mathbf{D}^{S}h\cdot\nabla S\right)\Big|_{Bank\,1} = M_s^{o1} \quad and \quad \mathbf{n}\cdot\left(\mathbf{q}S-\mathbf{D}^{S}h\cdot\nabla S\right)\Big|_{Bank\,2} = M_s^{o2} \tag{2.2.69}$$

where M_s^{o1} and M_s^{o2}, which appeared in Eq. (2.1.86), are the salt sources from overland into the rivers. These salt sources can be calculated using Eq. (2.1.88) if the salinity in the overland water and river water are discontinuous at the interfaces. If the salinity is continuous, then these salt sources should be formulated by imposing the continuity of salinity in the overland water and river water at the interface.

2.3 Water Flow in Three-Dimensional Subsurface Media

2.3.1 Water Flow

The governing equation of subsurface density dependent flow through saturated-unsaturated porous media can be derived based on the conservation law of water mass (Yeh, 1987; Yeh et al., 1994; Lin et al., 1997). It is written as follows.

$$\frac{\rho}{\rho_o}F\frac{\partial h}{\partial t} = \nabla\cdot\left[\mathbf{K}\cdot\left(\nabla h+\frac{\rho}{\rho_o}\nabla z\right)\right]+\frac{\rho^*}{\rho_o}q \tag{2.3.1}$$

where ρ is the density of water; ρ_o is the reference density of water; h is the referenced pressure head [L]; t is the time [t]; **K** is the hydraulic conductivity tensor [L/t]; z is the potential head [L]; ρ* is the density of source water; q is the source and/or sink [L^3/L^3/t]; and F is the water capacity [1/L] given by

$$F = a'\frac{\theta_e}{n_e}+\beta'\theta_e+n_e\frac{dS}{dh} \tag{2.3.2}$$

where a' is the modified compressibility of the medium [1/L], θ_e is the effective moisture content [L^3/L^3], n_e is the effectively porosity [L^3/L^3], β' is the compressibility of water [1/L], and S is the degree of saturation. The Darcy's velocity is given by

$$\mathbf{V} = -\mathbf{K} \cdot \left(\frac{\rho_o}{\rho} \nabla h + \nabla z \right) \tag{2.3.3}$$

To achieve transient simulation, the following initial condition needs to be given.

$$h = h_i(\mathbf{x}) \qquad in \quad R, \tag{2.3.4}$$

where R is the region of interest and h_i is the prescribed pressure head [L], which can be obtained by either field measurements or by solving the steady state version of Eq. (2.3.1).

Five types of boundary conditions are taken into account as follows.

Dirichlet boundary condition:

This boundary condition is used when pressure head can be prescribed on the boundary. It can be expressed as

$$h = h_d(\mathbf{x}, t) \qquad on \quad B_d(\mathbf{x}) = 0 \tag{2.3.5}$$

where $h_d(\mathbf{x},t)$ is the Dirichlet head on the boundary surface $B_d(\mathbf{x}) = 0$

Neumann boundary condition:

This boundary condition is employed when the flux results from pressure-head gradient is known as a function of time. It is written as

$$-\mathbf{n} \cdot \mathbf{K} \cdot \frac{\rho_o}{\rho} \nabla h = q_n(\mathbf{x}, t) \qquad on \quad B_n(\mathbf{x}) = 0 \tag{2.3.6}$$

where $q_n(\mathbf{x},t)$ is the Neumann flux and $B_n(\mathbf{x}) = 0$ is the Neumann boundary surface.

Cauchy boundary condition:

This boundary condition is employed when the flux results from total-head gradient is known as a function of time. It can be written as

$$-\mathbf{n} \cdot \left(\mathbf{K} \cdot \frac{\rho_o}{\rho} \nabla h + \mathbf{K} \cdot \nabla z \right) = q_c(\mathbf{x}, t) \qquad on \quad B_c(\mathbf{x}) = 0 \tag{2.3.7}$$

where $q_c(\mathbf{x},t)$ is the Cauchy flux and $B_c(\mathbf{x}) = 0$ is the Cauchy boundary surface.

River Boundary Condition:

This boundary condition is employed when there is a thin layer of medium separating the river and the subsurface media.

$$-\mathbf{n}\cdot\mathbf{K}\cdot\left(\frac{\rho_o}{\rho}\nabla h+\nabla z\right)=-\frac{K_R}{b_R}\left(h_R-h\right)\qquad on\quad B_r(\mathbf{x})=0 \tag{2.3.8}$$

where K_R is the hydraulic conductivity of the thin layer, b_R is the thickness of the thin layer, h_R is the water depth in the river, and $B_r(\mathbf{x}) = 0$ is the surface between the river and subsurface media.

Variable Boundary Condition:

This boundary condition is usually used for the ground surface boundary when the coupling of surface and subsurface systems is not taken into account.

(1) During precipitation periods:

$$h=h_p(\mathbf{x},t)\quad iff\quad -\mathbf{n}\cdot\mathbf{K}\cdot\left(\frac{\rho_o}{\rho}\nabla h+\nabla z\right)\geq q_p(\mathbf{x},t)\quad on\quad B_v(\mathbf{x})=0 \tag{2.3.9}$$

or

$$-\mathbf{n}\cdot\mathbf{K}\cdot\left(\frac{\rho_o}{\rho}\nabla h+\nabla z\right)=q_p(\mathbf{x},t)\quad iff\quad h\leq h_p\quad on\quad B_v(\mathbf{x})=0 \tag{2.3.10}$$

(2) During non-precipitation period:

$$h=h_p(\mathbf{x},t)\quad iff\quad -\mathbf{n}\cdot\mathbf{K}\cdot\left(\frac{\rho_o}{\rho}\nabla h+\nabla z\right)\geq 0\quad on\quad B_v(\mathbf{x})=0 \tag{2.3.11}$$

$$h=h_m(\mathbf{x},t)\quad iff\quad -\mathbf{n}\cdot\mathbf{K}\cdot\left(\frac{\rho_o}{\rho}\nabla h+\nabla z\right)\leq q_e\quad on\quad B_v(\mathbf{x})=0 \tag{2.3.12}$$

or

$$-\mathbf{n}\cdot\mathbf{K}\cdot\left(\frac{\rho_o}{\rho}\nabla h+\nabla z\right)=q_e(\mathbf{x},t)\quad iff\quad h\geq h_m\quad on\quad B_v(\mathbf{x})=0 \tag{2.3.13}$$

where $h_p(\mathbf{x},t)$ is ponding depth, $q_p(\mathbf{x},t)$ is the flux due to precipitation, $h_m(\mathbf{x},t)$ is the minimum pressure head, and $q_e(\mathbf{x},t)$ is the potential evaporation rate on the surfaces of the variable boundary condition $B_v(\mathbf{x}) = 0$. Only one of Eqs. (2.3.9) through (2.3.13) is used at any point on the variable boundary at any time.

2.3.2 Thermal Transport

The thermal transport equation is derived based on the conservation principle of energy as:

$$\frac{\partial\left[\left(\rho_w C_w\theta+\rho_b C_m\right)T\right]}{\partial t}+\nabla\cdot\left(\rho_w C_w\mathbf{V}T\right)-\nabla\cdot\left(\mathbf{D}^{\mathbf{H}}\cdot\nabla T\right)=H^a+H^c \tag{2.3.14}$$

where ρ_w is the water density [M/L^3]; C_w is the heat capacity of water [L^2/t^2/T]; θ is the moisture content [L^3/L^3]; ρ_b is the bulk density of the media [M/L^3]; C_m is the heat capacity of the matrix [L^2/t^2/T]; T is the temperature [T]; $\mathbf{D}^{\mathrm{H}}$ is the apparent thermal conductivity tensor including the effect of dispersion, diffusion, and conduction [E/t/L/T = ML/t^3/T, where E is the unit of energy]; H^a is the heat source due to artificial injection/withdraw [E/t/L^3 = M/L/t^3], and H^c is the heat source due to chemical reaction [E/t/L^3 = M/L/t^3].

In addition to the initial boundary condition, boundary conditions must be specified for the temperature. Five types of global boundary conditions are provided in this report as follows.

Dirichlet boundary condition:

This condition is applied when the temperature is prescribed as a function of time on the boundaries:

$$T(\mathbf{x},t) = T_{db}(\mathbf{x},t) \quad on \quad B_d(\mathbf{x}) = 0 \tag{2.3.15}$$

where $T_{db}(\mathbf{x},t)$ is a time-dependent temperature on the Dirichlet boundary $B_d(\mathbf{x}) = 0$ [T].

Variable boundary condition:

This boundary condition is employed when the flow direction would change with time during simulations. Two cases are considered, regarding to the flow direction on the boundary.

< Case 1 > Flow is coming in from outside:

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{V}T - \mathbf{D}^{\mathbf{H}}\cdot\nabla T\right) = \mathbf{n}\cdot\rho_w C_w \mathbf{V}T_{vb}(\mathbf{x},t) \quad on \quad B_v(\mathbf{x}) = 0 \tag{2.3.16}$$

< Case 2 > Flow is going out from inside:

$$-\mathbf{n}\cdot\mathbf{D}^{\mathbf{H}}\cdot\nabla T = 0 \quad on \quad B_v(\mathbf{x}) = 0 \tag{2.3.17}$$

where $T_{vb}(\mathbf{x},t)$ is a time-dependent temperature on the variable boundary, $B_v(\mathbf{x}) = 0$, [T], which is associated with the incoming flow.

Cauchy boundary condition*:*

This boundary condition is employed when the total heat-flow rate is given at the river/stream boundary. Usually, this boundary is an upstream boundary node. The conditions can be expressed as

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{V}T - \mathbf{D}^{\mathbf{H}}\cdot\nabla T\right) = H_{cb}(\mathbf{x},t) \quad on \quad B_c(\mathbf{x}) = 0 \tag{2.3.18}$$

where $H_{cb}(\mathbf{x},t)$ is total heat flux through the Cauchy boundary, $B_c(\mathbf{x}) = 0$, [E/L^2/t = M/t^3, where E denotes the unit of energy], which takes a positive value if it is going out of the region and a negative value if it is coming into the region.

Neumann boundary condition:

This boundary condition is used when the conductive heat-flow rate is known at the river/stream boundary node. It can be written as

$$-\mathbf{n}\cdot\mathbf{D}^{\mathbf{H}}\cdot\nabla T = H_{nb}(\mathbf{x},t) \quad on \quad B_n(\mathbf{x}) = 0 \tag{2.3.19}$$

where $H_{nb}(\mathbf{x},t)$ is the heat flux through the Neumann boundary, $B_n(\mathbf{x}) = 0$, [E/L^2/t].

Atmosphere-subsurface interface boundary condition:

At the interface of the atmosphere and subsurface media, a heat budget boundary condition is specified as

$$-\mathbf{n}\cdot\left(\rho_w C_w \mathbf{V}T - \mathbf{D}^{\mathbf{H}}\cdot\nabla T\right) = H_n - H_b - H_e - H_s \tag{2.3.20}$$

where H_n, H_b, H_e, and H_s are calculated using Eqs. (2.1.71) through (2.1.76).

In addition to the five types of global boundary conditions, two interface boundary conditions may be specified: one for the exchange of energy/heat flux between the subsurface media and river/stream network and the other for energy/heat exchange between the subsurface media and the overland. Mathematically, these boundary conditions are described below.

Subsurface-river interface boundary condition*:*

$$\int_P \mathbf{n}\cdot\left(\rho_w C_w \mathbf{V}T - \mathbf{D}^{\mathbf{H}}\cdot\nabla T\right)dP = S_h^i \tag{2.3.21}$$

where S_h^i is the heat sources in Eq. (2.1.67) and P is the wet perimeter of the river. The heat source can be calculated using Eq. (2.1.68) if the temperatures in the subsurface and river are discontinuous at the interfaces. If the temperatures are continues, then this heat source should be formulated by imposing the continuity of the temperatures in the subsurface and river water at the interfaces.

Subsurface-overland interface boundary condition:

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{V}T - \mathbf{D}^{\mathbf{H}}\cdot\nabla T\right) = H_i \tag{2.3.22}$$

where H_i is the heat source in Eq. (2.2.54). This heat source can be calculated using Eq. (2.2.55) if the temperatures in the subsurface and overland are discontinuous at the interface. If the temperatures are continues, then this heat source should be formulated by imposing the continuity of the temperatures in the subsurface and overland at the interface.

2.3.3 Salinity Transport

$$\frac{\partial(\theta S)}{\partial t} + \nabla\cdot(\mathbf{V}S) - \nabla\cdot\left(\theta\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right) = S^{as} \qquad \textbf{(2.3.23)}$$

where S is the salinity [M/L^3]; $\mathbf{D}^{\mathbf{S}}$ is the longitudinal dispersion coefficient [L^2/t]; and S^{as} is the artificial source of the salt [M/L^3/t].

As in thermal transport, four types of global boundary conditions for salinity transport are provided in this report as follows.

Dirichlet boundary condition:

This condition is applied when the salinity is prescribed as a function of time on the boundaries:

$$S(x,t) = S_{db}(\mathbf{x},t) \quad on \quad B_d(\mathbf{x}) = 0 \qquad \textbf{(2.3.24)}$$

where $S_{db}(\mathbf{x},t)$ is a time-dependent salinity on the Dirichlet boundary, $B_d(\mathbf{x}) = 0$, [M/L^3].

Variable boundary condition:

This boundary condition is employed when the flow direction would change with time during simulations. Two cases are considered, regarding to the flow direction on the boundary.

< Case 1 > Flow is coming in from outside:

$$\mathbf{n}\cdot\left(\mathbf{V}S - \theta\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right) = \mathbf{n}\cdot VS_{vb}(\mathbf{x},t) \quad on \quad B_v(\mathbf{x}) = 0 \qquad \textbf{(2.3.25)}$$

< Case 2 > Flow is going out from inside:

$$-\mathbf{n}\cdot\theta\mathbf{D}^{\mathbf{S}}\cdot\nabla S = 0 \quad on \quad B_v(\mathbf{x}) = 0 \qquad \textbf{(2.3.26)}$$

where $S_{vb}(\mathbf{x},t)$ is a time-dependent salinity [M/L^3] on the variable boundary, $B_v(\mathbf{x}) = 0$, which is associated with the incoming flow.

Cauchy boundary condition:

This boundary condition is employed when the total salt-flow rate is given at pervious boundaries. Usually, this boundary is a flow-in boundary. The conditions are expressed as

$$\mathbf{n}\cdot\left(\mathbf{V}S - \theta\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right) = Q_{scb}(\mathbf{x},t) \quad on \quad B_c(\mathbf{x}) = 0 \qquad \textbf{(2.3.27)}$$

where $Q_{scb}(\mathbf{x},t)$ is total salt-flow rate [M/L^2/t] through the Cauchy boundary, $B_c(\mathbf{x}) = 0$, which takes a positive value if it is going out of the region and a negative value if it is coming into the region.

Neumann boundary condition:

This boundary condition is used when the dispersive salt-flow rate is known at the boundary. It can be written as

$$-\mathbf{n}\cdot\theta\mathbf{D}^{\mathbf{S}}\cdot\nabla S = Q_{snb}\left(\mathbf{x},t\right) \tag{2.3.28}$$

where $Q_{snb}\left(\mathbf{x},t\right)$ is the salt flux through the Neumann boundary, $B_n(\mathbf{x}) = 0$, [M/L^2/t].

In addition to the four types of global boundary conditions, two interface boundary conditions may be specified: one for the exchange of salt flux between the subsurface media and river/stream network and the other for salt exchange between the subsurface media and the overland. Mathematically, these boundary conditions are described below.

Subsurface-river interface boundary condition:

$$\int_P \mathbf{n}\cdot\left(\mathbf{V}S - \theta\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right)dP = M_s^i \tag{2.3.29}$$

where M_s^i is the salt source in Eq. (2.1.86) and P is the wet perimeter of the river. The salt source can be calculated using Eq. (2.1.87) if the salinity in the subsurface and river is discontinuous at the interfaces. If the salinity is continuous, then this salt source should be formulated by imposing the continuity of the salinity in the subsurface and river at the interface.

Subsurface-overland interface boundary condition:

$$\mathbf{n}\cdot\left(\mathbf{V}S - \theta\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right) = M_s^{is} \tag{2.3.30}$$

where M_s^{is} is the salt source in Eq. (2.2.62). This salt source can be calculated using Eq. (2.2.63) if the salinity in the subsurface and overland is discontinuous at the interface. If the salinity is continuous, then this salt source should be formulated by imposing the continuity of the salinity in the subsurface and overland at the interface.

2.4 Coupling Fluid Flows Among Various Media

One of the critical issues in a first principle physics-based watershed model is its treatments of coupling among various media. There appear a number of watershed models that have dealt with each component medium on the bases of first principle in the past decade (MIKE11-MIKE SHE [Abbott et al., 1986a, 1986b], SHETRAN [Ewen et al., 2000], MODFLOW-HMS [HydroGeoLogic, Inc., 2001], InHM [VanderKwaak, 1999], GISWA [Wigmosta and Perkins, 1997], SFRSM-HSE [SFWMD, 2005], COSFLOW [Yeh et al., 1997], WASH123D Version 1.0 [Yeh et al., 1998]). However, rigorous considerations on coupling among media seemed lacking. For example, a linkage term is normally formulated between the river/stream/canal dynamics and subsurface fluid flow (e.g., MODNET [Walton et al., 1999]) or between overland and subsurface flows (e.g.,

MIKE11-MIKE SHE [http://www.dhisoftware.com/mikeshe/; http://www.dhisoftware.com/mikeshe/components]). The linkage term usually introduces non-physical parameters. As a result, such watershed models have degraded even though each media-component module has taken a first principle physics-based approach. A rigorous treatment of coupling media should be based the continuity of mass, momentum, and state variables. This is the approach taken in this report. Mathematical statements on coupling between pairs of media are address below.

2.4.1 Coupling between River/Stream/Canal and Overland Flows

The fluxes between overland regime and canals/streams/rivers network are dynamics and depend on the water surface elevations in the vicinity of the interface between canal/stream/river and overland regime (Fig. 2.4-1). The basic principle of coupling is to impose continuous of fluxes and the state variables (water surface elevations, temperature, and salinity in the overland and in the canal) if these state variables do not exhibit discontinuity. If the state variables exhibit discontinuity, then the linkage term is used to simulate the volumetric fluxes or simplified formulations of heat fluxes and salinity fluxes are imposed.

When a levee is present on the bank of the canal (left column in Fig. 2.4-1), there are several possibilities on the dynamic interactions between overland flow and river flow dynamics. If water surfaces in both the overland regime and river are below the top of the levee, the two flow systems are decoupled (Fig. 2.4-1a).

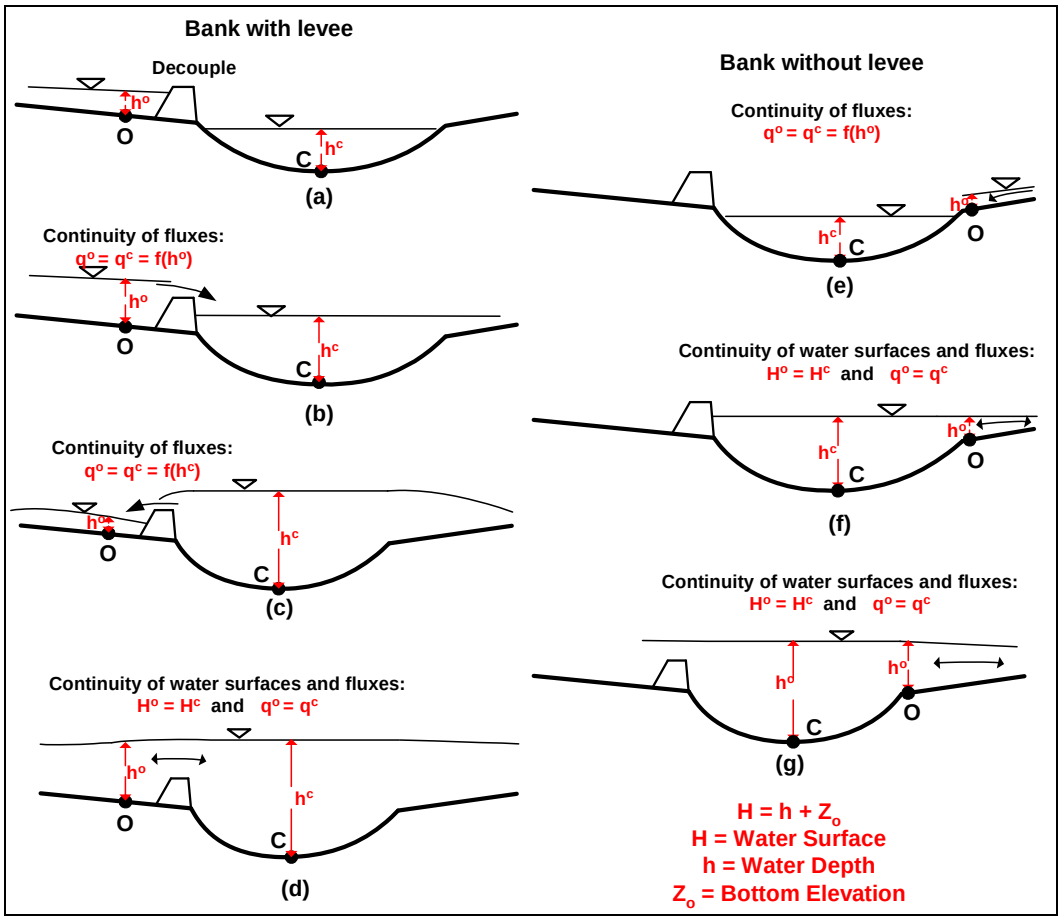


Fig. 2.4-1. Flow interactions between overland regime and canal: bank with levee (left column) and bank without levee (right column)

When the water surface in the overland regime is above the top of the levee and in the canal is below

the top of the levee (Fig. 2.4-1b), the flux is a function of the water depth in the overland regime given

$$q^{o} = q^{c} = f\left(h^{o}\right) \;\Rightarrow\; \mathbf{n}\cdot\mathbf{V}h\big|_{O} = S_1 = f\left(h^{o}; Z_{o|B}\right) \qquad \textbf{(2.4.1)}$$

where q^o is the outward normal flux of the overland flow, q^c is the lateral flow from the overland to the canal, h^o is the water depth in the overland regime, $f(h^o)$ is a prescribed function of h^o given by the shape and width of the levee, $\mathbf{n}$ is the outward unit vector (from the overland side) of the overland-canal interface, $\mathbf{V}$ is the velocity in the overland regime, S_1 is defined in Eq. (2.1.1), $Z_o|_B$ is the bottom elevation evaluated at the canal bank (in this case $Z_o|_B$ is the elevation of the top of the levee). The coupling of thermal and/or salinity transport between the overland regime and river networks for this case can be stated as

$$\begin{aligned} \mathbf{n}\cdot\left(\rho_w C_w \mathbf{q}T - \mathbf{D}^{\mathbf{H}} h\cdot\nabla T\right)\Big|_{Bank\,1} &= S_h^{o1} = \rho_w C_w S_1 T^o \qquad \textit{and} \\ \mathbf{n}\cdot\left(\mathbf{q}S - \mathbf{D}^{\mathbf{S}} h\cdot\nabla S\right)\Big|_{Bank\,1} &= M_s^{o1} = S_1 S^o \end{aligned} \qquad \textbf{(2.4.2)}$$

where T^o is the temperature of the overland water at the interface and S^o is the salinity of the overland water at the interface.

On the other hand, when the water surface in the overland regime is belowe the top of the levee and in the canal is above the top of the levee (Fig. 2.4-1c), the flux is a function of the water depth in the overland regime given by

$$q^{o} = q^{c} = f\left(h^{c}\right) \qquad \Rightarrow \qquad \mathbf{n}\cdot\mathbf{V}h\big|_{O} = S_1 = f\left(h^{c}; Z_o\big|_B\right) \qquad \textbf{(2.4.3)}$$

where h^c is the water depth in the canal and $f(h^c)$ is a prescribed function of h^c. The coupling of thermal and salinity transport between the overland regime and river networks for this case can be stated as

$$\begin{aligned} \mathbf{n}\cdot\left(\rho_w C_w \mathbf{q}T - \mathbf{D}^{\mathbf{H}} h\cdot\nabla T\right)\Big|_{Bank1} &= S_h^{o1} = \rho_w C_w S_1 T^c \qquad \textit{and} \\ \mathbf{n}\cdot\left(\mathbf{q}S - \mathbf{D}^{\mathbf{S}} h\cdot\nabla S\right)\Big|_{Bank1} &= M_s^{o1} = S_1 S^c \end{aligned} \qquad \textbf{(2.4.4)}$$

where T^c is the temperature of the canal water at the interface and S^c is the salinity of the canal water at the interface.

When the water surfaces in both the overland and canal are above the top of the levee (Fig. 2.4-1d), then the continuity of fluxes and state variables must be imposed as

$$q^o = q^c \;\Rightarrow \mathbf{n}\cdot\mathbf{V}h\big|_{O} = S_1 \quad \textit{and} \quad H^o = H^c \Rightarrow \left(h + Z_o\right)\big|_{O} = \left(h + Z_o\right)\big|_{C} \qquad \textbf{(2.4.5)}$$

where $(h + Z_o)|_O$ denotes that $(h + Z_o)$ is evaluated at point O (Fig. 2.4-1 d). Similarly, $(h + Z_o)|_C$ denotes that $(h + Z_o)$ is evaluated at point C. The coupling of thermal and/or salinity transport between the overland regime and river networks for this case can be obtained by formulating the fluxes

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{q}T - \mathbf{D}^{\mathbf{H}} h\cdot\nabla T\right)\Big|_{Bank1} = S_h^{o1} = \rho_w C_w S_1 \frac{1}{2}\left(1+sign\left(S_1\right)T^o + \left(1-sign\left(S_1\right)\right)T^c\right)$$
$$and \quad \mathbf{n}\cdot\left(\mathbf{q}S - \mathbf{D}^{\mathbf{S}} h\cdot\nabla S\right)\Big|_{Bank1} = M_S^{o1} = S_1 \frac{1}{2}\left(\left(1+sign\left(S_1\right)\right)S^o + \left(1-sign\left(S_1\right)\right)S^c\right) \quad \textbf{(2.4.6)}$$

where *sign(S_1)* is 1.0 if the flow is from overland to canal, -1.0 if the flow is from canal to overland. For this case, the temperature and salinity in the canal may be the same as those in the overland water at the interface. If this is the case, we impose the continuity of temperature and/or salinity to yield the fluxes

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{q}T - \mathbf{D}^{\mathbf{H}} h\cdot\nabla T\right)\Big|_{Bank1} = S_h^{o1} \quad and \quad T^o\Big|_{Bank1} = T^c$$
$$and \qquad \mathbf{n}\cdot\left(\mathbf{q}S - \mathbf{D}^{\mathbf{S}} h\cdot\nabla S\right)\Big|_{Bank1} = M_S^{o1} \quad and \quad S^o\Big|_{Bank1} = S^c \quad \textbf{(2.4.7)}$$

When a levee is not present on the bank of the canal (right column in Fig. 2.4-1), there are two possibilities on the dynamic interactions between overland flow and river flow dynamics. If water surface in the canal falls below the bank, the flux is either zero if the overland flow is not present or is nonzero and directed from the overland into the canal if overland flow is present (Fig. 2.4-1 e) as

$$q^o = q^c = f\left(h^o\right) \qquad \Rightarrow \qquad \mathbf{n}\cdot\mathbf{V}h\Big|_O = S_2 = f\left(h^o; Z_o\big|_B\right) \quad \textbf{(2.4.8)}$$

where S_2 is defined in Eq. (2.1.1) and $Z_o|_B$ is the bottom elevation evaluated at point *O* on the canal bank. The coupling of thermal and/or salinity transport between the overland regime and river networks for this case can be stated as

$$\mathbf{n}\cdot\left(\rho_w C_W \mathbf{q}T - \mathbf{D}^{\mathbf{H}} h\cdot\nabla T\right)\Big|_{Bank2} = S_h^{o2} = \rho_w C_w S_2 T^o \quad and$$
$$\mathbf{n}\cdot\left(\mathbf{q}S - \mathbf{D}^{\mathbf{S}} h\cdot\nabla S\right)\Big|_{Bank2} = M_s^{o2} = S_2 S^o \quad \textbf{(2.4.9)}$$

When the water surface in the canal is above the bank (Figs. 2.4-1f and 2.4-1.g), the flux direction can be either from the overland into the canal or from the canal into the overland depending on the flow dynamics in the overland and in the canal. The direction of the flux and its magnitude are obtained by imposing the continuity of flux and state variables

$$q^o = q^c \Rightarrow \mathbf{n}\cdot\mathbf{V}h\Big|_O = S_2 \quad and$$
$$H^o = H^c \Rightarrow \left(h+Z_o\right)\Big|_O = \left(h+Z_o\right)\Big|_C \quad \textbf{(2.4.10)}$$

The coupling of thermal and/or salinity transport between the overland regime and river networks for this case can be stated as

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{q}T - \mathbf{D}^{\mathbf{H}} h\cdot\nabla T\right)\Big|_{Bank\,2} = S_h^{o2}$$
$$= \rho_w C_w S_2 \frac{1}{2}\left(\left(1+sign\left(S_2\right)\right)T^o + \left(1-sign\left(S_2\right)\right)T^c\right) \quad and \tag{2.4.11}$$
$$\mathbf{n}\cdot\left(\mathbf{q}S - \mathbf{D}^{\mathbf{S}} h\cdot\nabla S\right)\Big|_{Bank\,2} = M_S^{o2} = S_2\frac{1}{2}\left(\left(1+sign\left(S_2\right)\right)S^o + \left(1-sign\left(S_2\right)\right)S^c\right)$$

For these two cases (Fig. 2.4-1f and 2.4-1g), the temperature and salinity in the canal may be the same as those in the overland water at the interface. If this is the case, we impose the continuity of temperature and/or salinity to yield the fluxes

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{q}T - \mathbf{D}^{\mathbf{H}} h\cdot\nabla T\right)\Big|_{Bank\,2} = S_h^{o1} \quad and \quad T^o\Big|_{Bank\,2} = T^c \quad and$$
$$\mathbf{n}\cdot\left(\mathbf{q}S - \mathbf{D}^{\mathbf{S}} h\cdot\nabla S\right)\Big|_{Bank\,2} = M_s^{o1} \quad and \quad S^o\Big|_{Bank\,2} = S^c \tag{2.4.12}$$

2.4.2 Coupling between Overland and Subsurface Flows

The fluxes between overland and subsurface media are obtained by imposing continuous of fluxes and state variables if these state variables do not exhibit discontinuity. If the state variables exhibit discontinuity, then a linkage term is used to simulate the fluxes. Consider the interaction between the overland subsurface and subsurface flows. There are two cases: in one case, there is no impermeable layers on the ground surface (Fig. 2.4-2a) and, in another case, there are thin layers of very impermeable layers such as pavements or sediment deposits on the ground surface (Fig. 2.4-2b).

For the case of no impermeable layers on the ground surface (Fig. 2.4-2a), it can easily be seen that the pressures in the overland flow (if it is present) and in the subsurface media will be continuous across the interface. Thus, the interaction must be simulated by imposing continuity of pressures and fluxes as

$$h^o = h^s \quad and \quad Q^o = Q^s \quad \Rightarrow \quad I = -\mathbf{n}\cdot\mathbf{K}\cdot\left(\frac{\rho_o}{\rho}\nabla h^s + \nabla z\right) \tag{2.4.13}$$

where h^o is the water depth in the overland if it is present, h^s is the pressure head in the subsurface, Q^o is the flux from the overland to the interface and Q^s is the flux from the interface to the subsurface media, I is defined in Eq. (2.2.1), **n** is an outward unit vector of the ground subsurface, **K** is the hydraulic conductivity tensor, and h^s is the pressure head in the subsurface media. The use of a linkage term such as $Q^o = Q^s = K(h^o - h^s)$, while may be convenient, is not appropriate because it introduces a non-physics parameter K. The calibration of K to match simulations with field data renders the coupled model ad hoc even though the overland and subsurface flows are each individually physics-based.

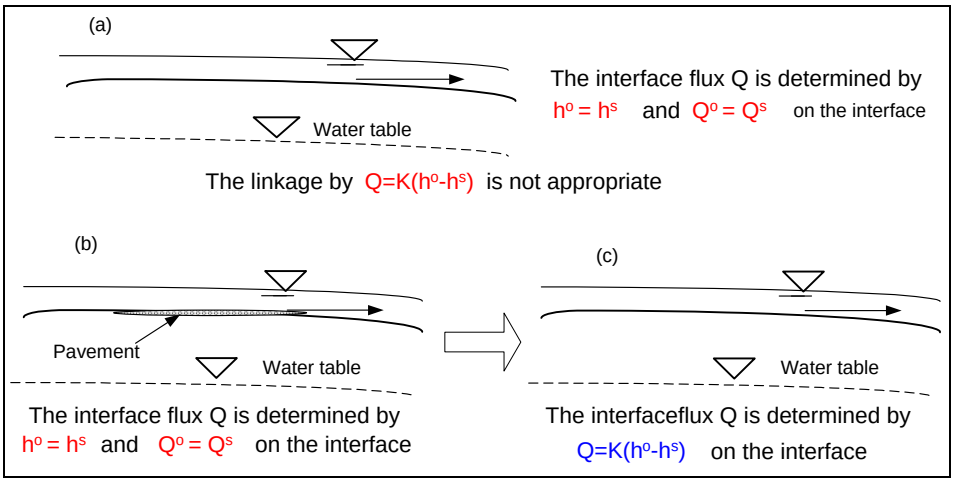


Fig. 2.4-2. Flow interactions between overland regime and subsurface media.

For the cases with thin impervious layers (Fig. 2.4-2b), one can include the impervious layers as part of the subsurface media or exclude these layers from the modeling. If one includes the thin layers, then it is obvious the pressures in the overland flow and in the layer are continuous across the interface, thus continuity of pressures and fluxes must imposed to simulate the interaction. On the other hand, if the thin layers are not included, it is obvious, the pressures in the overland flow and the subsurface are not continuous across the removed layers, then a linkage term is used to model the flux between across interface as

$$Q^o = Q^s \qquad \Rightarrow \qquad I = -n \cdot K \cdot \left(\frac{\rho_o}{\rho} \nabla h^s + \nabla z \right) = \frac{K_b}{b} \left(h^s - h^o \right) \tag{2.4.14}$$

where K_b and b are the hydraulic conductivity and thickness, respectively, of the removed bottom sediment layer. These parameters in the linkage term are the material properties and geometry of the removed layer. These parameters, in theory, can be obtained independent of model calibration.

The coupling of thermal and/or salinity transport between the overland regime and subsurface media can be stated as

$$\begin{aligned} &\mathbf{n} \cdot \left(\rho_w C_w V T - \mathbf{D^H} \cdot \nabla T \right) = H_i = \rho_w C_w I \frac{1}{2} \left(\left(1 + sign(I) \right) T^s + \left(1 - sign(I) \right) T^o \right) \\ &\textit{and} \quad \mathbf{n} \cdot \left(V S - \theta \mathbf{D^S} \cdot \nabla S \right) = M_s^{is} = I \frac{1}{2} \left(\left(1 + sign(I) \right) S^s + \left(1 - sign(I) \right) S^o \right) \end{aligned} \tag{2.4.15}$$

where *sign(I)* is 1.0 if I is positive and is -1.0 if negative; T^s is the temperature of subsurface water at the interface; T^o is the temperature of overland water at the interface; S^s is the salinity of subsurface water at the interface; and S^o is the salinity of overland water at the interface.

The temperature and salinity in the overland water may be the same as those in the subsurface water at the interface. If this is the case, we impose the continuity of temperature and/or salinity to yield the fluxes

$$\mathbf{n}\cdot\left(\rho_w C_w \mathbf{V}T - \mathbf{D}^{\mathbf{H}}\cdot\nabla T\right) = H_i \text{ and } T^s\Big|_{\text{on the surface}} = T^o \text{ and}$$
$$\mathbf{n}\cdot\left(\mathbf{V}S - \theta\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right) = M_s^{is} \quad \text{and} \quad S^s\Big|_{\text{on the surface}} = S^o \tag{2.4.16}$$

2.4.3 Coupling between Subsurface and River/Stream/Canal Flows

The fluxes between canal and subsurface are obtained by imposing continuous of fluxes and state variables if these state variables do not exhibit discontinuity. If the state variables exhibit discontinuity, then a linkage term is used to simulate the fluxes. Consider the interaction between the canal and subsurface. There are two cases: in one case, there is not any thin layer of sediment materials (Fig. 2.4-3a) and, in another case, there are thin layers of sediment materials between the canal bottom and the top of surface media (Fig. 2.4-3b).

For the case of no thin layer of sediments (Fig. 2.4-3a), it can easily be seen that the pressures in the canal and in the subsurface media will be continuous across the interface of canal bottom and subsurface media. Thus, the interaction must be simulated by imposing continuity of pressure and flux as follows.

$$h^c = h^s \quad \text{and} \quad Q^c = Q^s \Rightarrow S_I = \int_P \left[-\mathbf{n}\cdot\mathbf{K}\cdot\left(\frac{\rho_O}{\rho}\nabla h^s + \nabla z\right)\right] dP \tag{2.4.17}$$

where h^c is the water depth in the canal, h^s is the pressure head in the subsurface, Q^c is the flux from the canal to the interface and Q^s is the flux from the interface to the subsurface media, S_I is defined in Eq. (2.1.1), **n** is an outward unit vector of the subsurface media interfacing the canal, **K** is the hydraulic conductivity tensor of the subsurface media, h^s is the pressure head in the subsurface media, and P is the wet perimeter of the canal. The use of a linkage term such as $Q^c = Q^s = K(h^c - h^s)$, while may be convenient, is not appropriate because it introduces a non-physics parameter K. The calibration of K to match simulations with field data renders the coupled model ad hoc even though the canal and subsurface flows are each individually physics-based.

For the cases with thin layers of sediments (Fig. 2.4-3b), one can include the sediment layers as part of the subsurface media or exclude these layers from the modeling. If one includes the thin layers, then it is obvious the pressures in the canal and in the sediment layer are continuous across the interface of canal bottom and the top of the thin layers, thus continuity of pressures must imposed to simulate the interaction. On the other hand, if the thin layers are excluded (Fig. 2.4-3c), the pressures in the canal and subsurface are not continuous across the bottom of canal and the top of subsurface media, then, a linkage term can be used to model the flux between the canal and surface media as

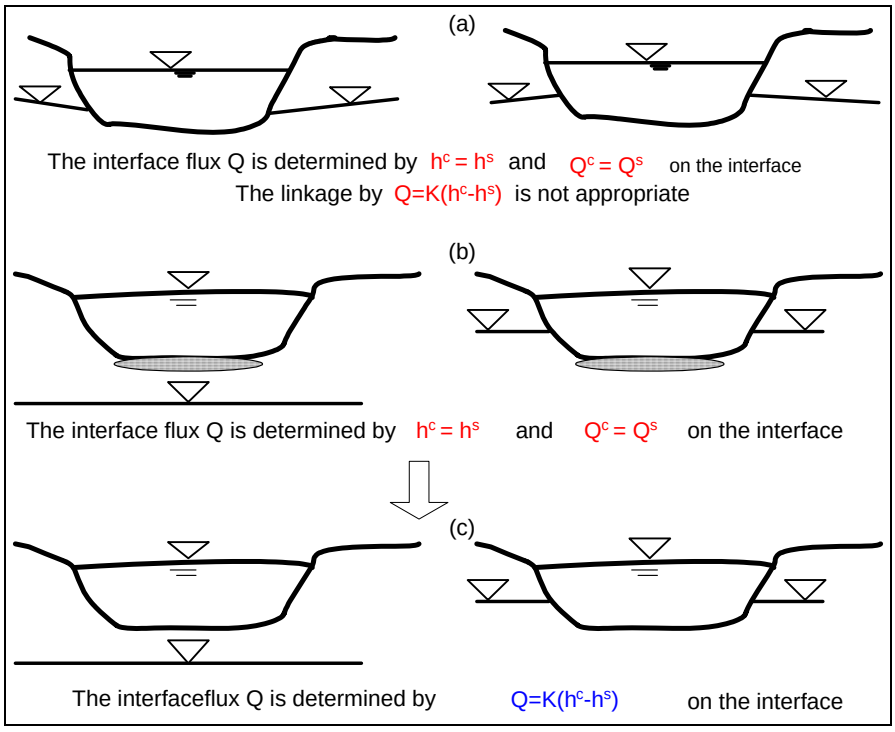


Fig. 2.4-3. Flow interactions between canal and subsurface media.

$$Q^c = Q^s \Rightarrow \int_P \left[-\mathbf{n}\cdot\mathbf{K}\cdot\left(\frac{\rho_o}{\rho}\nabla h^s + \nabla z\right)\right] dP = \int_P \frac{K_b}{b}\left(h^s - h^c\right) dP \qquad \textbf{(2.4.18)}$$

where K_b and b are the hydraulic conductivity and thickness, respectively, of the removed bottom sediment layer. These parameters in the linkage term are the material properties and geometry of the removed layer. These parameters, in theory, can be obtained independent of model calibration.

The coupling of thermal and/or salinity transport between the canal and subsurface media can be stated as

$$\int_P \mathbf{n}\cdot\left(\rho_w C_w \mathbf{V} T - \mathbf{D}^{\mathbf{H}}\cdot\nabla T\right) dP = S_h^i$$

$$= \rho_w C_w S_I \frac{1}{2}\left(\left(1+sign\left(S_I\right)\right)T^s + \left(1-sign\left(S_I\right)\right)T^c\right) \quad and \qquad \textbf{(2.4.19)}$$

$$\int_P \mathbf{n}\cdot\left(\mathbf{V}S - \theta\mathbf{D}^{\mathbf{S}}\cdot\nabla S\right) dP = M_s^i = S_I \frac{1}{2}\left(\left(1+sign\left(S_I\right)\right)S^s + \left(1-sign\left(S_I\right)\right)S^c\right)$$

where $sign(S_I)$ is 1.0 if S_I is positive and is -1.0 if negative; T^s is the temperature of subsurface water at the interface; T^c is the temperature of canal water at the interface; S^s is the salinity of subsurface water at the interface; and S^c is the salinity of canal water at the interface.

Similar to the interaction between the overland regime and subsurface media, the temperature and salinity in the canal water may be the same as those in the subsurface water at the interface. If this is

the case, we impose the continuity of temperature and/or salinity to yield the fluxes

$$\int_P \mathbf{n}\cdot\left(\rho_w C_w \mathbf{V}T - \mathbf{D}^{\mathbf{H}}\cdot\nabla T\right)dP = S_h^i \quad and \quad T^s\Big|_{on\ the\ surface} = T^c \quad and$$
$$\int_P \mathbf{n}\cdot\left(\mathbf{V}S - \theta\mathbf{D}^S\cdot\nabla S\right)dP = = M_s^i \quad and \quad S^s\Big|_{on\ the\ surface} = S^c \qquad \textbf{(2.4.20)}$$

2.5 Sediment and Water Quality Transport in 1D River/Stream/Canal Networks

In WASH123D, sediments are categorized based on their physical and chemical properties. For each category of sediment, we include mobile suspended sediment particles scattered in water column and immobile bed sediment particles accumulated in river/stream bed. The distribution of suspended sediment and bed sediment is controlled through hydrological transport as well as erosion and deposition processes.

In river/stream networks, there are six phases and three forms of biochemical species. As shown in Figure 2.5-1, the six phases are suspended sediment, bed sediment, mobile water, immobile water, suspension precipitate, and bed precipitate phases; and the three forms are dissolved biochemicals, particulate biochemicals sorbed onto sediments, and precipitates. Usually, biochemical species in the suspended sediment phase, the mobile water phase and the suspension precipitate phase are considered mobile. Biochemical species in the bed sediment phase, the immobile water phase and the bed precipitate phase are considered immobile.

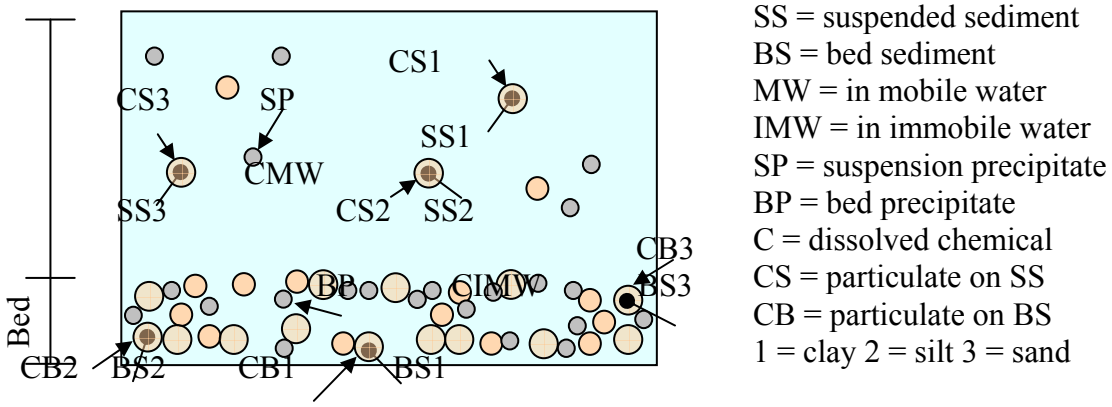


Fig. 2.5-1. Sediments and Chemicals in River/Stream Networks

A reactive system is completely defined by specifying biogeochemical reactions (Yeh, et al. 2001a). In the transport simulation, biogeochemical reactions can be divided into two classes (Rubin, 1983): (1) Fast/equilibrium reactions, and (2) Slow/kinetic reactions. The former are sufficiently fast compared to transport time scale and reversible, so that local equilibrium may be assumed. The latter are not sufficiently fast compared to transport time scale. They are either reversible or irreversible, where the local equilibrium formulation is inappropriate.

As shown in Figure 2.5-2, the biogeochemical reactions considered in the model can be categorized into ten types which take place between various phases: (1) aqueous complexation in column water, (2) adsorption/desorption or ion-exchange to suspended sediment, (3) precipitation/dissolution in water column, (4) adsorption/desorption or ion-exchange between column water and bed sediment, (5) aqueous complexation in pore water, (6) adsorption/desorption or ion-exchange to bed sediment, (7) precipitation/dissolution in bed, (8) volatilization reactions from water column to the atmopshere, (9) diffusion reactions between column and pore water, and (10) sedimentation reactions. Any individual reaction representing any of these chemical and physical processes may be simulated as kinetic or as equilibrium, which makes the code extremely flexible for application to a wide range of biogeochemical transport problems.

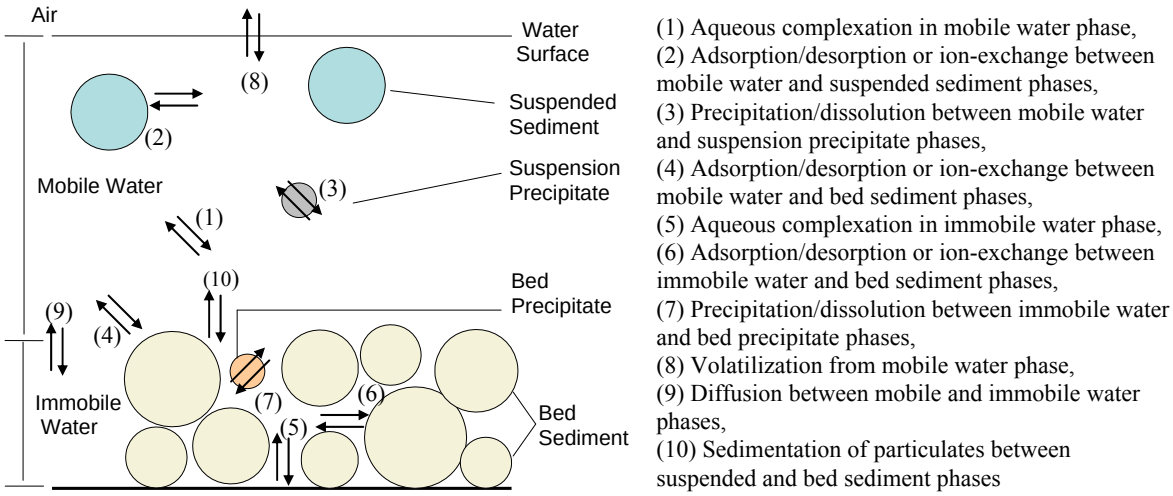


Fig. 2.5-2. Biogeochemical Reactions Considered in the Model

2.5.1 Bed Sediment

The balance equation for bed sediments is simply the statement that the rate of mass change is due to erosion/deposition as

$$\frac{\partial(PM_n)}{\partial t} = P(D_n - R_n) + M^{is}_{M_n}, \quad n \in [1, N_s] \qquad \textbf{(2.5.1)}$$

where P is the river/stream cross-sectional wetted perimeter [L], M_n is wetted perimeter-averaged concentration of the n-th bed sediment in mass per unit bed area [M/L^2], D_n is the deposition rate of the n-th sediment in mass per unit bed area per unit time [M/L^2/T], R_n is the erosion rate of the n-th sediment in mass per unit bed area per unit time [M/L^2/T], $M^{is}_{M_n}$ is the source of the n-th sediment from groundwater exfiltration in mass per unit river length [M/L/T], and N_S is the total number of sediment size fractions. Concentrations of all bed sediments must be given initially for transient simulations. No boundary condition is needed for bed sediments. In equation (2.5.1), we estimate the deposition and erosion rates using the different equations for cohesive and non-cohesive sediments.

For cohesive sediments, e.g., silt and clay, following equations are used (Yeh et al., 1998; Gerritsen

et al., 2000)

$$D_n = \min\left(V_{sn} S_n P_{Dn},\ S_n h/\Delta t\right) \qquad \text{where} \qquad P_{Dn} = \max\left(0,\ 1-\tau_b/\tau_{cDn}\right) \tag{2.5.2}$$

and

$$R_n = \min\left(E_{0n} P_{Rn},\ DMA_n/\Delta t\right) \qquad \text{where} \qquad P_{Rn} = \max\left(0,\ \tau_b/\tau_{cRn}-1\right) \tag{2.5.3}$$

where V_{sn} is the settling velocity of the n-th sediment [L/T], S_n is the cross-section-averaged suspended concentration of n-th sediment [M/L^3], h is the water depth [L], Δt is the time step size [T], τ_b is the bottom shear stress or the bottom friction stress [M/L/T^2], τ_{cDn} is the critical shear stress for the deposition of the n-th sediment [M/L/T^2], E_{0n} is the erodibility of the n-th sediment [M/L^2/T], DMA_n is the amount of locally available dry matter of n-th sediment, expressed as dry weight per unit area [M/L^2], τ_{cRn} is the critical shear stress for the erosion of the n-th sediment [M/L/T^2].

For Non-cohesive sediments, e.g., sand, we have two options.

Option 1 (Prandle et al., 2000)

$$D_n = \min\left(V_{sn} S_n N_{Dn},\ S_n h/\Delta t\right) \qquad \text{where} \qquad N_{Dn} = \max\left[0,\ 1-\left(V_{cDn}/V_{cRn}\right)^2\right] \tag{2.5.4}$$

and

$$R_n = \min\left(E_{0n} N_{Rn},\ DMA_n/\Delta t\right) \qquad \text{where} \qquad N_{Rn} = \max\left(0,\ V_{cDn}/V_{cRn}-1\right) \tag{2.5.5}$$

where V_{cDn} and V_{cRn} represent the critical friction velocities for the onset of deposition and erosion, respectively [L/T].

Option 2 (Yeh et al., 1998)

$$D_n = \max\left(\frac{G_{sAn}-G_{sn}}{\Delta L}, 0\right) \tag{2.5.6}$$

and

$$R_n = \max\left(\frac{G_{sn}-G_{sAn}}{\Delta L}, 0\right) \tag{2.5.7}$$

where G_{sAn} is the actual load rate of the n-th sediment per unit width at a upstream location [M/L/T], G_{sn} is the maximum load rate of the n-th size fraction sediment per unit width at a downstream location [M/L/T], ΔL is the distance between the upstream and the downstream locations.

$$G_{sAn} = S_n V R \tag{2.5.8}$$

and

$$G_{sn} = 10\frac{\rho^2 VRS(\tau_b-\tau_{crn})}{g d_n(\rho_{sn}-\rho)^2} \tag{2.5.9}$$

where V is the river/stream flow velocity [L/T], R is hydraulic radius [L], ρ is the density of water [M/L^3], S is the friction slope, τ_{crn} is the critical bottom shear stress of the n-th sediment at which sediment movement begins [M/L/T^2], g is gravity [L/T^2], d_n is the median diameter of the n-th sediment particle [L], and ρ_{sn} is the density of the n-th sediment [M/L^3].

It should be noted that equations (2.5.2) through (2.5.9) are the sample models programmed in the computer code to estimate sediment deposition and erosion rate. Any other phenomenological model equation can be easily incorporated in the code.

2.5.2 Suspended Sediments

The continuity equation of suspended sediment can be derived based on the conservation law of material mass as (Yeh et al., 2005):

$$\frac{\partial (AS_n)}{\partial t} + \frac{\partial (QS_n)}{\partial x} - \frac{\partial}{\partial x}\left(AK_x \frac{\partial S_n}{\partial x} \right) = M_{S_n}{}^{as} + M_{S_n}{}^{os1} + M_{S_n}{}^{os2} + M_{S_n}{}^{is} + (R_n - D_n)P, \quad n \in [1, N_s] \tag{2.5.10}$$

where S_n is the cross-sectional-averaged concentration of the *n*-th suspended sediment in the unit of mass per unit column volume [M/L^3], K_x is the dispersion coefficient [L^2/T], $M_{S_n}{}^{as}$ is the artificial source of the *n*-th suspended sediment [M/L/T], $M_{S_n}{}^{is}$ is the source of the n-th suspended sediment from groundwater exfiltration [M/L/T], and $M_{S_n}{}^{os1}$ and $M_{S_n}{}^{os2}$ are overland sources of the *n*-th suspended sediment from river bank *1* and *2*, respectively [M/L/T].

Concentrations of all suspended sediments must be given initially for transient simulations. Four types of boundary conditions are taken into account for suspended sediments, including Dirichlet, Variable, Cauchy, and Neumann boundary conditions (Yeh et al., 2005).

Dirichlet boundary condition: Dirichlet boundary conditions are prescribed on the boundary where the suspended sediment concentration is known,

$$S_n = S_{dn}(x_b, t) \qquad \text{on} \qquad B_d(x_b) \tag{2.5.11}$$

where x_b is the axis coordinate of the boundary node [L], $S_{dn}(x_b, t)$ is a time-dependent Dirichlet concentration of the *n*-th fraction size on the boundary $B_d(x_b)$ [M/L^3].

Variable boundary condition: Variable boundary conditions are normally specified on the boundary where the flow direction can change with time or on any open boundary. On the variable boundary, when the flow is directed into the region of the interest, the mass rate into the region is given by the product of the flow rate and concentration of the incoming fluid. When the flow is directed out of the region, the sediment mass is assumed carried out via advection. Mathematically, a variable boundary condition is given as

$$n\left(QS_n - AK_x \frac{\partial S_n}{\partial x} \right) = nQS_{vn}(x_b, t) \;\; if \;\; nQ \le 0 \;\; on \;\; B_v(x_b) \tag{2.5.12}$$

and

$$-nAK_x \frac{\partial S_n}{\partial x} = 0 \;\; if \;\; nQ \ge 0 \;\; on \;\; B_v(x_b) \tag{2.5.13}$$

where *n* is a unit outward direction, and $S_{vn}(x_b,t)$ is a time-dependent concentration at the boundary that is associated with the incoming flow on the variable boundary $B_v(x_b)$ [M/L^3].

Cauchy boundary condition: This boundary condition is employed when the total material flow rate is given. Usually, this boundary is an upstream flux boundary.

$$n\left(QS_n - AK_x\frac{\partial S_n}{\partial x}\right) = Q_{S_n c}(x_b,t) \;\; on \;\; B_c(x_b) \qquad \textbf{(2.5.14)}$$

where $Q_{S_n c}(x_b,t)$ is a time-dependent material flow rate at the Cauchy boundary boundary [M/t] $B_c(x_b)$.

Neumann boundary condition: This boundary condition is used when the diffusive material flow rate is known at the boundary node.

$$-nAK_x\frac{\partial S_n}{\partial x} = Q_{S_n n}(x_b,t) \;\; on \;\; B_n(x_b) \qquad \textbf{(2.5.15)}$$

where $Q_{S_n n}(x_b,t)$ is a time-dependent diffusive material flow rate at the boundary $B_n(x_b)$ [M/t].

2.5.3 Immobile Bed-Sediment Species

The balance equation for immobile species is simply the statement that the rate of mass change is due to biogeochemical reaction as:

$$\frac{\partial(Ph_b\rho_{bw}\theta_b C_{bw})}{\partial t} = Ph_b r_{Cbw}\big|_N' \qquad \textbf{(2.5.16)}$$

$$\frac{\partial(Ph_b\rho_{bw}\theta_b C_{bp})}{\partial t} = Ph_b r_{Cbp}\big|_N' \qquad \textbf{(2.5.17)}$$

$$\frac{\partial(PM_n C_{bsn})}{\partial t} = Ph_b r_{Cbsn}\big|_N' \qquad \textbf{(2.5.18)}$$

where h_b is the river/stream bed depth [L], ρ_{bw} is the density of bed pore-water [M/L^3], θ_b is the porosity of the bed sediment [L^3/L^3], C_{bw} is the concentration of dissolved chemical in the immobile pore-water phase in the unit of chemical mass per bed-water mass [M/M], $r_{Cbw}\big|_N$' is the production rate of C_{bw} due to all N reactions in the unit of chemical mass per bed volume per time [M/L^3/t], C_{bp} is the concentration of bed precipitate in the unit of chemical mass per bed-water mass [M/M], $r_{Cbp}\big|_N$' is the production rate of C_{bp} due to all N reactions in the unit of chemical mass per bed volume per time [M/L^3/t], C_{bsn} is the concentration of particulate sorbed on to bed sediment of the *n*-th fraction size in the unit of chemical mass per unit of bed-sediment mass [M/M], M_n is the concentration of the *n*-th bed sediment in the unit of sediment mass per bed area [M/L^2], $r_{Cbsn}\big|_N$' is the production rate of C_{bsn} due to all N reactions in the unit of chemical mass per bed volume per time [M/L^3/t].

Define

$$r_i\big|_N = Ph_b r_i\big|_N \,'/A \quad where \quad i = C_{bw},\ C_{bp},\ or\ C_{bsn} \tag{2.5.19}$$

Equation (2.5.16) through (2.5.18) can be modified as

$$\frac{\partial(Ph_b\rho_{bw}\theta_b C_{bw})}{\partial t} = Ar_{Cbw}\big|_N \tag{2.5.20}$$

$$\frac{\partial(Ph_b\rho_{bw}\theta_b C_{bp})}{\partial t} = Ar_{Cbp}\big|_N \tag{2.5.21}$$

$$\frac{\partial(PM_n C_{bsn})}{\partial t} = Ar_{Cbsn}\big|_N \tag{2.5.22}$$

Define

$$\rho_i = \begin{cases} Ph_b\rho_{bw}\theta_b / A, for\ C_{bw}\ and\ C_{bp} \\ PM_n / A, for\ C_{bsn} \end{cases} \tag{2.5.23}$$

Equation (2.5.20) through (2.5.22) can be summarized as

$$\frac{\partial(A\rho_i C_i)}{\partial t} = Ar_i\big|_N, \quad i \in M_{im} \tag{2.5.24}$$

where C_i is the concentration of species i, which is immobile, in the unit of chemical mass per unit phase mass [M/M], ρ_i is the density of the phase associated with species i [M/L^3], $r_i\big|_N$ is the production rate of species i due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], and M_{im} is the number of immobile species. The concentrations of all immobile species must be given initially for transient simulations. No boundary conditions are needed for immobile species.

2.5.4 Mobile Column-Water Species

The continuity equation of mobile species can be derived based on the conservation law of material mass stating that the rate of mass change is due to both advective-dispersive transport and biogeochemical reactions as:

$$\frac{\partial(A\rho_w C_w)}{\partial t} + L(\rho_w C_w) = Ar_{Cw}\big|_N \tag{2.5.25}$$

$$\frac{\partial(A\rho_w C_p)}{\partial t} + L(\rho_w C_p) = Ar_{Cp}\big|_N \tag{2.5.26}$$

$$\frac{\partial(AS_n C_{sn})}{\partial t} + L(S_n C_{sn}) = Ar_{Csn}\big|_N \tag{2.5.27}$$

where ρ_w is the density of column water [M/L^3], C_w is the concentration of dissolved chemical in the mobile water phase in the unit of chemical mass per column-water mass [M/M], $r_{Cw}\big|_N$ is the production rate of C_w due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], C_p is the concentration of suspension precipitate in the unit of chemical mass per column-water mass [M/M], $r_{Cp}\big|_N$ is the production rate of C_p due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], C_{sn} is the concentration of particulate sorbed on to suspended sediment of the n-th fraction size in the unit of chemical mass per unit of sediment mass [M/M], S_n is the concentration of suspended sediment in the unit of sediment mass per column volume [M/L^3], $r_{Csn}\big|_N$ is the production rate of C_{sn} due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], and L is an operator that will be defined in Eq. (2.5.30) later.

Define

$$\rho_i = \begin{cases} \rho_w \quad for \quad C_w \ and \ C_p \\ S_n \quad for \quad C_{sn} \end{cases} \tag{2.5.28}$$

Equation (2.5.25) through (2.5.27) can be summarized as

$$\frac{\partial(A\rho_i C_i)}{\partial t} + L(\rho_i C_i) = Ar_i\big|_N, \quad i \in M_m = M - M_{im} \tag{2.5.29}$$

where C_i is the concentration of species i, which is mobile, in the unit of chemical mass per unit phase mass [M/M], ρ_i is the density of the phase associated with species i [M/L^3], $r_i\big|_N$ is the production rate of species i due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], M is the total number of chemical species, M_m is the number of mobile chemical species, and operator L is defined as

$$L(\rho_i C_i) = \frac{\partial(Q\rho_i C_i)}{\partial x} - \frac{\partial}{\partial x}\left[AK_x \frac{\partial(\rho_i C_i)}{\partial x}\right] - (M_{C_i}^{as} + M_{C_i}^{rs} - M_{C_i}^{es} + M_{C_i}^{os1} + M_{C_i}^{os2} + M_{C_i}^{is}) \tag{2.5.30}$$

where $M_{C_i}^{as}$ is the artificial source of species i [M/L/T], $M_{C_i}^{rs}$ is the rainfall source of species i [M/L/T], $M_{C_i}^{rs}$ is the sink of species i due to evaporation, $M_{C_i}^{os1}$ and $M_{C_i}^{os2}$ are the overland sources of species i from river bank *1* and *2*, respectively [M/L/T], and $M_{C_i}^{is}$ is the mass rate of the source of species i in river/stream from subsurface [M/L/T].

Concentrations of all mobile species must be given initially for transient simulations. Four types of boundary conditions are taken into account for mobile species, including Dirichlet, Variable, Cauchy, and Neumann boundary conditions (Yeh et al., 2005), which are similar to those for suspended sediment transport and are presented below:

Dirichlet boundary condition: On a Dirichlet boundary, the concentrations of all mobile species are prescribed

$$C_i = C_{idb}(x_b, t) \qquad i \in M_m \qquad on \qquad B_d(x) = 0 \tag{2.5.31}$$

where $C_{idb}(x_b,t)$ is the prescribed concentration of the *i*-th mobile species on the Dirichlet boundary $B_d(x)=0$ [M/M].

Variable boundary condition: On a variable boundary, the concentrations of all mobile species are known and they contribute to the increase of chemical masses in the region of interest when the flow is coming into the region. When the flow is going out of the region, the transport of all mobile species out of the region is assumed due to advection only, which implies that one must put an outgoing boundary far away from the source.

< Case 1 > Flow is coming in from outside (nQ < 0)

$$n\left(Q\rho_i C_i - AK_x\frac{\partial\rho_i C_i}{\partial x}\right)=(nQ)\rho_i C_{ivb}(x_b,t) \qquad i\in M_m \qquad on \qquad B_v(x)=0 \tag{2.5.32}$$

< Case 2 > Flow is going out from inside (nQ > 0).

$$-nAK_x\frac{\partial\rho_i C_i}{\partial x}=0 \qquad i\in M_m \qquad on \qquad B_v(x)=0 \tag{2.5.33}$$

where *n* is the unit outward direction and $C_{ivb}(x_b,t)$ is the concentration of the *i*-th species in the incoming fluid on the variable boundary $B_v(x)=0$ [M/M].

Cauchy boundary condition: On a Cauchy boundary chemical flux for any mobile species is prescribed

$$n\left(Q\rho_i C_i - AK_x\frac{\partial\rho_i C_i}{\partial x}\right)=Q_{C_i cb}(x_b,t) \qquad i\in M_m \qquad on \qquad B_c(x)=0 \tag{2.5.34}$$

where $Q_{C_i cb}(x_b,t)$ is the mass flux of C_i through the Cauchy boundary $B_c(x)=0$ [M/t].

Neumann boundary condition: On a Neumann boundary, chemical flux of any mobile species due to dispersion is prescribed

$$-nAK_x\frac{\partial\rho_i C_i}{\partial x}=Q_{C_i nb}(x_b,t) \qquad i\in M_m \qquad on \qquad B_n(x)=0 \tag{2.5.35}$$

where $Q_{C_i nb}(x_b,t)$ is the mass flux of C_i through the Neumann boundary $B_n(x)=0$ [M/t].

2.5.5 Diagonalization of Species Transport Equations

The temporal-spatial distribution of chemical species is described by a system of M_{im} mass balance equations [equation (2.5.24)], and M_m reactive transport equations [equation (2.5.29)]. These two equations can be recast in the following form

$$\frac{\partial(A\rho_i C_i)}{\partial t} + \alpha_i L(\rho_i C_i) = A r_i\big|_N, \quad i \in M \tag{2.5.36}$$

where M is the total number of chemical species, α_i is 0 for immobile species and 1 for mobile species.

The determination of $r_i\big|_N$ and associated parameters is a primary challenge in biogeochemical modeling. Instead of using an ad hoc method to formulate $r_i\big|_N$, we use reaction-based formulations (Steefel and Cappellen, 1998). In a reaction-based formulation, $r_i\big|_N$ is given by the summation of rates of all reactions that the i-th species participates in,

$$r_i\big|_N = \frac{d(\rho_i C_i)}{dt}\Big|_{reaction} = \sum_{k=1}^{N}\left[(\nu_{ik} - \mu_{ik})r_k\right], \quad i \in M \tag{2.5.37}$$

where ν_{ik} is the reaction stoichiometry of the i-th species in the k-th reaction associated with the products, μ_{ik} is the reaction stoichiometry of the i-th species in the k-th reaction associated with the reactants, and r_k is the rate of the k-th reaction.

Substituting equation (2.5.37) into equation (2.5.36) results in the transport equations of M chemical species described by

$$\frac{\partial(A\rho_i C_i)}{\partial t} + \alpha_i L(\rho_i C_i) = A\sum_{k=1}^{N}\left[(\nu_{ik} - \mu_{ik})r_k\right], \quad i \in M; \quad or \quad \mathbf{U}\frac{\partial \mathbf{C_A}}{\partial t} + \boldsymbol{\alpha} L(\mathbf{C}) = A\boldsymbol{\nu}\mathbf{r} \tag{2.5.38}$$

where $\mathbf{U}$ is a unit matrix, $\mathbf{C_A}$ is a vector with its components representing M species concentrations multiply the cross section area of the river [M/L], $\boldsymbol{\alpha}$ is a diagonal matrix with α_i as its diagonal component, $\mathbf{C}$ is a vector with its components representing M species concentrations [M/L^3], $\boldsymbol{\nu}$ is the reaction stoichiometry matrix, and $\mathbf{r}$ is the reaction rate vector with N reaction rates as its components. Equation (2.5.38) represents a mass balance for species i, which states that the rate of change of any species mass is due to advection-dispersion coupled with contributing reactions that describe the biogeochemical processes.

In a primitive approach, equation (2.5.38) is integrated to yield the distributions and evolutions of chemical species in a region of interest. However, when some fast equilibrium reactions take place in the system, this approach is not adequate (Fang et al., 2003). Here, we will take a diagonalization approach through decomposition. Equation (2.5.38) written in matrix form can be decomposed based on the type of biogeochemical reactions via Gauss-Jordan column reduction of reaction matrix $\boldsymbol{\nu}$. Among all the fast/equilibrium and slow/kinetic reactions, "redundant reactions" are defined as fast reactions that are linearly dependent on other fast reactions, and "irrelevant reactions" are kinetic reactions that are linearly dependent on only equilibrium reactions. In order to avoid singularity of the reaction matrix, redundant fast reactions are omitted from the system prior to decomposition. The removal of irrelevant slow reactions alleviates problems associated with rate formulation uncertainty and parameterization for these reactions.

Decomposition is performed by pivoting on the N_E equilibrium reactions and decoupling them from the N_K kinetic reactions. In other words, each fast reaction can be used to eliminate one chemical

species from simultaneous consideration. An incomplete Gauss-Jordan row decomposition of the reaction matrix $\boldsymbol{\nu}$ by pivoting on N_E equilibrium reactions will result in N_E equilibrium-variables and N_{KIV} kinetic-variables. To analyze the system behavior, it is advantageous to perform a complete decomposition, in which the reduction of the reaction matrix is done by pivoting on N_E equilibrium reactions and on N_{KI} linearly independent kinetic reactions to result in N_E equilibrium-variables, N_{KI} kinetic-variables, and N_C components. The complete decomposition is given as follows:

$$\begin{bmatrix} \mathbf{A}_{11} & \mathbf{0}_{12} & \mathbf{0}_{13} \\ \mathbf{A}_{21} & \mathbf{A}_{22} & \mathbf{0}_{23} \\ \mathbf{A}_{31} & \mathbf{A}_{32} & \mathbf{U}_{33} \end{bmatrix} \begin{Bmatrix} \dfrac{\partial \mathbf{C}_{A1}}{dt} \\ \dfrac{\partial \mathbf{C}_{A2}}{dt} \\ \dfrac{\partial \mathbf{C}_{A3}}{dt} \end{Bmatrix} + \begin{bmatrix} \mathbf{B}_{11} & \mathbf{0}_{12} & \mathbf{0}_{13} \\ \mathbf{B}_{21} & \mathbf{B}_{22} & \mathbf{0}_{23} \\ \mathbf{B}_{31} & \mathbf{B}_{32} & \boldsymbol{\alpha}_{33} \end{bmatrix} \mathrm{L}\left(\begin{Bmatrix} \mathbf{C}_1 \\ \mathbf{C}_2 \\ \mathbf{C}_3 \end{Bmatrix} \right) = \mathrm{A} \begin{bmatrix} \mathbf{D}_{11} & \mathbf{K}_{12} & \mathbf{K}_{13} \\ \mathbf{0}_{21} & \mathbf{D}_{22} & \mathbf{K}_{23} \\ \mathbf{0}_{31} & \mathbf{0}_{32} & \mathbf{0}_{33} \end{bmatrix} \begin{Bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{r}_3 \end{Bmatrix} \quad \textbf{(2.5.39)}$$

where $\mathbf{A_{11}}$ is the submatrix of the reduced **U** matrix with size of $N_E \times N_E$, $\mathbf{A_{21}}$ is the submatrix of the reduced **U** matrix with size of $N_{KI} \times N_E$, and $\mathbf{A_{31}}$ is the submatrix of the reduced **U** matrix with size of $N_C \times N_E$; $\mathbf{0_{12}}$ is the zero submatrix of the reduced **U** matrix with size of $N_E \times N_{KI}$, $\mathbf{A_{22}}$ is the submatrix of the reduced **U** matrix with size of $N_{KI} \times N_{KI}$, and $\mathbf{A_{32}}$ is the submatrix of the reduced **U** matrix with size of $N_C \times N_{KI}$; $\mathbf{0_{13}}$ is the zero submatrix of the reduced **U** matrix with size of $N_E \times N_C$, $\mathbf{0_{23}}$ is the submatrix of the reduced **U** matrix with size of $N_{KI} \times N_C$, and $\mathbf{U_{33}}$ is the unit submatrix of the reduced **U** matrix with size of $N_C \times N_C$; $\mathbf{C_{A1}}$, $\mathbf{C_{A2}}$, and $\mathbf{C_{A3}}$ are the subvectors of the vector $\mathbf{C_A}$ with sizes of N_E, N_{KI}, and N_C, respectively; $\mathbf{B_{11}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_E$, $\mathbf{B_{21}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_{KI} \times N_E$, and $\mathbf{B_{31}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_C \times N_E$; $\mathbf{0_{12}}$ is the zero submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_{KI}$, $\mathbf{A_{22}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_{KI} \times N_{KI}$, and $\mathbf{B_{32}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_C \times N_{KI}$; $\mathbf{0_{13}}$ is the zero submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_C$, $\mathbf{0_{23}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_{KI} \times N_C$, and $\boldsymbol{\alpha_{33}}$ is the diagonal submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_C \times N_C$; $\mathbf{C_1}$, $\mathbf{C_2}$, and $\mathbf{C_3}$ are the subvectors of the vector **C** with sizes of N_E, N_{KI}, and N_C, respectively; $\mathbf{D_{11}}$ is the diagonal submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_E$, $\mathbf{K_{12}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_{KI}$, and $\mathbf{K_{13}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_{KD(k)}$; $\mathbf{0_{21}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KI} \times N_E$, $\mathbf{D_{22}}$ is the diagonal submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KI} \times N_{KI}$, and $\mathbf{K_{23}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KI} \times N_{KD(k)}$; $\mathbf{0_{13}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_C \times N_E$, $\mathbf{0_{32}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_C \times N_{KI}$, and $\mathbf{0_{33}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_C \times N_{KD(k)}$; $\mathbf{r_1}$, $\mathbf{r_2}$, and $\mathbf{r_3}$ are the subvectors of the vector **r** with sizes of N_E, N_{KI}, and $N_{KD(k)}$, respectively.

For incomplete decomposition of the reaction matrix $\boldsymbol{\nu}$, Equation (2.5.39) can be connoted as

$$\begin{bmatrix} \mathbf{A}_{11} & \mathbf{0}_{12} \\ \mathbf{A}_{21} & \mathrm{U}_{22} \end{bmatrix} \begin{Bmatrix} \dfrac{\partial \mathbf{C}_{A1}}{dt} \\ \dfrac{\partial \mathbf{C}_{A2}}{dt} \end{Bmatrix} + \begin{bmatrix} \mathbf{B}_{11} & \mathbf{0}_{12} \\ \mathbf{B}_{21} & \boldsymbol{\alpha}_{22} \end{bmatrix} \mathrm{L}\left(\begin{Bmatrix} \mathbf{C}_1 \\ \mathbf{C}_2 \end{Bmatrix} \right) = \mathrm{A} \begin{bmatrix} \mathbf{D}_{11} & \mathbf{K}_{12} \\ \mathbf{0}_{21} & \mathbf{K}_{22} \end{bmatrix} \begin{Bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \end{Bmatrix} \quad \textbf{(2.5.40)}$$

where $\mathbf{A_{11}}$ and $\mathbf{A_{21}}$ are the submatrices of the reduced **U** matrix with size of $N_E \times N_E$ and $N_{KIV} \times N_E$, respectively (note that $N_{KIV} = M - N_E = N_{KI} + N_C$); $\mathbf{0_{12}}$ and $\mathbf{U_{22}}$ are the zero- and unit-submatrices, respectively, of the reduced **U** matrix with size of $N_E \times N_{KIV}$ and $N_{KIV} \times N_{KIV}$, respectively; $\mathbf{C_{A1}}$ and $\mathbf{C_{A2}}$ are the subvectors of the vector $\mathbf{C_A}$ with sizes of N_E and N_{KIV}, respectively; $\mathbf{B_{11}}$ and $\mathbf{B_{21}}$ are the submatrices of the reduced $\boldsymbol{\alpha}$ matrix with sizes of $N_E \times N_E$ and $N_{KIV} \times N_E$, respectively; $\mathbf{0_{12}}$ and $\boldsymbol{\alpha}_{\mathbf{22}}$ are the zero- and unit- submatrices, respectively, of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_{KIV}$ and $N_{KIV} \times N_{KIV}$, respectively; $\mathbf{C_1}$ and $\mathbf{C_2}$ are the subvectors of the vector **C** with sizes of N_E and N_{KIV}, respectively; $\mathbf{D_{11}}$ is the diagonal submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_E$ and $\mathbf{K_{12}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_{KIV}$; $\mathbf{0_{21}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KIV} \times N_E$ and $\mathbf{K_{22}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KIV} \times N_E$; $\mathbf{r_1}$ and $\mathbf{r_2}$ are the subvectors of the vector **r** with sizes of N_E and N_{KIV}, respectively.

For reactions that are fast, equilibrium may be regarded as being reached instantaneously among the relevant species and the reaction rates may be regarded as infinite. An infinite rate is mathematically represented by a mass action equation or a user specified nonlinear algebraic equation. As a result, the decomposition of equation (2.5.38) to equation (2.5.40) effectively reduces a set of M species reactive transport equations into two subsets of equations. The first set contains N_E algebraic equations representing mass action laws for the equilibrium reactions, and the second set contains N_{KIV} kinetic-variable transport equations. These equation subsets are defined as

Algebraic Equations for Equilibrium Reactions

$$\frac{\partial(AE_i)}{\partial t} + L(E_i^m) = AD_{1ii}r_{1i} + A\sum_{j=1}^{N_K} K_{1ij}r_{2j},\ i \in N_E \quad \Rightarrow \quad r_{1i} = \infty \quad \Rightarrow \quad \frac{\partial(AE_i)}{\partial t} \approx \infty$$

which is replaced with a thermodynamically consistent equation: $K_i^e = \prod_{j\in M} A_j^{\nu_{ji}} \Big/ \prod_{j\in M} A_j^{\mu_{ji}}$ **(2.5.41)**

$$or\ \ F_i(C_1,..,C_M;p_1,p_2,..) = 0 \quad where\ E_i = \sum_{j=1}^{N_E} A_{1ij}C_{1j}\ \ and\ \ E_i^m = \sum_{j=1}^{N_E} B_{1ij}C_{1j}$$

where K_i^e is the equilibrium constant of the i-th fast reaction, A_j is the activity of the j-th species, $F_i(C_1,..,C_M; p_1,p_2,..)$ is an empirical function of all species and a number of parameters $p_1, p_2, \ldots$ for the i-th fast reaction. E_i was called an equilibrium-variable (Fang, et al., 2003) because $\frac{\partial(AE_i)}{\partial t} \approx \infty$ simply means that E_i can reach equilibrium instantaneously.

Transport Equations for Kinetic-Variables

$$\frac{\partial(AE_i)}{\partial t} + L(E_i^m) = A\sum_{j=1}^{N_K} K_{2nj}r_{2j},\ \ i \in N_{KIV} = M - N_E$$
$$where\ E_i = \sum_{j=1}^{N_E} A_{2ij}C_{1j} + C_{2i}\ and\ E_i^m = \sum_{j=1}^{N_E} B_{2ij}C_{1j} + \alpha_{1i}C_{2i} \qquad \textbf{(2.5.42)}$$

where E_i was called kinetic variable (Fang, et al., 2003) because as E_i is transported it is subject to only kinetic reactions. This is in contrast to Eq. (2.5.38) where as C_i is transported, it is subject to

both equilibrium and kinetic reactions.

Assign

$$R_i = \sum_{j=1}^{N_K} K_{2ij} r_{2j},\ \mathrm{i} \in N_{KIV} \qquad \textbf{(2.5.43)}$$

The reduction of Eq. (2.5.38) to Eq. (2.5.41) and (2.5.42) is equivalent to reducing M governing equations for immobile and mobile species to the mixed N_E algebraic equations for equilibrium variables and N_{KIV} transport equations for kinetic-variables specified as follows

$$\begin{aligned} &\frac{\partial (AE_i)}{\partial t} + \frac{\partial (QE_i^{\,m})}{\partial x} - \frac{\partial}{\partial x}\left(AK_x \frac{\partial E_i^{\,m}}{\partial x} \right) = M_{E_i}^{\ as} + M_{E_i}^{\ rs} - M_{E_i}^{\ es} \\ &+ M_{E_i}^{\ os1} + M_{E_i}^{\ os2} + M_{E_i}^{\ is} + AR_i,\ i \in N_{KIV} \end{aligned} \qquad \textbf{(2.5.44)}$$

where E_i is the concentration of the i-th kinetic-variable [M/L^3], E_i^m is the concentration of mobile part of the i-th kinetic-variable [M/L^3], $M_{E_i}^{\ as}$ is the artificial source of the i-th kinetic-variable [M/L/T], $M_{E_i}^{\ rs}$ is the rainfall source of the i-th kinetic-variable [M/L/T], $M_{E_i}^{\ es}$ is the evaporation sink of the i-th kinetic variable [M/L/T], $M_{E_i}^{\ os1}$ and $M_{E_i}^{\ os2}$ are overland sources of the i-th kinetic-variable from river banks *1* and *2*, respectively [M/L/T], $M_{E_i}^{\ is}$ is the mass rate of the source of the i-th kinetic-variable in river/stream from subsurface [M/L/T], R_i is the production rate of i-th kinetic-variable due to biogeochemical reactions [M/L^3/T], and N_{KIV} is the number of kinetic variable variables.

Boundary conditions for mobile species need to be transformed into corresponding boundary conditions for kinetic-variables, which are stated in the following.

Dirichlet boundary condition:

$$E_i^{\ m} = E_{i\ db}^{m}(x_b, t) \qquad i \in M_m \qquad on \qquad B_d(x) = 0 \qquad \textbf{(2.5.45)}$$

where $E_{i\ db}^{m}(x_b, t)$ is the specified concentration of the mobile portion of the i-th kinetic variable on the Dirichlet boundary $B_d(x) = 0$ [M/L3].

Variable boundary condition:

< Case 1 > Flow is coming in from outside (nQ < 0)

$$n\left(QE_i^m - AK_x \frac{\partial E_i^m}{\partial x} \right) = nQE_{i\ vb}^{m}(x_b, t) \qquad i \in M_m \qquad on \qquad B_v(x) = 0 \qquad \textbf{(2.5.46)}$$

< Case 2 > Flow is going out from inside (nQ > 0).

$$-nAK_x \frac{\partial E_i^m}{\partial x} = 0 \qquad i \in M_m \qquad on \qquad B_v(x) = 0 \tag{2.5.47}$$

where n is the unit outward direction and $E_{i\ vb}^{m}(x_b,t)$ is the concentration of the mobile portion of the i-th kinetic variable on the variable boundary $B_v(x) = 0$ [M/L^3].

Cauchy boundary condition:

$$n\left(QE_i^m - AK_x \frac{\partial E_i^m}{\partial x}\right) = Q_{E_i^m cb}(x_b,t) \qquad i \in M_m \qquad on \qquad B_c(x) = 0 \tag{2.5.48}$$

where $Q_{E_i^m cb}(x_b,t)$ is the mass flux of E_i^m through the Cauchy boundary $B_c(x) = 0$ [M/t].

Neumann boundary condition:

$$-nAK_x \frac{\partial E_i^m}{\partial x} = Q_{E_i^m{}_{nb}}(x_b,t) \qquad i \in M_m \qquad on \qquad B_n(x) = 0 \tag{2.5.49}$$

where $Q_{E_i^m nb}(x_b,t)$ is the mass flux of E_i^m through the Neumann boundary $B_n(x) = 0$ [M/t].

2.6 Sediment and Water Quality Transport in Two-Dimension Overland Regime

Researches on overland water quality modeling include studies of sediment (McDonald and Cheng, 1994; Harris and Wiberg, 2001; and Zeng and Beck, 2003) and water quality transport (Falconer and Lin, 1997; Tufford and McKellar, 1999; Shen et al., 2002; and Zheng et al., 2004) as well as thermal and salinity transport. Most of the existing overland water quality models simulate either specific systems (Cerco and Cole, 1995; Shen et al., 2002; and Zheng et al., 2004) or systems containing specific reactions (Brown and Barnwell, 1987; Ambrose et al, 1993; and Bonnet and Wessen, 2001). They may provide efficient monitoring and management tools because they are calibrated for specific environments, but the extension of a calibrated model to other environmental conditions needs to be carefully evaluated. With better understanding and mathematical formulation of complex biogeochemical interactions (Thomann, 1998; Somlyody et al., 1998; and Yeh et al., 2001a), models considering interactions among biogeochemicals based on reaction mechanism have a better potential for application to other systems (Steefel and Cappellen, 1998). Although a few reaction-based models can handle contaminant transport subject to kinetically controlled chemical reactions (Cheng et al., 2000; and Yeh et al., 2005), no existing overland water quality model, to our knowledge, has the design capability that permitts the use of a fully mechanistic approach to estimate both kinetically and equilibrium controlled reactive chemical transport in overland water systems.

This section presents a general two-dimensional depth-averaged numerical model simulating the water quality in overland shallow water systems using a general paradigm of diagonalized reaction-

based approaches. In our model, sediments are categorized based on their physical and chemical properties. For each category of sediment, we include mobile suspended sediment particles scattered in water column and immobile bed sediment particles accumulated in water bed. The distribution of suspended sediment and bed sediment is controlled through hydrological transport as well as erosion and deposition processes. There are six phases and three forms for biogeochemical species. As shown in Figure 2.6-1, the six phases are suspended sediment, bed sediment, mobile water, immobile water, suspension precipitate, and bed precipitate phases; and the three forms are dissolved chemicals, particulate chemicals sorbed onto sediments, and precipitates.

In the transport simulation, biogeochemical reactions can be divided into two classes (Rubin, 1983): (1) equilibrium-controlled "fast" reactions, and (2) kinetically-controlled "slow" reactions. The former are sufficiently fast compared to the transport time-scale and are reversible, so that local equilibrium may be assumed. The latter are not sufficiently fast compared to the transport time-scale. As shown in Figure 2.6-2, biogeochemical reactions taken into account in the model include aqueous complexation, adsorption/desorption, ion-exchange, precipitation/dissolution, volatilization, diffusion, and sedimentation, etc. Any individual reaction representing any of these chemical and physical processes may be simulated as kinetic or as equilibrium, which makes the code extremely flexible for application to a wide range of biogeochemical transport problems.

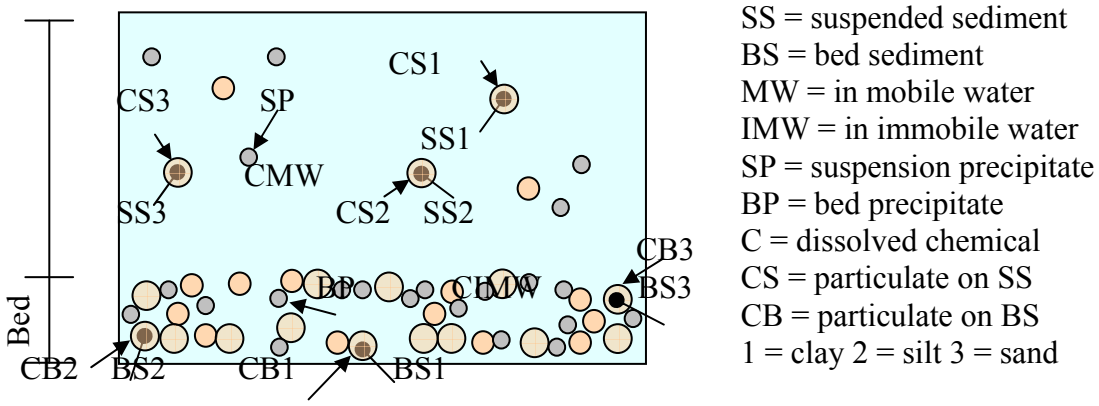


Fig. 2.6-1. Sediments and Chemicals in River/Stream Networks

2.6.1 Bed Sediment

The balance equation for bed sediments is simply the statement that the rate of mass change is due to erosion/deposition as (Yeh, et al., 2005)

$$\frac{\partial(M_n)}{\partial t} = (D_n - R_n) + M^{is}_{M_n}, \quad n \in [1, N_s] \qquad \textbf{(2.6.1)}$$

where M_n is the concentration of the n-th bed sediment in mass per unit bed area [M/L^2], D_n is the deposition rate of the n-th sediment in mass per unit bed area per unit time [M/L^2/T], R_n is the erosion rate of the n-th sediment in mass per unit bed area per unit time [M/L^2/T], $M^{is}_{M_n}$ is the source of the n-th sediment from groundwater exfiltration in mass per unit area [M/L^2/T], and N_S is the total number of sediment size fractions. Concentrations of all bed sediments must be given initially for

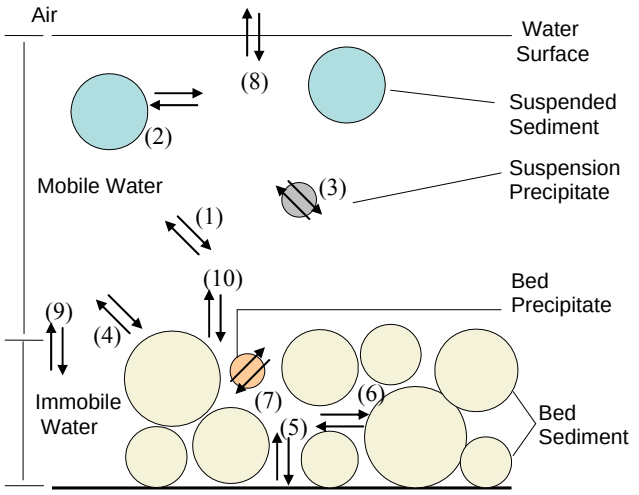
transient simulations. No boundary condition is needed for bed sediments. In equation (2.6.1), we estimate the deposition and erosion rates using the different equations for cohesive and non-cohesive sediments.

For cohesive sediments, e.g., silt and clay, following equations are used (Yeh et al., 1998; Gerritsen et al., 2000)

$$D_n = \min\left(V_{sn} S_n P_{Dn},\ S_n h/\Delta t\right) \qquad \text{where} \qquad P_{Dn} = \max\left(0,\ 1-\tau_b/\tau_{cDn}\right) \qquad \textbf{(2.6.2)}$$

and

$$R_n = \min\left(E_{0n} P_{Rn},\ DMA_n/\Delta t\right) \qquad \text{where} \qquad P_{Rn} = \max\left(0,\ \tau_b/\tau_{cRn}-1\right) \qquad \textbf{(2.6.3)}$$



(1) Aqueous complexation in mobile water phase,
(2) Adsorption/desorption or ion-exchange between mobile water and suspended sediment phases,
(3) Precipitation/dissolution between mobile water and suspension precipitate phases,
(4) Adsorption/desorption or ion-exchange between mobile water and bed sediment phases,
(5) Aqueous complexation in immobile water phase,
(6) Adsorption/desorption or ion-exchange between immobile water and bed sediment phases,
(7) Precipitation/dissolution between immobile water and bed precipitate phases,
(8) Volatilization from mobile water phase,
(9) Diffusion between mobile and immobile water phases,
(10) Sedimentation of particulates between suspended and bed sediment phases

Fig. 2.6-2. Biogeochemical Reactions Considered in the Model

where V_{sn} is the settling velocity of the n-th sediment [L/T], S_n is the depth-averaged suspended concentration of n-th sediment [M/L^3], h is the water depth [L], Δt is the simulation time step size [T], τ_b is the bottom shear stress or the bottom friction stress [M/L/T^2], τ_{cDn} is the critical shear stress for the deposition of the n-th sediment [M/L/T^2], E_{0n} is the erodibility of the n-th sediment [M/L^2/T], DMA_n is the amount of locally available dry matter of n-th sediment, expressed as dry weight per unit area [M/L^2], τ_{cRn} is the critical shear stress for the erosion of the n-th sediment [M/L/T^2].

For Non-cohesive sediments, e.g., sand, we have two options.

Option 1 (Prandle et al., 2000)

$$D_n = \min\left(V_{sn} S_n N_{Dn},\ S_n h/\Delta t\right) \qquad \text{where} \qquad N_{Dn} = \max\left[0,\ 1-\left(V_{cDn}/V_{cRn}\right)^2\right] \qquad \textbf{(2.6.4)}$$

and

$$R_n = \min\left(E_{0n} N_{Rn},\ DMA_n/\Delta t\right) \qquad \text{where} \qquad N_{Rn} = \max\left(0,\ V_{cDn}/V_{cRn}-1\right) \qquad \textbf{(2.6.5)}$$

where V_{cDn} and V_{cRn} represent the critical friction velocities for the onset of deposition and erosion, respectively [L/T].

Option 2 (Yeh et al., 1998)

$$D_n = \max\left(\frac{G_{sAn} - G_{sn}}{\Delta L}, 0\right) \tag{2.6.6}$$

and

$$R_n = \max\left(\frac{G_{sn} - G_{sAn}}{\Delta L}, 0\right) \tag{2.6.7}$$

where G_{sAn} is the actual load rate of the n-th sediment per unit width at a upstream location [M/L/T], G_{sn} is the maximum load rate of the n-th size fraction sediment per unit width at a downstream location [M/L/T], ΔL is the distance between the upstream and the downstream locations.

$$G_{sAn} = S_n VR \tag{2.6.8}$$

and

$$G_{sn} = 10\frac{\rho^2 VRS(\tau_b - \tau_{crn})}{g d_n (\rho_{sn} - \rho)^2} \tag{2.6.9}$$

where V is the overland flow velocity [L/t], R is hydraulic radius [L], ρ is the density of water [M/L^3], S is the friction slope, τ_{crn} is the critical bottom shear stress of the n-th sediment at which sediment movement begins [M/L/t^2], g is gravity [L/t^2], d_n is the median diameter of the n-th sediment particle [L], and ρ_{sn} is the density of the n-th sediment [M/L^3].

It should be noted that equations (2.6.2) through (2.6.9) are the sample models programmed in the computer code to estimate sediment deposition and erosion rate. Any other phenomenological model equation can be easily incorporated in the code.

2.6.2 Suspended Sediments

The continuity equation of suspended sediment can be derived based on the conservation law of material mass as (Yeh et al., 2005):

$$\frac{\partial(hS_n)}{\partial t} + \nabla\bullet(\mathbf{q}S_n) - \nabla\bullet(h\mathbf{K}\nabla S_n) = M_{S_n^{as}} + M_{S_n^{rs}} + M_{S_n^{is}} + R_n - D_n, \quad n \in [1, N_s] \tag{2.6.10}$$

where S_n is the depth-averaged concentration of the n-th suspended sediment in the unit of mass per unit column volume [M/L^3], $\mathbf{K}$ is the dispersion coefficient tensor [L^2/t], and $M_{S_n^{as}}$, $M_{S_n^{rs}}$, and $M_{S_n^{is}}$ are the mass rate of artificial source, rainfall source, and groundwater source of the n-th suspended sediment [M/L^2/t].

Concentrations of all suspended sediments must be given initially for transient simulations. Five types of boundary conditions are taken into account for suspended sediments, including Dirichlet, Variable, Cauchy, Neumann, and river/stream-overland interface boundary conditions (Yeh et al., 2005).

Dirichlet boundary condition: Dirichlet boundary conditions are prescribed on the boundary where

the suspended sediment concentration is known,

$$S_n = S_{ndb}(x_b, y_b, t) \quad on \quad B_d(\mathbf{x}) = 0 \tag{2.6.11}$$

where x_b and y_b are the coordinates of the boundary node [L], and $S_{ndb}(x_b, y_b, t)$ is a time-dependent concentration of the *n*-th sediment size on the Dirichlet boundary $B_d(\mathbf{x}) = 0$ [M/L^3].

Variable boundary condition: Variable boundary conditions are normally specified on the boundary where the flow direction can change with time or on any open boundary. On the variable boundary, when the flow is directed into the region of the interest, the mass rate into the region is given by the product of the flow rate and concentration of the incoming fluid. When the flow is directed out of the region, the sediment mass is assumed carried out via advection. Mathematically, a variable boundary condition is given as

$$\mathbf{n}\bullet\left(\mathbf{q}S_n - h\mathbf{K}\bullet\nabla S_n\right) = \mathbf{n}\bullet\mathbf{q}S_{nvb}(x_b, y_b, t) \quad if \quad \mathbf{n}\bullet\mathbf{q} \le 0 \quad on \quad B_v(\mathbf{x}) = 0 \tag{2.6.12}$$

and

$$-\mathbf{n}\bullet\left(h\mathbf{K}\bullet\nabla S_n\right) = 0 \quad if \quad \mathbf{n}\bullet\mathbf{q} \ge 0 \quad on \quad B_v(\mathbf{x}) = 0 \tag{2.6.13}$$

where **n** is a unit outward direction and $S_{nvb}(x_b, y_b, t)$ is a time-dependent concentration of the *n*-th sediment in the incoming fluid at the boundary [M/L^3] $B_v(\mathbf{x}) = 0$.

Cauchy boundary condition: This boundary condition is employed when the total material flow rate is given. Usually, this boundary is an upstream flux boundary.

$$\mathbf{n}\bullet\left(\mathbf{q}S_n - h\mathbf{K}\bullet\nabla S_n\right) = Q_{S_n cb}(x_b, y_b, t) \quad on \quad B_c(\mathbf{x}) = 0 \tag{2.6.14}$$

where $Q_{S_n cb}(x_b, y_b, t)$ is a time-dependent material flow rate of the *n*-th sediment through the Cauchy boundary $B_c(\mathbf{x}) = 0$ [M/t/L].

Neumann boundary condition: This boundary condition is used when the diffusive material flow rate is known at the boundary node.

$$-\mathbf{n}\bullet h\mathbf{K}\bullet\nabla S_n = Q_{S_n nb}(x_b, y_b, t) \quad on \quad B_{nb}(\mathbf{x}) = 0 \tag{2.6.15}$$

where $Q_{S_n nb}(x_b, y_b, t)$ is a time-dependent diffusive material flow rate of the *n*-th sediment trough the Neumann boundary $B_{nb}(\mathbf{x}) = 0$ [M/t/L].

Overland-River/Stream interface boundary condition: The boundary condition is needed when one-dimensional sediment transport in river/stream networks is coupled with two-dimensional sediment transport in overland regime. We assume that the exchange of sediment mass between river/stream and overland flows is mainly due to advection. Under such circumstances, the interfacial boundary condition is stated as

$$\mathbf{n}\cdot\left(\mathbf{q}S_n - h\mathbf{K}\cdot\nabla S_n\right) = \left(\mathbf{n}\cdot\mathbf{q}\right)\frac{1}{2}\left\{\left[1 + sign\left(\mathbf{n}\cdot\mathbf{q}\right)\right]S_n + \left[1 - sign\left(\mathbf{n}\cdot\mathbf{q}\right)\right]S_{n1D}(x_b, y_b, t)\right\} \tag{2.6.16}$$

where $S_{n1D}(x_b, y_b, t)$ is the time-dependent concentration of the *n*-th sediment at the 1-D node corresponding to the boundary [M/L^3]. It is the contribution of 1D transport to the overland boundary.

2.6.3 Immobile Species

The balance equation for immobile species is simply the statement that the rate of mass change is due to biogeochemical reaction as:

$$\frac{\partial(h_b \rho_{bw} \theta_b C_{bw})}{\partial t} = h_b r_{Cbw}\big|_N' \qquad \textbf{(2.6.17)}$$

$$\frac{\partial(h_b \rho_{bw} \theta_b C_{bp})}{\partial t} = h_b r_{Cbp}\big|_N' \qquad \textbf{(2.6.18)}$$

$$\frac{\partial(M_n C_{bsn})}{\partial t} = h_b r_{Cbsn}\big|_N' \qquad \textbf{(2.6.19)}$$

where h_b is the bed depth [L], ρ_{bw} is the density of bed pore-water [M/L^3], θ_b is the porosity of the bed sediment [L^3/L^3], C_{bw} is the concentration of dissolved chemical in the immobile pore-water phase in the unit of chemical mass per bed-water mass [M/M], $r_{Cbw}\big|_N'$ is the production rate of C_{bw} due to all N reactions in the unit of chemical mass per bed volume per time [M/L^3/t], C_{bp} is the concentration of bed precipitate in the unit of chemical mass per bed-water mass [M/M], $r_{Cbp}\big|_N'$ is the production rate of C_{bp} due to all N reactions in the unit of chemical mass per bed volume per time [M/L^3/t], C_{bsn} is the concentration of particulate sorbed on to bed sediment of the *n*-th fraction size in the unit of chemical mass per unit of bed-sediment mass [M/M], M_n is the concentration of the *n*-th bed sediment in the unit of sediment mass per bed area [M/L^2], $r_{Cbsn}\big|_N'$ is the production rate of C_{bsn} due to all N reactions in the unit of chemical mass per bed volume per time [M/L^3/t].

Define

$$r_i\big|_N = h_b \cdot r_i\big|_N' / h \quad where \quad i = C_{bw},\ C_{bp},\ or\ C_{bsn} \qquad \textbf{(2.6.20)}$$

Equation (2.6.16) through (2.6.18) can be modified as

$$\frac{\partial(h_b \rho_{bw} \theta_b C_{bw})}{\partial t} = h r_{Cbw}\big|_N \qquad \textbf{(2.6.21)}$$

$$\frac{\partial(h_b \rho_{bw} \theta_b C_{bp})}{\partial t} = h \cdot r_{Cbp}\big|_N \qquad \textbf{(2.6.22)}$$

$$\frac{\partial(h_b M_n C_{bsn})}{\partial t} = h r_{Cbsn}\big|_N \qquad \textbf{(2.6.23)}$$

Define

$$\rho_i = \begin{cases} h_b \rho_{bw} \theta_b / h, \ for \ \ C_{bw} \ and \ C_{bp} \\ M_n / h, \ for \ \ C_{bsn} \end{cases} \quad \textbf{(2.6.24)}$$

Equation (2.6.21) through (2.6.23) can be summarized as

$$\frac{\partial (h \rho_i C_i)}{\partial t} = hr_i \big|_N, \ \ i \in M_{im} \quad \textbf{(2.6.25)}$$

where C_i is the concentration of species i, which is immobile, in the unit of chemical mass per unit phase mass [M/M], ρ_i is the density of the phase associated with species i [M/L^3], $r_i \big|_N$ is the production rate of species i due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], and M_{im} is the number of immobile species. The concentrations of all immobile species must be given initially for transient simulations. No boundary conditions are needed for immobile species.

2.6.4 Mobile Species

The continuity equation of mobile species can be derived based on the conservation law of material mass stating that the rate of mass change is due to both advective-dispersive transport and biogeochemical reactions as:

$$\frac{\partial (h \rho_w C_w)}{\partial t} + L(\rho_w C_w) = hr_{Cw} \big|_N \quad \textbf{(2.6.26)}$$

$$\frac{\partial (h \rho_w C_p)}{\partial t} + L(\rho_w C_p) = hr_{Cp} \big|_N \quad \textbf{(2.6.27)}$$

$$\frac{\partial (h S_n C_{sn})}{\partial t} + L(S_n C_{sn}) = hr_{Csn} \big|_N \quad \textbf{(2.6.28)}$$

where ρ_w is the density of column water [M/L^3], C_w is the concentration of dissolved chemical in the mobile water phase in the unit of chemical mass per column-water mass [M/M], $r_{Cw} \big|_N$ is the production rate of C_w due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], C_p is the concentration of suspension precipitate in the unit of chemical mass per column-water mass [M/M], $r_{Cp} \big|_N$ is the production rate of C_p due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], C_{sn} is the concentration of particulate sorbed on to suspended sediment of the n-th fraction size in the unit of chemical mass per unit of sediment mass [M/M], S_n is the concentration of suspended sediment in the unit of sediment mass per column volume [M/L^3], $r_{Csn} \big|_N$ is the production rate of C_{sn} due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], and the operator L is defined in Eq. (2.6.31) later.

Define

$$\rho_i = \begin{cases} \rho_w \ \ for \ \ C_w \ and \ C_p \\ S_n \ \ for \ \ C_{sn} \end{cases} \quad \textbf{(2.6.29)}$$

Equation (2.6.26) through (2.6.28) can be summarized as

$$\frac{\partial(h\rho_i C_i)}{\partial t} + L(\rho_i C_i) = hr_i\big|_N, \quad i \in M_m = M - M_{im} \tag{2.6.30}$$

where C_i is the concentration of species i, which is mobile, in the unit of chemical mass per unit phase mass [M/M], ρ_i is the density of the phase associated with species i [M/L^3], $r_i\big|_N$ is the production rate of species i due to all N reactions in the unit of chemical mass per column volume per time [M/L^3/t], M is the total number of chemical species, M_m is the number of mobile chemical species, and operator L is defined as

$$L(\rho_i C_i) = \nabla\cdot(\mathbf{q}\rho_i C_i) - \nabla\cdot\left[h\mathrm{K}\cdot\nabla(\rho_i C_i)\right] - (M_{C_i^{as}} + M_{C_i^{rs}} - M_{C_i^{es}} + M_{C_i^{rs}}) \tag{2.6.31}$$

where $M_{C_i^{as}}$ is the mass ratte of artificial source of species i [M/L^2/T], $M_{C_i^{rs}}$ is the mass rate of the rainfall source of species i [M/L^2/T], $M_{C_i^{es}}$ is the mass rate of the evaporation sink of species i [M/L^2/T], and $M_{C_c^{is}}$ is mass rate of the source of species i in the overland from subsurface [M/L^2/T].

Concentrations of all mobile species must be given initially for transient simulations. Similar to suspended sediment transport, five types of boundary conditions are taken into account for mobile species, including Dirichlet, Variable, Cauchy, Neumann, and river/stream-overland interface boundary conditions (Yeh et al., 2005).

Dirichlet boundary condition: Dirichlet boundary conditions are prescribed on the boundary where the suspended sediment concentration is known,

$$C_i = C_{idb}(x_b, y_b, t) \qquad i \in M_m \quad on \quad B_d(\mathbf{x}) = 0 \tag{2.6.32}$$

where x_b and y_b are the coordinates of the boundary node [L], and $C_{idb}(x_b, y_b, t)$ is a time-dependent concentration of the i-th mobile species on the Dirichlet boundary $B_d(\mathbf{x}) = 0$ [M/M].

Variable boundary condition: Variable boundary conditions are normally specified on the boundary where the flow direction can change with time or on any open boundary. On the variable boundary, when the flow is directed into the region of the interest, the mass rate into the region is given by the product of the flow rate and concentration of the incoming fluid. When the flow is directed out of the region, the sediment mass is assumed carried out via advection. Mathematically, a variable boundary condition is given as

$$\mathbf{n}\cdot\left(\mathbf{q}\rho_i C_i - h\mathbf{K}\cdot\nabla(\rho_i C_i)\right) = \mathbf{n}\cdot\mathbf{q}\rho_i C_{ivb}(x_b, y_b, t) \; if \; \mathbf{n}\cdot\mathbf{q} \le 0 \; on \; B_v(\mathbf{x}) = 0, \; i \in M_m \tag{2.6.33}$$

and

$$-\mathbf{n}\cdot\left(h\mathbf{K}\cdot\nabla(\rho_i C_i)\right) = 0 \qquad if \qquad \mathbf{n}\cdot\mathbf{q} \le 0 \qquad on \qquad B_v(\mathbf{x}) = 0, \qquad i \in M_m \tag{2.6.34}$$

where $\mathbf{n}$ is a unit outward direction and $C_{ivb}(x_b, y_b, t)$ is a time-dependent concentration of the i-th mobile species in the incoming fluid at the boundary [M/M] $B_v(\mathbf{x}) = 0$.

Cauchy boundary condition: This boundary condition is employed when the total material flow rate

is given. Usually, this boundary is an upstream flux boundary.

$$\mathbf{n}\cdot\left(\mathbf{q}\rho_i C_i - h\mathbf{K}\cdot\nabla(\rho_i C_i)\right) = Q_{C_i cb}(x_b, y_b, t) \qquad i \in M_m \qquad on \qquad B_c(\mathbf{x}) = 0 \tag{2.6.35}$$

where $Q_{C_i cb}(x_b, y_b, t)$ is a time-dependent material flow rate of the *i*-th mobile species through the Cauchy boundary $B_c(\mathbf{x}) = 0$ [M/t/L].

Neumann boundary condition: This boundary condition is used when the diffusive material flow rate is known at the boundary node.

$$-\mathbf{n}\cdot h\mathbf{K}\cdot\nabla(\rho_i C_i) = Q_{C_i nb}(x_b, y_b, t) \qquad i \in M_m \qquad on \quad B_{nb}(\mathbf{x}) = 0 \tag{2.6.36}$$

where $Q_{C_i nb}(x_b, y_b, t)$ is a time-dependent diffusive material flow rate of the *i*-th mobile species through the Neumann boundary $B_{nb}(\mathbf{x}) = 0$ [M/t/L].

Overland-river/stream interface boundary condition: The boundary condition is needed when one-dimensional sediment transport in river/stream networks is coupled with two-dimensional sediment transport in overland regime. We assume that the exchange of sediment mass between river/stream and overland flows is mainly due to advection. Under such circumstances, the interfacial boundary condition is stated as

$$\mathbf{n}\cdot\left(\mathbf{q}\rho_i C_i - h\mathbf{K}\cdot\nabla(\rho_i C_i)\right) = \left(\mathbf{n}\cdot\mathbf{q}\right)\frac{1}{2}\left\{\left[1 + sign\left(\mathbf{n}\cdot\mathbf{q}\right)\right]\rho_i C_i + \left[1 - sign\left(\mathbf{n}\cdot\mathbf{q}\right)\right]\rho_i C_{i1D}(x_b, y_b, t)\right\} \tag{2.6.37}$$

where $C_{i1D}(x_b, y_b, t)$ is the time-dependent concentration of the *i*-th species at the 1-D node corresponding to the overland-river/stream interfacial boundary point [M/M].

2.6.5 Diagonalization of Species Transport Equations

The temporal-spatial distribution of chemical species is described by a system of M_{im} mass balance equations [equation (2.6.25)], and M_m reactive transport equations [equation (2.6.30)]. These two equations can be recast in the following form

$$\frac{\partial(h\rho_i C_i)}{\partial t} + \alpha_i L(\rho_i C_i) = hr_i\big|_N, \quad i \in M \tag{2.6.38}$$

where *M* is the total number of chemical species, α_i is 0 for immobile species and 1 for mobile species.

The determination of $r_i\big|_N$ and associated parameters is a primary challenge in biogeochemical modeling. Instead of using an ad hoc method to formulate $r_i\big|_N$, we use reaction-based formulations (Steefel and Cappellen, 1998). In a reaction-based formulation, $r_i\big|_N$ is given by the summation of rates of all reactions that the *i*-th species participates in,

$$r_i\big|_N = \frac{d\left(\rho_i C_i\right)}{dt}\Big|_{reaction} = \sum_{k=1}^{N}\left[(\nu_{ik} - \mu_{ik})r_k\right], \quad i \in M \qquad \textbf{(2.6.39)}$$

where ν_{ik} is the reaction stoichiometry of the *i*-th species in the *k*-th reaction associated with the products, μ_{ik} is the reaction stoichiometry of the *i*-th species in the *k*-th reaction associated with the reactants, and r_k is the rate of the *k*-th reaction.

Substituting equation (2.6.39) into equation (2.6.38) results in the transport equations of *M* chemical species described by

$$\frac{\partial(h\rho_i C_i)}{\partial t} + \alpha_i L(\rho_i C_i) = h\sum_{k=1}^{N}\left[(\nu_{ik} - \mu_{ik})r_k\right], \quad i \in M; \quad or \quad \mathbf{U}\frac{\partial \mathbf{C}_h}{\partial t} + \boldsymbol{\alpha} L(\mathbf{C}) = h\boldsymbol{\nu}\mathbf{r} \qquad \textbf{(2.6.40)}$$

where **U** is a unit matrix, $\mathbf{C}_h$ is a vector with its components representing *M* species concentrations multiply the water depth [M/L^2], $\boldsymbol{\alpha}$ is a diagonal matrix with α_i as its diagonal component, **C** is a vector with its components representing M species concentrations [M/L^3], $\boldsymbol{\nu}$ is the reaction stoichiometry matrix, and **r** is the reaction rate vector with *N* reaction rates as its components. Equation (2.6.40) represents a mass balance for species *i*, which states that the rate of change of any species mass is due to advection-dispersion coupled with contributing reactions that describe the biogeochemical processes.

In a primitive approach, equation (2.6.40) is integrated to yield the distributions and evolutions of chemical species in a region of interest. However, when some fast equilibrium reactions take place in the system, this approach is not adequate (Fang et al., 2003). Here, we will take a diagonalization approach through decomposition. Equation (2.6.40) written in matrix form can be decomposed based on the type of biogeochemical reactions via Gauss-Jordan column reduction of reaction matrix $\boldsymbol{\nu}$. Among all the fast/equilibrium and slow/kinetic reactions, "redundant reactions" are defined as fast reactions that are linearly dependent on other fast reactions, and "irrelevant reactions" are kinetic reactions that are linearly dependent on only equilibrium reactions. In order to avoid singularity of the reaction matrix, redundant fast reactions are omitted from the system prior to decomposition. The removal of irrelevant slow reactions alleviates problems associated with rate formulation uncertainty and parameterization for these reactions.

Decomposition is performed by pivoting on the N_E equilibrium reactions and decoupling them from the N_K kinetic reactions. In other words, each fast reaction can be used to eliminate one chemical species from simultaneous consideration. An incomplete Gauss-Jordan row decomposition of the reaction matrix $\boldsymbol{\nu}$ by pivoting on N_E equilibrium reactions will result in N_E equilibrium-variables and N_{KIV} kinetic-variables. To analyze the system behavior, it is advantageous to perform a complete decomposition, in which the reduction of the reaction matrix is done by pivoting on N_E equilibrium reactions and on N_{KI} linearly independent kinetic reactions to result in N_E equilibrium-variables, N_{KI} kinetic-variables, and N_C components. The complete decomposition is given as follows:

$$\begin{bmatrix} \mathbf{A_{11}} & \mathbf{0_{12}} & \mathbf{0_{13}} \\ \mathbf{A_{21}} & \mathbf{A_{22}} & \mathbf{0_{23}} \\ \mathbf{A_{31}} & \mathbf{A_{32}} & \mathbf{U_{33}} \end{bmatrix} \begin{Bmatrix} \frac{\partial \mathbf{C}_{h1}}{dt} \\ \frac{\partial \mathbf{C}_{h2}}{dt} \\ \frac{\partial \mathbf{C}_{h3}}{dt} \end{Bmatrix} + \begin{bmatrix} \mathbf{B_{11}} & \mathbf{0_{12}} & \mathbf{0_{13}} \\ \mathbf{B_{21}} & \mathbf{B_{22}} & \mathbf{0_{23}} \\ \mathbf{B_{31}} & \mathbf{B_{32}} & \boldsymbol{\alpha}_{33} \end{bmatrix} \mathrm{L}\left(\begin{Bmatrix} \mathbf{C_1} \\ \mathbf{C_2} \\ \mathbf{C_3} \end{Bmatrix} \right) = \mathrm{h} \begin{bmatrix} \mathbf{D_{11}} & \mathbf{K_{12}} & \mathbf{K_{13}} \\ \mathbf{0_{21}} & \mathbf{D_{22}} & \mathbf{K_{23}} \\ \mathbf{0_{31}} & \mathbf{0_{32}} & \mathbf{0_{33}} \end{bmatrix} \begin{Bmatrix} \mathbf{r_1} \\ \mathbf{r_2} \\ \mathbf{r_3} \end{Bmatrix} \quad \textbf{(2.6.41)}$$

where $\mathbf{A_{11}}$ is the submatrix of the reduced **U** matrix with size of $N_E \times N_E$, $\mathbf{A_{21}}$ is the submatrix of the reduced **U** matrix with size of $N_{KI} \times N_E$, and $\mathbf{A_{31}}$ is the submatrix of the reduced **U** matrix with size of $N_C \times N_E$; $\mathbf{0_{12}}$ is the zero submatrix of the reduced **U** matrix with size of $N_E \times N_{KI}$, $\mathbf{A_{22}}$ is the submatrix of the reduced **U** matrix with size of $N_{KI} \times N_{KI}$, and $\mathbf{A_{32}}$ is the submatrix of the reduced **U** matrix with size of $N_C \times N_{KI}$; $\mathbf{0_{13}}$ is the zero submatrix of the reduced **U** matrix with size of $N_E \times N_C$, $\mathbf{0_{23}}$ is the submatrix of the reduced **U** matrix with size of $N_{KI} \times N_C$, and $\mathbf{U_{33}}$ is the unit submatrix of the reduced **U** matrix with size of $N_C \times N_C$; $\mathbf{C_{h1}}$, $\mathbf{C_{h2}}$, and $\mathbf{C_{h3}}$ are the subvectors of the vector $\mathbf{C_h}$ with sizes of N_E, N_{KI}, and N_C, respectively; $\mathbf{B_{11}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_E$, $\mathbf{B_{21}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_{KI} \times N_E$, and $\mathbf{B_{31}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_C \times N_E$; $\mathbf{0_{12}}$ is the zero submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_{KI}$, $\mathbf{A_{22}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_{KI} \times N_{KI}$, and $\mathbf{B_{32}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_C \times N_{KI}$; $\mathbf{0_{13}}$ is the zero submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_C$, $\mathbf{0_{23}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_{KI} \times N_C$, and $\boldsymbol{\alpha}_{33}$ is the diagonal submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_C \times N_C$; $\mathbf{C_1}$, $\mathbf{C_2}$, and $\mathbf{C_3}$ are the subvectors of the vector **C** with sizes of N_E, N_{KI}, and N_C, respectively; $\mathbf{D_{11}}$ is the diagonal submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_E$, $\mathbf{K_{12}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_{KI}$, and $\mathbf{K_{13}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_{KD(k)}$; $\mathbf{0_{21}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KI} \times N_E$, $\mathbf{D_{22}}$ is the diagonal submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KI} \times N_{KI}$, and $\mathbf{K_{23}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KI} \times N_{KD(k)}$; $\mathbf{0_{13}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_C \times N_E$, $\mathbf{0_{32}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_C \times N_{KI}$, and $\mathbf{0_{33}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_C \times N_{KD(k)}$; $\mathbf{r_1}$, $\mathbf{r_2}$, and $\mathbf{r_3}$ are the subvectors of the vector **r** with sizes of N_E, N_{KI}, and $N_{KD(k)}$, respectively.

For incomplete decomposition of the reaction matrix $\boldsymbol{\nu}$, Equation (2.6.41) can be connoted as

$$\begin{bmatrix} \mathbf{A_{11}} & \mathbf{0_{12}} \\ \mathbf{A_{21}} & \mathrm{U}_{22} \end{bmatrix} \begin{Bmatrix} \frac{\partial \mathbf{C}_{h1}}{dt} \\ \frac{\partial \mathbf{C}_{h2}}{dt} \end{Bmatrix} + \begin{bmatrix} \mathbf{B_{11}} & \mathbf{0_{12}} \\ \mathbf{B_{21}} & \boldsymbol{\alpha}_{22} \end{bmatrix} \mathrm{L}\left(\begin{Bmatrix} \mathbf{C_1} \\ \mathbf{C_2} \end{Bmatrix} \right) = \mathrm{h} \begin{bmatrix} \mathbf{D_{11}} & \mathbf{K_{12}} \\ \mathbf{0_{21}} & \mathbf{K_{22}} \end{bmatrix} \begin{Bmatrix} \mathbf{r_1} \\ \mathbf{r_2} \end{Bmatrix} \quad \textbf{(2.6.42)}$$

where $\mathbf{A_{11}}$ and $\mathbf{A_{21}}$ are the submatrices of the reduced **U** matrix with size of $N_E \times N_E$ and $N_{KIV} \times N_E$, respectively (note that $N_{KIV} = M - N_E = N_{KI} + N_C$); $\mathbf{0_{12}}$ and $\mathbf{U_{22}}$ are the zero- and unit-submatrices, respectively, of the reduced **U** matrix with size of $N_E \times N_{KIV}$ and $N_{KIV} \times N_{KIV}$, respectively; $\mathbf{C_{h1}}$ and $\mathbf{C_{h2}}$ are the subvectors of the vector $\mathbf{C_h}$ with sizes of N_E and N_{KIV}, respectively; $\mathbf{B_{11}}$ and $\mathbf{B_{21}}$ are the submatrices of the reduced $\boldsymbol{\alpha}$ matrix with sizes of $N_E \times N_E$ and $N_{KIV} \times N_E$, respectively; $\mathbf{0_{12}}$ and $\boldsymbol{\alpha}_{22}$ are the zero- and unit- submatrices, respectively, of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_{KIV}$ and $N_{KIV} \times N_{KIV}$, respectively; $\mathbf{C_1}$ and $\mathbf{C_2}$ are the subvectors of the vector **C** with sizes of N_E and N_{KIV},

respectively; $\mathbf{D_{11}}$ is the diagonal submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_E$ and $\mathbf{K_{12}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_{KIV}$; $\mathbf{0_{21}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KIV} \times N_E$ and $\mathbf{K_{22}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KIV} \times N_E$; $\mathbf{r_1}$ and $\mathbf{r_2}$ are the subvectors of the vector $\mathbf{r}$ with sizes of N_E and N_{KIV}, respectively.

For reactions that are fast, equilibrium may be regarded as being reached instantaneously among the relevant species and the reaction rates may be regarded as infinite. An infinite rate is mathematically represented by a mass action equation or a user specified nonlinear algebraic equation. As a result, the decomposition of equation (2.6.40) to equation (2.6.42) effectively reduces a set of M species reactive transport equations into two subsets of equations. The first set contains N_E algebraic equations representing mass action laws for the equilibrium reactions, and the second set contains N_{KIV} kinetic-variable transport equations. These equation subsets are defined as

Algebraic Equations for Equilibrium Reactions

$$\frac{\partial(hE_i)}{\partial t} + L(E_i^m) = hD_{1ii}r_{1i} + h\sum_{j=1}^{N_K} K_{1ij}r_{2j},\ i \in N_E \quad \Rightarrow \quad r_{1i} = \infty \quad \Rightarrow \quad \frac{\partial(hE_i)}{\partial t} \approx \infty$$

which is replaced with a thermodynamically consistent equation: $K_i^e = \prod_{j\in M} A_j^{\nu_{ji}} \Big/ \prod_{j\in M} A_j^{\mu_{ji}}$ **(2.6.43)**

$$or\ \ F_i(C_1,..,C_M;p_1,p_2,..) = 0 \quad where\ E_i = \sum_{j=1}^{N_E} A_{1ij}C_{1j} \ \ and \ \ E_i^m = \sum_{j=1}^{N_E} B_{1ij}C_{1j}$$

where K_i^e is the equilibrium constant of the i-th fast reaction, A_j is the activity of the j-th species, $Fi(C_1,..,C_M; p_1,p_2,..)$ is an empirical function of all species and a number of parameters p, p2, … for the i-th fast reaction. E_i was called an equilibrium-variable (Fang, et al., 2003) because $\frac{\partial(hE_i)}{\partial t} \approx \infty$ simply means that E_i can reach equilibrium instantaneously.

Transport Equations for Kinetic-Variables

$$\frac{\partial(hE_i)}{\partial t} + L(E_i^m) = h\sum_{j=1}^{N_K} K_{2nj}r_{2j},\ \ i \in N_{KIV} = M - N_E$$
$$where\ E_i = \sum_{j=1}^{N_E} A_{2ij}C_{1j} + C_{2i}\ \ and\ \ E_i^m = \sum_{j=1}^{N_E} B_{2ij}C_{1j} + \alpha_{1i}C_{2i} \qquad \textbf{(2.6.44)}$$

where E_i was called a kinetic variable (Fang, et al., 2003) because as E_i is transported it is subject to only kinetic reactions. This is in contrast to Eq. (2.6.44) where as C_i is transported, it is subject to both equilibrium and kinetic reactions.

Assign

$$R_i = \sum_{j=1}^{N_K} K_{2ij}r_{2j},\ \mathrm{i} \in N_{KIV} \qquad \textbf{(2.6.45)}$$

The reduction of Eq. (2.6.40) to Eq. (2.6.43) and (2.6.44) is equivalent to reducing M governing

equations for immobile and mobile species to the mixed N_E algebraic equations for equilibrium variables and N_{KIV} transport equations for kinetic-variables specified as follows

$$\frac{\partial(hE_i)}{\partial t} + \nabla\bullet(\mathbf{q}E_i^m) - \nabla\bullet\left[(h\mathbf{K}\bullet\nabla E_i^m)\right] = M_{E_i^{as}} + M_{E_i^{rs}} + M_{E_i^{is}} + hR_i,\ i \in N_{KIV} \qquad \textbf{(2.6.46)}$$

where E_i is the concentration of the i-th kinetic-variable [M/L^3], E_i^m is the concentration of mobile part of the i-th kinetic-variable [M/L^3], $M_{E_i^{as}}$ is the artificial source of the i-th kinetic-variable [M/L^2/T], $M_{E_i^{rs}}$ is the rainfall source of the i-th kinetic-variable [M/L^2/T], $M_{E_i^{os1}}$ and $M_{E_i^{os2}}$ are overland sources of the i-th kinetic-variable from river banks *1* and *2*, respectively [M/L^2/T], $M_{E_i^{is}}$ is the mass rate of the source of the i-th kinetic-variable in the overland from subsurface [M/L^2/T], R_i is the production rate of i-th kinetic-variable due to biogeochemical reactions [M/L^3/T], and N_{KIV} is the number of kinetic variable variables.

Initial and boundary condition for chemical species need to be transformed into corresponding initial and boundary conditions for kinetic-variables, which are stated in the following.

Dirichlet boundary condition:

$$E_i^m = E_{i\ db}^m(x_b, y_b, t) \qquad i \in M_m \qquad on \qquad B_d(\mathbf{x}) = 0 \qquad \textbf{(2.6.47)}$$

where $E_{i\ db}^m(x_b, y_b, t)$ is the prescribed concentration of the mobile portion of the i-th kinetic variable on the Dirichlet boundary $B_d(\mathbf{x}) = 0$ [M/L^3].

Variable boundary condition:

< Case 1 > Flow is coming in from outside (nQ < 0)

$$\mathbf{n}\bullet\left(\mathbf{q}E_i^m - h\mathbf{K}\bullet\nabla E_i^m\right) = \mathbf{n}\bullet\mathbf{q}E_{i\ vb}^m(x_b, y_b, t) \qquad i \in M_i \qquad on \qquad B_v(\mathbf{x}) = 0 \qquad \textbf{(2.6.48)}$$

< Case 2 > Flow is going out from inside (nQ > 0).

$$-\mathbf{n}\bullet\left(h\mathbf{K}\bullet\nabla E_i^m\right) = 0 \qquad i \in M_m \qquad on \qquad B_v(\mathbf{x}) = 0 \qquad \textbf{(2.6.49)}$$

where $\mathbf{n}$ is the unit outward vector and $E_{i\ vb}^m(x_b, y_b, t)$ is the concentration of the mobile portion of the i-th kinetic variable on the variable boundary $B_v(\mathbf{x}) = 0$ [M/L^3].

Cauchy boundary condition:

$$\mathbf{n}\bullet\left(\mathbf{q}E_i^m - h\mathbf{K}\bullet\nabla E_i^m\right) = Q_{E_i^m cb}(x_b, y_b, t) \qquad i \in M_i \qquad on \qquad B_c(\mathbf{x}) = 0 \qquad \textbf{(2.6.50)}$$

where $Q_{E_i^m cb}(x_b, y_b, t)$ is the mass flux of E_i^m through the Cauchy boundary $B_c(\mathbf{x}) = 0$ [M/t/L].

Neumann boundary condition:

$$-\mathbf{n}\bullet\left(h\mathbf{K}\bullet\nabla E_i^m\right)=Q_{E_i^m nb}(x_b,y_b,t)\qquad i\in M_i\qquad on\qquad B_n(\mathbf{x})=0 \tag{2.6.51}$$

where $Q_{E_i^m nb}(x_b,y_b,t)$ is the mass flux of E_i^m through the Neumann boundary $B_n(\mathbf{x})=0$ [M/t/L].

Overland-river/stream interface boundary condition:

$$\mathbf{n}\cdot\left(\mathbf{q}E_i^m-h\mathbf{K}\cdot\nabla E_i^m\right)=\left(\mathbf{n}\cdot\mathbf{q}\right)\frac{1}{2}\left\{\left[1+sign\left(\mathbf{n}\cdot\mathbf{q}\right)\right]E_i^m+\left[1-sign\left(\mathbf{n}\cdot\mathbf{q}\right)\right]E_{i\ 1D}^m(x_b,y_b,t)\right\} \tag{2.6.52}$$

where $E_{i\ 1D}^m(x_b,y_b,t)$ is the time-dependent concentration of the mobile portion of the *i*-th kinetic variable at the 1-D node corresponding to the overland-river/stream interfacial boundary point [M/L^3].

2.7 Reactive Biogeochemical Transport in Three-Dimension Subsurface Media

Reactive chemical transport in the subsurface occurs over a broad range of geochemical environments at various space and time scales. Coupled models that simulate hydrological transport and complex biogeochemical reactions are important tools for quantitative predictions of the fate and transport of chemicals in groundwater. Biogeochemical reactions can be divided into two classes (Rubin, 1983): (1) equilibrium-controlled "fast" reactions, and (2) kinetically-controlled "slow" reactions. The former are sufficiently fast compared to the transport time-scale and are reversible, so that local equilibrium may be assumed. The latter are not sufficiently fast compared to the transport time-scale. They may be either reversible or irreversible. Local equilibrium conditions cannot be assumed.

Due to computational limitations, existing coupled models for subsurface reactive transport have various capabilities (Keum and Hahn, 2003). Some models couple transport with equilibrium chemistry (e.g., Cederberg et al., 1985; Liu and Narasimhan, 1989; Yeh and Tripathi, 1991; Parkhurst, 1995; and Parkhurst and Appelo, 1999), while some couple transport with kinetic chemistry (e.g., MacQuarrie et al., 1990; Tompson, 1993; Lensing et al., 1994; Wood et al., 1994; Adeel et al., 1995; Yeh et al., 1998; and Saiers et al., 2000). Models coupling transport with both equilibrium and kinetic reactions appeared in the mid-1990s (e.g., Steefel and Lasaga, 1994; Chilakapati, 1995; Chilakapati et al., 1998; Tebes-Stevens et al., 1998; Yeh et al., 2001b; Brun and Engesgaard, 2002). Most of these models either implicitly assumes that equilibrium reactions occur only among aqueous species or consider only limited reaction networks. These limitations affect the generality of the models. There appears to be few general-purpose transport models that can simulate generic reaction networks including mixed equilibrium/kinetic biochemical and geochemical reactions (Yeh et al., 2004).

This report presents a general mathematical framework and a three-dimensional numerical implementation to simulate reactive chemical transport in subsurface water subject to a defined flow field. Chemical species considered include dissolved species, suspension precipitates and surface species that encompass adsorbed species, ion-exchanged species and free sites. Biogeochemical

reactions taken into account in the model include aqueous complexation, adsorption/desorption, ion-exchange, precipitation/dissolution, reduction/oxidation, and volatilization. Any individual reaction representing any of these chemical and physical processes may be simulated as kinetic or as equilibrium, which makes the approach applicable to a wide range of biogeochemical transport problems. In the subsurface, all dissolved species are assumed mobile while all surface species and suspension precipitates are assumed immobile.

2.7.1 Immobile Species

The balance equation for immobile species is simply the statement that the rate of mass change is due to biogeochemical reaction as:

$$\frac{\partial(\theta\rho_w C_p)}{\partial t} = \theta r_{Cp}\big|_N \qquad \textbf{(2.7.1)}$$

and

$$\frac{\partial(\rho_b S_A C_s)}{\partial t} = \theta r_{Cs}\big|_N \qquad \textbf{(2.7.2)}$$

where ρ_w is the density of pore-water [M/L^3], θ is the porosity of the media [L^3/L^3], C_p is the concentration of precipitate in the unit of chemical mass per por-water mass [M/M], $r_{Cp}\big|_N$ is the production rate of C_p due to all N reactions in the unit of chemical mass per pore-water volume per time [M/L^3/t], ρ_b is the bulk density in dry media mass per unit media volume [M/L^3], S_A is the surface area per unit dry mass [L^2/M], C_s is the concentration of surface species in unit of chemical mass per surface area [M/L^2], and $r_{Cs}\big|_N$ is the production rate of C_s due to all N reactions in the unit of chemical mass per pore-water per time [M/L^3/t].

Equation (2.7.1) and (2.7.2) can be combined as

$$\frac{\partial(\theta\rho_i C_i)}{\partial t} = \theta r_i\big|_N, \quad i \in M_{im} \qquad \textbf{(2.7.3)}$$

where C_i is the concentration of the i-th immobile, $r_i\big|_N$ is the production rate of species i due to all N reactions in the unit of chemical mass per pore-water volume per time [M/L^3/t], M_{im} is the number of immobile species, and ρ_i is defined by

$$\rho_i = \begin{cases} \rho_w, & for\ C_p \\ \rho_b S_A / \theta, & for\ C_s \end{cases} \qquad \textbf{(2.7.4)}$$

The concentrations of all immobile species must be given initially for transient simulations. No boundary conditions are needed for immobile species.

2.7.2 Mobile Species

The continuity equation of mobile species, i.e. dissolved species in the water phase, can be derived

based on the mass conservation law stating that the rate of mass change is due to both advective-dispersive transport and biogeochemical reactions as

$$\frac{\partial(\theta\rho_i C_i)}{\partial t} + \nabla\cdot(\mathbf{V}\rho_i C_i) - \nabla\cdot[\theta\mathbf{D}\cdot\nabla(\rho_i C_i)] = M_{C_i}^{\ as} + \theta r_i\big|_N, \quad i \in M_m \qquad \textbf{(2.7.5)}$$

where C_i is the concentration of the i-th dissolved species in the unit of chemical mass per unit water mass [M/M], ρ_i is the density of water [i.e., $C_i = C_w$] [M/L^3], **V** is the Darcy velocity [L/t], **D** is the dispersion coefficient tensor [L^2/t], $r_i\big|_N$ is the production rate of species i due to all N reactions in the unit of chemical mass per volume of water per time [M/L^3/t], $M_{C_i}^{\ as}$ is the artificial source of C_i in unit of chemical mass per unit of medium volume [M/L^3/t], and M_m is the number of mobile chemical species.

Concentrations of all mobile species must be given initially for transient simulations. Similar to salinity transport, six types of boundary conditions are taken into account for mobile species, including Dirichlet, Variable, Cauchy, Neumann, river/stream-overland interface, and overland-subsurface interface boundary conditions (Yeh et al., 2005). These boundary conditions are stated below:

Dirichlet boundary condition: This condition is applied when the species concentration is prescribed as a function of time on the boundaries:

$$C_i(\mathbf{x},t) = C_{idb}(\mathbf{x},t) \quad on \quad B_d(\mathbf{x}) = 0 \qquad \textbf{(2.7.6)}$$

where $C_{idb}(\mathbf{x},t)$ is a time-dependent concentration of the i-th species on the Dirichlet boundary, $B_d(\mathbf{x}) = 0$, [M/M].

Variable boundary condition: This boundary condition is employed when the flow direction would change with time during simulations. Two cases are considered, regarding to the flow direction on the boundary.

< Case 1 > Flow is coming in from outside:

$$\mathbf{n}\cdot\left[\mathbf{V}\rho_i C_i - \theta\mathbf{D}\cdot\nabla(\rho_i C_i)\right] = (\mathbf{n}\cdot\mathbf{V})\rho_i C_{ivb}(\mathbf{x},t) \quad on \quad B_v(\mathbf{x}) = 0 \qquad \textbf{(2.7.7)}$$

< Case 2 > Flow is going out from inside:

$$-\mathbf{n}\cdot\left[\theta\mathbf{D}\cdot\nabla(\rho_i C_i)\right] = 0 \quad on \quad B_v(\mathbf{x}) = 0 \qquad \textbf{(2.7.8)}$$

where $C_{ivb}(\mathbf{x},t)$ is a time-dependent concentration of the i-th species [M/M] on the variable boundary, $B_v(\mathbf{x}) = 0$, which is associated with the incoming flow.

Cauchy boundary condition: This boundary condition is employed when the total salt-flow rate is given at pervious boundaries. Usually, this boundary is a flow-in boundary. The conditions are expressed as

$$\mathbf{n}\cdot\left[\mathbf{V}\rho_i C_i - \theta\mathbf{D}\cdot\nabla(\rho_i C_i)\right] = Q_{C_i cb}(\mathbf{x},t) \quad on \quad B_c(\mathbf{x}) = 0 \qquad \textbf{(2.7.9)}$$

where $Q_{C_i cb}(\mathbf{x},t)$ is total chemical flux of the *i*-th species [M/L^2/t] through the Cauchy boundary, $B_c(\mathbf{x}) = 0$, which takes a positive value if it is going out of the region and a negative value if it is coming into the region.

Neumann boundary condition: This boundary condition is used when the dispersive salt-flow rate is known at the boundary. It can be written as

$$-\mathbf{n}\cdot\left(\theta\mathbf{D}\cdot\nabla(\rho_i C_i)\right) = Q_{C_i nb}(\mathbf{x},t) \quad on \quad B_n(\mathbf{x}) = 0 \qquad \textbf{(2.7.10)}$$

where $Q_{C_i nb}(\mathbf{x},t)$ is the chemical flux of the *i*-th species through the Neumann boundary, $B_n(\mathbf{x}) = 0$, [M/L^2/t].

In addition to the four types of global boundary conditions, two interface boundary conditions may be specified: one for the exchange of chemicals between the subsurface media and river/stream network and the other for chemical exchange between the subsurface media and the overland. Mathematically, these boundary conditions are described below.

Subsurface-river interface boundary condition:

$$\mathbf{n}\cdot\left[\mathbf{V}\rho_i C_i - \theta\mathbf{D}\cdot\nabla(\rho_i C_i)\right] = (\mathbf{n}\cdot\mathbf{V})\frac{1}{2}\left\{\left[1+sign(\mathbf{n}\cdot\mathbf{V})\right]\rho_i C_i + \left[1-sign(\mathbf{n}\cdot\mathbf{V})\right]\rho_i C_{i1D}(x_b,y_b,z_b,t)\right\} \qquad \textbf{(2.7.11)}$$

where $C_{i1D}(x_b,y_b,z_b,t)$ is the time-dependent concentration of the *i*-th species at the 1-D node corresponding to the subsurface-river/stream interfacial boundary points [M/M].

Subsurface-overland interface boundary condition:

$$\mathbf{n}\cdot\left[\mathbf{V}\rho_i C_i - \theta\mathbf{D}\cdot\nabla(\rho_i C_i)\right] = (\mathbf{n}\cdot\mathbf{V})\frac{1}{2}\left\{\left[1+sign(\mathbf{n}\cdot\mathbf{V})\right]\rho_i C_i + \left[1-sign(\mathbf{n}\cdot\mathbf{V})\right]\rho_i C_{i2D}(x_b,y_b,z_b,t)\right\} \qquad \textbf{(2.7.12)}$$

where $C_{i2D}(x_b,y_b,z_b,t)$ is the time-dependent concentration of the *i*-th species at the 2-D node corresponding to the subsurface-overland interfacial boundary point [M/M].

2.7.3 Diagonalization of Species Transport Equations

The temporal-spatial distribution of chemical species is described by a system of M_{im} mass balance equations [equation (2.7.3)], and M_m reactive transport equations [equation (2.7.5)]. These two equations can be recast in the following form

$$\frac{\partial(\theta\rho_i C_i)}{\partial t} + \alpha_i L(\rho_i C_i) = \theta r_i\big|_N, \quad i \in M \qquad \textbf{(2.7.13)}$$

where L is an operator defined as

$$L(\rho_i C_i) = \nabla \cdot (\mathbf{V}\rho_i C_i) - \nabla \cdot [\theta \mathbf{D} \cdot \nabla(\rho_i C_i)] - M_{C_i}{}^{as} \qquad \textbf{(2.7.14)}$$

The determination of $r_i\,|_N$ and associated parameters is a primary challenge in biogeochemical modeling. Instead of using an ad hoc method to formulate $r_i\,|_N$, we use reaction-based formulations (Steefel and Cappellen, 1998). In a reaction-based formulation, $r_i\,|_N$ is given by the summation of rates of all reactions that the *i*-th species participates in,

$$r_i\,|_N = \frac{d(\rho_i C_i)}{dt}\Big|_{reaction} = \sum_{k=1}^{N}[(\nu_{ik} - \mu_{ik})r_k], \quad i \in M \qquad \textbf{(2.7.15)}$$

where ν_{ik} is the reaction stoichiometry of the *i*-th species in the *k*-th reaction associated with the products, μ_{ik} is the reaction stoichiometry of the *i*-th species in the *k*-th reaction associated with the reactants, and r_k is the rate of the *k*-th reaction.

Substituting equation (2.7.15) into equation (2.7.18) results in the transport equations of *M* chemical species described by

$$\frac{\partial(\theta\rho_i C_i)}{\partial t} + \alpha_i L(\rho_i C_i) = \theta\sum_{k=1}^{N}[(\nu_{ik} - \mu_{ik})r_k], \quad i \in M; \quad or \quad \mathbf{U}\frac{\partial \mathbf{C}_\theta}{\partial t} + \boldsymbol{\alpha} L(\mathbf{C}) = h\boldsymbol{\nu}\mathbf{r} \qquad \textbf{(2.7.16)}$$

where **U** is a unit matrix, $\mathbf{C}_{\boldsymbol{\theta}}$ is a vector with its components representing *M* species concentrations multiply the moisture content [M/L^3], $\boldsymbol{\alpha}$ is a diagonal matrix with α_i as its diagonal component, **C** is a vector with its components representing M species concentrations [M/L^3], $\boldsymbol{\nu}$ is the reaction stoichiometry matrix, and **r** is the reaction rate vector with *N* reaction rates as its components. Equation (2.7.16) represents a mass balance for species *i*, which states that the rate of change of any species mass is due to advection-dispersion coupled with contributing reactions that describe the biogeochemical processes.

In a primitive approach, equation (2.7.16) is integrated to yield the distributions and evolutions of chemical species in a region of interest. However, when some fast equilibrium reactions take place in the system, this approach is not adequate (Fang et al., 2003). Here, we will take a diagonalization approach through decomposition. Equation (2.7.16) written in matrix form can be decomposed based on the type of biogeochemical reactions via Gauss-Jordan column reduction of reaction matrix $\boldsymbol{\nu}$. Among all the fast/equilibrium and slow/kinetic reactions, "redundant reactions" are defined as fast reactions that are linearly dependent on other fast reactions, and "irrelevant reactions" are kinetic reactions that are linearly dependent on only equilibrium reactions. In order to avoid singularity of the reaction matrix, redundant fast reactions are omitted from the system prior to decomposition. The removal of irrelevant slow reactions alleviates problems associated with rate formulation uncertainty and parameterization for these reactions.

Decomposition is performed by pivoting on the N_E equilibrium reactions and decoupling them from the N_K kinetic reactions. In other words, each fast reaction can be used to eliminate one chemical species from simultaneous consideration. An incomplete Gauss-Jordan row decomposition of the reaction matrix $\boldsymbol{\nu}$ by pivoting on N_E equilibrium reactions will result in N_E equilibrium-variables and N_{KIV} kinetic-variables. To analyze the system behavior, it is advantageous to perform a

complete decomposition, in which the reduction of the reaction matrix is done by pivoting on N_E equilibrium reactions and on N_{KI} linearly independent kinetic reactions to result in N_E equilibrium-variables, N_{KI} kinetic-variables, and N_C components. The complete decomposition is given as follows:

$$\begin{bmatrix} \mathbf{A_{11}} & \mathbf{0_{12}} & \mathbf{0_{13}} \\ \mathbf{A_{21}} & \mathbf{A_{22}} & \mathbf{0_{23}} \\ \mathbf{A_{31}} & \mathbf{A_{32}} & \mathbf{U_{33}} \end{bmatrix} \begin{Bmatrix} \dfrac{\partial \mathbf{C}_{\theta 1}}{\mathrm{dt}} \\ \dfrac{\partial \mathbf{C}_{\theta 2}}{\mathrm{dt}} \\ \dfrac{\partial \mathbf{C}_{\theta 3}}{\mathrm{dt}} \end{Bmatrix} + \begin{bmatrix} \mathbf{B_{11}} & \mathbf{0_{12}} & \mathbf{0_{13}} \\ \mathbf{B_{21}} & \mathbf{B_{22}} & \mathbf{0_{23}} \\ \mathbf{B_{31}} & \mathbf{B_{32}} & \boldsymbol{\alpha}_{33} \end{bmatrix} \mathrm{L}\left(\begin{Bmatrix} \mathbf{C_1} \\ \mathbf{C_2} \\ \mathbf{C}_3 \end{Bmatrix} \right) = \theta \begin{bmatrix} \mathbf{D_{11}} & \mathbf{K_{12}} & \mathbf{K_{13}} \\ \mathbf{0_{21}} & \mathbf{D_{22}} & \mathbf{K_{23}} \\ \mathbf{0_{31}} & \mathbf{0_{32}} & \mathbf{0_{33}} \end{bmatrix} \begin{Bmatrix} \mathbf{r_1} \\ \mathbf{r_2} \\ \mathbf{r_3} \end{Bmatrix} \quad \textbf{(2.7.17)}$$

where $\mathbf{A_{11}}$ is the submatrix of the reduced **U** matrix with size of $N_E \times N_E$, $\mathbf{A_{21}}$ is the submatrix of the reduced **U** matrix with size of $N_{KI} \times N_E$, and $\mathbf{A_{31}}$ is the submatrix of the reduced **U** matrix with size of $N_C \times N_E$; $\mathbf{0_{12}}$ is the zero submatrix of the reduced **U** matrix with size of $N_E \times N_{KI}$, $\mathbf{A_{22}}$ is the submatrix of the reduced **U** matrix with size of $N_{KI} \times N_{KI}$, and $\mathbf{A_{32}}$ is the submatrix of the reduced **U** matrix with size of $N_C \times N_{KI}$; $\mathbf{0_{13}}$ is the zero submatrix of the reduced **U** matrix with size of $N_E \times N_C$, $\mathbf{0_{23}}$ is the submatrix of the reduced **U** matrix with size of $N_{KI} \times N_C$, and $\mathbf{U_{33}}$ is the unit submatrix of the reduced **U** matrix with size of $N_C \times N_C$; $\mathbf{C_{h1}}$, $\mathbf{C_{h2}}$, and $\mathbf{C_{h3}}$ are the subvectors of the vector $\mathbf{C_h}$ with sizes of N_E, N_{KI}, and N_C, respectively; $\mathbf{B_{11}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_E$, $\mathbf{B_{21}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_{KI} \times N_E$, and $\mathbf{B_{31}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_C \times N_E$; $\mathbf{0_{12}}$ is the zero submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_{KI}$, $\mathbf{A_{22}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_{KI} \times N_{KI}$, and $\mathbf{B_{32}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_C \times N_{KI}$; $\mathbf{0_{13}}$ is the zero submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_C$, $\mathbf{0_{23}}$ is the submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_{KI} \times N_C$, and $\boldsymbol{\alpha}_{33}$ is the diagonal submatrix of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_C \times N_C$; $\mathbf{C_1}$, $\mathbf{C_2}$, and $\mathbf{C_3}$ are the subvectors of the vector **C** with sizes of N_E, N_{KI}, and N_C, respectively; $\mathbf{D_{11}}$ is the diagonal submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_E$, $\mathbf{K_{12}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_{KI}$, and $\mathbf{K_{13}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_{KD(k)}$; $\mathbf{0_{21}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KI} \times N_E$, $\mathbf{D_{22}}$ is the diagonal submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KI} \times N_{KI}$, and $\mathbf{K_{23}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KI} \times N_{KD(k)}$; $\mathbf{0_{13}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_C \times N_E$, $\mathbf{0_{32}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_C \times N_{KI}$, and $\mathbf{0_{33}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_C \times N_{KD(k)}$; $\mathbf{r_1}$, $\mathbf{r_2}$, and $\mathbf{r_3}$ are the subvectors of the vector **r** with sizes of N_E, N_{KI}, and $N_{KD(k)}$, respectively.

For incomplete decomposition of the reaction matrix $\boldsymbol{\nu}$, Equation (2.7.17) can be connoted as

$$\begin{bmatrix} \mathbf{A_{11}} & \mathbf{0_{12}} \\ \mathbf{A_{21}} & \mathrm{U}_{22} \end{bmatrix} \begin{Bmatrix} \dfrac{\partial \mathbf{C}_{\theta 1}}{\mathrm{dt}} \\ \dfrac{\partial \mathbf{C}_{\theta 2}}{\mathrm{dt}} \end{Bmatrix} + \begin{bmatrix} \mathbf{B_{11}} & \mathbf{0_{12}} \\ \mathbf{B_{21}} & \boldsymbol{\alpha}_{22} \end{bmatrix} \mathrm{L}\left(\begin{Bmatrix} \mathbf{C_1} \\ \mathbf{C}_2 \end{Bmatrix} \right) = \theta \begin{bmatrix} \mathbf{D_{11}} & \mathbf{K_{12}} \\ \mathbf{0_{21}} & \mathbf{K_{22}} \end{bmatrix} \begin{Bmatrix} \mathbf{r_1} \\ \mathbf{r_2} \end{Bmatrix} \quad \textbf{(2.7.18)}$$

where $\mathbf{A_{11}}$ and $\mathbf{A_{21}}$ are the submatrices of the reduced **U** matrix with size of $N_E \times N_E$ and $N_{KIV} \times N_E$, respectively (note that $N_{KIV} = M - N_E = N_{\mathrm{KI}} + N_C$); $\mathbf{0_{12}}$ and $\mathbf{U_{22}}$ are the zero- and unit-submatrices,

respectively, of the reduced **U** matrix with size of $N_E \times N_{KIV}$ and $N_{KIV} \times N_{KIV}$, respectively; $\mathbf{C_{\theta 1}}$ and $\mathbf{C_{\theta 2}}$ are the subvectors of the vector $\mathbf{C_\theta}$ with sizes of N_E and N_{KIV}, respectively; $\mathbf{B_{11}}$ and $\mathbf{B_{21}}$ are the submatrices of the reduced $\boldsymbol{\alpha}$ matrix with sizes of $N_E \times N_E$ and $N_{KIV} \times N_E$, respectively; $\mathbf{0_{12}}$ and $\boldsymbol{\alpha}_{22}$ are the zero- and unit- submatrices, respectively, of the reduced $\boldsymbol{\alpha}$ matrix with size of $N_E \times N_{KIV}$ and $N_{KIV} \times N_{KIV}$, respectively; $\mathbf{C_1}$ and $\mathbf{C_2}$ are the subvectors of the vector **C** with sizes of N_E and N_{KIV}, respectively; $\mathbf{D_{11}}$ is the diagonal submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_E$ and $\mathbf{K_{12}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_E \times N_{KIV}$; $\mathbf{0_{21}}$ is the zero submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KIV} \times N_E$ and $\mathbf{K_{22}}$ is the submatrix of the reduced $\boldsymbol{\nu}$ matrix with size of $N_{KIV} \times N_E$; $\mathbf{r_1}$ and $\mathbf{r_2}$ are the subvectors of the vector **r** with sizes of N_E and N_{KIV}, respectively.

For reactions that are fast, equilibrium may be regarded as being reached instantaneously among the relevant species and the reaction rates may be regarded as infinite. An infinite rate is mathematically represented by a mass action equation or a user specified nonlinear algebraic equation. As a result, the decomposition of equation (2.7.16) to equation (2.7.18) effectively reduces a set of *M* species reactive transport equations into two subsets of equations. The first set contains N_E algebraic equations representing mass action laws for the equilibrium reactions, and the second set contains N_{KIV} kinetic-variable transport equations. These equation subsets are defined as

Algebraic Equations for Equilibrium Reactions

$$\frac{\partial(\theta E_i)}{\partial t} + L(E_i^m) = \theta D_{1ii} r_{1i} + \theta \sum_{j=1}^{N_K} K_{1ij} r_{2j},\ i \in N_E \quad \Rightarrow \quad r_{1i} = \infty \quad \Rightarrow \quad \frac{\partial(\theta E_i)}{\partial t} \approx \infty$$

which is replaced with a thermodynamically consistent equation: $K_i^e = \prod_{j \in M} A_j^{\nu_{ji}} \Big/ \prod_{j \in M} A_j^{\mu_{ji}}$ **(2.7.19)**

$$or\ \ F_i(C_1,..,C_M; p_1, p_2,..) = 0 \quad where\ E_i = \sum_{j=1}^{N_E} A_{1ij} C_{1j} \ \ and \ \ E_i^m = \sum_{j=1}^{N_E} B_{1ij} C_{1j}$$

where K_i^e is the equilibrium constant of the *i*-th fast reaction, A_j is the activity of the *j*-th species, $F_i(C_1,..,C_M; p_1,p_2,..)$ is an empirical function of all species and a number of parameters p, p2, … for the *i*-th fast reaction. E_i was called an equilibrium-variable (Fang, et al., 2003) because $\frac{\partial(\theta E_i)}{\partial t} \approx \infty$ simply means that E_i can reach equilibrium instantaneously.

Transport Equations for Kinetic-Variables

$$\frac{\partial(\theta E_i)}{\partial t} + L(E_i^m) = \theta \sum_{j=1}^{N_K} K_{2nj} r_{2j},\ \ i \in N_{KIV} = M - N_E$$
$$where\ E_i = \sum_{j=1}^{N_E} A_{2ij} C_{1j} + C_{2i} \ and \ E_i^m = \sum_{j=1}^{N_E} B_{2ij} C_{1j} + \alpha_{1i} C_{2i} \qquad \textbf{(2.7.20)}$$

where E_i was called a kinetic variable (Fang, et al., 2003) because as E_i is transported it is subject to only kinetic reactions. This is in contrast to Eq. (2.7.16) where as C_i is transported, it is subject to both equilibrium and kinetic reactions.

Assign

$$R_i = \sum_{j=1}^{N_K} K_{2ij} r_{2j},\ \mathrm{i} \in N_{KIV} \qquad \textbf{(2.7.21)}$$

The reduction of Eq. (2.7.15) to Eq. (2.7.18) and (2.7.19) is equivalent to reducing M governing equations for immobile and mobile species to N_E algebraic equations for equilibrium variables and N_{KIV} transport equations for kinetic-variables specified as follows

$$\frac{\partial(\theta E_i)}{\partial t} + \nabla\bullet(\mathbf{V}E_i^m) - \nabla\bullet\left[(\theta\mathbf{D}\bullet\nabla E_i^m)\right] = M_{E_i^{as}} + \theta R_i,\ i \in N_{KIV} \qquad \textbf{(2.7.22)}$$

where E_i is the concentration of the i-th kinetic-variable [M/L^3], E_i^m is the concentration of mobile part of the i-th kinetic-variable [M/L^3], $M_{E_i^{as}}$ is the artificial source of the i-th kinetic-variable [M/L^3/T], R_i is the production rate of i-th kinetic-variable due to biogeochemical reactions [M/L^3/T], and N_{KIV} is the number of kinetic variable variables.

Initial and boundary condition for chemical species need to be transformed into corresponding initial and boundary conditions for kinetic-variables, which are stated in the following.

Dirichlet boundary condition:

$$E_i^m = E_{id}^m(x_b, y_b, z_b, t) \qquad on \qquad B_d(\mathbf{x}) = 0 \qquad \textbf{(2.7.23)}$$

where $E_{id}^m(x_b, y_b, t)$ is the specified concentration of the mobile portion of the i-th kinetic variable on the Dirichlet boundary $B_d(\mathbf{x}) = 0$ [M/L^3].

Variable boundary condition:

< Case 1 > Flow is coming in from outside (nQ < 0)

$$\mathbf{n}\bullet\left(\mathbf{V}E_i^m - \theta\mathbf{D}\bullet\nabla E_i^m\right) = \mathbf{n}\bullet\mathbf{V}E_{iv}^m(x_b, y_b, z_b, t) \qquad on \qquad B_v(\mathbf{x}) = 0 \qquad \textbf{(2.7.24)}$$

< Case 2 > Flow is going out from inside (nQ > 0).

$$-\mathbf{n}\bullet\left(\theta\mathbf{D}\bullet\nabla E_i^m\right) = 0 \qquad on \qquad B_v(\mathbf{x}) = 0 \qquad \textbf{(2.7.25)}$$

where $\mathbf{n}$ is the unit outward vector and $E_{iv}^m(x_b, y_b, z_b, t)$ is the concentration of the mobile portion of the i-th kinetic variable on the variable boundary $B_v(\mathbf{x}) = 0$ [M/L^3].

Cauchy boundary condition:

$$\mathbf{n}\bullet\left(\mathbf{V}E_i^m - \theta\mathbf{D}\bullet\nabla E_i^m\right) = Q_{cE_i^m}(x_b, y_b, z_b, t) \qquad on \qquad B_c(\mathbf{x}) = 0 \qquad \textbf{(2.7.26)}$$

where $Q_{cE_i^m}(x_b, y_b z_b, t)$ is the mass flux of E_i^m through the Cauchy boundary $B_c(\mathbf{x}) = 0$ [M/t/L^2].

Neumann boundary condition:

$$-\mathbf{n}\bullet\left(\theta\mathbf{D}\bullet\nabla E_i^m\right)=Q_{nE_i^m}(x_b,y_b,z_b,t)\quad on\quad B_n(\mathbf{x})=0 \qquad \textbf{(2.7.27)}$$

where $Q_{nE_i^m}(x_b,y_b,z_b,t)$ is the mass flux of E_i^m through the Neumann boundary $B_n(\mathbf{x})=0$ [M/t/L^2].

Subsurface-river interface boundary condition:

$$\mathbf{n}\cdot\left[\mathbf{V}E_i^m-\theta\mathbf{D}\cdot\nabla(E_i^m)\right]=(\mathbf{n}\cdot\mathbf{V})\frac{1}{2}\left\{\left[1+sign(\mathbf{n}\cdot\mathbf{V})\right]E_i^m+\left[1-sign(\mathbf{n}\cdot\mathbf{V})\right]E_i^m(C_j^{1D}{}'s)\right\} \qquad \textbf{(2.7.28)}$$

Where $E_i^m(C_j^{1D}{}'s)$ is the mobile portion of the subsurface *i*-th kinetic variables with its argument being the linear combination of 1-D river/stream species concentrations $C_j^{1D}{}'s$ [M/L^3].

Subsurface-overland interface boundary condition:

$$\mathbf{n}\cdot\left[\mathbf{V}E_i^m-\theta\mathbf{D}\cdot\nabla(E_i^m)\right]=(\mathbf{n}\cdot\mathbf{V})\frac{1}{2}\left\{\left[1+sign(\mathbf{n}\cdot\mathbf{V})\right]E_i^m+\left[1-sign(\mathbf{n}\cdot\mathbf{V})\right]E_i^m(C_j^{2D}{}'s)\right\} \qquad \textbf{(2.7.29)}$$

where $E_i^m(C_j^{2D}{}'s)$ is the mobile portion of the subsurface *i*-th kinetic variables with its argument being the linear comination of 2-D overland species concentrations $C_j^{2D}{}'s$ [M/L^3].

2.8 Coupling Transport Among Various Media

As in coupling flows among various media, a rigorous treatment of coupling transport among media should be based the continuity of material fluxes and state variables. This rigorous treatment in coupling chemical transport among various media can be taken similar to the case of flows. We simply impose the continuity of material fluxes and species concentrations for all mobile (between river/stream networks and overland regime) dissolved aqueous species (between subsurface media and overland regime and between subsurface media and river/stream networks) .

However, because the state variables (dissolved chemical concentrations, suspend sediment concentrations, and mobile particulate chemical concentrations) in various media may not be continuous because these state variables are true three-dimensional distribution in subsurface media, but are vertically averaged quantities in overland regime and cross-sectional area averaged quantity in river/stream networks. Because of the averaging processes, mass fluxes between media can be considered due mainly to the advective transport. If this assumption is valid, the coupling of transport among various medial is much simpler than that for fluid flow.

2.8.1 Coupling between Overland Transport and River/StreamNetworks

The coupling of transport between overland and canal is similar to that of salinity transport. When a levee is present on the bank of the canal (left column in Fig. 2.4-1), there are several possibilities on the interactions between overland and river flow transport. If water surfaces in both the overland regime and river are below the top of the levee, the two flow systems are decoupled and transport in overland is decoupled from that in river networks (Fig. 2.4-1a).

When the water surface in the overland regime is above the top of the levee and in the canal is below the top of the levee (Fig. 2.4-1b), the flow is from the overland to river network and thus the transport is also one way from the overland to river network. The fluxes are given by

$$\mathbf{n}\cdot\left[\mathbf{q}\rho C-\mathbf{D}h\cdot\nabla(\rho C)\right]\Big|_{Bank\,1}=M_{C_i}^{\ osl}=S_1\rho C^{o} \qquad \textbf{(2.8.1)}$$

where C [denotes S_n with $\rho=1$ for supended sediment, C_w with $\rho=\rho_w$ for dissolved species, C_p with $\rho=\rho_w$ for precipitated species, C_{Sn} with $\rho=S_n$ for particulate species] is sediment concentration [M/L^3] or species concentrations [M/M] in the overland flow, $M_{C_i}^{\ osl}$ is the source rate of the i-th species in the canal from the overland via bank *1*, which appeared in Eq. (2.5.30) [M/t/L], C^o is the value of C in the overland water at the interface. When the water surface in the overland regime is below the top of the levee and in the canal is above the top of the levee (Fig. 2.4-1c), the flow is from the canal to overland and thus the transport is one way from the canal to overland. The fluxes are given by

$$\mathbf{n}\cdot\left[\mathbf{q}\rho C-\mathbf{D}h\cdot\nabla(\rho C)\right]\Big|_{Bank\,1}=M_{C_i}^{\ osl}=S_1\rho C^{c} \qquad \textbf{(2.8.2)}$$

where C^c is the value of C in the canal water. When the water surfaces in the overland and canal are above the top of the levee (Fig. 2.4-1d), flow direction can e either from the overland to the canl or from the canal to the overland depending on the flow dynamics in the overland and in the canal. If the state variable C is discontinues at the interface of the canal and overland, the fluxes are given by

$$\mathbf{n}\cdot\left[\mathbf{q}\rho C-\mathbf{D}h\cdot\nabla(\rho C)\right]\Big|_{Bank\,1}=M_{C_i}^{\ osl}=S_1\frac{1}{2}\left[\left(1+sign\left(S_1\right)\right)\rho C^{o}+\left(1-sign\left(S_1\right)\right)\rho C^{c}\right] \qquad \textbf{(2.8.3)}$$

If the state variable is continuous, the fluxes are modeled by imposing its continuity to yield the fluxes

$$\mathbf{n}\cdot\left[\mathbf{q}\rho C-\mathbf{D}h\cdot\nabla(\rho C)\right]\Big|_{Bank\,1}=M_{C_i}^{\ osl}\quad and\quad C^{o}\Big|_{Bank\,1}=C^{c} \qquad \textbf{(2.8.4)}$$

When a levee is not present on the bank of the canal (right column in Fig. 2.4-1), there are two possibilities on the interactions between overland and river transport. If water surface in the canal falls below the bank, the flux is either zero if the overland flow is not present or is nonzero and directed from the overland into the canal if overland flow is present (Fig. 2.4-1e). Under this circumstance, the fluxes are given by

$$\mathbf{n}\cdot\left[\mathbf{q}\rho C-\mathbf{D}h\cdot\nabla(\rho C)\right]\Big|_{Bank\,2}=M_{C_i}^{\ os2}=S_2\rho C^{o} \qquad \textbf{(2.8.5)}$$

where $M_{C_i}^{os2}$ is the source rate of the *i*-th species in the canal from the overland via bank *2*, which appeared in Eq. (2.5.30) [M/t/L],

When the water surface in the canal is above the bank (Figs. 2.4-1f and 2.4-1.g), the flow direction can be either from the overland into the canal or from the canal into the overland depending on the flow dynamics in the overland and in the canal. If the state variable is discontinuous, the fluxes are

$$\mathbf{n}\cdot\left[\mathbf{q}\rho C - \mathbf{D}h\cdot\nabla(\rho C)\right]\Big|_{Bank\,2} = M_{C_i}^{os2} = S_2\frac{1}{2}\left[\left(1+sign\left(S_2\right)\right)\rho C^{o} + \left(1-sign\left(S_2\right)\right)\rho C^{c}\right] \qquad \textbf{(2.8.6)}$$

If the state variable is continuous, we impose the continuity of the state variable to yield the fluxes

$$\mathbf{n}\cdot\left[\mathbf{q}\rho C - \mathbf{D}h\cdot\nabla(\rho C)\right]\Big|_{Bank\,2} = M_{C_i}^{os2} \quad and \quad C^{o}\Big|_{Bank\,2} = C^{c} \qquad \textbf{(2.8.7)}$$

Because kinetic variables *E* are chosen as the primary variables in the transport module, for reactive chemical transport, the interfacial boundary conditions in terms of species concentrations must be transformed into those in terms of kinetic variables. Since reaction networks in overland and river/stream/canal networks are identical, every corresponding kinetic variable in the overland and river/stream networks contains the same mobile portion. Thus, one simply replaces ρC with E_i^m in Eqs. (2.8.1) through (2.8.7). For completeness of this report, these equations are listed below.

For couling via bank 1:

When the water surface in the overland regime is above the top of the levee and in the canal is below the top of the levee (Fig. 2.4-1b), the flow is from the overland to river network and thus the transport is also one way from the overland to river network. The flux of the *i*-th kinetic variables are given by

$$\mathbf{n}\cdot\left[\mathbf{q}E_i^m - \mathbf{D}h\cdot\nabla E_i^m\right]\Big|_{Bank\,1} = M_{E_i}^{os1} = S_1\left(E_i^m\right)^{o} \qquad \textbf{(2.8.8)}$$

When the water surface in the overland regime is below the top of the levee and in the canal is above the top of the levee (Fig. 2.4-1c), the flow is from the canal to overland and thus the transport is one way from the canal to overland, the flux of the i-th kinetic variable is given as

$$\mathbf{n}\cdot\left[\mathbf{q}E_i^m - \mathbf{D}h\cdot\nabla E_i^m\right]\Big|_{Bank\,1} = M_{E_i}^{os1} = S_1\left(E_i^m\right)^{c} \qquad \textbf{(2.8.9)}$$

When the water surfaces in the overland and canal are above the top of the levee (Fig. 2.4-1d), flow direction can e either from the overland to the canl or from the canal to the overland depending on the flow dynamics in the overland and in the canal. If the state variable *E* is discontinues at the interface of the canal and overland, the fluxes are given by

$$\mathbf{n}\cdot\left[\mathbf{q}E_i^m - \mathbf{D}h\cdot\nabla E_i^m\right]\Big|_{Bank\,1} = M_{E_i}^{os1} = S_1\frac{1}{2}\left[\left(1+sign\left(S_1\right)\right)\left(E_i^m\right)^{o} + \left(1-sign\left(S_1\right)\right)\left(E_i^m\right)^{c}\right] \qquad \textbf{(2.8.10)}$$

If the state variable *E* is continuous, the fluxes are modeled by imposing its continuity to yield the

fluxes

$$\mathbf{n}\cdot\left[\mathbf{q}E_i^m - \mathbf{D}h\cdot\nabla E_i^m\right]\Big|_{Bank\,1} = M_{E_i}^{os1} \quad and \quad \left(E_i^m\right)^o\Big|_{Bank\,1} = \left(E_i^m\right)^c \tag{2.8.11}$$

In Equations (2.8.8) through (2.8.11), E_i^m is the concentration of the mobile portion of the *i*-th kinetic variable [M/L^3], $\left(E_i^m\right)^o$ is the value of E_i^m in the overland water at the interface [M/L^3], and $M_{E_i}^{os1}$ is the source of the kinetic variable E_i in the canal from the overland via bank *1* [M/t/L], which appeared in Eq. (2.5.44), and $\left(E_i^m\right)^c$ is the value of E_i^m in the canal water at the interface.

For couling via bank 2:

When a levee is not present on the bank of the canal (right column in Fig. 2.4-1), there are two possibilities on the interactions between overland and river transport. If water surface in the canal falls below the bank, the flux is either zero if the overland flow is not present or is nonzero and directed from the overland into the canal if overland flow is present (Fig. 2.4-1e). Under this circumstance, the fluxes are given by

$$\mathbf{n}\cdot\left[\mathbf{q}E_i^m - \mathbf{D}h\cdot\nabla E_i^m\right]\Big|_{Bank\,2} = M_{E_i}^{os2} = S_2\left(E_i^m\right)^o \tag{2.8.12}$$

When the water surface in the canal is above the bank (Figs. 2.4-1f and 2.4-1g), the flow direction can be either from the overland into the canal or from the canal into the overland depending on the flow dynamics in the overland and in the canal. If the state variable is discontinuous, the fluxes are

$$\mathbf{n}\cdot\left[\mathbf{q}E_i^m - \mathbf{D}h\cdot\nabla E_i^m\right]\Big|_{Bank\,2} = M_{E_i}^{os2} = S_2\frac{1}{2}\left[\left(1+sign\left(S_2\right)\right)\left(E_i^m\right)^o + \left(1-sign\left(S_2\right)\right)\left(E_i^m\right)^c\right] \tag{2.8.13}$$

If the state variable is continuous, we impose the continuity of the state variable to yield the fluxes

$$\mathbf{n}\cdot\left[\mathbf{q}E_i^m - \mathbf{D}h\cdot\nabla E_i^m\right]\Big|_{Bank\,2} = M_{E_i}^{os2} \quad and \quad \left(E_i^m\right)^o\Big|_{Bank\,2} = \left(E_i^m\right)^c \tag{2.8.14}$$

In Equstions (2.8.12) through (2.8.14), $M_{E_i}^{os2}$ is the source of the kinetic variable E_i in the canal from the overland via bank *2* [M/t/L], which appeared in Eq. (2.5.44).

2.8.2 Coupling between Subsurface and Overland Transport

The coupling of overland and subsurface transport is through the exchange of dissolved species only. Sediments, particulate species, and precipitated species in the overland flow will not exchange with adsorbed/ion exchanged and precipitated species in the subsurface flow. If the concentrations of dissolved chemicals in overland water and subsurface water at the ground surface are discontinuous, the chemical flux is given by

$$\mathbf{n}\cdot\left[\mathbf{V}\rho_w C_i^w - \theta\mathbf{D}\cdot\nabla(\rho_w C_i^w)\right] = M_{C_i^{is}} = \frac{S_I}{2}\left[\left(1+sign(S_I)\right)\rho_w\left(C_i^w\right)^s + \left(1-sign(S_I)\right)\rho_w\left(C_i^w\right)^o\right] \quad \textbf{(2.8.15)}$$

where $\left(C_i^w\right)^o$ is the concentration of the *i*-th dissolved species in the overland water and $\left(C_i^w\right)^s$ is the concentration of the *i*-th dissolved species of subsurface water at the interface and $M_{C_i^{is}}$ is mass rate of the source of the *i*-th dissolved species in overland from subsurface media [M/t/L^2], which appeared in Eq. (2.6.31). If the concentrations are continuous, we impose the continuity of dissolved concentration to yield the fluxes

$$\mathbf{n}\cdot\left[\mathbf{V}\rho_i C_i^w - \theta\mathbf{D}\cdot\nabla(\rho_i C_i^w)\right] = M_{C_i^{is}} \text{ and } \left(C_i^w\right)^s\Big|_{\text{on the interface}} = \left(C_i^w\right)^o \quad \textbf{(2.8.16)}$$

The transforemation of the interfacial boundary conditions, Eq. (2.8.15) and (2.8.16), to those in terms of kinetic variables is not straightforward because the reaction networks for the subsurface and overland may not be identical. If every kinetic-variable in the subsurface corresponding to that in the overland contains the same dissolved aqueous species, then the transformation is straightforwd as

$$\mathbf{n}\cdot\left[\mathbf{V}E_i^w - \theta\mathbf{D}\cdot\nabla(E_i^w)\right] = M_{E_i^{is}} = \frac{S_I}{2}\left[\left(1+sign(S_I)\right)\left(E_i^w\right)^s + \left(1-sign(S_I)\right)\left(E_i^w\right)^o\right] \quad \textbf{(2.8.17)}$$

for the case when the state variables are discontinuous, and

$$\mathbf{n}\cdot\left[\mathbf{V}E_i^w - \theta\mathbf{D}\cdot\nabla(E_i^w)\right] = M_{E_i^{is}} \text{ and } \left(E_i^w\right)^s\Big|_{\text{on the interface}} = \left(E_i^w\right)^o \quad \textbf{(2.8.18)}$$

for the case when the state variables are continuous. In Equstions (2.8.17) and (2.8.18), $\left(E_i^w\right)^o$ is the concentration of the dissolved portion of *i*-th kinetic variables in the overland water and $\left(E_i^w\right)^s$ is the concentration of the dissolved portion of the *i*-th kinetic variable in subsurface water at the interface and $M_{E_i^{is}}$ is the mass rate of the source of the *i*-th kinetic variable in overland from subsurface media [M/t/L^2], which appeared in Eq. (2.6.46).

It should be kept in mind that $\left(E_i^w\right)^o$ and $\left(E_i^w\right)^s$ (and as a matter of fact $\left(E_i^w\right)$) must have the same dissolved species content for Equations (2.8.17) and (2.8.18) to be valid. Otherwise, the coupling in terms of kinetic-variables requires further elaborations that will be addressed in Section 2.8.4.

2.8.3 Coupling between Subsurface and River/Stream/Canal Transport

Similar to the coupling between subsurface and overland, the transport between subsurface and canal is coupled and the fluxes between two media depend on if the dissolved concentration is continuous or not. For the case of discontinuous chemical concentration, the flux is given by

$$\mathbf{n}\cdot\left(\mathbf{V}\,\rho_w C_i^{\,w}-\theta\mathbf{D}\cdot\nabla\rho_w C_i^{\,w}\right)=\frac{\mathbf{n}\bullet\mathbf{V}}{2}\left(\left(1+sign\left(\mathbf{n}\bullet\mathbf{V}\right)\right)\rho_w\left(C_i^{\,w}\right)^s+\left(1-sign\left(\mathbf{n}\bullet\mathbf{V}\right)\right)\rho_w\left(C_i^{\,w}\right)^c\right)$$
$$M_{C_i}^{\,is}=\int_P\frac{\mathbf{n}\bullet\mathbf{V}}{2}\left(\left(1+sign\left(\mathbf{n}\bullet\mathbf{V}\right)\right)\rho_w\left(C_i^{\,w}\right)^s+\left(1-sign\left(\mathbf{n}\bullet\mathbf{V}\right)\right)\rho_w\left(C_i^{\,w}\right)^c\right)dP \qquad \textbf{(2.8.19)}$$

where $\left(C_i^{\,w}\right)^s$ and $\left(C_i^{\,w}\right)^c$ are the concentrations of the i-th dissolved species in the subsurface and canal waters. If the concentration is continuous, we impose its continuity to yield the flux

$$\int_P\mathbf{n}\cdot\left(\mathbf{V}\,\rho_w C_i^{\,w}-\theta\mathbf{D}\cdot\nabla(\rho_w C_i^{\,w})\right)dP=M_{C_i}^{\,is}\quad and\quad\left(C_i^{\,w}\right)^s\Big|_{\text{on the interface}}=\left(C_i^{\,w}\right)^c \qquad \textbf{(2.8.20)}$$

where $M_{C_i^{is}}$ is mass rate of the source of the *i*-th dissolved species in canal from subsurface media [M/t/L].

Similar to the coupling between subsurface and overland flows, the transforemation of the interfacial boundary conditions, Eq. (2.8.19) and (2.8.20), to those in terms of kinetic variables is not straightforward because the reaction networks for the subsurface and river/stream newtworks may not be identical. If every kinetic-variable in the subsurface corresponding to that in the river/stream contains the same dissolved aqueous species, then the transformation is straightforwd and is given in Eqs. (2.8.21) and (2.8.22), respectively, for the cases of discontinuity and conctinuity, respectively, in species concentrations,

$$\mathbf{n}\cdot\left(\mathbf{V}\,E_i^w-\theta\mathbf{D}\cdot\nabla E_i^w\right)=\frac{\mathbf{n}\bullet\mathbf{V}}{2}\left(\left(1+sign\left(\mathbf{n}\bullet\mathbf{V}\right)\right)\left(E_i^w\right)^s+\left(1-sign\left(\mathbf{n}\bullet\mathbf{V}\right)\right)\left(E_i^w\right)^c\right)$$
$$M_{E_i}^{\,is}=\int_P\frac{\mathbf{n}\bullet\mathbf{V}}{2}\left(\left(1+sign\left(\mathbf{n}\bullet\mathbf{V}\right)\right)\left(E_i^w\right)^s+\left(1-sign\left(\mathbf{n}\bullet\mathbf{V}\right)\right)\left(E_i^w\right)^c\right)dP \qquad \textbf{(2.8.21)}$$

and

$$\int_P\mathbf{n}\cdot\left(\mathbf{V}E_i^w-\theta\mathbf{D}\cdot\nabla(E_i^w)\right)dP=M_{E_i}^{\,is}\quad and\quad\left(E_i^w\right)^s\Big|_{\text{on the interface}}=\left(E_i^{\,w}\right)^c \qquad \textbf{(2.8.22)}$$

where $\left(E_i^{\,w}\right)^s$ and $\left(E_i^{\,w}\right)^c$ are the concentration of the dissolved portion of *i*-th kinetic variables in the subsurface and canal.

It should be kept in mind that $\left(E_i^{\,w}\right)^c$ and $\left(E_i^{\,w}\right)^s$ (and as a matter of fact $\left(E_i^{\,w}\right)$) must have the same content of dissolved species for Equations (2.8.21) and (2.8.22) to be valid. Otherwise, the coupling in terms of kinetic-variables requires further elaborations that will be addressed in Section 2.8.4.

2.8.4 Coupling of Reactive Transport between Groundwater and Surface Transport

Since reaction networks for groundwater and surface waters (in overland and river/stream flows) are likely to be different, the continuity of species fluxes and the continuity of species concentration or

the formulation of species fluxes must be transformed from those in terms of species concentration to those in terms of kinetic variables.

After decomposition of reaction networks, kinetic-variables and their corresponding dissolved portion are simply defined as linear combination of species

$$\{\mathbf{E}\}_g = [\mathbf{A}]_g \{\mathbf{C}\}_g, \quad \{\mathbf{E}^w\}_g = [\mathbf{B}]_g \{\mathbf{C}\}_g \qquad \textit{and} \qquad \{\mathbf{E}\}_s = [\mathbf{A}]_s \{\mathbf{C}\}_s, \quad \{\mathbf{E}^w\}_s = [\mathbf{B}]_s \{\mathbf{C}\}_s \tag{2.8.23}$$

where the subscript *g* denotes the groundwater system; the subscript *s* denote the surface water system; $\{\mathbf{E}\}$ and $\{\mathbf{E}^{\mathbf{w}}\}$ are the vectors of size *M*; and $[\mathbf{A}]$ and $[\mathbf{B}]$ are the decomposed unit matrices of size *M* x *M*. It is noted that the *i*-th reaction extent, E_i, is an equilibrium variable if its evolution is governed by an indepdendnt equilibrium raeaction and a set of linearly depending kinetic reactions; a kinetic variable if by an independent kinetic reaction and a set of linearly dependent kinetic reactions; a component if its concentration remains constant (Fang et al., 2003). Inverting Eq. (2.8.23), we have

$$\{\mathbf{C}\}_g = [\mathbf{A}]_g^{-1} \{\mathbf{E}\}_g \qquad \textit{and} \qquad \{\mathbf{C}\}_s = [\mathbf{A}]_s^{-1} \{\mathbf{E}\}_s \tag{2.8.24}$$

Continuity of flux of all aqueous requires

$$\begin{aligned} &\mathbf{n} \cdot \left(\mathbf{V} \{\mathbf{E}^w\}_g - \theta \mathbf{D} \cdot \nabla \{\mathbf{E}^w\}_g \right) = \mathbf{n} \cdot \left(\mathbf{V} [\mathbf{B}]_g \{\mathbf{C}^w\}_g - \theta \mathbf{D} \cdot \nabla [\mathbf{B}]_g \{\mathbf{C}^w\}_g \right), \\ &\textit{thus} \qquad \mathbf{n} \cdot \left(\mathbf{V} \{\mathbf{E}^w\}_g - \theta \mathbf{D} \cdot \nabla \{\mathbf{E}^w\}_g \right) = \mathbf{n} \cdot \left(\mathbf{V} [\mathbf{B}]_g \{\mathbf{C}^w\}_s - \theta \mathbf{D} \cdot \nabla [\mathbf{B}]_g \{\mathbf{C}^w\}_s \right) \\ &\qquad\qquad = \mathbf{n} \cdot \left(\mathbf{V} [\mathbf{B}]_g [\mathbf{A}]_s^{-1} \{\mathbf{E}\}_s - \theta \mathbf{D} \cdot \nabla [\mathbf{B}]_g [\mathbf{A}]_s^{-1} \{\mathbf{E}\}_s \right) \end{aligned} \tag{2.8.25}$$

Continuity of aqueous speces require

$$\{\mathbf{E}^w\}_g = [\mathbf{B}]_g \{\mathbf{C}^w\}_g = [\mathbf{B}]_g \{\mathbf{C}^w\}_s = [\mathbf{B}]_g [\mathbf{A}]_s^{-1} \{\mathbf{E}\}_s \tag{2.8.26}$$