**HMS Diagenesis Model Data Requirements**

The HMS diagenesis model is based on Dominic Di Toro’s *Sediment Flux Modeling* (2001). The diagenesis model is comprised of 24 state variables. These variables include particulate organic carbon (POC), particulate organic nitrogen (PON), and particulate organic phosphorus (POP), in three different reactivity classes G1—fast reacting G2—slow reacting, and G3—nonreactive. Inorganic phosphate, ammonia, and nitrate are modeled in two sediment layers, one surficial aerobic layer and one deeper anaerobic layer.



Water-column nutrients must be modeled (phosphate, ammonia, and nitrate) as the flux of nutrients to water depends on their valuations.

There are potential interactions between the HMS diagenesis model and animal and plants and organic matter state variables/models. If these state variables are not explicitly modeled within HMS, then time-series linkages from other models or estimates of impacts of animals, plants, and on diagenesis derivatives may be input into the model directly within the JSON files.

The list of time-series linkages into the diagenesis state variable derivatives are listed here. All units are **(g/d)**:

|  |  |  |  |
| --- | --- | --- | --- |
| **State Variable** | **Derivative Linkage** | **Name within JSON** | **Omit if explicitly modeling** |
| POC\_G1..G3 | *(Predation /* *Detr2OC)* | Predation\_Link | Detritivores |
| POC\_G1..G3 | *Deposition* | Deposition\_Link | All depositing animals, plants, organic matter.\* |
| POP\_G1..G3 | *(Predation \* P2Org)* | Predation\_Link | Detritivores |
| POP\_G1..G3 | *Deposition* | Deposition\_Link | All depositing animals, plants, organic matter.\* |
| PON\_G1..G3 | *(Predation /* *N2Org)* | Predation\_Link | Detritivores |
| PON\_G1..G3 | *Deposition* | Deposition\_Link | All depositing animals, plants, organic matter.\* |

\* This linkage will be added to existing model components that are explicitly depositing.

Example JSON data files for an organic-matter model may be found in the associated DOCS directory.

The following pages are excerpts from the relevant sections of the AQUATOX Release 3.2 Technical Documentation. The HMS diagenesis model was not changed from the AQUATOX Release 3.2 implementation and results were verified against AQUATOX Release 3.2 results.

**7. SEDIMENT DIAGENESIS**

AQUATOX has been modified to include a representation of the sediment bed as presented in Di Toro’s *Sediment Flux Modeling* (2001). This optional sediment submodel tracks the effects of organic matter decomposition on pore-water nutrients, and predicts the flux of nutrients from the pore waters to the overlying water column based on this decomposition. It is a more realistic representation of nutrient fluxes than the “classic” AQUATOX model. It includes silica, which will be modeled as a nutrient for diatoms in a later version.

**Sediment Diagenesis Model: Simplifying Assumptions**

* Model assumes a depositional environment (no scour is modeled).
* Two layers of sediment are modeled.
* Aerobic (top) layer is quite thin
* Model is best suited to represent predominantly anaerobic sediments.
* Deposition of particulate organic matter moves directly into Layer 2. Particulate organic matter in Layer 1 assumed to be negligible and is not modeled
* The fraction of POP and PON within defecated or sedimented matter is assumed equal to the ratio of phosphate or nitrate to organic matter for given species.
* All methane is oxidized or lost.

The model assumes a small aerobic layer (L1) above a larger anaerobic layer (L2). For this reason, it is best to apply this optional submodel in eutrophic sites where anaerobic sediments are prevalent.

Because AQUATOX simulates organic matter with stoichiometric ratios for nutrients and Di Toro’s model simulates separate organic nutrients, the organic-nutrient relationships are redefined for the sediments. The additional 21 state variables added when the sediment diagenesis model is enabled (and one driving variable) are as follows:

* **POC** (Particulate Organic Carbon) in sediment: three state variables to represent three reactivity classes (see below). A component of the particulate organic matter (POM) that settles from the water column into the anaerobic layer (Layer 2) and decomposes.
* **PON** (Particulate Organic Nitrate) in sediment: as with POC, three state variables to represent three reactivity classes in the anaerobic layer. Another component of POM.
* **POP** (Particulate Organic Phosphate) in sediment: as with POC, three state variables to represent three reactivity classes in the anaerobic layer. The third modeled component of POM.
* **Ammonia**:two state variables to represent two layers. Formed by the decomposition of PON, this process is also called the diagenesis flux. Ammonia in sediment undergoes nitrification and flux to or from the water column.
* **Nitrate**: two state variables (in Layers 1 and 2). Formed by nitrification of ammonia in the sediment bed. Undergoes denitrification and flux to or from the water column.
* **Orthophosphate**: two state variables (in Layers 1 and 2). Formed by the decomposition of POP in sediment (diagenesis flux). Flux to or from the water column is predicted but may be limited by strong P sorption to oxidated ferrous iron in the aerobic layer.
* **Methane**: (Layer 2) Methane is formed due to the decomposition of POC in the sediment bed under low-salinity conditions. Methane undergoes oxidation resulting in increased sediment oxygen demand.
* **Sulfide**: two state variables (in Layers 1 and 2). Hydrogen sulfide (H2S) is formed, rather than methane under saline conditions. Sulfide in sediment may undergo burial, flux to the water column, or oxidation (increasing SOD).
* **Biogenic Silica**: Silica in sediment is modeled using three state variables. Silica deposited from the water column is bioavailable or “biogenic silica” and is modeled in Layer 2. Biogenic silica can then either undergo deep burial or dissolution to dissolved silica.
* **Dissolved Silica:** two state variables (in Layers 1 and 2). Produced when biogenic silica breaks down due to dissolution. Available Silica in Layer 2 and Silica in Layers 1 & 2. Dissolved silica may undergo burial or flux to the water column.
* **COD**: Driving variable for chemical oxygen demand in the water column that affects the flux of sulfide to the water column.

Figure : Simplified schematic of the AQUATOX sediment diagenesis model

*(Diagram does not include Silica, Sulfide or COD)*



Particulate organic matter in the sediment bed (POC, PON, and POP) is divided into three reactivity classes as follows:

* G1 – reactivity class 1, equivalent to labile organic matter
* G2 – reactivity class 2, equivalent to refractory organic matter
* G3 – reactivity class 3, nonreactive

Within the system of equations governing these state variables, sediment oxygen demand (SOD) is a function of specific chemical reactions following the decomposition of organic matter. Specifically the oxidation of methane or sulfide and the nitrification of ammonia increases the predicted SOD . This in turn has effects on the amount of oxygen present in the water column. The amount of oxygen in the water column, however significantly affects the nitrification of ammonia **(275)**.

To optimize the solution of this feedback loop, an iterative solution is utilized to calculate SOD in each time-step. (see Eq 263) An initial value of SOD *(SODInitial)* is estimated. (In the first time-step, *SODInitial* is calculated by the model based on sediment initial conditions, in later time-steps the *SODInitial*  is assumed to equal the SOD in the previous time-step.) Based on *SODInitial*, the concentrations of ammonia, nitrate, and sulfide or methane can be calculated by the model Then, using those nutrient concentrations, a new estimate of SOD may be obtained. This becomes the new “initial” estimate of SOD until the initial estimate and “new” estimate of SOD converge (to within the relative error set in the AQUATOX setup screen).

This iterative solution is likely not mandatory within AQUATOX as the water column model is not decoupled from the sediment diagenesis model (all differential equations are solved simultaneously.) However, by including this iterative solution, the solution for SOD is not a limiting factor when setting the variable differentiation time-step.

Most implementations of Di Toro’s model solve state variables in the thin aerobic upper layer (Layer 1) using an assumption of steady-state. This option was added to AQUATOX Release 3.1. A checkbox at the top of the diagenesis initial conditions screen can be selected for running the model in this manner. Initial tests of the steady-state model produce results nearly identical to non-steady-state model results and the model runs up to ten times faster.

However, precise balancing of the mass of nutrients is not generally possible when the steady-state model is incorporated. If there are two interacting state variables and one is solved with a steady-state solution and the other is solved using differential equations, the conservation of mass is not possible. (For example, when solved under steady state, the nutrient mass in Layer 1 will change based on the conditions prior to the time-step but that nutrient mass is not explicitly added to or subtracted from another state variable.)

It would be advisable to simulate a site with steady state turned on during model calibration and off for production runs if balancing the mass of nutrients is important. When the steady-state model is not utilized, the state variables in sediment Layer 1 are solved using differential equations. The thickness of Layer 1 (a user input variable) might therefore have a significant effect on model run time, with larger layer thicknesses resulting in shorter run-times.

**7.1 Sediment Fluxes**

State variables in the two model layers are subject to a number of fluxes to and from other modeled and unmodeled compartments. Fluxes in the model include:

* Diffusion of the dissolved component of state variables to and from the water column;
* Diffusion of the dissolved component of the state variables between layers;
* Burial of the state variables below the lower layer and out of the modeled system; and
* Particulate mixing of the two layers and resultant exchange of state variable.

To calculate these fluxes, the diffusion velocity between layers must be solved as well as a particle mixing velocity between the two layers and a surface mass transfer coefficient.

**Diffusion Velocity Between Layers**

Diffusion between layers is specified by a diffusion coefficient, provided by the user and adjusted for the water temperature in the system. Enhanced diffusive mixing due to bioturbation is not currently included in the AQUATOX implementation, though direct mixing by bioturbation is.

 **(261)**

*KL* = diffusion velocity between layers (m/d);

*Dd* = diffusion coefficient for pore water (m2/d);

*θ*Dd = constant for temperature adjustment for *Dd* (unitless);

*Temp* = temperature of water (deg. C); and

*H2* = depth of sediment layer 2 (m).

**Particle Mixing Between Layers (Bioturbation)**

In a departure from Di Toro’s model, particle mixing between layers is a direct function of the modeled benthic biomass in the system. Di Toro’s formulation uses the assumption that benthic biomass is proportional to the labile carbon in the sediment. As AQUATOX calculates benthic biomass explicitly, this simplifying assumption is not required and a direct empirical relationship based on benthic biomass is utilized.

 **(262)**

where:

*ω1,2* = particle mixing velocity between layers (m/d)

*Benthic\_Biomass* = sum of benthic invertebrate biomass (g/m2 dry);

*H2* = depth of sediment layer 2 (m); and

1e-4 = pore water concentration (m2/cm2);

Figure : Relationship derived from Di Toro, 2001, Figure 13.1A  
“Diffusion coefficient for particle mixing versus benthic biomass”



Additionally, the calculation of benthic biomass by AQUATOX includes benthic invertebrate mortality due to low oxygen conditions and recovery when oxygen concentrations rise. Because of this, Di Toro’s benthic stress model incorporating accumulated stress and dissipation of stress is not required nor included within AQUATOX.

**Surface Mass Transfer Coefficient**

Di Toro has advanced the idea that the diffusive surface mass transfer coefficient can be successfully related to the sediment oxygen demand (Di Toro et al. 1990). The resulting equation is as follows.

 **(263)**

where:

*s* = surface diffusive transfer (m/d)

*SOD* = sediment oxygen demand (g O2 / m2 d);

CSOD = carbon based sediment oxygen demand (g O2 / m2 d) see **(287)** or **(291)**;

NSOD = sediment oxygen demand due to nitrification (g O2 / m2 d) see **(275)**, converted into oxygen equivalent units (1.714 gO2/gN);

*OxygenWater* = overlying water oxygen conc. (g O2 / m3) **(186)**.

As shown above, *SOD* is the sum of the carbon based sediment oxygen demand and sediment oxygen demand due to nitrification..

**7.2 POC**

Particulate Organic Carbon in sediment is assumed to be located exclusively in the second layer of sediment. Three state variables are utilized to represent three reactivity classes (G1 through G3). POC is a component of the particulate organic matter that settles from the water column into the anaerobic layer and decomposes; it is also subject to consumption by detritivores. In this case, the POC uptake from that predation must be calculated separately from the POP and PON.

 **(264)**

where:

*Deposition* = deposition from water column (g C/ m3 d) see **(266)**;

*Mineralization* = decomposition (g C/ m3 d) see **(267)** ;

*Burial* = deep burial below modeled layer (g C/ m3 d) see **(265)**;

*Predation* = predation by detritivores (g C/ m3 d) see **(99)**; and

*Detr2OC* = detrital organic matter is assumed to be 1.90 • organic carbon as derived from stoichiometry (Winberg 1971).

For all state variables burial is solved as a function of the user input burial rate *w2:*

 **(265)**

where:

*Burial* = burial below modeled layer (g C/ m3 d); and

*POM* = POP, POC, or PON (g C/ m3);

*w2* = user input burial rate (m/d); and

*Hn* = depth of sediment layer *n* (m).

Burial from the top layer is added to the second layer, whereas burial from the second layer is considered deep burial out of the modeled system.

Deposition is solved as

 **(266)**

where:

*DepositionPOM\_Gi* = deposition of Gi reactivity class of POP, POC, or PON from water column (g OM/ m3 d);

*Def =* defecation of animals, see **(97)** (g OM/m­3water d);

*Def2POM­Gi* = fraction of POP, POC, or PON reaction class Giin defecated matter;

*Sed =* sedimentation of plants or detritus, see **(165)**, (g OM/m­3water d);

*Sed2POM­Gi* = fraction of POP, POC, or PON reaction class Giin sedimented algae or detritus (unitless);

*Volwater* = water volume (m3); and

*Volsediment* = sediment volume (m3);

Assigning fractions of defecation to the relevant POM class (i.e., determining *Def2POMGi*)is a two-part process. First, the fraction of POM, POC, or PON in the defecated material must be determined. Second, each fraction must be again multiplied by a fraction to assign it to the three reactivity classes (G1 to G3). In this manner, particulate organic matter is separated into nine different state variables in the sediment.

The fractions of POP and PON within defecated matter are assumed to equal the ratios of phosphate or nitrate to organic matter for sedimented labile detritus; these are editable parameters (“remineralization” screen). The fraction of POC within defecated matter is set to 52.6% (Winberg 1971). Defecated matter is split evenly between reactivity classes G1 and G2, with no defecation assigned to the non-reactive G3 class (*Def2SedLabile*=0.5).

Similarly, assigning fractions of sedimentation to reactivity classes is a two-part process. As before, the fraction of POP and PON within sedimented matter is assumed equal to the ratio of phosphate or nitrate to organic matter for the given species or detritus (editable parameters). The fraction of POC within sedimented matter is again set to 52.6% (Winberg 1971). The amount of *refractory* detritus that is converted to reactivity class G3 is a user entered parameter. The rest of the refractory detritus is assigned to G2 and labile detritus becomes G1. 92% of sinking plants are assumed to be labile (G1) with no sinking algae being converted to the non-reactive compartment (G3).

The decomposition of organic matter is calculated as a first-order reaction with an exponential temperature sensitivity built in:

 **(267)**

where:

*MineralizationPOM\_Gi* = decomposition of Gi reactivity class of POP, POC, or PON in the sediment bed (g/m3 d);

*POMGi* = concentration of POM in reactivity class Gi (g/m3);

*KPOM\_Gi* = decay rate of POM class (1/d);

*θPOM\_Gi* = exponential temperature adjustment for decomposition of POM class Gi (unitless); and

*Temp* = temperature (deg.C).

Feeding on G1 is calculated based on preferences for labile detritus and feeding on G2 is based on preferences for refractory detritus; these are set in the animal data screens. As a simplifying assumption, there is no feeding on nonreactive G3.

**7.3 PON**

Particulate Organic Nitrogen in sediment is also assumed to be in the second layer of sediment. Three state variables are utilized to represent three reaction classes (G1 through G3).

 **(268)**

where:

*Deposition* = deposition from water column (g N/ m3 d) see **(266)**;

*Mineralization* = decomposition to ammonia (g N/ m3 d) see **(267)** ;

*Burial* = deep burial below modeled layer (g N/ m3 d) see **(265)**;

*Predation* = predation by detritivores (g N/ m3 d) see **(99)**; and

*N2Org* = user input conversion factor between N and refractory or labile detritus (g N / g OC).

**7.4 POP**

Particulate Organic Phosphate in sediment is solved in a very similar manner to POC and PON. Mineralization rates may be different, however.

 **(269)**

where:

*Deposition* = deposition from water column (g P/ m3 d) see **(266)**;

*Mineralization* = decomposition to orthophosphate (g P/ m3 d) see **(267)** ;

*Burial* = deep burial below modeled layer (g P/ m3 d) see **(265)**;

*Predation* = predation by detritivores (g P/ m3 d) see **(99)**; and

*P2Org* = user input conversion factor between P and refractory or labile detritus (g P / g OC).

**7.5 Ammonia**

Ammonia in the sediment is solved using two state variables to represent the two layers. Ammonia is formed by the decomposition of PON. Ammonia in sediment undergoes nitrification, burial, and flux to or from the water column. The ammonia in each state variable is the sum of dissolved and particulate ammonia. The fraction that is dissolved is solved below in equation **(274)**. The ammonia differential equations are as follows:

 **(270)**

 **(271)**

where:

*Diag\_Flux* = decomposition of PON, see **(267)** ;

*Burial* = burial below relevant layer (g N/ m3 d) see **(265)**;

*Flux2Anaerobic* =flux to layer 2 from layer 1 (g N/ m3 d, may be negative) see **(272)** ;

*Flux2Water* =flux to water from layer 1 (g N/ m3 d, may be negative); see **(273)**; *Nitrification* = conversion to nitrate (g N/ m3 d) see **(275)**;

 **(272)**

where:

*ω1,2* = particle mixing velocity between layers (m/d), see **(262)**;

*KL* = diffusion velocity between layers (m/d), see **(261)**;

*fp,layer* = particulate fraction in layer 1 or 2 (unitless); see **(274)**

*fd,layer* = dissolved fraction in layer 1 or 2 (unitless); see **(274)**

*Conclayer* = total concentration of state variable in layer (g/m3); and

*H*layer = depth of layer being evaluated (m);

 **(273)**

where:

*s* = surface diffusive transfer (m/d); **(263)**

*fd1* = dissolved fraction in layer 1;

*Conclayer* = total concentration of state variable in layer (g/m3); and

*H1*= depth of layer 1 (m);

The fraction of ammonia that is dissolved in each layer is calculated as follows:

 **(274)**

where:

*fd ammonia,layer*  = dissolved fraction in layer;

*mlayer* = user-input solids concentration in layer (kg/L);

*KdNH4*= editable partition coefficient for ammonium (L/kg); and

*fp ammonia,layer*  = particulate fraction in layer.

Ammonia in the top layer is converted to nitrate in the presence of oxygen, resulting in sediment oxygen demand. Since the nitrification reaction requires oxygen, no nitrification is assumed to occur in the lower anaerobic layer. *Nitrification* in the aerobic layer is calculated as follows:

 **(275)**

where:

 = conversion of ammonia to nitrate (g N/m3d);

*DOWC.* = dissolved oxygen in the water column (g/m3);

*KMNH4*= user-input nitrification half-saturation coefficient for ammonium  
 (g N/m3);

*KMO2*= user-input nitrification half-saturation coefficient for oxygen   
(g O2/m3);

*κ* = reaction velocity for nitrification (m/d); (user-input, differentiating between fresh and salt water)

*s* = surface diffusive transfer (m/d); **(263)**

*NH41* = concentration of ammonia in layer 1 (g/m3); **(168)**

*H1*= user-input depth of layer 1 (m);

*θ*= user-input exponential temperature adjustment for nitrification (unitless); and

*Temp* = temperature (deg.C).

**7.6 Nitrate**

Nitrate is formed by the nitrification of ammonia in the top layer of the sediment bed. Nitrate in sediment undergoes denitrification, burial and flux to or from the water column.

 **(276)**

 **(277)**

where:

*Burial* = burial to layer below modeled layer or out of the system(g N/ m3 d) see **(265)**;

*Flux2Anaerobic* =flux to layer 2 from layer 1 (g N/ m3 d, may be negative) see **(272)** ;

*Flux2Water* =flux to water from layer 1 (g N/ m3 d, may be negative); see **(273)**; *Nitrification* = conversion of ammonia to nitrate (g N/ m3 d), see **(275)**;

*Denitr* = denitrification of nitrate to free nitrogen (g N/ m3 d), see **(278)**;

Nitrate is assumed to be dissolved in the sediment bed so *fd­* = 1.0 and *fp* = 0.0.

Denitrification is solved as follows

 **(278)**

where:

*κ layer, No3* = user-input reaction velocity for denitrification given the layer and salinity regime (m/d);

*θ*= user-input exponential temperature adjustment for denitrification (unitless); and

*s* = surface diffusive transfer (m/d); **(263)**

*H layer*= depth of layer (m);

*NO3layer* = concentration of nitrate in layer (g/m3); and

*Temp* = temperature (deg.C).

**7.7 Orthophosphate**

Phosphate in the sediment is solved using two state variables to represent the two layers. Like ammonia, the phosphate in each state variable represents the sum of dissolved and particulate phosphate.

 **(279)**

 **(280)**

where:

*Diag\_Flux* = decomposition of POP, see **(267)** ;

*Burial* = burial to layer below modeled layer or out of the system(g P/ m3 d) see **(265)**;

*Flux2Anaerobic* =flux to layer 2 from layer 1 (g P/ m3 d, may be negative) see **(272)** ;

*Flux2Water* =flux to water from layer 1 (g P/ m3 d, may be negative); see **(273)**;

When oxygen is present in the water column, the diffusion of phosphorus from sediment pore waters is limited. This is due to strong P sorption to oxidated ferrous iron in the aerobic layer (iron oxyhydroxide precipitate). Under conditions of anoxia, phosphorus flux from sediments increases significantly.

Di Toro incorporates the effect of oxygen on phosphate flux into his model by making the dissolved fraction of phosphate a function of oxygen in the water column. When the oxygen in water decreases below a critical threshold the partition coefficient for phosphate is increased by a user-entered factor. As the oxygen goes to zero, the partition coefficient is smoothly reduced to the anaerobic coefficient using an exponential function:

 **(281)**

Partitioning of phosphate between the dissolved and particulate forms will affect on the flux of phosphate to the water column **(273)**.

 **(282)**

where:

*fd phosphate,layer*  = dissolved fraction in layer (unitless);

*mlayer* = user-input solids concentration in layer (kg/L); and

*KdPO4,2*= partition coefficient for phosphate in layer 2 (L/kg);

Δ*KdPO4,1*= fresh or saltwater factor to increase the aerobic (L1) partition coefficient of PO4 relative to the anaerobic (L2) coeff. (unitless);

*DOWC* = dissolved oxygen in the water column (g/m3), see **(186)**; and

*DOCrit,PO4.* = critical oxygen concentration for adjustment of partition coefficient for inorganic P (g/m3);

**7.8 Methane**

Methane is formed due to the decomposition of POC in the sediment bed under low-salinity conditions. Methane undergoes oxidation resulting in increased sediment oxygen demand.

 **(283)**

where:

*MethaneL2Sed* = methane in the anaerobic layer expressed in oxygen equivalence units (g O2equiv / m3)

*Diag\_Flux* = decomposition of POC in freshwater, adjusted for the organic carbon lost due to denitrification (g O2equiv / m3 d) see **(284)**;

*Flux2Water* =methane flux to water (g O2equiv / m3 d), see **(288)**; and

*Oxidation* = oxidation of methane (CSOD) (g O2equiv / m3 d) see **(287)**;

In the manner of Di Toro, methane and sulfide are tracked in units of oxygen equivalents (g O2equiv / m3) to easily balance the model’s computations.

In fresh water conditions, decomposing POC is converted to methane which is tracked in oxygen equivalents. In salt water, decomposing POC becomes sulfide. However, some POC is lost due to denitrification and does not decompose:

 **(284)**

where:

*Diag\_FluxMethane,Sulfide*

= decomposition of POC in water, adjusted for the organic carbon lost due to denitrification (g O2equiv / m3 d);

*MineralizationPOC* =decomposition of POC in freshwater, (g POC/ m3 d) see **(267)** ;

*Denitrification* = denitrification of nitrate, (g N/ m3 d) see **(278)**;

32/12 = conversion between POC and oxygen equivalents; and

2.86 = conversion between Nitrate and oxygen equivalents;

Oxidation of methane is solved as a function of the saturation concentration of methane in pore water.

 **(285)**

 **(286)**

 **(287)**

where:

*CH4Sat* = saturation concentration of methane in pore water (g O2equiv / m3);

*zmean* = mean depth of water column above the sediment bed (m);

*Temp* = temperature (deg.C);

*CSODMax* = maximum oxidation flux (g O2equiv / m2 d);

*KL* = diffusion velocity between layers (m/d); **(261)**

*Diag\_FluxMethane* = diagenesis flux of methane to water column, adjusted to be in units of (g O2equiv / m2 d);

*OxidationMethane* = oxidation of methane (g O2equiv / m3 d);

** = hyperbolic secant function

*s* = surface diffusive transfer (m/d); **(263)**

*κCH4* = reaction velocity for methane oxidation(m/d);

*θCH4* = exp. temperature adjustment for methane oxidation (unitless); and

*H2*= depth of layer 2 (m); *(methane mass arbitrarily tracked on the second layer)*

All methane is assumed to be oxidized or to escape from the sediment to water. Thus the derivative for methane will remain at zero and the solution for the flux to water can be solved as follows:

 **(288)**

where:

*Diag\_Flux* = decomposition of POC in freshwater, adjusted for the organic carbon lost due to denitrification (g O2equiv / m3 d), see **(284)**;

*Oxidation* = oxidation of methane (g O2equiv / m3 d), see **(287)**;

**7.9 Sulfide**

Sulfide is formed, rather than methane, under saline conditions. Sulfide in sediment may undergo burial, flux to the water column, or oxidation, which increases SOD.

 **(289)**

 **(290)**

where:

*SulfideLn Sed* = sulfide concentration in layer n of sediment, (g O2equiv / m3);

*Diag\_FluxSulfide* = decomposition of POC in salt water, adjusted for the organic carbon lost due to denitrification (g O2equiv / m3 d), see **(284)**;

*Burial* = burial to layer below modeled layer or out of the system (g O2equiv / m3 d); see **(265)**;

*Flux2Anaerobic* =flux to layer 2 from layer 1 (g O2equiv / m3 d, may be neg.) see **(272)** ;

*Flux2Water* =flux to water from L1 (g O2equiv / m3 d, may be neg.) *(Note the driving var. “COD” represents the water col. conc. of sulfide.)* see **(273)**;

*Oxidation* = oxidation of sulfide in the active layer;

 **(291)**

where:

*OxidationSulfide* = oxidation of sulfide (g O2equiv / m3 d);

*ConcH2S,L1* = concentration of sulfide in layer 1 (g O2equiv / m3);

*κH2S,d* = reaction velocity for dissolved sulfide oxidation (m/d);

*κH2S,p* = reaction velocity for particulate sulfide oxidation (m/d);

*DOWC.* = dissolved oxygen in the water column (g/m3);

*KMH2S,DP*= sulfide oxidation normalization constant for oxygen (g O2/m3);

*θH2S* = exp. temperature adjustment for sulfide oxidation (unitless);

*s* = surface diffusive transfer (m/d); and

*H1*= depth of layer 1 (m);

The fraction of sulfide that is dissolved in each layer is calculated as follows:

 **(292)**

where:

*fd sulfide,layer*  = dissolved fraction in layer;

*mlayer* = solids concentration in layer (kg/L); and

*KdNH4*= partition coefficient for sulfide for layer (L/kg);

The particulate fraction of sulfide in each layer is calculated as one minus the dissolved fraction.

**7.10 Biogenic Silica**

Silica in sediment is modeled using three state variables. Silica associated with diatoms and deposited from the water column is biogenic silica and is modeled in Layer 2. Biogenic silica can then either undergo deep burial or dissolution to dissolved silica.

 **(293)**

where:

*Deposition* = deposition from water column (g Si/ m3 d) see **(294)**;

*Dissolution* = dissolution of biogenic silica (g Si/ m3 d)

*Burial* = deep burial below modeled layer (g Si/ m3 d) see **(265)**; and

Deposition of silica is a function of the sinking of diatoms:

 **(294)**

where:

*DepositionSi* = deposition of silica from water column (g Si/ m3 d);

*FracSilica* = user-input fraction of silica in diatoms, (unitless);

*Sed =* sedimentation of diatoms, see **(165)**, (g OM/m­3water d);

*Volwater* = water volume (m3); and

*Volsediment* = sediment volume (m3);

Biogenic silica can undergo dissolution to dissolved silica. This reaction can also operate in reverse:

 **(295)**

where:

*Dissolution* = dissolution of biogenic silica (g Si/ m3 d);

*κSi* = user-input reaction velocity for dissolved silica dissolution (1/d);

*θSi* = user-input exponential temperature adjustment for silica dissolution (unitless);

*Concvar,layer* = concentration of available silica or silica in layer 2 (g Si/ m3);

*KMPSi*= user input silica dissolution half-saturation constant for biogenic silica (g Si/m3);

*SiSat* = user-input saturation concentration of silica in pore water (g Si/m3);

*fd silica,layer*  = dissolved fraction of silica in layer.

**7.11 Dissolved Silica**

Dissolved silica is produced when biogenic silica breaks down due to dissolution, and could potentially be modeled as a limiting nutrient for diatoms in a later version of AQUATOX. Dissolved silica (referred to hereafter as “silica”) is modeled in two layers:

 **(296)**

 **(297)**

where:

*Dissolution* = dissolution of biogenic silica (g Si/ m3 d), see **(295)**;

*Burial* = burial to layer below modeled layer or out of the system (g Si/ m3 d); see **(265)**;

*Flux2Anaerobic* =flux to layer 2 from layer 1 (g Si/ m3 d, may be negative) see **(272)** ;

*Flux2Water* =flux to water from layer 1 (g Si/ m3 d, may be negative); see **(273)**;

Similar to inorganic phosphate, dissolved oxygen causes a barrier to silica flux to the water column. This is modeled by increasing the partition coefficient by a factor when the dissolved oxygen decreases below a critical threshold.

 **(298)**

 **(299)**

where:

*fd silica,layer*  = dissolved fraction in layer (unitless);

*mlayer* = solids concentration in layer (kg/L); and

*KdSi,2*= partition coefficient for silica in layer 2 (L/kg);

Δ*KdSi,1*= fresh or saltwater factor to increase the aerobic (L1) partition coefficient of silica relative to the anaerobic (L2) coeff. (unitless);

*DOWC* = dissolved oxygen in the water column (g/m3); and

*DOCrit,Si.* = critical oxygen concentration for adjustment of partition coefficient for silica (g/m3);