Chapter 2. Model Development

2.1 Conceptual Model

SEAM3D is capable of depicting subsurface transport of multiple solutes in a three-dimensional, anisotropic, heterogeneous domain as influenced by advection, dispersion, adsorption, and biodegradation. The solutes may be biodegradable substrates, nutrients, and electron acceptors (EAs) for microbial growth; products of biodegradation, daughter products of the substrates; or nonreactive tracers. Typically, the substrates are hydrocarbons that act as electron donors, and the nutrients are inorganic compounds such as phosphate or ammonia. Biodegradation of each substrate is assumed to follow Monod kinetics, although other kinetic models have been proposed (see de Blanc et al., 1995). The Monod equations are modified to include effects of EA and nutrient availability (Bailey and Ollis, 1977), inhibition (Widdowson et al., 1988), and threshold concentrations (Button, 1985). Microbial growth occurs only when substrate concentrations are sufficient to permit the population to double (Simkins and Alexander, 1984).

The Monod equation is empirically derived, and is often written in terms of the maximum specific growth rate μ^{max} [$M_b\ M_b^{-1}\ T^{-1}$] rather than the maximum specific rate of substrate utilization ν^{max} [$M_s\ M_b^{-1}\ T^{-1}$]. Nevertheless, SEAM3D uses the latter formulation to allow values of the use coefficients (see Section 2.1.2) for EAs and nutrients to be estimated from stoichiometric relationships (e.g. Borden et al., 1995). The model assumes that biomass yield (see Section 2.1.2) and ν^{max} are constant with respect to time, even though environmental factors may affect their value (Button, 1985). In part, this assumption may be justified since yield often remains constant when carbon sources are the limiting substrate (Simkins and Alexander, 1984).

When multiple EAs are available, microbes tend to utilize them in sequence, starting with the one that provides the highest Gibbs free energy (Table 2.1). SEAM3D simulates a sequence of six EAs, which are used in the following order (Jørgensen, 1989): oxygen (O_2), nitrate (NO_3^-), oxidized manganese (Mn(IV)), ferric iron (Fe(III)), sulfate (SO_4^{2-}), and carbon dioxide (CO_2). The model is flexible with respect to EA utilization, since user defined inhibition coefficients can allow some or all of the EAs to be used simultaneously rather than in sequence. Due to the low

solubility of most Fe(III) and Mn(IV) compounds, these constituents are assumed to occur as solid phase ions, while the other EAs are dissolved in the aqueous phase. Substrate utilization includes a Monod term for the aqueous phase EAs (see Section 2.1.2); however, utilization is zero order with respect to solid phase Mn(IV) and Fe(III), based on the assumption that these ions are readily available over a range of concentrations. If the concentration of Mn(IV) or Fe(III) falls below a minimum value, then utilization ceases.

SEAM3D can simulate a user specified nitrogenous compound (N_{user}), reduced manganese (Mn(II)), ferrous iron (Fe(II)), hydrogen sulfide (H_2S), and methane (CH_4) as products of biodegradation, with each hydrocarbon substrate potentially serving as a source of CH_4. Nitrate serves as the source of N_{user}, Mn(IV) is the source of Mn(II), Fe(III) is the source of Fe(II), and SO_4^{2-} is the source of H_2S. The model handles only a single product of NO_3^- reduction in order to avoid the complexities of the denitrification process. While products may not be of regulatory concern, these geochemical parameters are easily measured at petroleum contaminated sites and are viewed as indicators of biodegradation (Landmeyer et. al, 1996). Thus, their inclusion in a simulation may assist in the calibration of biodegradation parameters and interpretation of site conditions. In addition, SEAM3D allows each substrate to produce a single daughter product that cannot undergo further biodegradation, but can undergo first order decay.

The microbial phase is conceptualized as six independent heterotrophic groups (Table 2.1) that exist as scattered microcolonies attached to the porous medium. Although transport of microbes within the pore water has been reported (Kim and Corapcioglu, 1996), these organisms are assumed to have a negligible effect on biodegradation. The microcolonies and diffusional layer thickness are assumed to be small enough that solute diffusion from the aqueous phase occurs on a much smaller time scale than biodegradation. Thus microbial growth depends directly on the aqueous phase concentrations. Since Mn(IV) and Fe(III) are part of the aquifer solids, they are assumed to be in sufficient contact with the microbes that diffusional limitations do not restrict their use (Brauner and Widdowson, in press).

SEAM3D does not explicitly simulate an acclimation period (Chapelle, 1993) in which microbes prepare to utilize new subtrates. Thus the time scale for acclimation to substrate is assumed to be much smaller than the overall time scale (often many years) for biodegradation. In

addition, the model does not simulate changes in pH or geochemical reactions such as the precipitation of sufides, carbonates, and hydroxides. While these reactions do occur and may influence biodegradation, their explicit simulation was considered beyond the scope of the model.

Non-aqueous phase liquid (NAPL) mass can be placed at any block in the model domain in order to simulate dissolution of contaminants from the NAPL into the aqueous phase. The NAPL is conceptualized as being entirely residual, or trapped, within the porous medium, and NAPL flow is not simulated. This simplifying requirement is based on the assumption that the time scale for aqueous phase transport is much greater than the time duration of NAPL mobility. This assumption is likely to be valid for relatively small NAPL spills. For the initial condition, the user specifies the initial mass of NAPL for each dissolution block, and additional mass can be added to the NAPL according to user defined schedules as the simulation progresses. SEAM3D allows the NAPL to be composed of a maximum of 8 biodegradable substrates and 5 nonbiodegradable tracers, each of which can dissolve into the aqueous phase. The user defines the composition of the NAPL by specifying the mass fraction of each soluble substrate and tracer in the NAPL. If the sum of the mass fractions is less than 1.0, SEAM3D assigns the remaining NAPL mass as a relatively insoluble, or inert, fraction.

Table 2.1. Electron acceptors (EAs) used by the six heterotrophic microbial populations for biodegradation of hydrocarbon substrates. The EAs are listed in order of highest to lowest Gibbs free energy provided. Utilization of each EA is inhibited by the presence of an EA that provides higher energy.

x	Microbial Population	*le*	EA	Utilization Possibly Inhibited by	End products
1	strict aerobes	1	O_2	--	H_2O, CO_2*
2	facultative NO_3 reducers	1	O_2	--	H_2O, CO_2*
		2	NO_3	O_2	N_{user}
3	anaerobic Mn(IV) reducers	3	Mn(IV)	O_2, NO_3	Mn(II)
4	anaerobic Fe(III) reducers	4	Fe(III)	O_2, NO_3, Mn(IV)	Fe(II)
5	anaerobic SO_4 reducers	5	SO_4	O_2, NO_3, Mn(IV), Fe(III)	H_2O, H_2S
6	anaerobic methanogens	6	CO_2*	O_2, NO_3, Mn(IV), Fe(III), SO_4	H_2O, CH_4

* H_2O and CO_2 are not simulated in SEAM3D

2.1.1 Transport equations

Aqueous phase transport is described by the advection-dispersion equation, which may be written for each hydrocarbon substrate as

$$-\frac{\partial}{\partial x_i}\left(\bar{v}_i S_{ls}\right)+\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial S_{ls}}{\partial x_j}\right)+\frac{q_s}{\theta}S_{ls}^{*}-R_{sink,ls}^{bio}+R_{source,ls}^{NAPL}=R_{ls}\frac{\partial S_{ls}}{\partial t} \qquad (2.1)$$

where S_{ls} is the aqueous phase substrate concentration [M_{ls} L^{-3}] for *ls*=1,2,...,NS (number of substrates); S_{ls}^{*} is the substrate point source concentration [M_{ls} L^{-3}]; $\bar{v}_i$ is the average pore water velocity [L T^{-1}]; x_i is distance [L]; D_{ij} is the tensor for the hydrodynamic dispersion coefficient [L^2 T^{-1}]; $R_{sink,ls}^{bio}$ is the substrate biodegradation sink term [M_{ls} L^{-3} T^{-1}]; $R_{source,ls}^{NAPL}$ is a substrate source term due to non-aqueous phase liquid (NAPL) dissolution [M_{ls} L^{-3} T^{-1}]; R_{ls} is the retardation factor for substrate *ls* [L^o]; t is time [T]; and q_s is the volumetric flux of water per unit volume of aquifer [T^{-1}] with $q_s > 0$ for sources and $q_s < 0$ for sinks. In the case of a point sink, the concentration is generally not specified, and the model uses $S_{ls}^{*}=S_{ls}$. Nonbiodegradable tracers are simulated with a first order decay term replacing the biodegradation sink term in equation (2.1).

For each aqueous phase EA, transport follows

$$-\frac{\partial}{\partial x_i}\left(\bar{v}_i E_{le}\right)+\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial E_{le}}{\partial x_j}\right)+\frac{q_s}{\theta}E_{le}^{*}-R_{sink,le}^{bio}=\frac{\partial E_{le}}{\partial t} \qquad (2.2)$$

where E_{le} is the EA concentration [M_{le} L^{-3}] for *le*=1,2, and 5; E_{le}^{*} is the EA point source concentration [M_{le} L^{-3}]; $R_{sink,le}^{bio}$ is the EA biodegradation sink term [M_{le} L^{-3} T^{-1}]. A retardation factor does not appear in equation (2.2) since O_2, NO_3^-, and SO_4^{2-} are not typically adsorbed to aquifer solids. Equation (2.2) does not apply when *le* = 3 or 4, since Mn(IV) and Fe(III) are bound to the solid phase (the change in Mn(IV) and Fe(III) concentrations over time will be described in Section 2.1.2). For each nutrient, transport follows

$$-\frac{\partial}{\partial x_i}\left(\bar{v}_i N_{ln}\right)+\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial N_{ln}}{\partial x_j}\right)+\frac{q_s}{\theta}N_{ln}^{*}-R_{sink,ln}^{bio}=R_{ln}\frac{\partial N_{ln}}{\partial t} \qquad (2.3)$$

where N_{ln} is the aqueous phase nutrient concentration [M_{ln} L^{-3}] for *ln*=1,2,...,NN (number of nutrients); N_{ln}^{*} is the nutrient point source concentration [M_{ln} L^{-3}]; $R_{sink,ln}^{bio}$ is the nutrient biodegradation sink term [M_{ln} L^{-3} T^{-1}]; and R_{ln} is the retardation factor for nutrient *ln* [L^{o}]. For each biodegradation product (including daughters products), transport follows

$$-\frac{\partial}{\partial x_i}\left(\bar{v}_i P_{lp}\right)+\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial P_{lp}}{\partial x_j}\right)+\frac{q_s}{\theta}P_{lp}^{*}-\lambda_{lp}P_{lp}+R_{source}^{bio}=R_{lp}\frac{\partial P_{lp}}{\partial t} \tag{2.4}$$

where P_{lp} is the aqueous phase product concentration [M_{lp} L^{-3}] for *lp*=1,2,...,NP (number of products); P_{lp}^{*} is the product point source concentration [M_{lp} L^{-3}]; λ_{lp} is the product first order decay coefficient [T^{-1}]; R_{source}^{bio} is a biodegradation source term [M_{lp} L^{-3} T^{-1}]; and R_{lp} is the retardation factor for product *lp* [L^{o}].

The biodegradation source/sink term is evaluated by summing the effect of each microbial population on the substrates, EAs, nutrients, and products of biodegradation. The *x* subscripts for the six microbial populations and the *le* subscripts for the valid EAs within a microbial population are given in Table 2.1. Currently, SEAM3D allows microbial population 2 to utilize both O_2 and NO_3^-, while the other microbial populations utilize only one EA. For each substrate degraded by microbial population *x*, the sink term is

$$R_{sink,ls}^{bio}=\sum_{x}\frac{M_x}{\theta}r_{x,ls} \tag{2.5}$$

where M_x is the microbial biomass concentration [M_b L_{pm}^{-3}] for *x* = 1,2,...,NM (number of microbial populations); θ is effective transport porosity [L^{o}]; and $r_{x,ls}$ is the utilization rate of substrate *ls* in microbial population *x* [M_{ls} M_b^{-1} T^{-1}]. For each EA, the sink term is

$$R_{sink,le}^{bio}=\sum_{x}\frac{M_x}{\theta}r_{x,le} \tag{2.6}$$

where $r_{x,le}$ is the utilization rate of EA *le* in microbial population *x* [M_{le} M_b^{-1} T^{-1}]. For each nutrient, the sink term is

$$R_{sink,ln}^{bio}=\sum_{x}\frac{M_x}{\theta}r_{x,ln} \tag{2.7}$$

where $r_{x,ln}$ is the utilization rate of nutrient *ln* in microbial population *x* [M_{ln} M_b^{-1} T^{-1}]. For the product CH_4, the source term is

$$R^{bio}_{source,CH_4} = \sum_{ls} \zeta_{x,ls} \frac{M_x}{\theta} r_{x,ls} \tag{2.8}$$

where $\zeta_{x,ls}$ is the product generation coefficient [M_{lp} M_{ls}^{-1}], with *x* = 6 for CH_4 production. For the daughter products of the substrates, the source term is

$$R^{bio}_{source,ls} = \zeta^{dau}_{x,ls} \frac{M_x}{\theta} r_{x,ls} \tag{2.9}$$

where $\zeta^{dau}_{x,ls}$ is the daughter product generation coefficient [M_{ld} M_{ls}^{-1}]. For the EA products, the source term is

$$R^{bio}_{source,le} = \zeta_{x,le} \frac{M_x}{\theta} r_{x,le} \tag{2.10}$$

with *x* = *le* = 2 for N_{user}, *x* = *le* = 3 for Mn(II), *x* = *le* = 4 for Fe(II), and *x* = *le* = 5 for H_2S.

2.1.2 NAPL dissolution

When groundwater contacts a non-aqueous phase liquid (NAPL), components of the NAPL will dissolve into the aqueous phase until equilibrium is reached or NAPL mass is depleted. Since model handling of the dissolution of nonbiodegradable tracers is identical to biodegradable substrates, the following description will focus on substrates only. For each substrate *ls*, the driving force for dissolution is the difference between the actual aqueous phase concentration (S_{ls}), and the equilibrium concentration (S^{eq}_{ls}). In general, the rate of dissolution of S_{ls} into groundwater depends on the interfacial area between the NAPL and water, (Imhoff et al., 1993), aquifer heterogeneity (Mayer and Miller, 1996), the size and shape of the NAPL blobs (Powers et al., 1994) and the groundwater velocity (Pfannkuch, 1984). Thus, if transport processes occur at a high rate relative to the NAPL dissolution rate, S_{ls} may remain lower than S^{eq}_{ls}. This effect can be described mathematically (Imhoff et al., 1993; Parker et al., 1991) by a mass transfer rate coefficient (k^{NAPL}), such that the NAPL dissolution term (equation 2.1) for substrate *ls* becomes

$$R_{source,ls}^{NAPL} = \max\left[0,\, k^{NAPL}\left(S_{ls}^{eq} - S_{ls}\right)\right]. \tag{2.11}$$

Using Raoult's Law, S_{ls}^{eq} can be calculated (Corapcioglu and Baehr, 1987; Parker et al., 1991) as

$$S_{ls}^{eq} = f_{ls} S_{ls}^{sol} \tag{2.12}$$

where f_{ls} is the mole fraction of substrate *ls* in the NAPL [mol_{ls} mol_{NAPL}^{-1}]; and S_{ls}^{sol} is the solubility of pure substrate *ls* in water. During each time step, f_{ls} is computed as

$$f_{ls} = \frac{S_{ls}^{NAPL} / \omega_{ls}}{I^{NAPL} / \omega_{I} + \sum_{ls=1}^{NS} S_{ls}^{NAPL} / \omega_{ls} + \sum_{lt=1}^{NT} T_{lt}^{NAPL} / \omega_{lt}} \tag{2.13}$$

where S_{ls}^{NAPL} is the NAPL mass of substrate *ls* per unit mass dry soil [M_{ls} M_{solid}^{-1}]; I^{NAPL} is the NAPL concentration of inert (i.e., relatively insoluble constituents) [M_I M_{solid}^{-1}]; T_{lt}^{NAPL} is the NAPL concentration of nonbiodegradable tracer *lt* [M_{ls} M_{solid}^{-1}], and ω_j is the molecular weight of NAPL constituent *j*. Equations (2.12) and (2.13) represent the concept that the effective solubility of any NAPL constituent is reduced when other constituents are simultaneously dissolving into the aqueous phase. With each time step, S_{ls}^{NAPL} is updated as

$$\frac{dS_{ls}^{NAPL}}{dt} = -\frac{\theta}{\rho_b} R_{source,ls}^{NAPL} \tag{2.14}$$

where ρ_b is the bulk density of the porous medium [M_{solid} L_{pm}^{-3}]. Thus, dissolution causes the NAPL concentration of substrate *ls* to decrease as the aqueous phase concentration increases.

2.1.3 Utilization equations

Utilization of each substrate within microbial population *x* follows

$$r_{x,ls} = \sum_{le} \nu_{x,ls,le} \tag{2.15}$$

where $\nu_{x,ls,le}$ is the specific rate of substrate utilization (see equation (2.19)) for microbial population *x* growing on substrate *ls* and EA *le* [M_{ls} M_b^{-1} T^{-1}], and the summation over *le* includes only the valid EAs for microbial population *x* (Table 2.1). Utilization of each EA follows

$$r_{x,le} = \sum_{ls} \gamma_{x,ls,le}\ \nu_{x,ls,le} \tag{2.16}$$

where $\gamma_{x,ls,le}$ is the EA use coefficient [$M_{le}\ M_{ls}^{-1}$], representing the mass of EA *le* used per unit mass of substrate *ls*. Since Mn(IV) and Fe(III) are assumed to be attached to the solid phase, transport is not considered and utilization follows

$$-\frac{M_x}{\rho_b}\ r_{x,le} = \frac{dE_{le}}{dt} \tag{2.17}$$

where $x = le = 3$ for Mn(IV) and $x = le = 4$ for Fe(III); and E_{le} is the solid phase concentration [$M_{le}\ M_{solid}^{-1}$]. Utilization of each nutrient follows

$$r_{x,ln} = \sum_{le}\ \sum_{ls} \psi_{x,ls,le}\ \nu_{x,ls,le} \tag{2.18}$$

where $\psi_{x,ls,le}$ is the nutrient use coefficient [$M_{ln}\ M_{ls}^{-1}$] representing the mass of nutrient *ln* used per unit mass of substrate *ls*.

Using Monod kinetics modified for nutrient and EA availability, $\nu_{x,ls,le}$ may be written

$$\nu_{x,ls,le} = \nu_{x,ls,le}^{max}\left[\frac{\overline{S}_{ls}}{\overline{K}^{s}_{x,ls,le} + \overline{S}_{ls}}\right]\left[\frac{\overline{E}_{le}}{\overline{K}^{e}_{x,le} + \overline{E}_{le}}\right] N_x\ I_{le,li} \tag{2.19}$$

where $\overline{K}^{s}_{x,ls,le}$ is the effective half saturation constant for substrate *ls* utilizing EA *le* [$M_{ls}\ L^{-3}$]; $\overline{K}^{e}_{x,le}$ is the effective half saturation constant for EA *le* [$M_{le}\ L^{-3}$]; $\overline{S}_{ls}$ is the effective concentration of substrate *ls* [$M_{ls}\ L^{-3}$]; $\overline{E}_{le}$ is the effective concentration of EA *le* [$M_{le}\ L^{-3}$]; and N_x is a Monod function describing nutrient limitations. $I_{le,li}$ is an inhibition function (Widdowson et al., 1988) defined by

$$I_{le,li} = 1 \qquad \text{for } le = 1 \tag{2.20a}$$

and

$$I_{le,li} = \prod_{li=1}^{le-1}\left[\frac{\kappa_{le,li}}{\kappa_{le,li} + \overline{E}_{li}}\right] \qquad \text{for } le = 2, 3, 4, 5 \text{ or } 6 \tag{2.20b}$$

where $\kappa_{le,li}$ is the EA inhibition coefficient [$M_{le}\ L^{-3}$] representing inhibition of the use of EA *le* by EA *li*. If an EA is not specified in a particular simulation, then it is not included in equation

(2.20b). The inhibition function represents the concept that the availability of any EA may inhibit utilization of other EAs that provide less Gibbs free energy to the microbes. As $\kappa_{le,li}$ is assigned a larger value or $\overline{E}_{li}$ decreases, then the inhibitory effect decreases. Therefore, if the user assigns $\kappa_{le,li}$ a value that is much larger than the maximum value for $\overline{E}_{li}$, the inhibition term will be essentially equal to one, and simultaneous use of EAs may occur. N_x may be defined (Widdowson et al., 1988) as

$$N_x = \prod_{ln} \left[\frac{\overline{N}_{ln}}{\overline{K}^n_{x,ln} + \overline{N}_{ln}} \right] \tag{2.21}$$

where $\overline{K}^n_{x,ln}$ is the effective half saturation constant for nutrient *ln* [M_{ln} L^{-3}]; and $\overline{N}_{ln}$ is the effective concentration of nutrient *ln* [M_{ln} L^{-3}]. Since equation (2.21) uses the product of each nutrient Monod term, all nutrients are allowed to limit microbial growth simultaneously. Alternatively, a user option permits only the minimum nutrient to limit growth as follows:

$$N_x = \min_{ln} \left[\frac{\overline{N}_{ln}}{\overline{K}^n_{x,ln} + \overline{N}_{ln}} \right] \tag{2.22}$$

where the minimum is taken over the range of specified nutrients.

Effective concentrations are used in equations (2.19) through (2.22) to account for threshold concentrations below which the cells cannot grow (Button, 1985; Bosma et al., 1996). $\overline{S}_{ls}$ is defined as

$$\overline{S}_{ls} = \max(S_{ls} - S^t_{ls}, 0) \tag{2.23}$$

where S^t_{ls} is the threshold concentration of substrate *ls*. Likewise, $\overline{K}^s_{x,ls,le}$ is defined as

$$\overline{K}^s_{x,ls,le} = \max(K^s_{x,ls,le} - S^t_{ls}, 0) \tag{2.24}$$

where $K^s_{x,ls,le}$ is the half saturation constant for substrate *ls* utilizing EA *le* [M_{ls} L^{-3}]. In analogous fashion, $\overline{E}_{le}$, $\overline{N}_{ln}$, $\overline{K}^e_{x,le}$, and $\overline{K}^n_{x,ln}$ are defined using E^t_{le} and N^t_{ln} as the threshold concentrations. When actual concentrations are below threshold, lack of growth is generally attributed to endogenous requirements for cell maintenance (Button, 1985). Another explanation is that low concentrations of substrate, EAs, or nutrients may fail to induce enzymes for carrier proteins that transport these components into the cell (Bosma et al., 1996).

For the Mn(IV) and Fe(III) reducing populations, the substrate utilization rate is assumed to be independent of the EA concentration (E_{le}) over a range of values. Therefore, when E_{le} exceeds E^t_{le}, the expression is zero order with respect to the EA, and equation (2.19) becomes

$$\nu_{x,ls,le} = \nu^{max}_{x,ls,le}\left[\frac{\overline{S}_{ls}}{\overline{K}^s_{x,ls,le} + \overline{S}_{ls}}\right] N_x \; I_{le,li} \tag{2.25}$$

Conversely, when E_{le} falls below E^t_{le}, $\nu^{max}_{x,ls,le}$ is set to zero in equation (2.25) and substrate utilization due to that population ceases. This approach, suggested by Chapelle (1996, personal communication) is designed to simulate bioavailability of solid phase constituents; i.e. when $E_{le} < E^t_{le}$ the microbes no longer have direct access to EA on the solid phase. The model assumes that all Mn(IV) and Fe(III) is in a form that is available to the microbes. Therefore, Mn(IV) and Fe(III) forms that are relatively unavailable for microbial use should not be included in the specified concentrations of these EAs.

SEAM3D also assumes that methanogenesis is not limited by EA availability, since CO_2 is typically produced during oxidation of substrates under all other TEAP's modeled. These TEAP's precede methanogenesis and tend to occur at higher rates. Thus, CO_2 is assumed to be abundant, and the rate of substrate utilization follows equation (2.25) under methanogenesis. This simplification allows SEAM3D to avoid simulating the complexities of the carbon cycle in the subsurface environment. To fully describe the fate and transport of CO_2, an existing geochemical model could be coupled with the biodegradation model.

2.1.4 Microbial growth equations

In deriving the microbial growth equations, we distinguish between background substrates, which are not modeled explicitly, and the hydrocarbon (HC) substrates being modeled. Background substrates are the carbon sources that microbes utilize prior to aquifer contamination by HC substrates. When the aquifer is uncontaminated, the background substrate, EA, nutrient, and biomass concentrations are assumed to be at steady state. Thus the background death rate

($k_{d_x}^{bk}$) is equal to the growth rate at time zero ($G_x^{bk,0}$), just prior to HC contamination. SEAM3D calculates $G_x^{bk,0}$ as

$$G_x^{bk,0} = Y_x^{bk}\ \nu_x^{max,\,bk}\left[\frac{\overline{E}_{le}}{\overline{K}_{x,le}^{e} + \overline{E}_{le}}\right] N_x \tag{2.26}$$

where $Y_x^{bk} = \frac{1}{NS}\sum_{ls} Y_{x,ls,le}$ and $\nu_x^{max,\,bk} = \frac{1}{NS}\sum_{ls} \nu_{x,ls,le}^{max}$ for *le* representing the final EA utilized by population *x*. The use of averaged values for Y_x^{bk} and $\nu_x^{max,\,bk}$ ensures that $k_{d_x}^{bk}$ will be of the same order of magnitude as the growth rates ($G_{x,ls,le}$) due to HC substrates (see equation 2.28). Initial values for $\overline{E}_{le}$ and N_x are obtained as the spatial average of the initial concentrations, thus requiring the user to input initial concentrations that represent pristine conditions. In equation (2.26), the substrate Monod term has been set to one, under the assumption that the half saturation constant for background substrate is quite small, as is often the case in oligotrophic systems. The inhibition term does not appear in equation (2.26) since we assume that each population has reached steady state in the presence of inhibitory EAs.

When contamination occurs, steady state no longer applies, as HC substrates cause biomass growth accompanied by depletion of EAs and nutrients. As a result, periods of rapid microbial growth may be followed by rapid death. The mass balance equation for growth and death of microbial population *x* is written

$$\frac{1}{M_x}\frac{dM_x}{dt} = -k_{d_x} + G_{x,ls,le} \tag{2.27}$$

where k_{d_x} is the "effective" death rate [T^{-1}], and $G_{x,ls,le}$ is the growth rate due to the HC substrates, defined as

$$G_{x,ls,le} = \sum_{le}\ \sum_{ls} Y_{x,ls,le}\,\nu_{x,ls,le} \tag{2.28}$$

where $Y_{x,ls,le}$ is the biomass yield coefficient [$M_b\ M_{ls}^{-1}$], representing the mass of microbial population *x* produced per unit mass of substrate *ls* while utilizing EA *le*. The effective death rate (k_{d_x}) is computed as the difference between $k_{d_x}^{bk}$ (assumed constant over time) and the current growth rate as follows:

$$k_{d_x} = \max\left[0,\ k_{d_x}^{bk} - \left(G_x^{bk} + G_{x,ls,le}\right)\right] \tag{2.29}$$

where G_x^{bk} is given by equation (2.26) with $\overline{E}_{le}$ and N_x computed from current concentrations at each block in the model domain. In regions having no HC substrate, EAs and nutrients remain at background levels; thus $k_{d_x} = 0$, and biomass concentrations also remain at background levels. When HC substrates cause sufficient microbial utilization of EA and nutrient, G_x^{bk} and $G_{x,ls,le}$ decrease such that $k_{d_x} > 0$. The value of k_{d_x} will return to zero if HC subtrates are transported out of a zone, and EA and nutrient concentrations return to backgound levels.

If necessary, biomass size is limited by switching to Monod, no growth kinetics (Simkins and Alexander, 1984) when substrate concentrations are insufficient to allow the microbes to double. Thus, G_x^{bk} and $G_{x,ls,le}$ are set to zero when

$$M_x \geq \theta \sum_{ls} \left(Y_{x,ls,le} S_{ls}\right) \tag{2.30}$$

where *le* is the index of the predominant TEAP for population *x*. Overall, equations (2.26) to (2.30) link biomass concentrations to the available substrates, EAs, and nutrients, thereby preventing excessive growth or death. The intent of these equations is to provide a mathematical method for maintaining the size of each microbial population within a reasonable range. The exact behavior of microbial growth dynamics in the subsurface is not well described by current research, and simulation of biomass may not be desireable in all situations, perhaps due to lack of data. Thus, microbial death and growth can be eliminated from the model by setting the input values of $k_{d_x}^{bk}$ and $Y_{x,ls,le}$ to zero.

2.2 Model Implementation

The sequential electron acceptor model is implemented as a numerical, block-centered, finite difference computer algorithm (SEAM3D). An existing code MT3D (Zheng, 1990; Zheng, 1993) was used as the starting point for code development. MT3D is capable of simulating a single solute in groundwater under the influence of advection, dispersion, source/sink mixing, adsorption, and first order decay. SEAM3D extends the modular structure of MT3D such that

computer memory is not reserved for unused options. For example, if the user chooses to model aerobic biodecay only, then memory is not reserved for the anaerobic processes. SEAM3D interfaces with the groundwater flow model MODFLOW (McDonald and Harbaugh, 1988); thus it supports a variety of aquifer configurations and boundary conditions, including (1) confined or unconfined aquifer layers; (2) inclined and/or variable thickness layers; (3) specified concentration or mass flux boundaries; (4) and sources/sinks due to wells, drains, rivers, recharge, and evapotranspiration.

In solving the advection term in the transport equations, SEAM3D supports only the explicit finite difference algorithm. In contrast to the particle tracking algorithms, the finite difference option ensures that mass will be conserved as constituents are utilized or produced during biodegradation. Numerical dispersion error can be minimized by setting the grid spacing on the order of the dispersivity values (Zheng and Bennett, 1995). During each transport time step, SEAM3D calculates concentration changes due to advection, dispersion, and source/sink mixing. The resulting values for $\overline{S}_{ls}$, $\overline{E}_{le}$, and $\overline{N}_{ln}$ are used in equation (2.18) or (2.24) to obtain $\nu_{x,ls,le}$, from which the utilization rates are calculated in equations (2.15), (2.16), and (2.18), and biomass concentrations are calculated in equation (2.27). The code allows the transport time step to be subdivided into smaller increments for the biodegradation calculations.

Computational time and memory requirements vary, depending on user specifications for the number of blocks in the finite difference grid and the number of constituents. SEAM3D extends the modular structure of MT3D such that computer memory is not reserved for unused options. For example, if the user chooses to model aerobic biodecay only, then memory is not reserved for the anaerobic processes.