

## 1.0 INTRODUCTION

This document is the users' guide for the Coupled Model of **HYDRO**logic Transport and Mixed **BIOGEOCHEM**ical Reactions in Saturated-Unsaturated Media (HYDROBIOGEOCHEM). This code is a modification of HYDROGEOCHEM2.0 (Yeh and Salvage, 1995), a general purpose computer program written in FORTRAN 77 which is designed to solve coupled hydrologic transport and mixed kinetic and equilibrium geochemical reaction problems. The modification includes replacement of the KEMOD chemical reaction subroutines by a mixed micro**BIO**logical and chemical Kinetic and Equilibrium MODEl (BIOKEMOD) to deal with species whose concentrations are affected by microbiological and/or geochemical reactions.

This document is intended to assist modelers in using this code for site-specific applications.

- Chapter 2.0 derives the governing equations and initial and boundary conditions solved by HYDROBIOGEOCHEM.
- Chapter 3.0 details the numerical method used in solving the equations for transport and for mixed biogeochemical kinetic and equilibrium reactions.
- Chapter 4.0 describes the program structure of HYDROBIOGEOCHEM. It is intended to assist users in modifying or extending the code to better meet their needs.
- Chapter 5.0 describes the program's storage and memory requirements and relates it via the parameter statements to the problem size (the finite-element grid size as well as the number of chemical and microbial species). The chapter also describes the input-output format and specifications of HYDROBIOGEOCHEM.
- Chapter 6.0 provides sample problems demonstrating use of the program.
- Appendix A contains a complete description of all the problem-specific input necessary for running a simulation.
- APPENDIX B contains example problem input and output files on floppy disk.
- APPENDIX C contains FORTRAN 77 Source Program on floppy disk.

The program must be run with a consistent set of units. Units of mass (M), length (L), and time (T) are indicated in the input description in Appendix A. The unit of length should be decimeter (dm). The unit of mass for any chemical species should be mole and for any other parameter should be kilogram (kg). The concentration unit of all individual species (aqueous, sorbed, and precipitated species) is mole/mass of phase (mol/kg); the corresponding unit for the sorption distribution coefficient is  $\text{dm}^3/\text{kg}$  (= ml/g). The ion-exchange capacity is in equivalents/mass of

solid. The units of concentration for total concentrations of components is mole/unit total volume ( $\text{mol}/\text{dm}^3$ ). Any units of time may be used as long as the same unit is used consistently throughout the input file.

HYDROBIOGEOCHEM is a flexible and comprehensive package. It is designed to:

- Treat heterogeneous and anisotropic media.
- Consider spatially and temporally distributed sources/sinks as well as point sources/sinks.
- Accept the prescribed initial conditions or obtain initial conditions by simulating the steady-state version of the system under consideration.
- Deal with prescribed transient concentrations distributed over a Dirichlet boundary.
- Handle time-dependent fluxes over variable boundaries.
- Include the off-diagonal dispersion coefficient tensor components in the governing equation for dealing with cases in which the coordinate system does not coincide with the principal directions of the dispersion coefficient tensor.
- Provide two options for treating the mass matrix (consistent and lumping).
- Give three options for estimating the nonlinear matrix (exact relaxation, under-relaxation, and over-relaxation).
- Include six options for solving the linearized matrix equations (direct solution with Gaussian elimination method, successive point iterations, and four preconditioned conjugate gradient methods).
- Include both quadrilateral and triangular elements to facilitate the discretization of the region.
- Include chemical processes of aqueous complexation, precipitation/dissolution, adsorption, ion-exchange, redox, and acid-base reactions.
- Handle multiple adsorption sites and multiple ion-exchange sites.
- Include colloid transport.
- Include microbial processes affecting chemical species concentrations as well as microbial growth and decay.

### Limitations and Future Plans

There are some limitations in HYDROBIOGEOCHEM. Further development of the model to address these limitations may be warranted. These include:

- Inability to simulate co-precipitation (solid solution).
- The need to import hydrologic variables of flow velocity, moisture content, and pressure head generated by a subsurface flow model.
- The assumption of isothermal conditions.
- Applications limited to two-dimensional problems.
- Applications limited to single-fluid phase flows.

## 2.0 MATHEMATICAL FORMULATION

Hydrologic variables, including the Darcy's velocity, moisture content, and pressure head, are necessary in determining the transport of solutes through saturated-unsaturated subsurface systems. These hydrological variables can be specified by the user as described in the User's Guide (Data Set 16 in Appendix A) or a numerical model can be used to solve the saturated-unsaturated flow problem prior to simulation of solute transport with the HYDROBIOGEOCHEM code. A finite-element model has been constructed to achieve this purpose (Yeh, 1987). The relevant governing equations for saturated-unsaturated flow problems are briefly stated below.

### 2.1 Flow Equations

The derivation of the governing equations for flow through saturated-unsaturated media can be derived based on (Yeh and Ward, 1980; Yeh, 1987):

- Continuity of fluid.
- Continuity of solid.
- Motion of fluid (Darcy's law).
- Consolidation of the media.
- Compressibility of water.

Neglecting the compressibility of the media and water, we can write these equations as

$$\frac{\partial \rho_\ell \theta}{\partial t} = - \nabla \cdot (\rho_\ell \theta \mathbf{V}_{fs}) + \rho^* Q \quad , \quad (2.1.1)$$

$$\theta \mathbf{V}_{fs} = -\mathbf{K} \cdot \left( \frac{\rho_0}{\rho_\ell} \nabla h + \nabla z \right) \quad , \quad (2.1.2)$$

where

$$\mathbf{V}_f = \mathbf{V}_{fs} + \mathbf{V}_s \quad , \quad (2.1.3)$$

$$\mathbf{V} = \theta (\mathbf{V}_f - \mathbf{V}_s) = \theta \mathbf{V}_{fs} \quad . \quad (2.1.4)$$

where

- $\theta$  = moisture content ( $L^3/L^3$ ).
- $\rho_\ell$  = density of the liquid phase (M of liquid/ $L^3$  of liquid).
- $\rho_0$  = reference density = density of pure water at STP (M of liquid/ $L^3$  of liquid).
- $t$  = time (T).
- $\mathbf{V}_{fs}$  = fluid velocity relative to the solid (L/T).
- $\mathbf{V}_f$  = fluid velocity (L/T).
- $\mathbf{V}_s$  = solid velocity (L/T).
- $\mathbf{V}$  = Darcy's velocity (specific discharge) (L/T).

<b>K</b>	= hydraulic conductivity tensor (L/T).
<b>Q</b>	= source or sink representing the artificial injection or withdrawal of water, volume of water per volume of porous media per time [(L <sup>3</sup> /L <sup>3</sup> )/T].
<b>ρ*</b>	= density of source/sink liquid, (M of liquid/L <sup>3</sup> of liquid) = ρ <sub>ℓ</sub> if sink or withdrawal (negative Q), or = ρ <sub>in</sub> if source or injection (positive Q).
<b>h</b>	= pressure head (L).
<b>z</b>	= potential head (L).

Equations (2.1.1) through (2.1.4) and the constitutive relationships among the pressure head, moisture content, and the hydraulic conductivity tensor, together with appropriate initial conditions and boundary conditions, can be used to compute the temporal-spatial distributions of the hydrological variables, including pressure head, total head, moisture content, and Darcy's velocity. Equations (2.1.1) through (2.1.4) are provided in this report because they are needed for deriving the advective form of the hydrological transport equations in the next section.

## 2.2 Hydrological Transport Equations

Two of the most frequently mentioned terms in chemical transport modeling are components and species. Definitions of these terms used in this document loosely follow those of Westall et al. (1976). Components are a set of linearly independent "basis" chemical entities through which every species can be uniquely represented as a linear combination. A component cannot be represented as a linear combination of components other than itself. For example, in a simple system containing water, carbon, and calcium, we can choose Ca<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, and H<sup>+</sup> as the components, and all other species can be considered the products of these three chemical components: Ca<sup>2+</sup> cannot be represented as a product of CO<sub>3</sub><sup>2-</sup> and H<sup>+</sup>, CO<sub>3</sub><sup>2-</sup> cannot be represented as a combination of Ca<sup>2+</sup> and H<sup>+</sup>, and H<sup>+</sup> cannot be represented as a product of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>. In addition, we require that the global mass of a component be chemical reaction invariant (Rubin, 1983). A chemical species is the product of a chemical reaction involving the components as reactants (Westall et al., 1976). For example, in the above simple system the species HCO<sub>3</sub><sup>-</sup> is the product of H<sup>+</sup> and CO<sub>3</sub><sup>2-</sup>.

Let us consider a system of N chemical components and M<sub>B</sub> microbial species. In HYDROBIOGEOCHEM, the N chemical components include N<sub>a</sub> aqueous components (mobile components), N<sub>s</sub> adsorbent components (immobile adsorbent sites), and NSITE immobile ion-exchange sites. The N<sub>a</sub> aqueous components will react with each other to form M<sub>x</sub> aqueous complexed species and M<sub>p</sub> precipitated species. In addition, each aqueous component has a species that is not bound with other components. This "free" species is termed the aqueous component species. The total number of aqueous species, M<sub>c</sub>, is the sum of N<sub>a</sub> aqueous component species and M<sub>x</sub> complexed species. The N<sub>a</sub> aqueous components and N<sub>s</sub> adsorbent components will react to form M<sub>y</sub> adsorbed species for the case of sorption via surface complexation (adsorption). Each adsorbent component has a species that is not bound with other components. This "free" species is termed the adsorbent component species. In addition, M<sub>z</sub> of N<sub>a</sub> aqueous component species and M<sub>x</sub> complexed species may compete with each other for the

ion-exchange sites. The total number of sorbent species,  $M_s$ , is the sum of  $N_s$  adsorbent component species,  $M_y$  adsorbed species, and  $M_z$  ion-exchanged species. The total number of chemical species,  $M$ , is equal to the sum of  $M_c$ ,  $M_s$ , and  $M_p$ . For the purpose of deriving the chemical transport equations, we assume that the aqueous component species and complexed species are subject to hydrological transport, whereas the precipitated species, adsorbent component species, adsorbed species, and ion-exchanged species are not subject to hydrological transport. Table 2.1 summarizes the relations among chemical components and species considered in HYDROBIOGEOCHEM.

Microorganisms can exist in both the aqueous and adsorbed phases. The  $M_B$  microbial species consist of  $M_b$  aqueous phase species and  $M_a$  adsorbed phase species. We assume that the aqueous microbial species are subject to hydrological transport, whereas the adsorbed microbial species are not subject to hydrological transport. A phase transfer reaction may be specified, allowing for the simulation of the attachment and detachment of microorganisms from the porous media. In HYDROBIOGEOCHEM, the term “microbial species” may refer to either an individual type of organism or a consortia of organisms. The parameters chosen to describe the microbiological reactions must be specified accordingly.

The general transport equation governing the temporal-spatial distribution of any chemical species in a multicomponent system can be derived on the basis of the principle of balance of mass. Let  $c_j$  be the concentration of the  $j$ -th aqueous component species. The governing equation for  $c_j$  can be obtained by applying this principle in integral form as follows:

$$\begin{aligned} \frac{D}{Dt} \int_v \theta \rho_\ell c_j \, dv &= - \int_\Gamma \mathbf{n} \cdot (\theta \rho_\ell c_j) \mathbf{V}_{fs} \, d\Gamma - \int_\Gamma \mathbf{n} \cdot \mathbf{J}_j \, d\Gamma + \int_v \theta \rho_\ell r_j^c \, dv \\ &\quad - \int_v \theta \rho_\ell i_j^c \, dv + \int_v m_j^c \, dv \quad , \quad j \in N_a \quad , \end{aligned} \quad (2.2.1)$$

where

$v$  = material volume containing constant amount of media ( $L^3$ ).

$c_j$  = concentration of the  $j$ -th aqueous component species (M/M of liquid).

$\Gamma$  = surface enclosing the material volume  $v$  ( $L^2$ ).

$\mathbf{n}$  = outward unit vector normal to the surface  $\Gamma$ .

$\mathbf{J}_j$  =  $\rho_\ell \theta c_j (\mathbf{V}_j - \mathbf{V}_f)$  is the surface flux of the  $j$ -th aqueous component species with respect to fluid velocity  $\mathbf{V}_f$  [ $(M/T)/L^2$ ].

$r_j^c$  = production rate of the  $j$ -th aqueous component species per unit fluid mass due to all chemical and microbial reactions [ $(M/M \text{ of liquid})/T$ ].



Table 2.1 Chemical Components and Species Considered in HYDROBIOGEOCHEM

	Components													Charge $v$
	Aqueous						Adsorbed							
	1	2	...	j	...	$N_a$	1	2	...	j	...	$N_s$		
Concentrations	1	2	...	j	...	$N_a$	1	2	...	j	...	$N_s$		
Aqueous Components	$c_1$	1	0	...	0	...	0	0	0	...	0	...	0	$v_1^a$
	$c_2$	0	1	...	0	...	0	0	0	...	0	...	0	$v_2^a$
	.													
	$c_j$	0	0	...	1	...	0	0	0	...	0	...	0	$v_j^a$
	.													
$N_a$	0	0	...	0	...	1	0	0	0	...	0	...	0	$N_a$
Adsorbent Components	$s_1$	0	0	...	0	...	0	1	0	...	0	...	0	$v_2^s$
	$s_2$	0	0	...	0	...	0	0	1	...	0	...	0	$v_1^s$
	.													
	$s_j$	0	0	...	0	...	0	0	0	...	1	...	0	$v_j^s$
	.													
$N_s$	0	0	...	0	...	0	0	0	0	...	0	...	1	$v_{N_s}^-$



Table 2.1 Components and Species Considered in HYDROBIOGEOCHEM (Concluded)

		Components										Charge		
		Aqueous					Adsorbed							
Concentrations		1	2	...	j	...	N <sub>a</sub>	1	2	...	j	...	N <sub>s</sub>	v
Complexed Species	X <sub>1</sub>	a <sub>11</sub> <sup>x</sup>	a <sub>12</sub> <sup>x</sup>	...	a <sub>1j</sub> <sup>x</sup>	...	a <sub>IN<sub>a</sub></sub> <sup>x</sup>	0	0	...	0	...	0	v <sub>1</sub> <sup>x</sup>
	X <sub>2</sub>	a <sub>21</sub> <sup>x</sup>	a <sub>22</sub> <sup>x</sup>	...	a <sub>2j</sub> <sup>x</sup>	...		0	0	...	0	...	0	v <sub>2</sub> <sup>x</sup>
	.						a <sub>2N<sub>a</sub></sub> <sup>x</sup>	0	0	...	0	...	0	v <sub>1</sub> <sup>x</sup>
	M <sub>x</sub>	a <sub>11</sub> <sup>x</sup>	a <sub>12</sub> <sup>x</sup>	...	a <sub>1j</sub> <sup>x</sup>	...	a <sub>IN<sub>a</sub></sub> <sup>x</sup>	0	0	...	0	...	0	v <sub>1</sub> <sup>x</sup>
	.							0	0	...	0	...	0	m <sub>x</sub>
Adsorbed Species	Y <sub>1</sub>	a <sub>11</sub> <sup>y</sup>	a <sub>12</sub> <sup>y</sup>	...	a <sub>1j</sub> <sup>y</sup>	...	a <sub>IN<sub>a</sub></sub> <sup>y</sup>	a <sub>1(Na+1)</sub> <sup>y</sup>	a <sub>1(Na+2)</sub> <sup>y</sup>	...	a <sub>1(Na+i)</sub> <sup>y</sup>	...	a <sub>1(Na+Ns)</sub> <sup>y</sup>	v <sub>1</sub> <sup>y</sup>
	Y <sub>2</sub>	a <sub>21</sub> <sup>y</sup>	a <sub>22</sub> <sup>y</sup>	...	a <sub>2j</sub> <sup>y</sup>	...	a <sub>2N<sub>a</sub></sub> <sup>y</sup>	a <sub>2(Na+1)</sub> <sup>y</sup>	a <sub>2(Na+2)</sub> <sup>y</sup>	...	a <sub>2(Na+i)</sub> <sup>y</sup>	...	a <sub>2(Na+Ns)</sub> <sup>y</sup>	v <sub>2</sub> <sup>y</sup>
	.							a <sub>i(Na+1)</sub> <sup>y</sup>	a <sub>i(Na+2)</sub> <sup>y</sup>	...	a <sub>i(Na+i)</sub> <sup>y</sup>	...	a <sub>i(Na+Ns)</sub> <sup>y</sup>	v <sub>1</sub> <sup>y</sup>
	M <sub>y</sub>	a <sub>11</sub> <sup>y</sup>	a <sub>12</sub> <sup>y</sup>	...	a <sub>1j</sub> <sup>y</sup>	...	a <sub>IN<sub>a</sub></sub> <sup>y</sup>	a <sub>i(Na+1)</sub> <sup>y</sup>	a <sub>i(Na+2)</sub> <sup>y</sup>	...	a <sub>i(Na+i)</sub> <sup>y</sup>	...	a <sub>i(Na+Ns)</sub> <sup>y</sup>	v <sub>1</sub> <sup>y</sup>
	.							a <sub>M<sub>-</sub>(Na+1)</sub> <sup>y</sup>	a <sub>M<sub>-</sub>(Na+2)</sub> <sup>y</sup>	...	a <sub>M<sub>-</sub>(Na+i)</sub> <sup>y</sup>	...	a <sub>M<sub>-</sub>(Na+Ns)</sub> <sup>y</sup>	v' <sub>M<sub>y</sub></sub>
Ion-Exchange Species	Z <sub>1</sub>	a <sub>11</sub> <sup>z</sup>	a <sub>12</sub> <sup>z</sup>	...	a <sub>1j</sub> <sup>z</sup>	...	a <sub>IN<sub>a</sub></sub> <sup>z</sup>	0	0	...	0	...	0	v <sub>1</sub> <sup>z</sup>
	Z <sub>2</sub>	a <sub>21</sub> <sup>z</sup>	a <sub>22</sub> <sup>z</sup>	...	a <sub>2j</sub> <sup>z</sup>	...	a <sub>2N<sub>a</sub></sub> <sup>z</sup>	0	0	...	0	...	0	v <sub>2</sub> <sup>z</sup>
	.							0	0	...	0	...	0	v <sub>1</sub> <sup>z</sup>
	M <sub>z</sub>	a <sub>11</sub> <sup>z</sup>	a <sub>12</sub> <sup>z</sup>	...	a <sub>1j</sub> <sup>z</sup>	...	a <sub>IN<sub>a</sub></sub> <sup>z</sup>	0	0	...	0	...	0	v <sub>1</sub> <sup>z</sup>
	.							0	0	...	0	...	0	v <sub>M<sub>z</sub></sub> <sup>-</sup>

		Components												
		Aqueous					Adsorbed					Charge		
		1	2	...	j	...	$N_a$	1	2	...	j	...	$N_s$	v
Precipitated Species	$p_1$	$a_{11}^p$	$a_{12}^p$	...	$a_{1j}^p$	...	$a_{1N_a}^r$	0	0	...	0	...	0	$v_1^p$
	$p_2$	$a_{21}^p$	$a_{22}^p$	...	$a_{2j}^p$	...	$a_{2N_a}^r$	0	0	...	0	...	0	$v_2^p$
	⋮													
	$p_i$	$a_{i1}^p$	$a_{i2}^p$	...	$a_{ij}^p$	...	$a_{iN_a}^r$	0	0	...	0	...	0	$v_i^p$
Total	$P_{M_p}$	$a_{M_p 1}^r$	$a_{M_p 2}^r$	...	$a_{M_p j}^r$	...	$a_{M_p N_a}^r$	0	0	...	0	...	0	$v_{M_p}^r$
	Concentrations	$T_1$	$T_2$	...	$T_j$	...	$T_{N_a}$	$W_1$	$W_2$	...	$W_j$	...	$W_{N_s}$	

$\nu_j^c$  = rate of decay of the j-th aqueous component species [(M/M of liquid)/T].

$m_j^c$  = external source/sink rate of the j-th aqueous component species per unit volume of media [(M/L<sup>3</sup>)/T].

$N_a$  = number of aqueous component species.

By the Reynolds transport theorem (Owczarek, 1964), Equation (2.2.1) can be written as

$$\int_v \frac{\partial \theta \rho_\ell c_j}{\partial t} dv + \int_\Gamma \mathbf{n} \cdot (\theta \rho_\ell c_j \mathbf{V}_f) d\Gamma + \int_\Gamma \mathbf{n} \cdot \mathbf{J}_j d\Gamma = \int_v \theta \rho_\ell r_j^c dv - \int_v \theta \rho_\ell \nu_j^c dv + \int_v m_j^c dv, \quad j \in N_a \quad (2.2.2)$$

Applying the Gaussian divergence theorem to Equation (2.2.2) and using the fact that  $v$  is arbitrary, one can obtain the following continuity equation for the j-th aqueous component species:

$$\frac{\partial \theta \rho_\ell c_j}{\partial t} + \nabla \cdot (\theta \rho_\ell c_j \mathbf{V}_f) + \nabla \cdot \mathbf{J}_j = \theta \rho_\ell (r_j^c - \nu_j^c) + m_j^c, \quad j \in N_a. \quad (2.2.3)$$

The surface flux  $\mathbf{J}_j$  has been postulated to be proportional to the gradient of  $c_j$  as (Nguyen et al., 1982)

$$\mathbf{J}_j = -\rho_\ell \theta \mathbf{D} \cdot \nabla c_j, \quad j \in N_a \quad (2.2.4)$$

and

$$\theta \mathbf{D} = a_T |\mathbf{V}| \delta + (a_L - a_T) \frac{\mathbf{V} \mathbf{V}}{|\mathbf{V}|} + a_m \theta \tau \delta, \quad (2.2.5)$$

where

$a_T$  = transverse diffusivity (L).

$\delta$  = Kronecker delta tensor.

$|\mathbf{V}|$  = magnitude of the Darcy velocity  $\mathbf{V}$  (L/T).

$a_L$  = longitudinal diffusivity (L).

$a_m$  = molecular diffusion coefficient (L<sup>2</sup>/T).

$\tau$  = tortuosity.  
 $\mathbf{D}$  = dispersion coefficient tensor, (L<sup>2</sup>/T)

Substitution of Equations (2.1.3), (2.2.4), and (2.2.5) into Equation (2.2.3) and assuming vertical deformation only yields

$$\frac{\partial \rho_\ell \theta c_j}{\partial t} + \nabla \cdot (\rho_\ell \theta c_j \mathbf{V}_{fs}) - \nabla \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla c_j) = \rho_\ell \theta (r_j^c - \iota_j^c) - \rho_\ell \theta c_j \left( \alpha \frac{\partial p}{\partial t} \right) + m_j^c \quad (2.2.6)$$

$$j \in \mathbf{N}_a \text{ .}$$

where

$\alpha$  = compressibility of the media, (L T<sup>2</sup> /M).  
 $p$  = pressure, (M/L T<sup>2</sup>).

Equation (2.2.6) is simply the statement of mass balance over a differential volume. The first term represents the rate of mass accumulation, the second term represents the net rate of mass flux due to advection, the third term is the net mass flux due to dispersion and diffusion, the fourth term is the rate of mass production and reduction due to biogeochemical reactions and radioactive decay, the fifth term is the change in concentration due to compressibility of the media and the last term is for sources/sinks corresponding to artificial injection and/or withdrawal.

Since any aqueous complexed product species is subject to the same hydrological transport mechanism as the aqueous component species, its governing transport equation would be identical in form to Equation (2.2.6). If we let  $x_i$  denote the concentration of the  $i$ -th aqueous complexed species, we have the following transport equation:

$$\frac{\partial \rho_\ell \theta x_i}{\partial t} + \nabla \cdot (\rho_\ell \theta x_i \mathbf{V}_{fs}) - \nabla \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla x_i) = \rho_\ell \theta (r_i^x - \iota_i^x) - \rho_\ell \theta x_i \left( \alpha \frac{\partial p}{\partial t} \right) + m_i^x \quad (2.2.7)$$

$$i \in \mathbf{M}_x \text{ .}$$

where

$x_i$  = concentration of the  $i$ -th aqueous complexed species (M/M of liquid).

$r_i^x$  = production rate of i-th complexed species per unit fluid mass due to all microbial and chemical reactions [(M/M of liquid)/T].

$\iota_i^x$  = rate of decay of the i-th complexed species per unit fluid mass [(M/M of liquid)/T].

$m_i^x$  = external source/sink rate of the i-th complexed species per unit medium volume [(M/L<sup>3</sup>)/T].

Similarly, microorganisms which exist in the aqueous phase are subject to the same hydrological transport mechanism as the aqueous chemical species. The governing transport equation for aqueous microbial species is therefore identical in form to Equation (2.2.6). Letting  $b_i$  denote the concentration of the i-th aqueous microbial species, we have the following transport equation:

$$\frac{\partial \rho_\ell \theta b_i}{\partial t} + \nabla \cdot (\rho_\ell \theta b_i \mathbf{V}_{fs}) - \nabla \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla b_i) = \rho_\ell \theta (r_i^b - \iota_i^b) - \rho_\ell \theta b_i \left( \alpha \frac{\partial p}{\partial t} \right) + m_i^b \quad (2.2.8)$$

$i \in \mathbf{M}_b$  .

where

$b_i$  = concentration of the j-th aqueous microbial species (M/M of liquid).

$r_i^b$  = production rate of i-th aqueous microbial species per unit fluid mass due to all microbial reactions [(M/M of liquid)/T].

$\iota_i^b$  = rate of decay of the i-th microbial species per unit fluid mass [(M/M of liquid)/T].

$m_i^b$  = external source/sink rate of the i-th microbial species per unit medium volume [(M/L<sup>3</sup>)/T].

Because it is assumed that adsorbent component species are not subject to hydrological transport, their transport equations (or more precisely the mass balance equations for these species) can be obtained by dropping the second and third terms on the left-hand side of Equation (2.2.6) and replacing  $(\rho_\ell \theta c_j)$  with  $(\rho_b s_j)$ :

$$\frac{\partial \rho_b s_j}{\partial t} = \rho_b (r_j^s - \iota_j^s) - \left( \alpha \frac{\partial p}{\partial t} \right) \rho_b s_j + m_j^s, \quad j \in N_s. \quad (2.2.9)$$

where

$\rho_b$  = bulk density of the porous medium, mass of solid per unit medium volume (M of solid/L<sup>3</sup>).

$s_j$  = concentration of the j-th adsorbent component (M/M of solid).

$r_j^s$  = production rate of the j-th adsorbent component species per unit solid mass due to all chemical and microbial reactions [(M/M of solid)/T].

$m_j^s$  = external source/sink rate of the j-th adsorbent component species per unit medium volume [(M/L<sup>3</sup>)/T].

$\iota_j^s$  = rate of decay of the j-th adsorbent component species per unit solid mass [(M/M of solid)/T].

Similarly, it is assumed that adsorbed chemical and microbial species, ion-exchanged species, and precipitated species are not subject to hydrological transport, so the mass balance equations for these species are identical in form to Equation (2.2.9):

$$\frac{\partial \rho_b y_i}{\partial t} = \rho_b (r_i^y - \iota_i^y) - \left( \alpha \frac{\partial p}{\partial t} \right) \rho_b y_i + m_i^y, \quad i \in M_y. \quad (2.2.10)$$

$$\frac{\partial \rho_b z_i}{\partial t} = \rho_b (r_i^z - \iota_i^z) - \left( \alpha \frac{\partial p}{\partial t} \right) \rho_b z_i + m_i^z, \quad i \in M_z. \quad (2.2.11)$$

$$\frac{\partial \rho_b p_i}{\partial t} = \rho_b (r_i^p - \iota_i^p) - \left( \alpha \frac{\partial p}{\partial t} \right) \rho_b p_i + m_i^p, \quad i \in M_p. \quad (2.2.12)$$

and

$$\frac{\partial \rho_b a_i}{\partial t} = \rho_b (r_i^a - \iota_i^a) - \left( \alpha \frac{\partial p}{\partial t} \right) \rho_b a_i + m_i^a, \quad i \in M_a. \quad (2.2.13)$$

where

$r_i^y$  = production rate of the i-th adsorbed species per unit mass of solid due to all chemical and microbial reactions [(M/M of solid)/T].

$m_i^y$  = external source/sink rate of the i-th adsorbed species per unit medium volume [(M/L<sup>3</sup>)/T].

$\nu_i^y$  = rate of decay of the i-th adsorbed species per unit mass of solid [(M/M of solid)/T].

$r_i^z$  = production rate of the i-th ion-exchanged species per unit mass of solid due to all chemical and microbial reactions [(M/M of solid)/T].

$m_i^z$  = external source/sink rate of the i-th ion-exchanged species per unit medium volume [(M/L<sup>3</sup>)/T].

$\nu_i^z$  = rate of decay of the i-th ion-exchanged species per unit mass of solid [(M/M of solid)/T].

$r_i^p$  = production rate of the i-th precipitated species per unit mass of solid due to all chemical and microbial reactions [(M/M of solid)/T].

$m_i^p$  = external source/sink rate of the i-th precipitated species per unit medium volume [(M/L<sup>3</sup>)/T].

$\nu_i^p$  = rate of decay of the i-th precipitated species per unit mass of solid [(M/M of solid)/T].

$r_i^a$  = production rate of the i-th adsorbed microbial species per unit mass of solid due to all microbial reactions [(M/M of solid)/T].

$m_i^a$  = external source/sink rate of the i-th adsorbed microbial species per unit medium volume [(M/L<sup>3</sup>)/T].

$\nu_i^a$  = rate of decay of the i-th adsorbed microbial species per unit mass of solid [(M/M of solid)/T].

Equations (2.2.6) through (2.2.13) constitute eight sets of equations for eight sets of unknowns:  $c_j$ ,  $x_i$ ,  $b_i$ ,  $s_j$ ,  $y_i$ ,  $z_i$ ,  $p_i$ , and  $a_i$ . These equations form a closed system if the biogeochemical production rates  $r_j^c$ ,  $r_i^x$ ,  $r_j^b$ ,  $r_j^s$ ,  $r_i^y$ ,  $r_i^z$ ,  $r_i^p$  and  $r_i^a$  are known functions of  $c_j$ ,  $x_i$ ,  $b_i$ ,  $s_j$ ,  $y_i$ ,  $z_i$ ,  $p_i$ , and  $a_i$ .

The functional relationships can be postulated from the chemical and microbiological reactions.

Equations (2.2.6) through (2.2.13) can be further simplified regardless of whether the chemical reactions are in equilibrium or controlled by kinetics. The simplification is demonstrated in Section 2.2.1.

### 2.2.1 Transport of Aqueous Chemical Components

The chemical components are assumed to be in equilibrium with those chemical product species that are formed by relatively fast, reversible reactions. The chemical components can also be transformed into chemical product species by relatively slow or irreversible reactions. The first type of product species will be termed “equilibrium” product species and the second “kinetic” product species in this document. In HYDROBIOGEOCHEM, transport of the aqueous chemical components’ free species and all equilibrium product species which contain that component are solved together. This total “equilibrium” concentration of each aqueous component is subjected to transport, and is allowed to re-equilibrate to determine the new concentrations of the equilibrium product species and free component species formed. Transport of the aqueous kinetic product species is solved separately. The reaction term couples changes in the total “equilibrium” concentration of the components with changes in the kinetic products species’ concentrations.

Let  $a_{ij}$  denote the stoichiometric coefficient of the  $j$ -th chemical component in the  $i$ -th chemical product species. As identified previously,  $M_x$ ,  $M_y$ ,  $M_z$ , and  $M_p$  are the total number of aqueous complexed, adsorbed, ion-exchanged, and precipitated product species, respectively. Let  $K_x$ ,  $K_y$ ,  $K_z$ , and  $K_p$  denote the number of kinetic aqueous complexed, adsorbed, ion-exchanged, and precipitated product species, respectively. Then  $(M_x - K_x)$ ,  $(M_y - K_y)$ ,  $(M_z - K_z)$ , and  $(M_p - K_p)$  are the number of equilibrium aqueous complexed, adsorbed, ion-exchanged, and precipitated product species, respectively. Multiplying Equation (2.2.7) by  $a_{ij}$  and summing over  $i$  from 1 to  $(M_x - K_x)$ , multiplying Equation (2.2.10) by  $a_{ij}$  and summing over  $i$  from 1 to  $(M_y - K_y)$ , multiplying Equation (2.2.11) by  $a_{ij}$  and summing over  $i$  from 1 to  $(M_z - K_z)$ , multiplying Equation (2.2.12) by  $a_{ij}$  and summing over  $i$  from 1 to  $(M_p - K_p)$ , and adding the results to Equation (2.2.6), we obtain



$$\frac{\partial \rho_\ell \theta T'_j}{\partial t} + \nabla \cdot (\rho_\ell \theta C'_j \mathbf{V}_{fs}) - \nabla \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla C'_j) = \mathbb{R}_j^c - \Lambda_j^c - \rho_\ell \theta T'_j \left( \alpha \frac{\partial p}{\partial t} \right) + M_j^c \quad (2.2.14)$$

$$j \in N_a .$$

in which

$$T'_j = \frac{T_j}{\rho_\ell \theta} , \quad j \in N_a , \quad (2.2.15)$$

$$T_j = \rho_\ell \theta \left( c_j + \sum_{i=1}^{(M_x - K_x)} a_{ij} x_i \right) + \rho_b \left( \sum_{i=1}^{(M_y - K_y)} a_{ij} y_i + \sum_{i=1}^{(M_z - K_z)} a_{ij} z_i + \sum_{i=1}^{(M_p - K_p)} a_{ij} p_i \right) , \quad j \in N_a , \quad (2.2.16)$$

$$C'_j = \frac{C_j}{\rho_\ell \theta} , \quad j \in N_a , \quad (2.2.17)$$

$$C_j = \rho_\ell \theta \left( c_j + \sum_{i=1}^{(M_x - K_x)} a_{ij} x_i \right) , \quad j \in N_a , \quad (2.2.18)$$

$$\mathbb{R}_j^c = \rho_\ell \theta \left( r_j^c + \sum_{i=1}^{(M_x - K_x)} a_{ij} r_i^x \right) + \rho_b \left( \sum_{i=1}^{(M_y - K_y)} a_{ij} r_i^y + \sum_{i=1}^{(M_z - K_z)} a_{ij} r_i^z + \sum_{i=1}^{(M_p - K_p)} a_{ij} r_i^p \right) , \quad j \in N_a , \quad (2.2.19)$$

$$\Lambda_j^c = \rho_\ell \theta \left( l_j^c + \sum_{i=1}^{(M_x - K_x)} a_{ij} l_i^x \right) + \rho_b \left( \sum_{i=1}^{(M_y - K_y)} a_{ij} l_i^y + \sum_{i=1}^{(M_z - K_z)} a_{ij} l_i^z + \sum_{i=1}^{(M_p - K_p)} a_{ij} l_i^p \right) , \quad j \in N_a , \quad (2.2.20)$$

and

$$M_j^c = m_j^c + \sum_{i=1}^{(M_x - K_x)} a_{ij} m_i^x + \sum_{i=1}^{(M_y - K_y)} a_{ij} m_i^y + \sum_{i=1}^{(M_z - K_z)} a_{ij} m_i^z + \sum_{i=1}^{(M_p - K_p)} a_{ij} m_i^p , \quad j \in N_a . \quad (2.2.21)$$

where

$T_j$  = total equilibrium concentration of the j-th aqueous component, mass per unit medium volume ( $M/L^3$ ).

$T'_j$  = total equilibrium concentration of the j-th aqueous component, mass per mass of liquid ( $M/M$  of liquid).

$C_j$  = total dissolved concentration of the j-th aqueous component ( $M/L^3$ ).

- $C'_j$  = total dissolved concentration of the j-th aqueous component (M/M of liquid).  
 $M_j^c$  = total rate of source/sink of the j-th aqueous component (M/L<sup>3</sup>/T).  
 $\Lambda_j^c$  = total decay rate of the j-th aqueous component (M/L<sup>3</sup>/T).  
 $\mathbb{R}_j^c$  = total production/consumption of the j-th aqueous component due to all chemical and microbiological reactions (M/L<sup>3</sup>/T).

Equation (2.2.14) is written in conservative form. It has been suggested that using the advective form is sometimes more appropriate, especially if the finite-element method is used to simulate the chemical transport equation (Huyakorn et al., 1985). More importantly, an advective form of transport equations allows one to use the mixed Lagrangian-Eulerian approach, which can better solve advection-dominant transport problems (Yeh et al., 1995). To derive an advective form of the transport equation, we expand the first and second terms of Equation (2.2.14) and use the definition of the Darcy velocity to obtain

$$\begin{aligned}
 \rho_\ell \theta \frac{\partial T'_j}{\partial t} + T'_j \frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot C'_j + C'_j \nabla \cdot (\rho_\ell \mathbf{V}) - \nabla \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla C'_j) \\
 = \mathbb{R}_j^c - \Lambda_j^c - \rho_\ell \theta T'_j \left( \alpha \frac{\partial p}{\partial t} \right) + M_j^c \\
 j \in N_a .
 \end{aligned} \tag{2.2.22}$$

Since it is preferable to use the total concentrations of the aqueous components as the primary dependent variables (Yeh and Tripathi, 1989), the terms involving the total dissolved concentration,  $C'_j$  will be expressed in terms of  $T'_j$  :

$$\begin{aligned}
 \rho_\ell \theta \frac{\partial T'_j}{\partial t} + T'_j \frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot \left( \frac{C'_j}{T'_j} T'_j \right) + \left( \frac{C'_j}{T'_j} T'_j \right) \nabla \cdot (\rho_\ell \mathbf{V}) \\
 - \nabla \cdot \left[ \rho_\ell \theta \mathbf{D} \cdot \nabla \left( \frac{C'_j}{T'_j} T'_j \right) \right] = \mathbb{R}_j^c - \Lambda_j^c - \rho_\ell \theta T'_j \left( \alpha \frac{\partial p}{\partial t} \right) + M_j^c \\
 j \in N_a .
 \end{aligned} \tag{2.2.23}$$

This can be rearranged into a more convenient form for implementation in the numerical code by expanding the  $\nabla (\{C/T\} T)$  terms:

$$\begin{aligned}
& \rho_\ell \theta \frac{\partial T'_j}{\partial t} + T'_j \frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \frac{C'_j}{T'_j} \nabla \cdot T'_j + \left( \rho_\ell \mathbf{V} \nabla \cdot \frac{C'_j}{T'_j} \right) T'_j + \left( \frac{C'_j}{T'_j} T'_j \right) \nabla \cdot (\rho_\ell \mathbf{V}) \\
& - \nabla \cdot \left[ \rho_\ell \theta \mathbf{D} \frac{C'_j}{T'_j} \cdot \nabla T'_j \right] - \nabla \cdot \left[ \left( \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right) T'_j \right] \\
& = \mathbb{R}_j^c - \Lambda_j^c - \rho_\ell \theta T'_j \left( \alpha \frac{\partial p}{\partial t} \right) + \mathbf{M}_j^c \\
& \quad \mathbf{j} \in \mathbf{N}_a \quad .
\end{aligned} \tag{2.2.24}$$

Separating the last term on the right hand side and combining similar terms:

$$\begin{aligned}
& \rho_\ell \theta \frac{\partial T'_j}{\partial t} + \left[ \rho_\ell \mathbf{V} \frac{C'_j}{T'_j} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right] \nabla \cdot T'_j - \nabla \cdot \left[ \rho_\ell \theta \mathbf{D} \frac{C'_j}{T'_j} \cdot \nabla T'_j \right] \\
& + \left[ \frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot \frac{C'_j}{T'_j} + \frac{C'_j}{T'_j} \nabla \cdot (\rho_\ell \mathbf{V}) - \nabla \cdot \left( \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C'_j}{T'_j} \right) + \rho_\ell \theta \left( \alpha \frac{\partial p}{\partial t} \right) \right] T'_j \tag{2.2.25} \\
& = \mathbb{R}_j^c - \Lambda_j^c + \mathbf{M}_j^c \\
& \quad \mathbf{j} \in \mathbf{N}_a \quad .
\end{aligned}$$

Substituting the continuity equation for water flow, Equation (2.1.1), Equation (2.2.25) can be expressed as:

$$\rho_\ell \theta \frac{\partial T_j'}{\partial t} + L(C_j') + K T_j' + \rho^* Q \frac{C_j'}{T_j'} T_j' = R_j^c + M_j^c \quad (2.2.26)$$

$$j \in N_a \quad .$$

where  $L(C_j')$  and  $K$  are an advection-dispersion operator and first order rate term, respectively, given by

$$L(C_j') = \left[ \rho_\ell \mathbf{V} \frac{C_j'}{T_j'} - \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C_j'}{T_j'} \right] \nabla \cdot T_j' - \nabla \cdot \left[ \rho_\ell \theta \mathbf{D} \frac{C_j'}{T_j'} \cdot \nabla T_j' \right] \quad (2.2.27)$$

and

$$K = \left[ \frac{\partial \rho_\ell \theta}{\partial t} + \rho_\ell \mathbf{V} \nabla \cdot \frac{C_j'}{T_j'} - \frac{C_j'}{T_j'} \frac{\partial \rho_\ell \theta}{\partial t} - \nabla \cdot \left( \rho_\ell \theta \mathbf{D} \cdot \nabla \frac{C_j'}{T_j'} \right) + \rho_\ell \theta \left( \alpha \frac{\partial p}{\partial t} \right) + \lambda_j^c \right] \quad (2.2.28)$$

The decay term has been expressed as

$$\Lambda_j^c = \lambda_j^c T_j' \quad , \quad j \in N_a \quad , \quad (2.2.29)$$

where

$$\lambda_j^c = \text{decay rate constant of the } j\text{-th aqueous component (1/T)}.$$

The source/sink term  $M_j^c$  can be defined by

$$M_j^c = \rho^* C_j^* Q \quad , \quad j \in N_a \quad (2.2.30)$$

where

$$\begin{aligned} C_j^* &= \text{concentration of the } j\text{-th aqueous component in the source/sink liquid,} \\ &\quad (\text{M/M of liquid}). \\ &= C_j' \text{ if sink or withdrawal (negative } Q), \text{ or} \\ &= C_{in}, \text{ input concentration, if source or injection (positive } Q). \end{aligned}$$

By the definition of  $C_j^*$  the terms  $M_j^c$  and  $(\rho^* Q C_j^*)$  cancel each other for the case of sink (withdrawal). Thus, another advantage of using the advection form of the transport equation is that one does not need to include the sink in the equation.

Equation (2.2.26) can be simplified by separating the reaction term into the contributions from chemical and microbial reactions:

$$\mathbb{R}_j^c = \mathbf{R}_j^{c(\text{bio})} + \mathbf{R}_j^{c(\text{chem})} \quad , \quad \text{or}$$

$$\mathbb{R}_j^c = \rho_\ell \theta \left( \mathbf{r}_j^c |^{\text{bio}} + \sum_{i=1}^{(M_x - K_x)} a_{ij} \mathbf{r}_i^x |^{\text{bio}} \right) + \rho_b \left( \sum_{i=1}^{(M_y - K_y)} a_{ij} \mathbf{r}_i^y |^{\text{bio}} + \sum_{i=1}^{(M_z - K_z)} a_{ij} \mathbf{r}_i^z |^{\text{bio}} + \sum_{i=1}^{(M_p - K_p)} a_{ij} \mathbf{r}_i^p |^{\text{bio}} \right) \quad (2.2.31)$$

$$+ \rho_\ell \theta \left( \mathbf{r}_j^c |^{\text{chem}} + \sum_{i=1}^{(M_x - K_x)} a_{ij} \mathbf{r}_i^x |^{\text{chem}} \right) + \rho_b \left( \sum_{i=1}^{(M_y - K_y)} a_{ij} \mathbf{r}_i^y |^{\text{chem}} + \sum_{i=1}^{(M_z - K_z)} a_{ij} \mathbf{r}_i^z |^{\text{chem}} + \sum_{i=1}^{(M_p - K_p)} a_{ij} \mathbf{r}_i^p |^{\text{chem}} \right)$$

where

$\mathbf{R}_j^{c(\text{bio})}$  = production/consumption of the j-th aqueous component due to microbiological reactions ( $M/L^3/T$ ).

$\mathbf{R}_j^{c(\text{chem})}$  = production/consumption of the j-th aqueous component due to chemical reactions ( $M/L^3/T$ ).

and the superscripts “|<sup>bio</sup>” and “|<sup>chem</sup>” after the individual species reaction terms denotes “due to microbiological reactions” and “due to chemical reactions”, respectively.

A chemical component must be chemical reaction invariant; the rate at which a component is consumed in chemical reactions is balanced by the rate at which chemical product species containing that component are produced. That is:

$$\rho_\ell \theta \left( \mathbf{r}_j^c |^{\text{chem}} + \sum_{i=1}^{M_x} a_{ij} \mathbf{r}_i^x |^{\text{chem}} \right) + \rho_b \left( \sum_{i=1}^{M_y} a_{ij} \mathbf{r}_i^y |^{\text{chem}} + \sum_{i=1}^{M_z} a_{ij} \mathbf{r}_i^z |^{\text{chem}} + \sum_{i=1}^{M_p} a_{ij} \mathbf{r}_i^p |^{\text{chem}} \right) = 0 \quad , \quad (2.2.32)$$

$$j \in N_a$$

Chemical component mass may not be conserved with respect to microbiological reactions. Separating the equilibrium and kinetic chemical product species and rearranging, Equation (2.2.32) becomes:

$$\begin{aligned} & \rho_\ell \theta \left( r_j^c |^{\text{chem}} + \sum_{i=1}^{(M_x - K_x)} a_{ij} r_i^x |^{\text{chem}} \right) + \rho_b \left( \sum_{i=1}^{(M_y - K_y)} a_{ij} r_i^y |^{\text{chem}} + \sum_{i=1}^{(M_z - K_z)} a_{ij} r_i^z |^{\text{chem}} + \sum_{i=1}^{(M_p - K_p)} a_{ij} r_i^p |^{\text{chem}} \right) \\ & = - \rho_\ell \theta \sum_{i=1}^{K_x} a_{ij} r_i^x |^{\text{chem}} - \rho_b \left( \sum_{i=1}^{K_y} a_{ij} r_i^y |^{\text{chem}} + \sum_{i=1}^{K_z} a_{ij} r_i^z |^{\text{chem}} + \sum_{i=1}^{K_p} a_{ij} r_i^p |^{\text{chem}} \right) \end{aligned} \quad (2.2.33)$$

Equation (2.2.26) may therefore be rewritten as

$$\begin{aligned} \rho_\ell \theta \frac{\partial T'_j}{\partial t} + L(C'_j) + K T'_j + \rho^* Q \frac{C'_j}{T'_j} T'_j = R_j^c + M_j^c \\ j \in N_a \end{aligned} \quad (2.2.34)$$

in which the reaction term is given by combining Equations (2.2.19), (2.2.31), and (2.2.33):

$$\begin{aligned} R_j^c = \rho_\ell \theta \left( r_j^c |^{\text{bio}} + \sum_{i=1}^{(M_x - K_x)} a_{ij} r_i^x |^{\text{bio}} \right) + \rho_b \left( \sum_{i=1}^{(M_y - K_y)} a_{ij} r_i^y |^{\text{bio}} + \sum_{i=1}^{(M_z - K_z)} a_{ij} r_i^z |^{\text{bio}} + \sum_{i=1}^{(M_p - K_p)} a_{ij} r_i^p |^{\text{bio}} \right) \\ - \rho_\ell \theta \sum_{i=1}^{(K_x)} a_{ij} r_i^x |^{\text{chem}} - \rho_b \left( \sum_{i=1}^{(K_y)} a_{ij} r_i^y |^{\text{chem}} + \sum_{i=1}^{(K_z)} a_{ij} r_i^z |^{\text{chem}} + \sum_{i=1}^{(K_p)} a_{ij} r_i^p |^{\text{chem}} \right) \end{aligned} \quad (2.2.35)$$

## 2.2.2 Mass Balance of Adsorbent Components

Similarly, we can derive the governing equations for the total equilibrium concentration of adsorbent components and the number of equivalents occupying the ion-exchange sites. Multiplying Equation (2.2.10) by  $a_{ij}$ , summing over  $i$  from 1 to  $M_y$ , and adding the results to Equation (2.2.9), we obtain

$$\frac{\partial W_j}{\partial t} = \mathbf{R}_j^s - \Lambda_j^s - \alpha \frac{\partial p}{\partial t} W_j + M_j^s, \quad j \in N_s, \quad (2.2.36)$$

in which

$$W_j = \rho_b \left( s_j + \sum_{i=1}^{M_y - K_y} a_{ij} y_i \right), \quad j \in N_s, \quad (2.2.37)$$

$$M_j^s = m_j^s + \sum_{i=1}^{(M_y - K_y)} a_{ij} m_i^y, \quad j \in N_s, \quad (2.2.38)$$

$$\Lambda_j^s = \rho_b \left( v_j^s + \sum_{i=1}^{(M_y - K_y)} a_{ij} v_i^y \right), \quad j \in N_s, \quad (2.2.39)$$

and

$$\mathbf{R}_j^s = \rho_b \left( r_j^{s|\text{bio}} + \sum_{i=1}^{(M_y - K_y)} a_{ij} r_i^{y|\text{bio}} \right) - \rho_b \sum_{i=1}^{K_y} a_{ij} r_i^{y|\text{chem}}, \quad j \in N_s, \quad (2.2.40)$$

where

$W_j$	= total equilibrium concentration of the j-th adsorbent component (M/L <sup>3</sup> ).
$M_j^s$	= total rate of source/sink of the j-th adsorbent component (M/L <sup>3</sup> /T).
$\Lambda_j^s$	= total decay rate of the j-th adsorbent component (M/L <sup>3</sup> /T).
$\mathbf{R}_j^{s(\text{bio})}$	= production/consumption of the j-th adsorbent component due to chemical and microbiological reactions (M/L <sup>3</sup> /T).

The relationship that results from the requirement that adsorption be chemical reaction-invariant with respect to any adsorbent component has been used in deriving Equation (2.2.36):

$$\mathbf{R}_j^{s(\text{chem})} = \rho_b \left( r_j^{s|\text{chem}} + \sum_{i=1}^{M_y} a_{ij} r_i^{y|\text{chem}} \right) = 0, \quad j \in N_s, \quad (2.2.41)$$

where

$\mathbf{R}_j^{s(\text{chem})}$	= production/consumption of the j-th adsorbent component due to chemical reactions (M/L <sup>3</sup> /T).
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In addition, the source/sink term  $M_j^s$  is assumed to be zero:

$$M_j^s = 0 \quad , \quad j \in N_s \quad . \quad (2.2.42)$$

The decay term  $\Lambda_j^s$  can be defined as

$$\Lambda_j^s = \lambda_j^s W_j \quad , \quad j \in N_s \quad , \quad (2.2.43)$$

where

$$\lambda_j^s = \text{decay rate constant of the } j\text{-th adsorbent component (1/T).}$$

Equation (2.2.36) can therefore be restated as:

$$\frac{\partial W_j}{\partial t} = R_j^s - \left( \lambda_j^s + \alpha \frac{\partial p}{\partial t} \right) W_j \quad , \quad j \in N_s \quad (2.2.44)$$

### 2.2.3 Mass Balance of Ion-Exchange Sites

The governing equations for the ion-exchange sites are obtained similarly but with the exception that we have assumed that there are no free ion-exchange sites (i.e., the sites are completely occupied). Multiplying Equation (2.2.11) by  $v_k$  and summing over  $k$  from (NOMZJ(i)+1) to (NOMZJ(i)+NOMZI(i)), we obtain

$$\frac{\partial N_{eqi}}{\partial t} = R_{eqi}^{(bio)} - \Lambda_{eqi} - \alpha \frac{\partial p}{\partial t} N_{eqi} + M_{eqi} \quad , \quad i \in \text{NSITE} \quad (2.2.45)$$

in which

$$N_{eqi} = \rho_b \sum_{k=\text{NOMZJ}(i)+1}^{\text{NOMZJ}(i)+\text{NOMZI}(i)} v_k z_k \quad , \quad i \in \text{NSITE} \quad (2.2.46)$$

$$M_{eqi} = \sum_{k=\text{NOMZJ}(i)+1}^{\text{NOMZJ}(i)+\text{NOMZI}(i)} v_k m_k^z \quad , \quad i \in \text{NSITE} \quad (2.2.47)$$

$$\Lambda_{eqi} = \rho_b \sum_{k=\text{NOMZJ}(i)+1}^{\text{NOMZJ}(i)+\text{NOMZI}(i)} v_k \lambda_k^z \quad , \quad i \in \text{NSITE} \quad (2.2.48)$$

and



$$\mathbf{R}_{\text{eqi}}^{(\text{bio})} = \rho_b \sum_{k=\text{NOMZJ}(i)+1}^{\text{NOMZJ}(i)+\text{NOMZI}(i)} v_k r_k^z |^{\text{bio}}, \quad i \in \text{NSITE} \quad (2.2.49)$$

where

- $v_k$  = charge of the k-th ion exchanged species (equivalents/mol).  
 $N_{\text{eqi}}$  = number of equivalents of the ion-exchange sites per liter of solution for the i-th site (equivalents/L<sup>3</sup>).  
 $M_{\text{eqi}}$  = total rate of source/sink of the ion-exchange site for the i-th site (equivalents/L<sup>3</sup>/T).  
 $\Lambda_{\text{eqi}}$  = total decay rate of the ion-exchange site for the i-th site (equivalents/L<sup>3</sup>/T).  
 $R_{\text{eqi}}^{(\text{bio})}$  = production/consumption of the ion-exchange site for the i-th site due to microbiological reactions (equivalents/L<sup>3</sup>/T).  
 $\text{NSITE}$  = number of ion-exchange sites.  
 $\text{NOMZI}(i)$  = number of ion-exchanged species involved in the i-th ion-exchanged site.  
 $\text{NOMZJ}(i)$  = number of ion-exchanged species involved in the first through (i-1)-th ion-exchanged site.

The following relationship that results from the requirement of invariability for the ion-exchange site in the absence of microbiological reactions and decay has been used in deriving Equation (2.2.45):

$$\mathbf{R}_{\text{eqi}}^{(\text{chem})} = \rho_b \sum_{k=\text{NOMZJ}(i)+1}^{\text{NOMZJ}(i)+\text{NOMZI}(i)} v_k r_k^z |^{\text{chem}} = 0, \quad i \in \text{NSITE} \quad (2.2.50)$$

In addition, the source/sink term  $M_{\text{eqi}}$  is assumed to be zero; that is,

$$\mathbf{M}_{\text{eqi}} = 0. \quad (2.2.51)$$

The decay term  $\Lambda_{\text{eqi}}$  can be defined as

$$\Lambda_{\text{eqi}} = \lambda_{\text{eqi}} N_{\text{eqi}}, \quad (2.2.52)$$

where

$$\lambda_{\text{eqi}} = \text{decay rate constant of the ion-exchange site (1/T)}.$$

Equation (2.2.45) can therefore be restated as

$$\frac{\partial N_{\text{eqi}}}{\partial t} = R_{\text{eqi}}^{(\text{bio})} - \left( \lambda_{\text{eqi}} + \alpha \frac{\partial p}{\partial t} \right) N_{\text{eqi}}, \quad i \in \text{NSITE} \quad (2.2.53)$$

#### 2.2.4 Summary of Governing Equations

The transport equations for the aqueous complexed species and the aqueous microbial species can also be expressed in advective form for numerical implementation. The derivation is analogous to that for the aqueous components, except that the dissolved and total concentrations for these species are always equal; ie. the term  $\{C/T\}$  always equals one and the gradient of  $\{C/T\}$  always equals zero in the definition of the advection-dispersion operator,  $L(!)$ , and the first order term,  $K$ , defined by Equations (2.2.27) and (2.2.28), respectively. Equations (2.2.7) and (2.2.8) are replaced by

$$\rho_{\ell} \theta \frac{\partial x_i}{\partial t} + L(x_i) + K x_i + \rho^* Q x_i = \rho_{\ell} \theta r_i^x + m_i^x \quad (2.2.54)$$

$i \in M_x$  .

$$\rho_{\ell} \theta \frac{\partial b_i}{\partial t} + L(b_i) + K b_i + \rho^* Q b_i = \rho_{\ell} \theta r_i^b + m_i^b \quad (2.2.55)$$

$i \in M_b$  .

Equations (2.2.34), (2.2.15), (2.2.17), (2.2.44), (2.2.37), (2.2.53), (2.2.46), (2.2.54), (2.2.10), (2.2.11), (2.2.12), (2.2.55), and (2.2.13) constitute  $(3 \times N_a, 2 \times N_s, 2 \times \text{NSITE}, M_x, M_y, M_z, M_p, M_b, M_a)$  sets of equations defining  $(3 \times N_a, 2 \times N_s, \text{NSITE}, M_x, M_y, M_z, M_p, M_b, M_a)$  sets of unknowns ( $T_j$ 's,  $c_j$ 's,  $C_j$ 's,  $W_j$ 's,  $s_j$ 's,  $N_{\text{eq}}$ 's,  $x_i$ 's,  $y_i$ 's,  $z_i$ 's,  $p_i$ 's,  $b_i$ 's, and  $a_i$ 's). However, the formulation is not complete; the chemical and biological reaction rate terms in these equations ( $R_j^c, R_j^s, R_{\text{eqi}}, r_i^x, r_i^y, r_i^z, r_i^p, r_i^b, r_i^a$ ) must be prescribed to complete the formulation. For coupled hydrological transport and biogeochemical reaction modeling in HYDROBIOGEOCHEM, a mixed chemical microbiological model is adopted to give the implicit functional relationships among  $T_j$ 's,  $C_j$ 's,  $c_j$ 's,  $W_j$ 's,  $N_{\text{eq}}$ 's,  $s_j$ 's,  $x_i$ 's,  $y_i$ 's,  $z_i$ 's,  $p_i$ 's,  $b_i$ 's, and  $a_i$ 's as described in Sections 2.3 and 2.4.

## 2.2.5 Transport of Operational Electrons

Redox reactions are a class of chemical reactions involving a transfer of electrons. Hence, when redox reactions are present in a system, we must invoke the principle of conservation of electrons to ensure that all electrons donated by chemical species are accepted by another species. This is equivalent to the statement that oxidation numbers must be conserved in a chemical reaction.

In nonredox systems, the total concentrations of all components and the number of equivalents of the ion-exchange site must be known before one can calculate the concentrations of all species. In redox systems, the unknowns are not only the concentrations of all species but also include a redox parameter that describes the oxidation state of the system. To be consistent with the approach that uses concentrations or activities as unknowns, the "activity of electrons" designated by the symbol  $X_e$  is normally used as the redox parameter. Hence, in redox systems the total concentrations of all components, the number of equivalents of the ion-exchange site, and the total concentration of the "operational electrons" must be known before the concentrations of all species and the activity of electrons (or the pE value) can be computed (Walsh et al. 1984). Total concentrations of all components are determined by solving the transport equation, Equation (2.2.34), for aqueous components and the mass balance equation, Equation (2.2.44), for adsorbent components, respectively. The number of equivalents of the ion-exchange site is obtained by solving the mass balance equation, Equation (2.2.53). A transport equation for operational electrons is needed to determine the total concentration of operational electrons. (Walsh et al. use the term "available electrons." We think the term "operational electrons" is more appropriate.)

Let

- $a_{je}^c$  = stoichiometric coefficient of the electron in the j-th aqueous component species;
- $a_{ie}^x$  = stoichiometric coefficient of the electron in the i-th complexed species;
- $a_{je}^s$  = stoichiometric coefficient of the electron in the j-th adsorbent component species;
- $a_{ie}^y$  = stoichiometric coefficient of the electron in the i-th adsorbed species;
- $a_{ie}^z$  = stoichiometric coefficient of the electron in the i-th ion-exchanged species;
- $a_{ie}^p$  = stoichiometric coefficient of the electron in the i-th precipitated species.

By multiplying Equation (2.2.6) by  $a_{je}^c$  and summing over j from 1 to  $N_a$ , multiplying Equation (2.2.7) by  $a_{ie}^x$  and summing over i from 1 to  $M_x$ , multiplying Equation (2.2.9) by  $a_{je}^s$  and summing over j from 1 to  $N_s$ , multiplying Equation (2.2.10) by  $a_{ie}^y$  and summing over i from 1 to  $M_y$ , multiplying Equation (2.2.11) by  $a_{ie}^z$  and summing over i from 1 to  $M_z$ , multiplying Equation (2.2.12) by  $a_{ie}^p$  and summing over i from 1 to  $M_p$ , adding the results, and invoking the principle

of conservation of electrons, one obtains

$$\rho_\ell \theta \frac{\partial T_e'}{\partial t} + L(C_e') + K T_e' + \rho^* Q C_e' = R_j^e + M_j^e . \quad (2.2.56)$$

which is identical in form to Equation (2.2.34) and describes the transport of operational electrons. However, the definitions of  $C_e$ ,  $T_e$ ,  $M_e$ , and  $\Lambda_e$  are slightly different from those of  $C_j$ ,  $T_j$ ,  $M_j^c$  and  $\Lambda_j^c$ . The quantities  $C_e'$ ,  $T_e'$ ,  $C_e$ ,  $T_e$ ,  $M_e$ , and  $\Lambda_e$  are given by

$$T_e' = \frac{T_e}{\rho_\ell \theta} \quad (2.2.57)$$

$$T_e = \rho_\ell \theta \left( \sum_{j=1}^{N_a} a_{je}^c c_j + \sum_{i=1}^{(M_x - K_x)} a_{ie}^x x_i \right) + \rho_b \left( \sum_{i=1}^{(M_z - K_z)} a_{ie}^z z_i + \sum_{j=1}^{N_s} a_{je}^s s_j + \sum_{i=1}^{(M_y - K_y)} a_{ie}^y y_i + \sum_{i=1}^{(M_p - K_p)} a_{ie}^p p_i \right) \quad (2.2.58)$$

$$C_e' = \frac{C_e}{\rho_\ell \theta} \quad (2.2.59)$$

$$C_e = \rho_\ell \theta \left( \sum_{j=1}^{N_a} a_{je}^c c_j + \sum_{i=1}^{(M_x - K_x)} a_{ie}^x x_i \right) , \quad (2.2.60)$$

$$\begin{aligned} M_e &= \sum_{j=1}^{N_a} a_{je}^c m_j^c + \sum_{i=1}^{(M_x - K_x)} a_{ie}^x m_i^x + \sum_{i=1}^{(M_z - K_z)} a_{ie}^z m_i^z \\ &+ \sum_{j=1}^{N_s} a_{je}^s m_j^s + \sum_{i=1}^{(M_y - K_y)} a_{ie}^y m_i^y + \sum_{i=1}^{(M_p - K_p)} a_{ie}^p m_i^p , \end{aligned} \quad (2.2.61)$$

$$\begin{aligned} \Lambda_e &= \rho_\ell \theta \left( \sum_{j=1}^{N_a} a_{je}^c l_j^c + \sum_{i=1}^{(M_x - K_x)} a_{ie}^x l_i^x \right) + \\ &\rho_b \left( \sum_{i=1}^{(M_z - K_z)} a_{ie}^z l_i^z + \sum_{j=1}^{N_s} a_{je}^s l_j^s + \sum_{i=1}^{(M_y - K_y)} a_{ie}^y l_i^y + \sum_{i=1}^{(M_p - K_p)} a_{ie}^p l_i^p \right) , \end{aligned} \quad (2.2.62)$$

and

$$\begin{aligned}
R_e = & \rho_\ell \theta \left( \sum_{j=1}^{N_a} a_{je}^c r_e^c |^{bio} + \sum_{i=1}^{(M-K)_x} a_{ie}^x r_i^x |^{bio} \right) + \\
& \rho_b \left( \sum_{j=1}^{N_s} a_{je}^s r_e^s |^{bio} + \sum_{i=1}^{(M-K)_y} a_{ie}^y r_i^y |^{bio} + \sum_{i=1}^{(M-K)_z} a_{ie}^z r_i^z |^{bio} + \sum_{i=1}^{(M-K)_p} a_{ie}^p r_i^p |^{bio} \right) \\
& - \rho_\ell \theta \left( \sum_{i=1}^{K_x} a_{ie}^x r_i^x |^{chem} \right) - \rho_b \left( \sum_{i=1}^{K_y} a_{ie}^y r_i^y |^{chem} + \sum_{i=1}^{K_z} a_{ie}^z r_i^z |^{chem} + \sum_{i=1}^{K_p} a_{ie}^p r_i^p |^{chem} \right) , \tag{2.2.63}
\end{aligned}$$

where

- $C_e$  = concentration of operational electrons in aqueous phase (M/L<sup>3</sup>) .
- $C'_e$  = concentration of operational electrons in aqueous phase (M/M).
- $T_e$  = total concentration of operational electrons (M/L<sup>3</sup>) .
- $T'_e$  = total concentration of operational electrons (M/M).
- $M_e$  = external source/sink rate of the free electron species [(M/L<sup>3</sup>)/T].
- $\iota_e$  = rate of decay of the free electron species [(M/L<sup>3</sup>)/T].
- $\Lambda_e$  = total rate of decay of the operational electron [(M/L<sup>3</sup>)/T].
- $R_e$  = production/consumption of operational electrons due to chemical and microbiological reactions (M/L<sup>3</sup>/T).

The above stoichiometric coefficients are given by

$$a_{je}^c = \sum_{k=1}^{N_e} h_{jk}^c (v_{mk} - v_{jk}^c) , \quad j \in N_a , \tag{2.2.64}$$

$$a_{ie}^x = \sum_{k=1}^{N_e} h_{ik}^x (v_{mk} - v_{ik}^x) , \quad i \in M_x , \tag{2.2.65}$$

$$a_{je}^s = \sum_{k=1}^{N_e} h_{jk}^s (v_{mk} - v_{jk}^s) , \quad j \in N_s , \tag{2.2.66}$$

$$a_{ie}^y = \sum_{k=1}^{N_e} h_{ik}^y (v_{mk} - v_{ik}^y) , \quad i \in M_y , \tag{2.2.67}$$

$$a_{ie}^z = \sum_{k=1}^{N_e} h_{ik}^z (v_{mk} - v_{ik}^z) , \quad i \in M_z , \tag{2.2.68}$$

and

$$a_{ie}^p = \sum_{k=1}^{N_e} h_{ik}^p (v_{mk} - v_{ik}^p) , \quad i \in M_p , \quad (2.2.69)$$

where

$h_{jk}^c$  = stoichiometric coefficient of the k-th chemical element in the j-th aqueous component species.

$h_{ik}^x$  = stoichiometric coefficient of the k-th chemical element in the i-th complexed species.

$h_{jk}^s$  = stoichiometric coefficient of the k-th chemical element in the j-th adsorbent component species.

$h_{ik}^y$  = stoichiometric coefficient of the k-th chemical element in the i-th adsorbed species.

$h_{ik}^z$  = stoichiometric coefficient of the k-th chemical element in the i-th ion-exchanged species.

$h_{ik}^p$  = stoichiometric coefficient of the k-th chemical element in the i-th precipitated component species.

$v_{jk}^c$  = valence of the k-th chemical element in the j-th aqueous component species.

$v_{ik}^x$  = valence of the k-th chemical element in the i-th complexed species.

$v_{jk}^s$  = valence of the k-th chemical element in the j-th adsorbent component species.

$v_{ik}^y$  = valence of the k-th chemical element in the i-th adsorbed species.

$v_{ik}^z$  = valence of the k-th chemical element in the i-th ion-exchanged species.

$v_{ik}^p$  = valence of the k-th chemical element in the i-th precipitated species.

$v_{mk}$  = valence of the k-th chemical element in its maximum oxidation state except for oxygen, in which  $v_{mk} = -2$ .

$N_e$  = number of chemical elements considered in the system (Walsh et al. 1984).

If component species are chosen such that they contain only chemical elements in their maximum oxidation state, then the  $a_{je}^c$ 's and  $a_{je}^s$ 's are equal to zero, and Equations (2.2.58) through (2.2.63) have identical formulae to Equations (2.2.15) through (2.2.21). Choosing such components is very useful for describing the computation of electron activity involving redox reactions because

the operational electron can be considered computationally as an aqueous component. Nevertheless, even without such a choice the operational electron can still be considered an aqueous component, but with a possibility of having a negative total concentration of operational electrons.

### 2.2.5 Transport of Excess Protons

In a system involving acid-base reactions, an additional parameter describing the acidity of the system is needed. This additional parameter is the proton activity (or the pH value). The pH value may be simulated by using either the electroneutrality equation or proton condition. These two approaches are mathematically equivalent but not computationally equivalent. In coupling the hydrological transport and chemical reactions, it is preferable to use the proton-condition approach, in which the total concentration of the excess protons ( $H^+ - OH^-$ ) must be known before activity of protons can be computed. Therefore, a transport equation for excess protons is needed to determine the total concentration of excess protons.

Applying the principle of conservation of mass to both oxygen and hydrogen yields two transport equations: one for hydrogen H and the other for oxygen  $O_2$ . Adding these two equations with appropriate multipliers produces a transport equation for hydroxide OH. Taking the difference of the transport equation for H and that for OH, one obtains (Miller 1983):

$$\rho_t \theta \frac{\partial T'_H}{\partial t} + L(C'_H) + K T'_H + \rho^* Q C'_H = R_j^H + M_j^H \quad (2.2.70)$$

which is identical in form to Equation (2.2.34) and which describes the transport of excess protons. The algebraic equations defining  $T_H$ ,  $C_H$ ,  $M_H$ ,  $\lambda_H$  and  $R_H$  are identical in form to Equations (2.2.15) through (2.2.21), with the subscript j replaced by the subscript H.

Because the simulation of pH and/or pe uses transport equations identical in form to Equation (2.2.34), we can treat protons and/or electrons as aqueous components, and no special consideration to distinguish protons and/or electrons from other regular aqueous components is needed. The only thing we must keep in mind is that we use proton activity and electron activity rather than proton concentration and electron concentration as master variables in the geochemical reaction model.

### 2.2.6 Transport of Gas Component

In HYDROBIOGEOCHEM, one gas phase component may be specified. HYDROBIOGEOCHEM does not simulate the transport of gas within the porous media, but does allow the gas component to react to form aqueous product species, which are subject to transport. This capability was added specifically to provide the capability of simulating a system in which the partial pressure of  $CO_{2(gas)}$  is specified and the resultant formation and transport of  $H_2CO_3^*$ ,

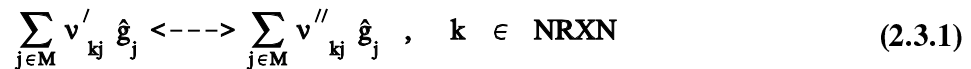
$\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  is simulated. This capability could be used to simulate any other gaseous species' interaction with the aqueous phase, as long as the transport of the gaseous species itself is not of significance to the problem.

### 2.3 Geochemical Reaction Equations

Chemical equilibrium can be dealt with in essentially two ways: the ion association theory (Bjerrum 1926; Fuoss 1935) and the mixed electrolyte theory (Reilly et al. 1971). Nearly all computerized models are based on the ion association theory (Nordstrom et al. 1979). Within this framework the species distribution can be formulated in two distinct but thermodynamically equivalent ways: the equilibrium-constant approach and the Gibbs free-energy approach. In the Gibbs free-energy approach, the species distributions are obtained by minimizing the total Gibbs free-energy function of a given set of species subject to the constraints of mass balance equations. In the equilibrium-constant approach, the set of nonlinear algebraic equations is obtained based on the law of mass action and the principle of mole balance (Morel and Morgan 1972). This set of nonlinear algebraic equations is then solved to yield the species distributions. In the latter approach, equilibrium constants are needed for the data base, whereas in the former approach, free energy values are needed. The equilibrium constant approach is chosen for handling of equilibrium geochemical reactions in HYDROBIOGEOCHEM. In the equilibrium-constant approach, the formation of an aqueous complexed species  $x_i$ , an adsorbed species  $y_i$ , an ion-exchanged species  $z_i$ , or a precipitated (solid) species  $p_i$  is described at equilibrium by the law of mass action.

Rate expressions based on collision theory are used to handle the kinetic geochemical reactions. Rate expressions based on Monod kinetics are used to describe biogeochemical reactions. The program has been developed in a modular fashion so that the user may readily incorporate rate expressions based on alternate theories to describe the kinetic reactions.

A general chemical reaction can be represented by



where

$M$  =  $(N_a + N_s + M_x + M_y + M_z + M_p)$  is the total number of chemical species.

$v'_{kj}$  = reactant stoichiometric coefficient of the  $j$ -th global species<sup>1</sup> in the  $k$ -th

---

<sup>1</sup> "Global species" refers to all of the species, both components and products, in the simulation. The global species are numbered in the following order:  $N_a$  aqueous component species,  $N_s$  adsorbent component species,  $M_x$  aqueous complexed species,  $M_y$  adsorbed species,  $M_z$  ion-exchanged species,  $M_p$  precipitated species,  $M_b$  aqueous



chemical reaction.

$v_{kj}''$  = product stoichiometric coefficient of the j-th global species in the k-th chemical reaction.

$\hat{g}_j$  = chemical formula for the j-th species.

NRXN = number of reactions in the simulation.

We will divide chemical reactions into two groups: one group is comprised of equilibrium reactions and the other of kinetic reactions. Denoting NRXNE the number of equilibrium reactions and NRXNK the number of kinetic reactions, we have  $NRXN = NRXNE + NRXNK$ .

To quantitatively describe the chemical reactions, a rate law must be given for each reaction. For equilibrium reactions, the net reaction rate is zero resulting in the law of mass action. For kinetic chemical reactions, the reaction rate is assumed to be governed by collision theory in HYDROBIOGEOCHEM. However, to make this computer code general, any kinetic reaction may instead be described by an optional rate law prescribed by the user. Thus, three chemical reaction types are included in HYDROBIOGEOCHEM: (1) equilibrium reactions, (2) kinetic reactions whose rate laws are given by collision theory, and (3) kinetic reactions whose rate laws are prescribed by the users.

For an equilibrium reaction, the rate of the reaction is given by

$$\Omega_k = 0 = k_k^f \prod_{j \in M} (\gamma_j g_j)^{v'_{kj}} - k_k^b \prod_{j \in M} (\gamma_j g_j)^{v''_{kj}} \quad (2.3.2)$$

if  $KTYP(k) = 0$

where

$\Omega_k$  = reaction rate of the k-th reaction, (1/T).

$g_j$  = concentration of the j-th global species, mass of chemical/mass of phase, (M/M). (i.e. mass/liquid mass or mass/solid mass).

$\gamma_j$  = activity coefficient of the j-th global species, mass of phase/mass of chemical, (M/M).

$k_k^f$  = forward rate constant for the k-th reaction, (1/T).

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phase microbial species, and  $M_a$  adsorbed phase microbial species.

$k_k^b$  = backward rate constant for the k-th reaction, (1/T).

KTYP(k) = reaction type of the k-th reaction,  
 = 0 if chemical equilibrium,  
 = 1 if chemical kinetic by collision theory,  
 = 2 if microbial by Monod kinetics,  
 = 3 if microbial phase transfer reaction,  
 = 4 if chemical kinetic using other rate law.

In HYDROBIOGEOCHEM, equilibrium species can appear in only one of the NRXNE equilibrium reactions and we associate this species with that equilibrium reaction. This restriction is made to facilitate the development of the mass action equations. For equilibrium reactions producing an aqueous complexed product species, Eq. (2.3.2) therefore simplifies to

$$\Omega_k = 0 = K_k^{eq} \prod_{j \in N_a} (\gamma_j g_j)^{v'_{kj}} - (\gamma_i x_i)^{v''_{ki}}, \text{ if KTYP(k) = 0} \quad (2.3.2a)$$

where  $K_k^{eq}$  = equilibrium constant for the k-th reaction

Similarly, for equilibrium reactions producing an adsorbed product species, Eq. (2.3.2) simplifies to

$$\Omega_k = 0 = K_k^{eq} \prod_{j \in (N_a + N_s)} (\gamma_j g_j)^{v'_{kj}} - (\gamma_i y_i)^{v''_{ki}}, \text{ if KTYP(k) = 0} \quad (2.3.2b)$$

And for equilibrium reactions producing a precipitated product species, Eq. (2.3.2) becomes

$$\Omega_k = 0 = K_k^{eq} \prod_{j \in N_a} (\gamma_j g_j)^{v'_{kj}} - (\gamma_i p_i)^{v''_{ki}}, \text{ if KTYP(k) = 0} \quad (2.3.2c)$$

In ion exchange reactions, free ions in solution are exchanged for ions of the same sign bound at the solid phase surface. Therefore each ion exchange reaction will involve an aqueous species and an ion exchanged species both as reactants and as products. Equilibrium controlled ion exchange species are subject to the constraint noted above that they participate in only one equilibrium reaction. Ion exchange reactions are discussed further in Section 2.3.1.

For a kinetic reaction with its rate law given by collision theory, the reaction rate is given by

$$\Omega_k = k_k^f \prod_{j \in M} (\gamma_j g_j)^{v'_{kj}} - k_k^b \prod_{j \in M} (\gamma_j g_j)^{v''_{kj}} \quad (2.3.3)$$

if  $\text{KTYP}(k) = 1$

For a kinetic reaction with its rate law prescribed the users, the reaction rate can be written as

$$\Omega_k = f_k(A_1, A_2, \dots, A_M; K_{k1}, K_{k2}, \dots, K_{kp}) \quad (2.3.4)$$

if  $\text{KTYP}(k) = 4$

where  $f_k$  is the prescribed rate law for the  $k$ -th reaction written as a function of the activities of all  $M$  species and a number of parameters.

The contribution of the  $k$ -th reaction to the production/consumption rate of the  $i$ -th species is

$$r_{i|k}^{\text{chem}} = \frac{v''_{ki} - v'_{ki}}{\gamma_i} \Omega_k, \quad i \in M, k \in \text{NRXNK} \quad (2.3.5)$$

where

$r_{i|k}^{\text{chem}}$  = the contribution of the  $k$ -th chemical reaction to the rate of production or consumption of the  $i$ -th chemical species, (mass/mass of phase)/time, ((M/M)/T).

The total production/consumption of the  $i$ -th species due to chemical reactions is the sum of the contributions from each of the reactions in which the species participates:

$$r_i^{\text{chem}} = \sum_{k=1}^{\text{NRXNK}} r_{i|k}^{\text{chem}} = \sum_{k=1}^{\text{NRXNK}} \frac{v''_{ki} - v'_{ki}}{\gamma_i} \Omega_k, \quad i \in M \quad (2.3.6)$$

where

$r_i^{\text{chem}}$  = total production/consumption rate of the  $i$ -th chemical species due to chemical reactions, (mass/mass of phase)/time, ((M/M)/T)

Before concluding this section, we note that if the users specify the kinetic reaction rates, these rates cannot be arbitrary. They must satisfy the following constraints

$$\sum_{i=1}^M a_{ij} \sum_{k=1}^{NRXN} \frac{v_{ki}'' - v_{ki}'}{\gamma_i} \Omega_k = 0, \text{ for } j \in N \quad (2.3.7)$$

$$\sum_{i=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} v_i \sum_{k=1} \frac{v_{ki}'' - v_{ki}'}{\gamma_i} \Omega_k = 0, \quad (2.3.8)$$

for  $j \in \text{NSITE}$

where  $a_{ij}$  = stoichiometry of the  $j$ -th component in the  $i$ -th species.

Eq. (2.3.7) results from the requirement that every component's mass must be conserved with respect to chemical reactions, i.e. that the rate at which a component is consumed must be balanced by the rate at which product species containing that component are produced. Similarly, Eq. (2.3.8) results from the fact that every ion-exchange site must be conserved with respect to ion-exchange reactions.

### 2.3.1 Ion Exchange

One class of surface-solution interaction reactions are ion-exchange reactions. Free ions in solution can be exchanged with an ion of the same sign bound at the solid-aqueous phase interface (Stumm and Morgan, 1981). Ion exchange sites possess a user specified ion exchange capacity and are assumed in HYDROBIOGEOCHEM to be fully occupied. Each ion-exchange reaction involves the removal of aqueous ions from solution (one of the  $N_a$  aqueous components or of the  $M_x$  aqueous complexed species) and the concurrent release of a previously existing ion-exchanged (immobile) species back into solution. In HYDROBIOGEOCHEM as many types of surfaces or ion-exchange sites as necessary to describe a scenario may be specified. For each site, it is necessary to specify one of the ion-exchanged species as a "reference species". All ion-exchange reactions at that site must then be written in terms of exchange of this reference species with the free ions in solution. The selectivity coefficient for all ion-exchange reactions at that site are therefore defined with respect to this reference species. The choice of this reference species is arbitrary; the user may choose the most prevalent ion bound initially to the surface material, or the most easily displaced ion that may participate in exchanges at that site, or any other ion which may participate in reactions at that site.

### 2.3.2 Adsorption

In the preceding sections, we model adsorption with a simple surface complexation approximation, i.e., the effect of electrostatic forces are not included. A simple surface complexation model can be treated numerically in the same manner as the aqueous complexation

model. No special consideration in the numerical approach is needed.

The distribution of the  $j$ -th aqueous component between the aqueous and adsorbed phases can be described empirically using the “ $K_d$  partitioning concept”:

$$T_j = R_{dj} C_j, \quad R_{dj} = 1 + \frac{\rho_b K_{dj}}{\theta}, \quad j \in N_a \quad (2.3.9)$$

and

$$S_j = \frac{\rho_b K_{dj}}{\theta} C_j, \quad j \in N_a, \quad (2.3.10)$$

where

- $S_j$  = total sorbed concentration of the  $j$ -th aqueous component ( $M/L^3$ ).
- $R_{dj}$  = retardation factor of the  $j$ -th component (dimensionless).
- $K_{dj}$  = distribution coefficient of the  $j$ -th aqueous component ( $L^3$  liquid/ $M$  solid).

In HYDROBIOGEOCHEM,  $T_j$ ,  $C_j$ , and  $S_j$  are determined once a solution has been reached for all individual species concentrations.  $K_{dj}$  and  $R_{dj}$  can then be determined from these values.

When the effect of electrostatic forces is to be included in modeling chemical adsorption, HYDROBIOGEOCHEM incorporates either the Constant Capacitance Model or the Triple Layer Model (Davis, et al., 1978; Stumm and Morgan, 1981). If the Constant Capacitance Model is used, one additional unknown ( $c_o$ ) is needed for each adsorbent component. If the Triple Layer Model is employed, two additional unknowns ( $c_o$  and  $c_b$ ) are introduced for each adsorbent component. These two additional unknowns are defined as

$$c_o = \exp\left(-\frac{e\psi_o}{kT}\right) \quad (2.3.11)$$

and

$$c_b = \exp\left(-\frac{e\psi_b}{kT}\right) \quad (2.3.12)$$

where  $k$  is the Boltzman constant,  $T$  is the absolute temperature,  $e$  is the electronic charge,  $\psi_o$  is the electric potential at the surface, and  $\psi_b$  is the electric potential at the beta layer.

In the case of the Constant Capacitance Model, the additional unknown  $c_o$  defined by Eq. (2.3.11) can be obtained by setting up one additional equation. This additional equation is obtained by assuming that the total charge calculated by summing over the charges on the 'o' plane is equal

to the total charge calculated by electro-static theory as

$$\mathbf{BC}\psi_o = \sum_{i=1}^{M_y} a_{io}^y y_i \quad (2.3.13)$$

where C is the capacitance of the region, B is a conversion factor from charge per unit area to moles per mass of solid, and  $a_{io}^y$  is the stoichiometric coefficient of  $c_o$  in the i-th adsorbed species

$y_i$ . For the evaluation of Jacobian, one needs to compute  $\frac{\partial \psi_o}{\partial c_o}$ , which can be easily computed

from Eq. (2.3.11) as follows:

$$\frac{\partial \psi_o}{\partial c_o} = -\frac{kT}{e} c_o \quad (2.3.13)$$

In the case of the Triple Layer Model, the two additional unknowns  $c_o$  and  $c_b$  can be obtained by assuming that the total charge calculated by summing over the charges of all surface species is equal to the total charge calculated by electro-static theory as given by

$$\mathbf{BC}_1(\psi_o - \psi_b) - \mathbf{B}\sigma_o = 0 \quad (2.3.15)$$

$$\mathbf{B}\sigma_o = \sum_{i=1}^{M_y} a_{io}^y y_i \quad (2.3.16)$$

and

$$\mathbf{C}_1(\psi_b - \psi_o)\mathbf{B} + \mathbf{C}_2(\psi_b - \psi_d)\mathbf{B} - \mathbf{B}\sigma_b = 0 \quad (2.3.17)$$

$$\mathbf{B}\sigma_b = \sum_{i=1}^{M_y} a_{ib}^y y_i \quad (2.3.18)$$

where  $C_1$  is the capacitance of the region between the "o" plane and "b" plane, B is a conversion factor from charge per unit area to moles per unit solid mass,  $\sigma_o$  is the charge density in moles per unit area on the "o" plane,  $a_{io}^y$  is the stoichiometric coefficient of  $c_o$  in the i-th adsorbed species  $y_i$ ,  $C_2$  is the capacitance of the region between the "b" plane and "d" plane,  $\sigma_b$  is the charge density in moles per unit area on the "b" plane, and  $a_{ib}^y$  is the stoichiometric coefficient of  $c_b$  in the i-th adsorbed species  $y_i$ .

Electroneutrality requires that the following relationship must be satisfied

$$\sigma_o + \sigma_b + \sigma_d = 0 \quad (2.3.19)$$

and the Gouy-Chapman diffuse layer theory yields

$$\sigma_d = -\left(8\epsilon\epsilon_o RT\right)^{\frac{1}{2}} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad (2.3.20)$$

where  $\sigma_d$  is the charge density in moles per unit area in the diffusive layer "d", R is the universal gas constant, I is ionic strength,  $\epsilon$  is the relative dielectric constant,  $\epsilon_o$  is the permittivity of the free space, and z is valence of the ion. It should be noted that Eq. (2.3.20) is valid only for the cases of symmetrical monovalent electrolyte. The charge potential relationship gives

$$C_2(\psi_d - \psi_b) = \sigma_d \quad (2.3.21)$$

Combining Eqs. (2.3.20) and (2.3.21), we relate the unknowns  $\psi_d$  to  $\psi_b$  implicitly as follows

$$C_2(\psi_d - \psi_b) = -\left(8\epsilon\epsilon_o RT\right)^{\frac{1}{2}} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad (2.3.22)$$

To solve Eqs. (2.3.15) and (2.3.17) with Newton-Raphson method, we need to evaluate  $\sigma_o$ ,  $\sigma_b$ ,

$\psi_o$ ,  $\psi_b$ , and  $\psi_d$ , and their partial derivatives with respect to  $c_o$  and  $c_b$  - -  $\frac{\partial\sigma_o}{\partial c_o}$ ,  $\frac{\partial\sigma_o}{\partial c_b}$ ,  $\frac{\partial\sigma_b}{\partial c_o}$ ,

$\frac{\partial\sigma_b}{\partial c_b}$ ,  $\frac{\partial\psi_o}{\partial c_o}$ ,  $\frac{\partial\psi_o}{\partial c_b}$ ,  $\frac{\partial\psi_b}{\partial c_o}$ ,  $\frac{\partial\psi_b}{\partial c_b}$ ,  $\frac{\partial\psi_d}{\partial c_o}$ ,  $\frac{\partial\psi_d}{\partial c_b}$ . The evaluation of  $B\sigma_o$  and  $B\sigma_b$ ,

and  $B\frac{\partial\sigma_o}{\partial c_o}$ ,  $B\frac{\partial\sigma_o}{\partial c_b}$ ,  $B\frac{\partial\sigma_b}{\partial c_o}$ , and  $B\frac{\partial\sigma_b}{\partial c_b}$  can be performed similarly to the evaluation for

other aqueous components. The evaluation of  $\psi_o$ ,  $\psi_b$ , and  $\psi_d$ , and  $\frac{\partial\psi_o}{\partial c_o}$ ,  $\frac{\partial\psi_o}{\partial c_b}$ ,  $\frac{\partial\psi_b}{\partial c_o}$ ,

$\frac{\partial \psi_b}{\partial c_b}$ ,  $\frac{\partial \psi_d}{\partial c_o}$ , and  $\frac{\partial \psi_d}{\partial c_b}$  requires a little further elaboration. Knowing  $c_o$  and  $c_b$  from previous iteration, we compute  $\psi_o$  and  $\psi_b$  from inverting Eqs. (2.3.11) and (2.3.12) as

$$\psi_o = -\frac{kT}{e} \ln(c_o) \quad (2.3.23)$$

and

$$\psi_b = -\frac{kT}{e} \ln(c_b) \quad (2.3.24)$$

respectively. Having computed  $\sigma_o$  and  $\sigma_b$  from Eqs. (2.3.16) and (2.3.18), respectively, we compute  $\sigma_d$  from Eq. (2.3.19) and then invert Eq. (2.3.20) to obtain  $\psi_d$  as

$$\psi_d = \frac{2kT}{ze} \sinh^{-1} \left[ \frac{\frac{\sigma_d}{B}}{(8\epsilon\epsilon_{RIT})^{\frac{1}{2}}} \right] \quad (2.3.25)$$

Differentiating Eq. (2.3.10) with respect to  $c_o$  and  $c_b$ , respectively, we obtain

$$\frac{\partial \psi_o}{\partial c_o} = \left( -\frac{kT}{e} \frac{1}{c_o} \right) \quad (2.3.26)$$

and

$$\frac{\partial \psi_o}{\partial c_b} = 0 \quad (2.3.27)$$

Similarly, taking the derivative of Eq. (2.3.12) with respect to  $c_o$  and  $c_b$ , respectively, we obtain

$$\frac{\partial \psi_b}{\partial c_o} = 0 \quad (2.3.28)$$

and



$$\frac{\partial \psi_b}{\partial c_b} = \left( -\frac{kT}{e} \frac{1}{c_b} \right) \quad (2.3.29)$$

Finally, taking the differentiation of Eq. (2.3.22) with respect to  $c_o$  and  $c_b$ , respectively, and substituting Eqs. (2.3.28) and (2.3.29) into the resulting equation, we obtain

$$\frac{\partial \psi_d}{\partial c_o} = 0 \quad (2.3.30)$$

and

$$\frac{\partial \psi_d}{\partial c_b} = \left( -\frac{kT}{e} \frac{1}{c_b} \right) \frac{1}{1 + \frac{e}{2kT} \left( 8\epsilon\epsilon_o RIT \right)^{\frac{1}{2}} \cosh \left( \frac{ze\psi_d}{2kT} \right) \frac{1}{C_2}} \quad (2.3.31)$$

### 2.3.3 Precipitation-Dissolution

According to convention (Stumm and Morgan, 1981), the activities of pure solid species are assumed to be constant and equal to one. (HYDROBIOGEOCHEM does not handle “solid solutions” which are characterized by activities equal to their mole fractions). The absence of the precipitated species activities from the chemical action expressions characterizes the chemical reaction of precipitation-dissolution and distinguishes it from other heterogeneous classes of chemical reactions such as adsorption and ion exchange, and from homogeneous reactions such as soluble complexation. This implies that models developed specifically for dealing with complexation and sorption are not necessarily capable of handling precipitation-dissolution.

In HYDROBIOGEOCHEM, a check is made on the solubility of the potentially precipitated species and whether conditions permit the precipitated species to exist. A check is made that a phase rule violation does not occur if an equilibrium precipitated species is allowed to form. These checks and a detail of the treatment of precipitation in the numerical solution routines in HYDROBIOGEOCHEM are discussed further in Section 3.3.4.

### 2.3.4 Activity Coefficients and Thermodynamic Equilibrium Constants

Since the activity coefficients of all aqueous chemical species are functions of the ionic strength of the system, the ionic strength must be known before one can compute the activity coefficients. The ionic strength,  $I$ , is given by the following formula:

$$I = \frac{1}{2} \sum_{i=1}^{M_{aq}} a_i v_i^2, \quad (2.3.32)$$

where

$v_i$  = charge of the  $i$ -th aqueous species.

$a_i$  = the molality of the  $i$ -th aqueous species.

$M_{aq}$  = the number of aqueous chemical species = the number of aqueous component species plus the number of aqueous complexed species.

Many semi-empirical formulae, usually based on the Debye-Huckel theory of ion clustering, have been proposed to calculate activity coefficients of aqueous species. All these semi-empirical formulae have the same generalized form (Kincaid et al., 1984):

$$\text{Log}(\gamma_i) = -A v_i^2 \left( \frac{\sqrt{I}}{1 + a_i B \sqrt{I}} + B' I \right) + b_i I + B_i I^2, \quad (2.3.33)$$

where  $A$ ,  $B$ , and  $B'$  are constants, depending only on the dielectric constant, the density of water, and the temperature of the solution, and  $a_i$ ,  $b_i$ , and  $B_i$  are species-dependent, adjustable parameters. For example, to obtain the Davies Formula (1962), one simply sets  $b_i$  and  $B_i$  equal to 0; for the Debye-Huckel Formula, one sets  $B'$ ,  $b_i$ , and  $B_i$  equal to 0; and for the extended Debye-Huckel Formula used in WATEQ (Truesdell and Jones, 1974), one sets  $B'$  and  $B_i$  equal to zero.

In HYDROBIOGEOCHEM, the Davies Formula is used to determine aqueous activity coefficients, with  $A = 0.5$ ,  $a_i B = 1$ ,  $B' = -0.3$ ,  $b_i = 0$  and  $B_i = 0$ . The activity coefficients of all adsorbed species are assumed to be 1. The activity coefficients of the ion-exchanged species are assumed to be the inverse of the total molal concentration at the exchange site. By convention, the activity of precipitated species is unity; in HYDROBIOGEOCHEM, the activity coefficients of precipitated species are set to 1 for convenience. In other words, the following equations are used to compute the activity coefficients for all species

$$\begin{aligned}
\gamma_j^c \text{ or } \gamma_i^x &= \text{given by Eq. (2.3.32)}, \quad j \in N_a \text{ or } i \in M_x \\
\gamma_j^s \text{ or } \gamma_i^y &= 1.0, \quad j \in N_s \text{ or } i \in M_y \\
\gamma_i^z &= \frac{1}{\sum_{k=NOMZI(j)+1}^{NOMZI(j)+NOMZI(j)} z_k}, \quad i \in NOMZI(j), \quad j \in NSITE \\
\gamma_i^p p_i &= 1.0, \quad i \in M_p
\end{aligned} \tag{2.3.34}$$

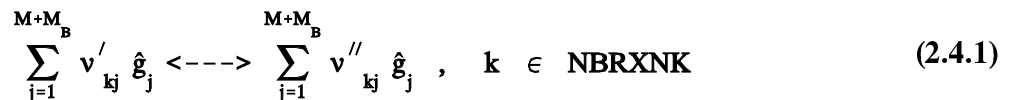
where

$$\begin{aligned}
\gamma_j^c &= \text{activity coefficient of the } j\text{-th aqueous component species,} \\
\gamma_i^x &= \text{activity coefficient of the } i\text{-th aqueous complexed species,} \\
\gamma_j^s &= \text{activity coefficient of the } j\text{-th adsorbent component species,} \\
\gamma_i^y &= \text{activity coefficient of the } i\text{-th adsorbed species,} \\
\gamma_i^z &= \text{activity coefficient of the } i\text{-th ion-exchanged species,} \\
\gamma_i^p &= \text{activity coefficient of the } i\text{-th precipitated species.}
\end{aligned}$$

The thermodynamic equilibrium constants or chemical kinetic forward and backward rate constants are normally given for conditions of 25°C and 1 atm. Under conditions other than this, the thermodynamic equilibrium constants must be corrected for temperature and pressure (Truesdell and Jones, 1974). This correction is not done within the HYDROBIOGEOCHEM code; it must be done by the user prior to running a simulation.

## 2.4 Microbiological Reaction Equations

Microbiological reactions can be defined using the same general form as Eq. (2.3.1) for chemical reactions, but one of the species involved is a microbial species:



Typically, reactant species will include a substrate, an electron acceptor, and other necessary

nutrients. Product species will include the byproducts of the biodegradation reaction and new biomass. Using modified Monod kinetics to describe the rate of the k-th microbiological reaction,

$$\Omega_k = \Gamma_k \left[ \frac{S_k}{K_{S-k} + S_k} \right] \left[ \frac{A_k}{K_{A-k} + A_k} \right] \left[ \frac{N_k}{K_{N-k} + N_k} \right] \quad (2.4.2)$$

if  $KRTYP(k) = 2$

where

$\Omega_k$  = rate of the k-th reaction per unit biomass activity, (1/T).

$\Gamma_k$  = growth rate constant for the k-th microbial reaction per unit biomass activity, (1/T).

$S_k$  = concentration of the substrate in the k-th microbial reaction, mass/mass of phase (M/M).

$A_k$  = concentration of the electron acceptor in the k-th microbial reaction, mass/mass of phase (M/M).

$N_k$  = concentration of the nutrient in the k-th microbial reaction, mass/mass of phase (M/M).

$K_{S-k}$  = half saturation constant for the substrate in the k-th microbial reaction, mass/mass of phase (M/M).

$K_{A-k}$  = half saturation constant for the electron acceptor in the k-th microbial reaction, mass/mass of phase (M/M).

$K_{N-k}$  = half saturation constant for the nutrient in the k-th microbial reaction, mass/mass of phase (M/M).

$NBRXNK$  = number of kinetic microbiological reactions.

In HYDROBIOGEOCHEM, the substrate, electron acceptor, and nutrients may be any chemical species in any phase (i.e.,  $(S_k, A_k, N_k) \in (N_a + N_s + M_x + M_y + M_z + M_p)$ ).

A metabolic lag coefficient (Kono, 1968; Wood et al., 1994) is used to allow for an acclimation period, if any, of microorganisms to new substrates:

$$\begin{aligned}
\mathcal{L}_k &= 0 && \text{if } t \leq \tau_{L-k}, \\
&= \frac{\tau_k - \tau_{L-k}}{\tau_{E-k} - \tau_{L-k}} && \text{if } \tau_{L-k} < t \leq \tau_{E-k}, \\
&= 1 && \text{if } t > \tau_{E-k}
\end{aligned} \tag{2.4.3}$$

where

$\mathcal{L}_k$  = lag coefficient for the k-th reaction.

$\tau_k$  = time microorganisms in the k-th reaction have been exposed to the substrate, (T).

$\tau_{L-k}$  = lag time for the k-th reaction, (T).

$\tau_{E-k}$  = time for microorganisms in the k-th reaction to reach exponential growth, (T).

Incorporating this lag coefficient, Eq. (2.4.2) becomes:

$$\begin{aligned}
\Omega_k &= \Gamma_k \left[ \frac{S_k}{K_{S-k} + S_k} \right] \left[ \frac{A_k}{K_{A-k} + A_k} \right] \left[ \frac{N_k}{K_{N-k} + N_k} \right] \mathcal{L}_k \\
&\text{if } \mathbf{KRTYP}(k) = 2
\end{aligned} \tag{2.4.4}$$

Microbial processes can be hindered by the presence of toxicants or excess amounts of certain substances. Inhibition may occur by different mechanisms (Bailey and Olis, 1986) and as a result affect the magnitude of the growth rate for the reaction and/or the the half velocity coefficient for the substrate, as summarized in Table 2.2.

Table 2.2 Effect of Inhibition on Microbiological Reactions.

Competitive Inhibition	$\Gamma_{k \text{ (apparent)}} = \Gamma_{k \text{ (no inhibitor)}}$	$K_{S \text{ (apparent)}} > K_{S \text{ (no inhibitor)}}$
Noncompetitive Inhibition	$\Gamma_{k \text{ (apparent)}} < \Gamma_{k \text{ (no inhibitor)}}$	$K_{S \text{ (apparent)}} = K_{S \text{ (no inhibitor)}}$
Uncompetitive Inhibition	$\Gamma_{k \text{ (apparent)}} < \Gamma_{k \text{ (no inhibitor)}}$	$K_{S \text{ (apparent)}} < K_{S \text{ (no inhibitor)}}$
Mixed Inhibition	$\Gamma_{k \text{ (apparent)}} < \Gamma_{k \text{ (no inhibitor)}}$	$K_{S \text{ (apparent)}} > K_{S \text{ (no inhibitor)}}$

Two inhibition coefficients are used to incorporate the effects of inhibition in HYDROBIOGEOCHEM:

$$I_{1k} = \left( 1 + \frac{[I]}{K_{11}} \right)^p, \quad I_{2k} = \left( 1 + \frac{[I]}{K_{12}} \right)^q \quad (2.4.5)$$

where

$I_{1k}$  = inhibition factor for the growth rate for the k-th reaction.

$I_{2k}$  = inhibition factor for the half saturation constant for the substrate in the k-th reaction.

$[I]$  = concentration of the inhibitory substance, (M/M).

$K_{11}$  = inhibition coefficient for the growth rate for the k-th reaction, (M/M).

$K_{12}$  = inhibition coefficient for the half saturation constant for the substrate in the k-th reaction, (M/M).

$p$  = fitting parameter, generally 0 (no inhibition), 1, or -1 (inhibition).

$q$  = fitting parameter, generally 0 (no inhibition), 1, or -1 (inhibition).

The inhibitory substance may be any of the chemical or microbial species. Incorporating these inhibition factors into Eq. (2.4.4), the rate of the k-th reaction becomes:

$$\Omega_k = (\Gamma_k I_{1k}) \left[ \frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right] \left[ \frac{A_k}{K_{A-k} + A_k} \right] \left[ \frac{N_k}{K_{N-k} + N_k} \right] \mathcal{Q}_k \quad (2.4.6)$$

if  $KRTYP(k) = 2$

The production/consumption rate of the j-th chemical species due to the k-th microbial biodegradation reaction is:

$$r_j|_k^{biodeg} = \frac{(v''_{kj} - v'_{kj})}{\gamma_j} \Omega_k (\gamma_{Bk} B_k), \quad j \in M \quad (2.4.7)$$

where

$r_j|_k^{\text{biodeg}}$  = the contribution of the k-th microbial biodegradation reaction to the rate of production or consumption of the j-th chemical species, (mass/mass of phase)/time, ((M/M)/T).

$B_k$  = concentration of the k-th microbial species, either aqueous ( $b_k$ ) or adsorbed ( $a_k$ ), mass/mass of phase (M/M).

$\gamma_{Bk}$  = activity coefficient for the microbial species  $B_k$ , (M/M).

The activity coefficients for microbial species are assumed to be unity. The total production/consumption rate of the j-th chemical species due to microbial degradation reactions is the sum of the contributions from all of the reactions in which the j-th species participates:

$$r_j|_{\text{biodeg}} = \sum_{k=1}^{\text{NBRXNK}} r_j|_k^{\text{biodeg}} = \sum_{k=1}^{\text{NBRXNK}} \frac{(v''_{kj} - v'_{kj})}{\gamma_j} \Omega_k (\gamma_{Bk} B_k), \quad j \in M \quad (2.4.8)$$

The production rate of biomass due to the k-th microbial reaction is given by:

$$r_i^{\text{Bg}}|_k = \frac{(v''_{ki} - v'_{ki})}{\gamma_i} \Omega_k (\gamma_{Bk} B_k), \quad i \in M_B \quad (2.4.9)$$

where

$r_i^{\text{Bg}}|_k$  = growth rate of the i-th microbial species, either aqueous ( $b_k$ ) or adsorbed ( $a_k$ ), due to the k-th microbial reaction, (mass/mass of phase)/time, ((M/M)/T).

The total growth of each microbial species is the sum of the contributions from each biodegradation reaction in which the microbial species participates:

$$r_i^{Bg} = \sum_{k=1}^{NBRXNK} r_i^{Bg|_k} = \sum_{k=1}^{NBRXNK} \frac{(v''_{ki} - v'_{ki})}{\gamma_i} \Omega_k (\gamma_{Bk} B_k), \quad i \in M_B \quad (2.4.10)$$

where

$$r_i^{Bg} = \text{total growth rate of the } i\text{-th microbial species, either aqueous or adsorbed,} \\ \text{(mass/mass of phase)/time, ((M/M)/T).}$$

The commonly used Monod kinetic parameters are incorporated in the above equations using the following relationships:

$$\mu_{\max-k} = (v''_{ki} - v'_{ki}) \Gamma_k, \quad i \in M_B \quad (2.4.11)$$

$$Y_{j-k} = \frac{(v''_{ki} - v'_{ki})}{(v''_{kj} - v'_{kj})}, \quad i \in M_B, \quad j \in M \quad (2.4.12)$$

where

$$\mu_{\max-k} = \text{maximum specific growth rate for the } k\text{-th microbial reaction, (1/T).}$$

$$Y_{j-k} = \text{growth yield coefficient for the } j\text{-th species in the } k\text{-th microbial reaction, mass} \\ \text{of microorganisms produced/mass of the } j\text{-th chemical species utilized, (M/M).}$$

The user provides values for  $\mu_{\max-k}$  and the reaction stoichiometry. HYDROBIOGEOCHEM determines the value for  $\Gamma_k$  accordingly. It should be noted that the above formulation allows for a unique growth yield coefficient for each chemical species participating in the reaction.

#### 2.4.1 Microbial Death/Decay and Endogenous Respiration

The rate of microbial death/decay is assumed to be proportional to the concentration of biomass present:

$$r_i^{Bd} = K_i^d B_i, \quad i \in M_B \quad (2.4.13)$$

where

$$r_i^{Bd} = \text{death/decay rate of the } i\text{-th microbial species, either aqueous or adsorbed,}$$



(mass/mass of phase)/time, ((M/M)/T).

$K_i^d$  = rate constant for death/decay of the i-th microbial species (1/T).

Cellular maintenance and cellular decay processes can utilize chemical species, most commonly oxygen as an electron acceptor. Endogenous respiration's effect on electron acceptor concentration has been observed to follow Monod type kinetics ( Kappeler and Gujer, 1992). Although it is likely that only oxygen or another electron acceptor will be consumed in endogenous maintenance, HYDROBIOGEOCHEM allows the flexibility of specifying any chemical species' consumption through this process:

$$r_j^{\text{bioresp}} = \sum_{i=1}^{M_B} \alpha_{ij} K_i^d B_i \left[ \frac{g_j}{\kappa_{ij} + g_j} \right], \quad j \in M \quad (2.4.14)$$

where

$r_j^{\text{bioresp}}$  = rate of consumption of j-th chemical species due to cellular maintenance/decay processes.

$\alpha_{ij}$  = stoichiometric coefficient for use of the j-th chemical species due to maintenance/decay of the i-th microbial species.

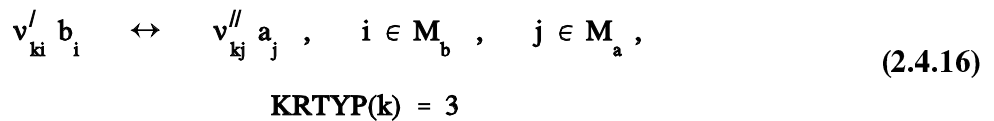
$\kappa_{ij}$  = half saturation constant for the j-th chemical species in the maintenance/decay processes of the i-th microbial species.

Incorporating consumption of chemical species due to microbial decay, the total rate of production/consumption of chemical species due to microbiological reactions combines Eqs. (2.4.8) and (2.4.14) and becomes:

$$r_j^{\text{bio}} = r_j^{\text{biodeg}} - r_j^{\text{bioresp}}, \quad j \in M \quad (2.4.15)$$

#### 2.4.2 Adsorption of Microbial Species

In HYDROBIOGEOCHEM, microorganisms may be either aqueous phase or adsorbed phase species, and may be transferred from one phase to the other. Transfer of microbial species between phases is handled by a simple kinetic transfer reaction:



The reaction rate is described using forward and backward rate constants, as for kinetic chemical reactions, but microbial species activities are used instead of chemical species activities:

$$\Omega_k = k_k^f (\gamma_i b_i)^{v_{ki}'} - k_k^b (\gamma_j a_j)^{v_{kj}''}, \quad i \in M_b, \quad j \in M_a \quad (2.4.17)$$

if  $KTYP(k) = 3$

where

$\Omega_k$  = reaction rate of the k-th reaction, (1/T).

$k_k^f$  = forward rate constant for the k-th reaction, (1/T).

$k_k^b$  = backward rate constant for the k-th reaction, (1/T).

So the rate of change of the i-th microbial species between phases is:

$$r_i^{xfr} = \frac{(v_{ki}'' - v_{ki}')}{\gamma_i} \Omega_k, \quad i \in M_B \quad (2.4.18)$$

## 2.5 Treatment of Colloids

Colloids are water borne particles with diameters less than approximately 10  $\mu\text{m}$  (Stumm and Morgan 1981). The surface of colloids can act as sites for adsorption of chemical species. Any chemical species adsorbed to the colloid will be transported with the colloid as it moves through the porous media. In HYDROBIOGEOCHEM's handling of hydrologic transport, colloids are treated as aqueous components which are subject to advective-dispersive transport per Equation (2.2.34). In the model's handling of biogeochemical reactions, colloids are treated as adsorbent components which may provide sites for adsorption of aqueous chemical species. Adsorption to the colloid may be equilibrium or kinetic and may be simulated using the surface complexation, Constant Capacitance, or Triple Layer Models. The colloids themselves are considered stable particles; HYDROBIOGEOCHEM does not address aggregation of colloids or colloid stability.

## 2.6 Initial and Boundary Conditions

To complete the description of the hydrological transport and mass balance Equations (2.2.34), (2.2.44), (2.2.53), (2.2.54), (2.2.55) and (2.2.10) through (2.2.13), initial and boundary conditions must be specified in accordance with dynamic and physical considerations. It will be assumed

initially that the total equilibrium concentrations for all components and all kinetically controlled chemical and microbiological species and the number of equivalents of the ion-exchange site are known throughout the region of interest; that is,

$$T_j = T_{j0} \quad \text{at } t = 0, \quad j \in N_a, \quad (2.6.1)$$

$$W_j = W_{j0} \quad \text{at } t = 0, \quad j \in N_s, \quad (2.6.2)$$

$$N_{eqi} = N_{eqio} \quad \text{at } t = 0, \quad i \in \text{NSITE} \quad (2.6.3)$$

$$x_j = x_{j0} \quad \text{at } t = 0, \quad j \in K_x, \quad (2.6.4)$$

$$y_j = y_{j0} \quad \text{at } t = 0, \quad j \in K_y, \quad (2.6.5)$$

$$z_j = z_{j0} \quad \text{at } t = 0, \quad j \in K_z, \quad (2.6.6)$$

$$p_j = p_{j0} \quad \text{at } t = 0, \quad j \in K_p, \quad (2.6.7)$$

$$b_j = b_{j0} \quad \text{at } t = 0, \quad j \in M_b, \quad (2.6.8)$$

and

$$a_j = a_{j0} \quad \text{at } t = 0, \quad j \in M_a, \quad (2.6.9)$$

where

- $T_{j0}$  = initial total equilibrium concentration of the j-th aqueous component (M/L<sup>3</sup>).
- $W_{j0}$  = initial total equilibrium concentration of the j-th adsorbent component (M/L<sup>3</sup>).
- $N_{eqio}$  = initial number of equivalents of the i-th ion-exchange site (equivalents/L<sup>3</sup>).
- $x_{j0}$  = initial concentration of the j-th kinetically controlled aqueous complexed species, (M/M of liquid).
- $y_{j0}$  = initial concentration of the j-th kinetically controlled adsorbed species (M/M of solid).
- $z_{j0}$  = initial concentration of the j-th kinetically controlled ion-exchanged species (M/M of solid).
- $p_{j0}$  = initial concentration of the j-th kinetically controlled precipitated species (M/M of solid).
- $b_{j0}$  = initial concentration of the j-th aqueous phase microbial species (M/M of liquid).
- $a_{j0}$  = initial concentration of the j-th adsorbed phase microbial species (M/M of solid).

Equilibrium product species concentrations are obtained from mass action equations involving the components, and hence do not have to be independently specified. Initial concentrations for

aqueous components may be obtained from field measurements or by solving the steady-state version of Equation (2.2.34) with time-invariant boundary conditions.

The specification of boundary conditions is the most difficult and intricate task in multicomponent transport modeling. From the dynamic point of view, a boundary segment may be classified as either flow-through or impervious. From a physical point of view, it is a soil-air interface, a soil-soil interface, or a soil-water interface. From the mathematical point of view, it may be treated as a Dirichlet boundary, for which the total concentration is prescribed; a Neumann boundary, for which the flux due to the gradient of total concentration is known; or a Cauchy boundary, for which the total flux is given. An even more difficult mathematical boundary is the variable condition, in which the boundary conditions are not known a priori but are themselves part of the solution. In other words, on the mathematically variable boundary, either Neumann or Cauchy conditions may prevail and change with time. Which condition prevails at a particular time can be determined only in the cyclic processes of solving the governing equations (Freeze 1972a, 1972b; Yeh and Ward 1980, 1981).

Whatever point of view is chosen, all boundary conditions eventually must be transformed into mathematical equations for quantitative simulations. Thus, we can specify the boundary conditions from the mathematical point of view in concert with dynamic and physical considerations. Boundary conditions must be specified for all entities that are subject to hydrologic transport, that is all aqueous chemical components (Eq. (2.2.34)), all kinetically controlled aqueous product species (Eq. (2.2.54)), and all aqueous phase microbial species (Eq. (2.2.55)). (Equilibrium aqueous complexed species concentrations are obtained from mass action equations involving the aqueous components, and hence do not have to be independently specified). The boundary conditions imposed on any segment of the boundary can be either Dirichlet, Neumann, Cauchy, or variable for  $T_j$  with  $j = 1, 2, \dots, N_a$ , for  $x_j$  with  $j = 1, 2, \dots, K_x$ , and for  $b_j$  with  $j = 1, 2, \dots, M_b$  independently of each other. Thus, for any  $T_j$ ,  $x_j$ , or  $b_j$ , the global boundary may be split into four parts:  $B_D$ ,  $B_N$ ,  $B_C$ , and  $B_V$ , denoting Dirichlet, Neumann, Cauchy, and variable boundaries, respectively. The conditions imposed on the first three types of boundaries are given as

$$T_j = T_{jD} \quad \text{on} \quad B_D, \quad j \in N_a, \quad (2.6.10)$$

$$x_j = x_{jD} \quad \text{on} \quad B_D, \quad j \in K_x, \quad (2.6.11)$$

$$b_j = b_{jD} \quad \text{on} \quad B_D, \quad j \in M_b, \quad (2.6.12)$$

$$-\mathbf{n} \cdot [\rho_\ell \theta \mathbf{D} \cdot \nabla(C_j/\rho_\ell \theta)] = q_{jN} \quad \text{on} \quad B_N, \quad j \in N_a, \quad (2.6.13)$$

$$-\mathbf{n} \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla x_j) = q_{jN} \quad \text{on} \quad B_N, \quad j \in K_x, \quad (2.6.14)$$

$$-\mathbf{n} \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla \mathbf{b}_j) = q_{jN} \quad \text{on} \quad \mathbf{B}_N, \quad j \in \mathbf{M}_b, \quad (2.6.15)$$

$$\mathbf{n} \cdot [\rho_\ell \mathbf{V}(C_j/\rho_\ell \theta) - \rho_\ell \theta \mathbf{D} \cdot \nabla(C_j/\rho_\ell \theta)] = q_{jC} \quad \text{on} \quad \mathbf{B}_C, \quad j \in \mathbf{N}_a, \quad (2.6.16)$$

$$\mathbf{n} \cdot (\rho_\ell \mathbf{V} \mathbf{x}_j - \rho_\ell \theta \mathbf{D} \cdot \nabla \mathbf{x}_j) = q_{jC} \quad \text{on} \quad \mathbf{B}_C, \quad j \in \mathbf{K}_x, \quad (2.6.17)$$

$$\mathbf{n} \cdot (\rho_\ell \mathbf{V} \mathbf{b}_j - \rho_\ell \theta \mathbf{D} \cdot \nabla \mathbf{b}_j) = q_{jC} \quad \text{on} \quad \mathbf{B}_C, \quad j \in \mathbf{M}_b, \quad (2.6.18)$$

where

$T_{jD}$  = prescribed Dirichlet total equilibrium concentration for aqueous component  $j$  ( $M/L^3$ ).

$x_{jD}$  = prescribed Dirichlet total concentration for kinetic aqueous complexed species  $j$  ( $M/M$  of liquid).

$b_{jD}$  = prescribed Dirichlet total concentration for aqueous microbial species  $j$  ( $M/M$  of liquid).

$q_{jN}$  = normal Neumann flux ( $M/L^2/T$ ).

$q_{jC}$  = normal Cauchy flux ( $M/L^2/T$ ).

$\mathbf{n}$  = an outward unit vector normal to the boundary.

The conditions imposed on the variable-type boundary, which is normally the soil-air interface or soil-water interface, are either the Neumann with zero gradient flux or the Cauchy with given total flux. The former is specified when the water flow is directed out of the region from the far away boundary, whereas the latter is specified when the water flow is directed into the region. This type of variable condition would normally occur at flow-through boundaries. Written mathematically, the variable boundary condition is given by

$$-\mathbf{n} \cdot [\rho_\ell \theta \mathbf{D} \cdot \nabla(C_j/\rho_\ell \theta)] = q_{jV} \quad \text{if} \quad \mathbf{V} \cdot \mathbf{n} > 0 \quad \text{on} \quad \mathbf{B}_V, \quad j \in \mathbf{N}_a \quad (2.6.19)$$

$$-\mathbf{n} \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla \mathbf{x}_j) = q_{jV} \quad \text{if} \quad \mathbf{V} \cdot \mathbf{n} > 0 \quad \text{on} \quad \mathbf{B}_V, \quad j \in \mathbf{K}_x \quad (2.6.20)$$

$$-\mathbf{n} \cdot (\rho_\ell \theta \mathbf{D} \cdot \nabla \mathbf{b}_j) = q_{jV} \quad \text{if} \quad \mathbf{V} \cdot \mathbf{n} > 0 \quad \text{on} \quad \mathbf{B}_V, \quad j \in \mathbf{M}_b \quad (2.6.21)$$

and

$$\mathbf{n} \cdot [\rho_\ell \mathbf{V}(C_j/\rho_\ell \theta) - \rho_\ell \theta \mathbf{D} \cdot \nabla(C_j/\rho_\ell \theta)] = q_{jV} \quad \text{if} \quad \mathbf{V} \cdot \mathbf{n} < 0 \quad \text{on} \quad \mathbf{B}_V, \quad j \in \mathbf{N}_a. \quad (2.6.22)$$

$$\mathbf{n} \cdot (\rho_\ell \mathbf{V} \mathbf{x}_j - \rho_\ell \theta \mathbf{D} \cdot \nabla \mathbf{x}_j) = q_{jV} \quad \text{if} \quad \mathbf{V} \cdot \mathbf{n} < 0 \quad \text{on} \quad \mathbf{B}_V, \quad j \in \mathbf{K}_x. \quad (2.6.23)$$

$$\mathbf{n} \cdot (\rho_\ell \mathbf{V} \mathbf{b}_j - \rho_\ell \theta \mathbf{D} \cdot \nabla \mathbf{b}_j) = q_{jV} \quad \text{if} \quad \mathbf{V} \cdot \mathbf{n} < 0 \quad \text{on} \quad \mathbf{B}_V, \quad j \in \mathbf{M}_b. \quad (2.6.24)$$

HYDROBIOGEOCHEM allows specification of Dirichlet and variable type boundary conditions to handle the range of physical boundaries needed for subsurface transport problems.