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Supplement to Water Analysis Simulation Program User Documentation

WASP Sediment Diagenesis Routines: Model Theory and User's Guide

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1. Introduction

One of the processes long been known to impact the water quality of surface waters is the oxygen demand by, and nutrient release from, sediments. Sediment oxygen demand (SOD) and nutrient releases, due to the mineralization (diagenesis) of organic materials in bottom sediments, can contribute to eutrophication, harmful algal oxygen blooms and hypoxia. Hypoxic or dead zones are becoming more common in estuarine and coastal environments and have, as reported in Science (Diaz and Rosenberg, 2008), spread exponentially since the 1960s and resulting in serious consequences for ecosystem functioning. As of 2008 (Diaz and Rosenberg 2008), dead zones have been reported from more than 400 systems, affecting a total area of more than 245,000 square kilometers. Seasonal hypoxia (and/or anoxia) frequently occurs in the hypolimnion of many lakes and reservoirs.

Because of their importance, SOD and sediment nutrient releases have been included in essentially all modern numerical water quality models, including the Water Analysis Simulation Program (WASP). However, formerly WASP, like most available models, only had the capability of describing, rather than predicting SOD and sediment nutrient releases. SOD and sediment nutrient releases were included as temperature-corrected zeroth order rates (in units of g m^{-2} day^{-1} or mg m^{-2} day^{-1}), so that the rate of change in concentrations in the overlying water are predicted from

Equation 1

$$\frac{dC}{dt} = -\frac{R}{H}\mathbf{\Theta}^{(T-\mathbf{20})}$$

where H = water depth,

R = rate (of SOD or nutrient release),

t = time

C = concentration in the overlying water,

T = temperature

Θ = temperature coefficient.

That is, the rates of SOD and nutrient release vary only with temperature, and those rates are not impacted by the concentrations of materials in the sediments or the overlying water column. This option is still retained in the present version of WASP as well as the predictive submodel described in this supplement.

The zeroth order rates of SOD and nutrient release have commonly been estimated by model calibration. That is, the rates are adjusted until the observed oxygen and nutrient concentrations are close to those observed. While a commonly used method, this approach is flawed. The approach assumes that all other model processes impacting dissolved oxygen and nutrient concentrations are known with confidence, which is rarely the case. For example, inadequate predictions of hydrodynamics alone can result in rates determined by model calibration being highly uncertain.

A second commonly used, and preferable, method for the determination of the rates is through direct measurement. Methods developed, such as chamber and core methods, for measuring SOD and nutrient releases have been successfully applied in a variety of studies. However, the costs involved and difficulty in obtaining direct measurements often limits the number of such measurements available for use. A second limitation is often a lack of correlation of measured rates to other measurable sediment characteristics, making the interpolation between limited samples over a waterbody problematic.

The use of a zeroth order rate, or constant source term, in water quality model applications has an additional major limitation. That is it does not provide for a mechanistic link between sediment organic matter and its conversion into oxygen demand and nutrient release. In the absence of this missing link, one of two alternative approaches have commonly been employed. The first and most commonly used approach has been to assume the rates of SOD and nutrient release are unchanged following waste load reductions, or implementation of other water quality management alternatives. Clearly, this should not be the case in that reduction in loads of organic matter to a waterbody should impact organic loads to sediments and the resulting sediment oxygen demand and nutrient release. However, the "no change" approach has often been justified as being a "conservative" assumption. An alternative approach has been to assume linearity and lower SOD in direct proportion to a load reduction (Chapra 1997). However, there are rarely sufficient data available to estimate the magnitude and rate for the reduction.

The preferable approach would be the utilization of mechanistic models that provide a link between the influxes of organic materials to sediments, physical, biological and chemical processes occurring within the sediments, and consequent sediment oxygen demand and nutrient release. A number of approaches have been attempted. One limitation, as described by Chapra (1997), has been that some of the early and more simplified approaches have tended to overestimate the sediment oxygen demand and fail to capture the non-linear (e.g., Fair et al. 1964), or "square root" relationship, between loads and oxygen demand observed in natural waters.

In a landmark paper, Di Toro et al. (1990) developed a model of the SOD that mechanistically arrives at the observed non-linear relationships (Chapra 1997). Di Toro's approach, as described in his book on *Sediment Flux Modeling* (Di Toro 2001), calculates sediment oxygen demand and phosphorus and nitrogen release as functions of the downward flux of carbon, nitrogen, and phosphorus from the water column. This approach, well founded in diagenetic theory and supported by field and laboratory measurements, was an important advancement in the field of sediment-water interactions.

This supplement to the WASP user documentation (Wool et al. 2003) describes the incorporation of a sediment diagenesis model into the WASP modeling framework. The diagenesis model was based Di Toro's (2001) framework as implemented in a model code developed by Quantitative Environmental Analysis, LLC (QEA) and provided to the U.S. EPA Region 4. The model was reviewed and predictions compared to similar models by Martin (2002). The model code was then modified and enhanced, and linked to WASP, resulting in the diagenesis model described in this supplement. The theoretical structure of the diagenesis model is first provided followed by a brief user's guide.

2. Theoretical Overview

The basic framework of the sediment diagenesis model consists of two well-mixed sediment layers, underlying each surface water column segment: a thin upper sediment layer (the aerobic layer, on the order of 0.1 cm thick, Di Toro 2001) and a thicker active layer (anaerobic, on the order of 10 cm thick; Di Toro 2001, Figure 1). Three major processes included in the sediment model are the:

- Fluxes of particulate organic matter from the water column to the sediments (note that since the upper sediment layer is assumed to have a negligible thickness, the fluxes are deposited directly into the second, or anaerobic layer),
- Mineralization (or diagenesis) of the particulate organic matter, and
- Reactions and transfers (between sediment layers, to the water column and deep inactive sediments) of the reaction products.

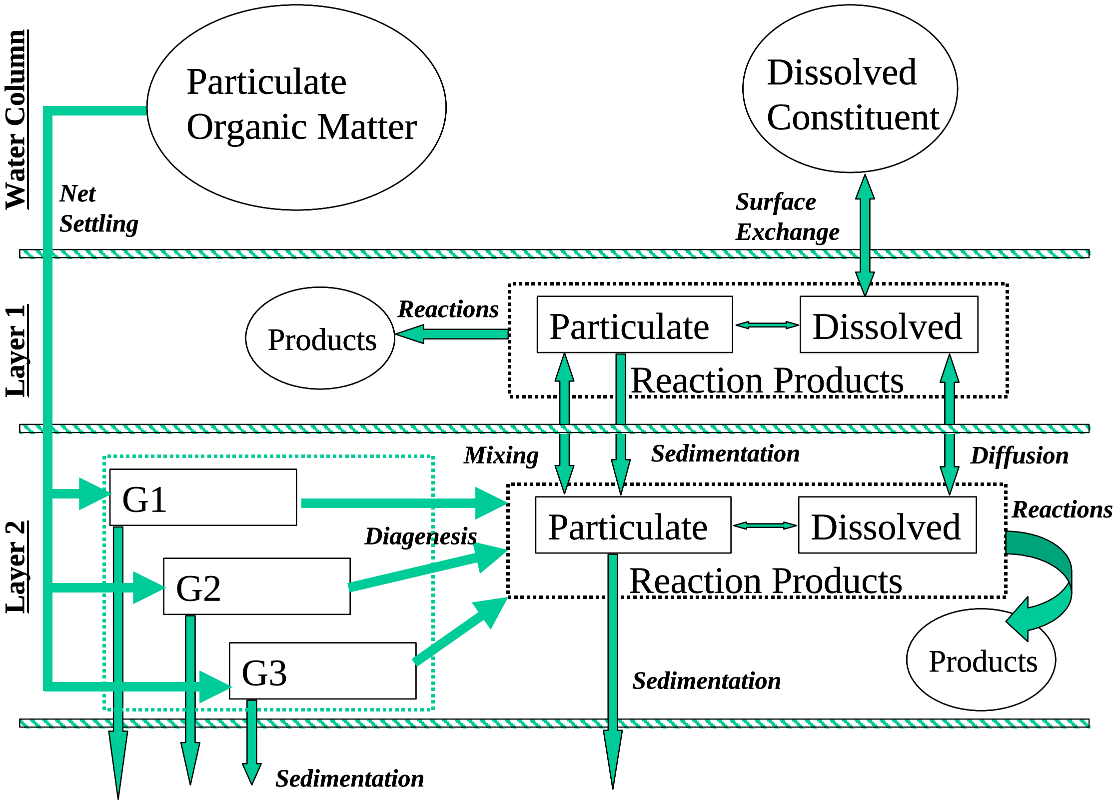


Figure 1. Basic structure of the diagenesis model.

The sediments receive fluxes from the water column of particulate organic carbon (POC), nitrogen (PON), and phosphorus (POP), collectively referred to as particulate organic matter (POM). In WASP, the POC fluxes are in oxygen equivalents. The flux from the water column to the sediment is computed as the product of the user specified settling rates and the water column particulate organic matter concentration.

Organic matter initially mineralizes rapidly in the sediments, but then slows down. In order to capture this process, the settled POM is fractionated to one of three “G classes” (Figure 1, Di Toro 2001). The three G classes represent a relatively rapidly mineralizing labile class (G1), a more refractory form (G2) and a relatively inert form (G3).

Diagenesis (mineralization) reactions occur in the second (anaerobic) sediment layer. The diagenesis equations solved for each form of particulate organic matter (N, P and C) and for each G class (1-3) are analogous. In order to compute the time-varying diagenesis for each modeled variable, a mass balance equation is written for each form and type of POM (e.g. POC, PON and POP in each G class).

The mass balance equations are conveniently solved algebraically for the concentration at the present time step. Once the concentrations at the present time step are computed, the diagenesis source terms for reactions and transfers are computed. Diagenesis source terms are computed for C, N and P from the sum of the product of the chemical specific reaction velocities and computed concentrations in each of the three G classes.

Once the sediment particulate organic matter (C, N and P) concentrations and source terms are computed for the present time step, the reactions and transfers are computed. Concentrations or ammonia, nitrates, methane, sulfates, sulfides, silica and phosphorus are computed, and then used to compute fluxes to the overlying water column, including sediment oxygen demand.

The total chemical concentrations are computed from mass balance relationships for each of the two sediment layers. Since the surface layer is thin compared to the active anaerobic layer, it can be assumed that layer 1 is at steady-state in comparison to the slower processes occurring in layer 2, where it is assumed that the thickness of the layers is constant. The equations are conveniently solved for the new concentrations using a matrix solution. Once the concentrations have been updated, the flux of the material to the overlying water column is computed. Given the chemical concentrations in layer 1, the SOD and release rates are then computed. However, with the exception of phosphates and silica, each of these constituents affects SOD, which in turn affects the surface transfer rate. Therefore, an iterative solution is required. The procedure employed in the sediment diagenesis model is as follows:

1. Start with an initial estimate of the SOD.
2. Solve layer 1 and 2 equations (for ammonia, nitrate, sulfate, sulfide, and methane).
3. Refine the estimate of SOD. A root finding method is used to make the new estimate.
4. Go to step (2) if no convergence.

Once the SOD is determined, then the layer 1 and 2 equations for phosphate and silica are solved and the flux rates determined.

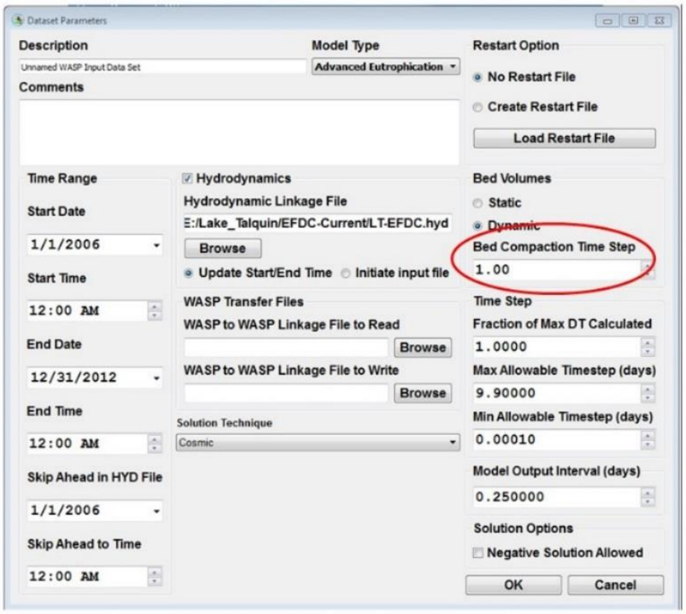
3. Model Input

Time step and General run-time information considerations

General information required for the execution of the sediment diagenesis model includes a selection for its use and the computational time step. The use of the sediment diagenesis model is optional. To use the sediment diagenesis model, the user must go the kinetic constants, select the Sediment Oxygen Demand Constant Group (see below), set the SOD switch, and input the appropriate data. Input data specific to the diagenesis model are described below. Presently, the diagenesis model is only function when using the advanced eutrophication model.

Data set parameter Screen: Set Diagenesis Model Time Step

The diagenesis model is only functional when using the advanced eutrophication model, so the first step is to select that model. Secondly, the diagenesis model can be executed using a larger computational time step than the model time step. Typically, since processes in anoxic sediments or response times are slower than those in the water column, the sediment diagenesis time step would be greater than the model computational time step. As indicated above, the POM is fractionated into "G classes" in the diagenesis model, reflecting different rates of reactivity. While labile components may respond relatively quickly (months), the more refractory components may take many years to reach equilibrium with the water column. Where the sediment diagenesis time step is greater than the model computational time step the fluxes of particulate organic matter to the sediment are accumulated and water column concentrations are averaged over the diagenesis time step interval. If not specified by the user, the sediment diagenesis time step is set to 1.0 day ().



Description: Unnamed WASP Input Data Set
Model Type: Advanced Eutrophication
Restart Option: ● No Restart File ○ Create Restart File
Start Date: 1/1/2006
Start Time: 12:00 AM
End Date: 12/31/2012
End Time: 12:00 AM
Skip Ahead in HYD File: 1/1/2006
Skip Ahead to Time: 12:00 AM
☑ Hydrodynamics
Hydrodynamic Linkage File: E:/Lake_Talquin/EFDC-Current/LT-EFDC.hyd
● Update Start/End Time ○ Initiate input file
WASP to WASP Linkage File to Read:
WASP to WASP Linkage File to Write:
Solution Technique: Cosmic
Bed Volumes: ○ Static ● Dynamic
Bed Compaction Time Step: 1.00
Fraction of Max DT Calculated: 1.0000
Max Allowable Timestep (days): 9.90000
Min Allowable Timestep (days): 0.00010
Model Output Interval (days): 0.250000
☐ Negative Solution Allowed

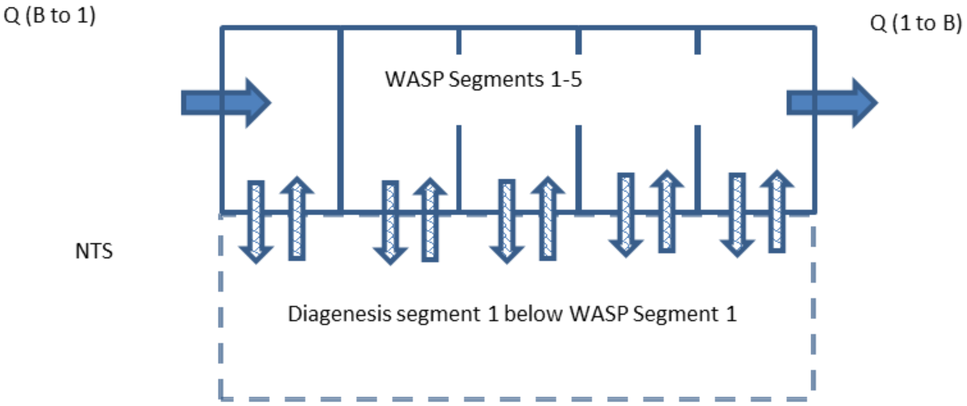
Figure 2 SOD Sub Module Timestep

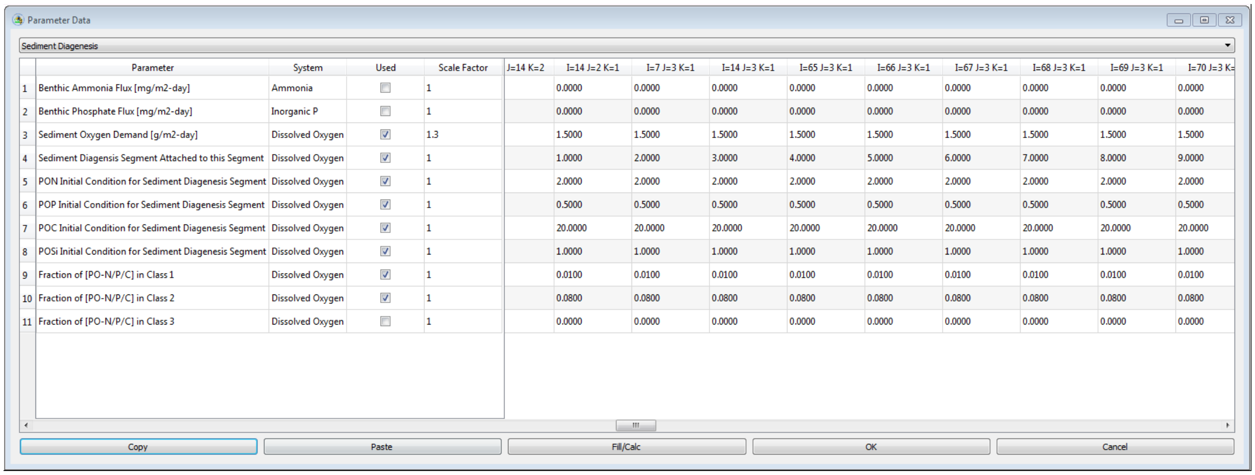
Segment Parameter Input

Once the segmentation for the simulation has been established, the model parameters are used to specify the diagenesis segments and initial conditions. If the diagenesis model is not used, the user can still input parameter values for sediment fluxes using the parameters:

- Benthic Ammonia Flux (mg/m^2-day)
- Benthic Phosphate Flux (mg/m^2-day)
- Sediment Oxygen Demand (g/m^2-day)

If the diagenesis model is to be used, the determination of how many diagenesis segments there are and which water column segment above them is based on user input. For example, in the illustration below there are five WASP water column segments overlying a single diagenesis segment. The diagenesis segment below a specific WASP segment is specified using the parameter "Sediment Diagenesis Segment Attached to this Segment"





	Parameter	System	Used	Scale Factor	J=14 K=2	I=14 J=2 K=1	I=7 J=3 K=1	I=14 J=3 K=1	I=65 J=3 K=1	I=66 J=3 K=1	I=67 J=3 K=1	I=68 J=3 K=1	I=69 J=3 K=1	I=70 J=3 K=
1	Benthic Ammonia Flux [mg/m2-day]	Ammonia	☐	1		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	Benthic Phosphate Flux [mg/m2-day]	Inorganic P	☐	1		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
3	Sediment Oxygen Demand [g/m2-day]	Dissolved Oxygen	☑	1.3		1.5000	1.5000	1.5000	1.5000	1.5000	1.5000	1.5000	1.5000	1.5000
4	Sediment Diagensis Segment Attached to this Segment	Dissolved Oxygen	☑	1		1.0000	2.0000	3.0000	4.0000	5.0000	6.0000	7.0000	8.0000	9.0000
5	PON Initial Condition for Sediment Diagenesis Segment	Dissolved Oxygen	☑	1		2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
6	POP Initial Condition for Sediment Diagenesis Segment	Dissolved Oxygen	☑	1		0.5000	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000
7	POC Initial Condition for Sediment Diagenesis Segment	Dissolved Oxygen	☑	1		20.0000	20.0000	20.0000	20.0000	20.0000	20.0000	20.0000	20.0000	20.0000
8	POSi Initial Condition for Sediment Diagenesis Segment	Dissolved Oxygen	☑	1		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
9	Fraction of [PO-N/P/C] in Class 1	Dissolved Oxygen	☑	1		0.0100	0.0100	0.0100	0.0100	0.0100	0.0100	0.0100	0.0100	0.0100
10	Fraction of [PO-N/P/C] in Class 2	Dissolved Oxygen	☑	1		0.0800	0.0800	0.0800	0.0800	0.0800	0.0800	0.0800	0.0800	0.0800
11	Fraction of [PO-N/P/C] in Class 3	Dissolved Oxygen	☐	1		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

The user must also input initial conditions for the particulate organic matter in the diagenesis layer as well as the G class fractions (representing the rate of reactivity, G1-G3) for that POM, using the parameters:

- PON Initial Condition for Sediment Diagenesis Segment (mg N/g sediment)
- POP Initial Condition for Sediment Diagenesis Segment (mg P/g sediment)
- POC Initial Condition for Sediment Diagenesis Segment (mg C/g sediment in O_2 equivalents)
- POSi Initial Condition for Sediment Diagenesis Segment(mg Si/g sediment)
- Fraction of (PO-N/P/C) in Class 1
- Fraction of (PO-N/P/C) in Class 2

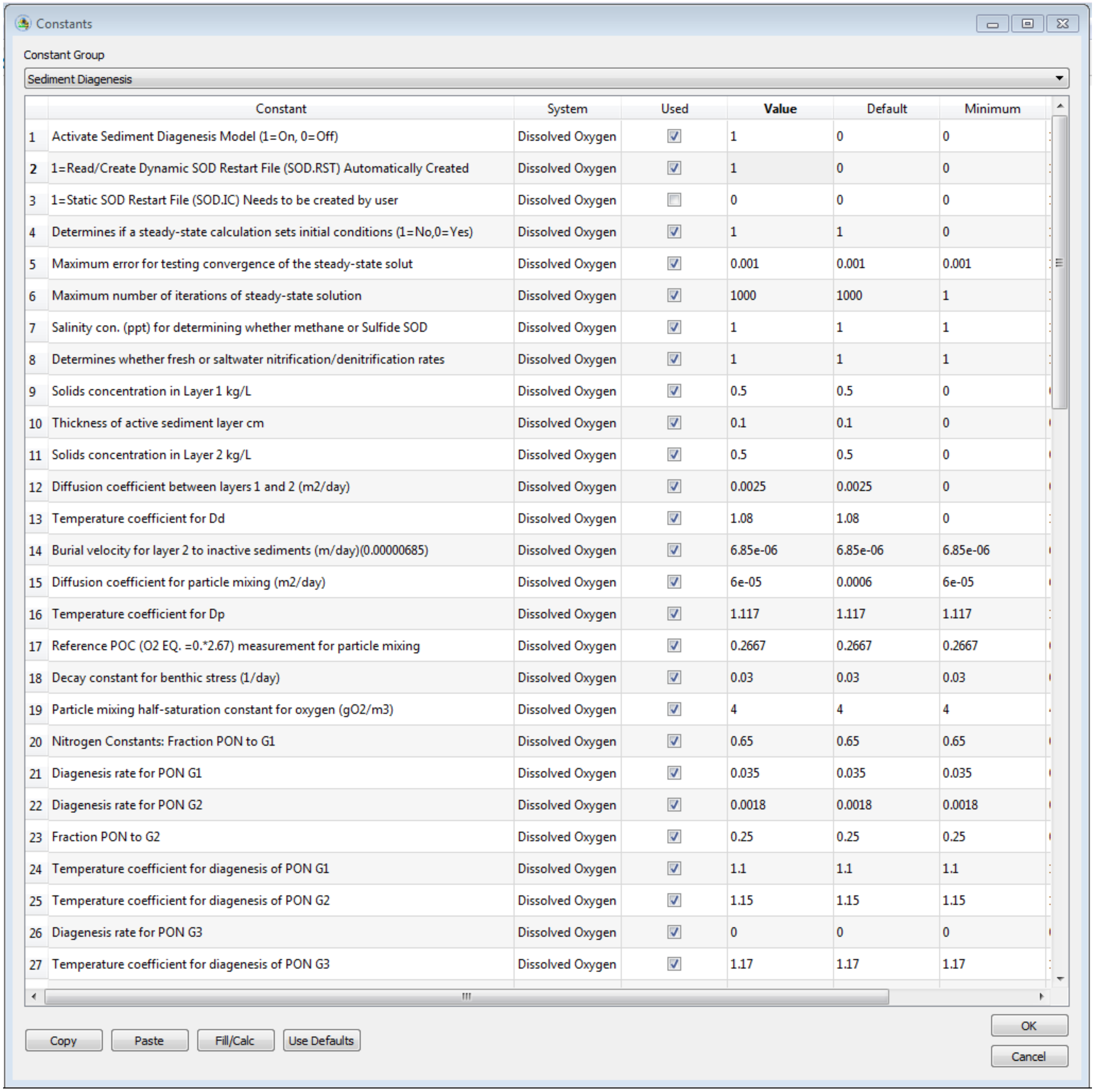
As with all WASP parameters, the parameters to be used must be checked under the parameter screen while the specific values are set under the segment screen. Note that presently there are no provisions to set the initial dissolved concentrations in the sediment pore waters.

Fluxes to Sediments

The diagenesis is driven by the fluxes to the sediments. The fluxes are controlled by the user selected model systems, associated input and specified rates of settling. The settling rates is specified the “old way” using flow fields and set from the segment to the boundary, and WASP will recognize which diagenesis segment receives the flux from the “diagenesis segment below” parameter.

Diagenesis constants

The diagenesis options and constants are set under the constant screen and by selecting the option is still retained to allow the user to specify (rather than predict) rates of sediment oxygen demand and release of phosphorus and ammonia (model parameters; if the SOD switch=0). The user must use caution since as explained later the model parameter for SOD has a different meaning if the SOD switch >0. For that case, the parameter specifies the sediment diagenesis layer below the model segment, while for SOD switch = 0 the parameter specifies the SOD rate (g m^{-2} day^{-1}).



Constant Group: Sediment Diagenesis

	Constant	System	Used	Value	Default	Minimum
1	Activate Sediment Diagenesis Model (1=On, 0=Off)	Dissolved Oxygen	☑	1	0	0
2	1=Read/Create Dynamic SOD Restart File (SOD.RST) Automatically Created	Dissolved Oxygen	☑	1	0	0
3	1=Static SOD Restart File (SOD.IC) Needs to be created by user	Dissolved Oxygen	☐	0	0	0
4	Determines if a steady-state calculation sets initial conditions (1=No,0=Yes)	Dissolved Oxygen	☑	1	1	0
5	Maximum error for testing convergence of the steady-state solut	Dissolved Oxygen	☑	0.001	0.001	0.001
6	Maximum number of iterations of steady-state solution	Dissolved Oxygen	☑	1000	1000	1
7	Salinity con. (ppt) for determining whether methane or Sulfide SOD	Dissolved Oxygen	☑	1	1	1
8	Determines whether fresh or saltwater nitrification/denitrification rates	Dissolved Oxygen	☑	1	1	1
9	Solids concentration in Layer 1 kg/L	Dissolved Oxygen	☑	0.5	0.5	0
10	Thickness of active sediment layer cm	Dissolved Oxygen	☑	0.1	0.1	0
11	Solids concentration in Layer 2 kg/L	Dissolved Oxygen	☑	0.5	0.5	0
12	Diffusion coefficient between layers 1 and 2 (m2/day)	Dissolved Oxygen	☑	0.0025	0.0025	0
13	Temperature coefficient for Dd	Dissolved Oxygen	☑	1.08	1.08	0
14	Burial velocity for layer 2 to inactive sediments (m/day)(0.00000685)	Dissolved Oxygen	☑	6.85e-06	6.85e-06	6.85e-06
15	Diffusion coefficient for particle mixing (m2/day)	Dissolved Oxygen	☑	6e-05	0.0006	6e-05
16	Temperature coefficient for Dp	Dissolved Oxygen	☑	1.117	1.117	1.117
17	Reference POC (O2 EQ. =0.*2.67) measurement for particle mixing	Dissolved Oxygen	☑	0.2667	0.2667	0.2667
18	Decay constant for benthic stress (1/day)	Dissolved Oxygen	☑	0.03	0.03	0.03
19	Particle mixing half-saturation constant for oxygen (gO2/m3)	Dissolved Oxygen	☑	4	4	4
20	Nitrogen Constants: Fraction PON to G1	Dissolved Oxygen	☑	0.65	0.65	0.65
21	Diagenesis rate for PON G1	Dissolved Oxygen	☑	0.035	0.035	0.035
22	Diagenesis rate for PON G2	Dissolved Oxygen	☑	0.0018	0.0018	0.0018
23	Fraction PON to G2	Dissolved Oxygen	☑	0.25	0.25	0.25
24	Temperature coefficient for diagenesis of PON G1	Dissolved Oxygen	☑	1.1	1.1	1.1
25	Temperature coefficient for diagenesis of PON G2	Dissolved Oxygen	☑	1.15	1.15	1.15
26	Diagenesis rate for PON G3	Dissolved Oxygen	☑	0	0	0
27	Temperature coefficient for diagenesis of PON G3	Dissolved Oxygen	☑	1.17	1.17	1.17

Diagenesis constants and typical values are provided below. The first option determines if the diagenesis model is to be included in the simulation. The second option impacts how the initial conditions are determined. They may input as model parameters or read from the restart file. Alternatively, the user may elect to have the model compute the initial conditions assuming the sediment is at steady-state with the initial fluxes to the sediment layer (based on initial conditions and settling fluxes). The steady-state is computed using an iterative solution, so in addition to selecting this option the user also specifies that maximum number of iteratons and an error (convergence) criteria.

Diagenesis Constants	Use?	Value
Activate Sediment Diagenesis Model (1=On, 0=Off)	Y	1
1=Read/Create Dynamic SOD Restart File (Wif_File Name.SOD_RST) Automatically Created	Y	1
1=Static SOD Restart File (Wif_File Name.SOD_IC) Needs to be created by user	N	0
Determines if a steady-state diagenesis calculation(1=No,0=Yes)	Y	1
Maximum error for testing convergence of the steady-state solute	Y	0.001
Maximum number of iterations of steady-state solution (new)	Y	1000
Salinity con. (ppt) for determining whether methane or Sulfide SOD	Y	1
Determines whether fresh or saltwater nitrification/denitrification rates	Y	1
Solids concentration in Layer 1 kg/L	Y	0.5
Solids concentration in Layer 2 kg/L	Y	0.5
Diffusion coefficient between layers 1 and 2 (m2/day)	Y	0.0025
Temperature coefficient for Dd	Y	1.08
Thickness of active sediment layer cm	Y	0.1
Burial velocity for layer 2 to inactive sediments (m/day)(0.00000685)	Y	6.85E-06
Diffusion coefficient for particle mixing (m2/day)	Y	6.00E-05
Temperature coefficient for Dp	Y	1.117
Reference POC (O2 EQ. =0.*2.67) measurement for particle mixing	Y	0.2667
Decay constant for benthic stress (1/day)	Y	0.03
Particle mixing half-saturation constant for oxygen (gO2/m3)	Y	4
Nitrogen Constants: Fraction PON to G1	Y	0.65
Fraction PON to G2	Y	0.25
Diagenesis rate for PON G1	Y	0.035
Temperature coefficient for diagenesis of PON G1	Y	1.1

Diagenesis rate for PON G2	Y	0.0018
Temperature coefficient for diagenesis of PON G2	Y	1.15
Diagenesis rate for PON G3	Y	0
Temperature coefficient for diagenesis of PON G3	Y	1.17
Freshwater nitrification reaction velocity (m/day) (new)	Y	0.1313
Saltwater nitrification reaction velocity (m/day) (new)	Y	0.1313
Temperature coefficient for nitrification	Y	1.123
Half-saturation coefficient for ammonia in the nitrification reaction (mg/L)	Y	0.728
Half-saturation coefficient for oxygen in the nitrification reaction (mg/L)	Y	0.37
2nd step reaction reaction velocity for nitrification (NO2 to NO3) (m/day)	Y	100
Temperature coefficient for 2nd step reaction velocity	Y	1.123
Half-saturation coefficient for oxygen in the 2nd reaction step (mg O2/L)	Y	0.37
Freshwater denitrification reaction velocity in layer 1(m/day)	Y	0.1
Saltwater denitrification reaction velocity in layer 1 (m/day)	Y	0.1
Temperature coefficient for denitrification	Y	1.08
Denitrification reaction velocity in layer 2 (m/day)	Y	0.25
Nitrogen partition coefficient (L/kg)	Y	1
Phosphorus: Fraction POP to G1	Y	0.65
Fraction POP to G2	Y	0.2
Diagenesis rate for POP G1	Y	0.035
Temperature coefficient for diagenesis of POP G1	Y	1.1
Diagenesis rate for POP G2	Y	0.0018
Temperature coefficient for diagenesis of POP G2	Y	1.15
Diagenesis rate for POP G3	Y	0

Temperature coefficient for diagenesis of POP G3	Y	1.17
Phosphorus partition coefficient in layer 2 (L/kg)	Y	20
Incremental freshwater partition coefficient in layer 1 (new)	Y	20
Incremental saltwater partition coefficient in layer 1	Y	20
Critical oxygen concentration in layer 1 incremental phosphate sorption (mgO2/L)	Y	2
Carbon Constants: Fraction CBODu to G1	Y	0.65
Fraction CBODu to G2	Y	0.2
Diagenesis rate for CBODu G1	Y	0.035
Temperature coefficient for diagenesis of CBODu G1	Y	1.1
Diagenesis rate for CBODu G2	Y	0.0018
Temperature coefficient for diagenesis of CBODu G2	Y	1.15
Diagenesis rate for CBODu G3	Y	0
Temperature coefficient for diagenesis of CBODu G3	Y	1.17
Methane oxidation reaction velocity (m/day)	Y	0.7
Temperature coefficient for methane oxidation	Y	1.079
Half-saturation coefficient for oxygen in oxidation of methane (mg/L)	Y	0.37
Reaction velocity for dissolved sulfide oxidation in layer 1 (m/day)	Y	0.2
Reaction velocity for particulate sulfide oxidation in layer 1 (m/day)	Y	0.4
Temperature coefficient for sulfide oxidation (new)	Y	1.079
Sulfide oxidation normalization constant (mg/L) (new)	Y	4
Sulfide partition coefficient in layer 1 (L/kg) (new)	Y	100
Sulfide partition coefficient in layer 2 (L/kg) (new)	Y	100
Algae Constants: Fraction settled algae to G1 (new)	Y	0.65
Fraction settled algae to G2 (new)	Y	0.2

Dissolution Rate of particulate biogenic silica at 20c (1/day)	Y	0.5
Temperature Effect on Silica Dissolution	Y	1.1
Silica Saturation Concentration in Porewater (mg si/m**3)	Y	4000
Incremental Change (Mult) for freshwater in Partition Coeff. Si as DO	Y	10
Partition Coefficient between Dissolved/Sorbed Silica in Layer 2	Y	100
Half Saturation Constant of Dissolved Silica in Dissolution Reaction	Y	50000000
Critical Oxygen Concentration for Silica Sorption	Y	1

4. Running the diagenesis model:

Once setting up the diagenesis model

Initial Conditions

Initial conditions are required for the dynamic simulation for each of the diagenesis segments specified under the model parameter input, as described above. Initial conditions are required for each form of organic matter (N, P, C and Si) in each of the three G-classes. Note that organic carbon is specified in oxygen equivalents. Note that presently there are no provisions for providing initial concentrations of pore water dissolved ammonia, nitrite, nitrate, and phosphate concentrations.

Initial conditions would ideally be derived from field measurements, such as pore water concentrations and particulate organic matter concentrations (POM), further subdivided into G-classes. In practice, the lack of field data and/or accepted analytical procedures from fractionating G-classes makes this difficult. For example, older sediments with low rates of deposition from the water column may be largely composed of G Class 3, while in highly productive systems there may be a greater G Class 2 component. The relative proportions directly impacts response times since the rates of diagenesis are so different.

One common practice is to estimate initial conditions by modeling. The modeling estimations may typically be based upon steady state or quasi-dynamic predictions.

A model option ("steady-state" selected under the diagenesis kinetic constants menu) allows the model to compute the initial conditions based upon the initial water column concentrations and settling fluxes, assuming steady-state conditions (see Appendix A for a description of the steady-state computations). Some caution should be exercised using this option, particularly for phosphorus and silica. As indicated by Di Toro (2001), a steady-state model cannot be used to successfully predict the range of phosphorus fluxes from the sediments, particularly under anoxic water column conditions. As a result, the steady-state option for computing initial conditions of diagenesis segments should not be used where the initial dissolved oxygen concentrations in the overlying water column are near zero.

A more commonly used approach to estimate initial conditions is through use of a quasi-dynamic approach. In this approach, the model is run for a period of a year or more, with reasonably repeating water column conditions, and the predicted concentrations in diagenesis segments at the end of that period used to refine and replace the specified initial conditions. The process is repeated until the resulting predictions approach a quasi-steady state. An option is also provided for a restart file to be written at the end of a simulation period and then be read and provide initial conditions in subsequent simulations.

Deposition Fluxes

The sediment diagenesis is driven by the deposition fluxes from the water column. The flux of organic matter (PON, POP and POC) to the diagenesis segments is computed based upon the water column concentrations and specified settling rates. The deposition fluxes used as input for the sediment diagenesis are those OUT of a water column segment. That is, the deposition fluxes are specified as those from a water column segment to the model boundary.

Relationship to WASP State Variables and Parameters

The state variables in the diagenesis model include:

- Particulate organic nitrogen (3 G-classes)
- Particulate organic phosphorus (3 G-classes)
- Particulate organic carbon (3 G-classes)
- Reaction products and dissolved constituents
  - ammonia
  - nitrite-nitrogen
  - nitrate-nitrogen
  - phosphate
  - sulfides
  - methane
  - silica

In the diagenesis model POC is computed in oxygen equivalents. The deposition fluxes of particulate organic matter from the water column to the diagenesis segment are subdivided into organic N, P and C and Si based on the model state variables and model stoichiometry. The fluxes are further subdivided into G classes based on user provide input constants. Water column concentrations of dissolved ammonia, nitrate and phosphates impact the transfer of these constituents between the diagenesis segments and the overlying water column segment. In the present version of the WASP model, the nitrite concentration of the water column is assumed to be zero. The rates of transfer and reactions also vary with the computed dissolved oxygen concentration in the overlying water column.

A number of the reactions also vary between fresh and saltwater systems, so that the predicted salinity also impacts the diagenesis model predictions. In addition, for fresh water systems methane reactions are computed, while sulfides are computed for saltwater systems.

There is no provision presently included in the WASP model for a gradual transition between methane or sulfide reactions. Therefore, the user should use caution when applying the model to estuarine systems that may rapidly alternate between salt and fresh water conditions.

Reaction rates vary with temperature, and in the diagenesis model, the segment temperature is assumed to equal the temperature of the overlying water column. The segment temperatures are specified using the WASP model parameters and time functions. The user should note that the temperature is assumed to be 0 ^oC if not specified.

Model Coefficients and Constants

The simulation of sediment diagenesis and prediction of the resulting fluxes from the sediments to the water column requires the specification of a number of constants and coefficients related to diagenesis, sediment properties, mixing and kinetics. Coefficients and constants related to the diagenesis model can be subdivided into four groups as listed in the tables below. The first group includes model options as well as constants used to define the geometry of the diagenesis layers, solids concentrations, and salinity (fresh or salt water) for reactions. The second group of constants is used to partition the settled organic matter among type (PON, POP, and POC) and G-classes. The third group contains terms related to the diagenesis of organic matter. The final group contains terms related to the kinetic reactions.

The typical values specified in the tables below are based upon the MERL studies, and the user is referred to Di Toro (2001, Tables 15.5-15.6) for the values of constants and coefficients from other studies (Chesapeake Bay, Long Island Sound, Massachusetts Bay, and Jamaica Bay). A detailed presentation of the utilization of these constants and coefficients in model equations is provided in Appendix A.

Table 1. General diagenesis constants and sediment properties

Typical value	Description
0.001	Maximum error (fraction of change) for testing convergence of the steady-state solution for the initial conditions
1000	Maximum number of iterations of steady-state solution
1	Salinity concentration (ppt) for determining whether methane or sulfide SOD formulation
1	Salinity concentration (ppt) that determines whether fresh or saltwater nitrification/denitrification rates are used
0.5	Solids concentration in Layer 1 kg/L
0.5	Solids concentration in Layer 2 kg/L
0.1	Thickness of active sediment layer (cm)

Table 2. Diagenesis model coefficients and constants related to mixing and transfers

Typical value	Description
0.0025	Diffusion coefficient between layers 1 and 2 (m^2/day)
1.08	Temperature coefficient for Dd
6.85E-06	Burial velocity for layer 2 to inactive sediments (m/day)
0.00006	Diffusion coefficient for particle mixing (m^2/day)
1.117	Temperature coefficient for Dp
0.2667	Reference POC (O_2 EQ. =0.*2.67) measurement for particle mixing (mg/g)
0.03	Decay constant for benthic stress (day^{-1})
4	Particle mixing half-saturation constant for oxygen (gO_2/m^3)

Table 3. Diagenesis model coefficients and constants related to organic matter fractionation in the water column (for fluxes to sediments)

Typical value	Description
0.65	Fraction PON to G-class 1
0.25	Fraction PON to G-class 2
0.65	Fraction POP to G-class 1
0.2	Fraction POP to G-class 2
0.65	Fraction CBODu to G-class 1
0.2	Fraction CBODu to G-class 2

Table 4. Diagenesis model coefficients and constants related to organic matter diagenesis

Typical value	Description
0.035	Diagenesis rate for PON G1
1.1	Temperature coefficient for diagenesis of PON G1
0.0018	Diagenesis rate for PON G2
1.15	Temperature coefficient for diagenesis of PON G2
0	Diagenesis rate for PON G3
1.17	Temperature coefficient for diagenesis of PON G3
0.035	Diagenesis rate for POP G1
1.1	Temperature coefficient for diagenesis of POP G1
0.0018	Diagenesis rate for POP G2
1.15	Temperature coefficient for diagenesis of POP G2
0	Diagenesis rate for POP G3
1.17	Temperature coefficient for diagenesis of POP G3
0.035	Diagenesis rate for POC G1
1.1	Temperature coefficient for diagenesis of POC G1

0.0018	Diagenesis rate for POC G2
1.15	Temperature coefficient for diagenesis of POC G2
0	Diagenesis rate for POC G3
1.17	Temperature coefficient for diagenesis of POC BODu G3

Table 5. Diagenesis model coefficients and constants related to reactions

Typical value	Description
0.1313	Freshwater nitrification reaction velocity (m/day) (new)
0.1313	Saltwater nitrification reaction velocity (m/day) (new)
1.123	Temperature coefficient for nitrification
0.728	Half-saturation coefficient for ammonia in the nitrification reaction (mg/L)
0.37	Half-saturation coefficient for oxygen in the nitrification reaction (mg/L)
100	2nd step reaction velocity for nitrification (NO_2 to NO_3) (m/day)
1.123	Temperature coefficient for 2nd step reaction velocity
0.37	Half-saturation coefficient for oxygen in the 2nd reaction step (mg O_2/L)
0.1	Freshwater denitrification reaction velocity in layer 1(m/day)
0.1	Saltwater denitrification reaction velocity in layer 1 (m/day)
1.08	Temperature coefficient for denitrification
0.25	Denitrification reaction velocity in layer 2 (m/day)
1	Nitrogen partition coefficient (L/kg)
20	Phosphorus partition coefficient in layer 2 (L/kg)
20	Incremental freshwater partition coefficient in layer 1
20	Incremental saltwater partition coefficient in layer 1
2	Critical oxygen concentration in layer 1 incremental phosphate sorption (mgO2/L)
0.7	Methane oxidation reaction velocity (m/day)
1.079	Temperature coefficient for methane oxidation
0.37	Half-saturation coefficient for oxygen in oxidation of methane (mg/L)
0.2	Reaction velocity for dissolved sulfide oxidation in layer 1 (m/day)

0.4	Reaction velocity for particulate sulfide oxidation in layer 1 (m/day)
1.079	Temperature coefficient for sulfide oxidation
4	Sulfide oxidation normalization constant (mg/L)
100	Sulfide partition coefficient in layer 1 (L/kg)
100	Sulfide partition coefficient in layer 2 (L/kg)

5. SOD Model Restart Options

There are two types of restart files that can be used to set initial concentrations of the major components of the SOD module.

1. Dynamic Restart File – this file will be created at the end of the simulation period automatically by the SOD module. The final conditions of the SOD module calculations are stored and can be automatically read in on the next execution of the WASP model. The dynamic restart file will automatically be named whatever of the WIF file with the extension .SOD_RST.
2. Static Restart File –this file will need to be created/edited by the user. You can use the option above to create the file initially. This file will be read by the SOD module at the start of the simulation. The static restart file must be called whatever of the WIF file with the extension .SOD_IC.

6. Diagenesis Model Outputs

Outputs to the water quality routines from the diagenesis model incorporated into the binary model data (BMD) or CSV files include:

- Sediment oxygen demand
- Ammonia flux
- Nitrate flux
- Phosphate flux

These output variables are included for both the descriptive (specified fluxes) or predictive (diagenesis mode) approach. In addition to the WASP model output, there is an output file or the Additional variables computed but not presently used by the WASP model include:

Table 6. Sediment Diagenesis output

Total PON concentration in the overlying water	TPON WC	mg N/L
PON G Class 1 Concentration in Layer 2	PON(1) 2	mg N/g
PON G Class 2 Concentration in Layer 2	PON(2) 2	mg N/g
PON G Class 3 Concentration in Layer 2	PON(3) 2	mg N/g
NH_3 concentration in overlying water	NH3 WC	mg N/L
NH_3 concentration in layer 1	NH3 1	mg N/L
NH_3 concentration in layer 2	NH3 2	mg N/L
NO_2 concentration in overlying water (not used = 0)	NO2 WC	mg N/L
NO_2 concentration in layer 1 (not used = 0)	NO2 1	mg N/L
NO_2 concentration in layer 2 (not used = 0)	NO2 2	mg N/L
NO_3 concentration in overlying water	NO3 WC	mg N/L
NO_3 concentration in layer 1	NO3 1	mg N/L
NO_3 concentration in layer 2	NO3 2	mg N/L
Total POP concentrations in the overlying water	TPOP WC	mg P/L
POP G Class 1 Concentration in Layer 2	POP(1) 2	mg P/g
POP G Class 1 Concentration in Layer 2	POP(2) 2	mg P/g
POP G Class 1 Concentration in Layer 2	POP(3) 2	mg P/g
PO_4 concentration in overlying water	PO4 WC	mg P/L
PO_4 concentration in layer 1	PO4 1	mg P/L
PO_4 concentration in layer 2	PO4 2	mg P/L
Total POC concentration in the water column	TPOC WC	mg O_2/L
POC G Class 1 Concentration in Layer 2	POC(1) 2	mg O_2/g
POC G Class 1 Concentration in Layer 2	POC(2) 2	mg O_2/g
POC G Class 1 Concentration in Layer 2	POC(3) 2	mg O_2/g
Methane concentration in overlying water (not used = 0)	CH4 WC	mg O_2/L

Dissolved Oxygen concentration in overlying water	DO WC	mg O_2/L
Computed PON flux to sediments	JPON WC->Sed	mg N m^{-2} d^{-1}
Computed NH_3 flux to overlying water	JNH3 Sed->WC	mg N m^{-2} d^{-1}
Computed NO_2 flux to overlying water	JNO2 Sed->WC	mg N m^{-2} d^{-1}
Computed NO_3 flux to overlying water	JNO3 Sed->WC	mg N m^{-2} d^{-1}
Computed denitrification flux	JDenit Sed->WC	mg N m^{-2} d^{-1}
Computed POP flux to sediments	JPOP WC->Sed	mg P m^{-2} d^{-1}
Computed PO_4 flux to overlying water	JPO4 Sed->WC	mg P m^{-2} d^{-1}
Computed POC flux to sediments	JPOC WC->Sed	mg O_2 m^{-2} d^{-1}
Computed aqueous methane flux to overlying water	JCH4aq Sed->WC	mg O_2 m^{-2} d^{-1}
Computed gaseous methane flux to overlying water	JCH4g Sed->WC	mg O_2 m^{-2} d^{-1}
Computed sulfide flux to overlying water	JHS Sed->WC	mg O_2 m^{-2} d^{-1}
Computed sediment oxygen demand	SOD WC->Sed	g O_2 m^{-2} d^{-1}
Computed surface transfer rate between water and sediment	s	m/d

7. References:

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8. Appendix A: Detailed Description of Sediment Diagenesis Model

Introduction

The basic framework of the sediment model consists of two well-mixed sediment layers, underlying each surface water column segment: a thin upper sediment layer (the aerobic layer) and a thicker active (anaerobic) layer (Figure 3). In WASP, the thickness of the active layer is specified by the user (input) and assumed constant among all sediment columns. Three major processes included in the sediment model are the:

- Fluxes of particulate organic matter from the water column to the sediments (note that since the upper sediment layer is assumed to have a negligible thickness, the fluxes are deposited directly into the second, or anaerobic layer),
- Mineralization (or diagenesis) of the particulate organic matter, and
- Reactions and transfers (between sediment layers, to the water column and deep inactive sediments) of the reaction products.

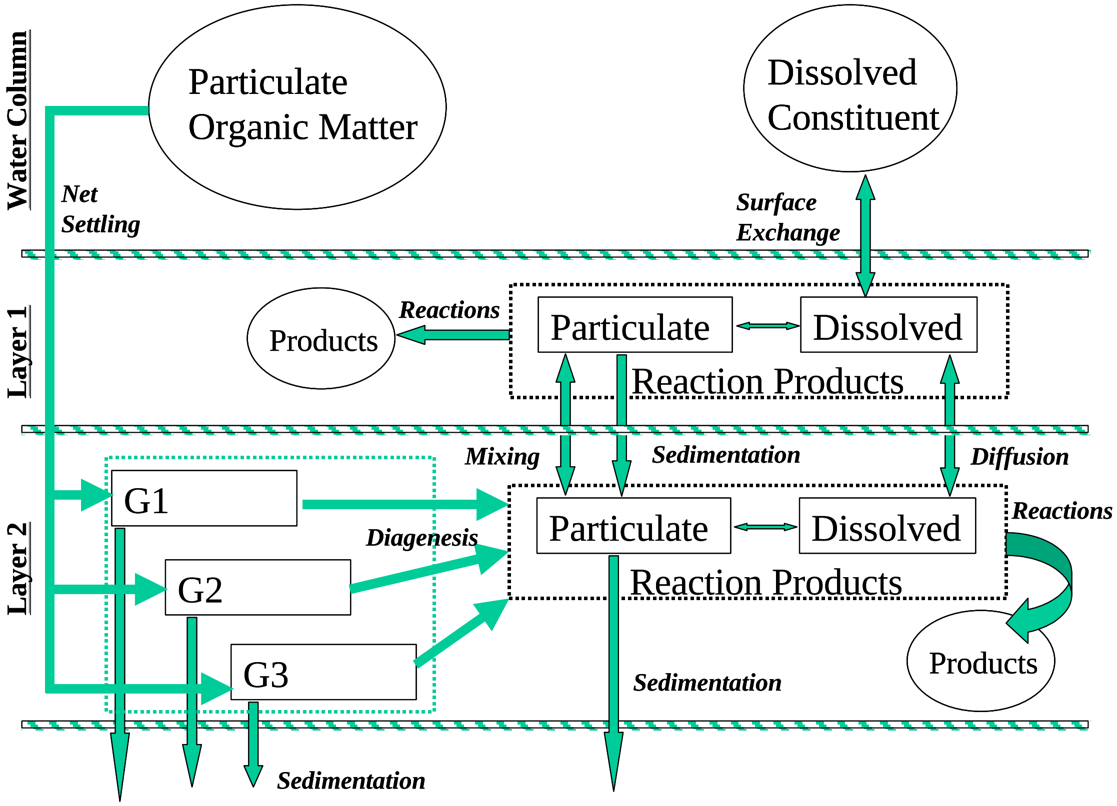

Figure 3. Sediment model framework.

Particulate Organic Matter Fluxes (Deposition)

Fluxes of particulate organic matter (POM) from the water column represent a source term for the sediments. The particulate organic matter fluxes are subdivided into particulate organic carbon (C, in oxygen equivalents), nitrogen (N) and phosphorus forms (POC, PON and POP) and then into separate forms (G-classes) based upon their reactivity.

The flux of POM from the water column to the sediments is computed using the standard WASP transport conventions for the following state variables: CBOD, algae, organic nitrogen and organic phosphorus. In WASP, settling fluxes for these state variables are computed based upon the specified fraction dissolved (which can vary by segment and state variable), specified particulate transport field (for the state variable) and the specified rates of solids transport (flow fields 1 to 3). The particulate organic carbon, in the diagenesis model, is in oxygen equivalent units (CBOD) as opposed to carbon units in similar models. The flux of algae to the sediment model is subdivided into carbon (oxygen equivalents), nitrogen and phosphorus using specified stoichiometric constants.

Internal sediment state variables for diagenesis are based upon the multi-class G model, in which the organic forms are divided based upon their reactivity into reactive (G1), refractory (G2), and inert (G3) forms (Figure 3). Therefore the fluxes of particulate organic carbon (oxygen equivalents), nitrogen, and phosphorus are subdivided into G-class fractions, based upon user specified ratios. Due to the negligible thickness of the upper layer, deposition (as described later) is assumed to proceed directly from the water column to the lower (anoxic) sediment layer.

Diagenesis

Diagenesis reactions are assumed to occur in the second (anaerobic) sediment layer. The diagenesis equations are solved for each form of particulate organic matter (POM; forms for N, P and C where C is in oxygen equivalents) and for each G class (1-3) using the same basic formulation. In order to compute the time-varying diagenesis for each modeled variable, a mass balance equation is written as

Equation 2

$$\frac{\partial C_{T2}}{\partial t} = \frac{J_2}{H_2} - \frac{W_2}{H_2} C_{T2}^{t+\Delta t} - K_2 C_{T2}^{t+\Delta t} \approx \frac{C_{T2}^{t+\Delta t} - C_{T2}^{t}}{\Delta t}$$

where

$C_{T2}^{t+\Delta t}$ = total concentration in layer 2 at time t+Δt

C_{T2}^{t} = total concentration in layer 2 at time t (from initial conditions or computed value from previous time step)

Δt = time step (from the water quality model converted to internal units)

J_2 = flux from the water column,

H_2 = thickness of the active sediment layer (input variable),

K_2 = reaction velocity (specific to chemical and G class, temperature corrected), and

W_2 = net sedimentation velocity (input variable)

The mass balance equation is solved algebraically for the concentration at the present time step, as

Equation 3

$$C_{T2}^{t+\Delta t} = \frac{J_2 \dfrac{\Delta t}{H_2} + C_{T2}^{t}}{\mathbf{1} + K_2 H_2 \dfrac{\Delta t}{H_2} + W_2 \dfrac{\Delta t}{H_2}}$$

Once the concentrations at the present time step are computed, the diagenesis source terms for reactions and transfers ($J_{T2}^{t+\Delta t}$) are computed. Diagenesis source terms are computed for C, N and P from the sum of the product of the chemical specific reaction velocities (K_2) and computed concentrations in each of the three G classes. For example,

Equation 4

$$J_{T2}^{t+\Delta t} = \sum_{i=1}^{3} K_{2.i} C_{T2,i}^{t+\Delta t}$$

where

$J_{T2}^{t+\Delta t}$ = source term for total chemical in layer 2 at time $t+\Delta t$

K2,i = reaction velocity for total chemical in G class i

$C_{T2,i}^{t+\Delta t}$ = total chemical concentration for G class i

The WASP diagenesis model also contains an option for steady-state computations for use in computing the initial conditions for the model. The steady-state computations involve an iterative solution for kinetic reactions, as discussed in a following section. That is, an initial guess for the solution is specified (the initial conditions) and the computations iterated until the solution converges. The maximum number of allowable iterations and convergence criteria are specified in input. For POM diagenesis, the steady-state solution to Equation 2 is given by

Equation 5

$$C_{T2} = \frac{\dfrac{J_2}{H_2}}{K_2 + \dfrac{W_2}{H_2}}$$

Reactions and Transfers

Overview

Once the sediment particulate organic matter (C, N and P) concentrations and source terms are computed for the present time step, as described above, the reactions and transfers are computed. Concentrations of ammonia, nitrates, methane, sulfides, silica and phosphorus are computed, and then used to compute fluxes to the overlying water column.

The total chemical concentrations are computed from mass balance relationships for each of the two sediment layers. Since the surface layer is thin (on the order of 0.1 cm) compared to the active anaerobic layer (on the order of 10 cm), it is assumed that layer 1 can be considered at steady-state in comparison to the slower processes occurring in layer 2. From DiToro (2001; Equations 13.28 and 13.30), the two equations solved are

Layer 1

Equation 6

$$\mathbf{0} = -s\left(f_{d\mathbf{1}}C_{T\mathbf{1}}^{t+\Delta t} - C_{dO}^{t+\Delta t}\right) + \boldsymbol{\omega}_{\mathbf{12}}\left(f_{p\mathbf{2}}C_{T\mathbf{2}}^{t+\Delta t} - f_{p\mathbf{1}}C_{T\mathbf{1}}^{t+\Delta t}\right) + K_{L\mathbf{12}}\left(f_{d\mathbf{2}}C_{T\mathbf{2}}^{t+\Delta t} - f_{d\mathbf{1}}C_{T\mathbf{1}}^{t+\Delta t}\right)$$

$$-\boldsymbol{\omega}_{\mathbf{2}}\, C_{T\mathbf{1}}^{t+\Delta t} - \frac{\boldsymbol{\kappa}_{\mathbf{1}}^{\mathbf{2}}}{s} C_{T\mathbf{1}}^{t+\Delta t} + J_{T\mathbf{1}}^{t+\Delta t} + C_{T\mathbf{2}}^{t+\Delta t}\,\dot{H}_{\mathbf{1}}^{+} - C_{T\mathbf{1}}^{t+\Delta t}\left(\dot{H}_{\mathbf{1}} + \dot{H}_{\mathbf{1}}^{-}\right)$$

Layer 2

Equation 7

$$\mathbf{0} = -\boldsymbol{\omega}_{\mathbf{12}}\left(f_{p\mathbf{2}}C_{T\mathbf{2}}^{t+\Delta t} - f_{p\mathbf{1}}C_{T\mathbf{1}}^{t+\Delta t}\right) - K_{L\mathbf{12}}\left(f_{d\mathbf{2}}C_{T\mathbf{2}}^{t+\Delta t} - f_{d\mathbf{1}}C_{T\mathbf{1}}^{t+\Delta t}\right) - \boldsymbol{\kappa}_{\mathbf{2}}C_{T\mathbf{2}}^{t+\Delta t} + \boldsymbol{\omega}_{\mathbf{2}}\left(C_{T\mathbf{1}}^{t+\Delta t} - C_{T\mathbf{2}}^{t+\Delta t}\right)$$

$$-\frac{H_{\mathbf{2}}C_{T\mathbf{2}}^{t+\Delta t}}{\boldsymbol{\Delta t}} + J_{T\mathbf{2}}^{t+\Delta t} + \frac{H_{\mathbf{2}}C_{T\mathbf{2}}^{t}}{\boldsymbol{\Delta t}} + C_{T\mathbf{2}}^{t+\Delta t}\,\dot{H}_{\mathbf{1}}^{+} - C_{T\mathbf{2}}^{t+\Delta t}\left(\dot{H}_{\mathbf{2}} + \dot{H}_{\mathbf{1}}^{+}\right)$$

s = surface transfer rate; SOD/[$O_2(0)$], where SOD=SOD rate and $O_2(0)$ is the overlying water concentration

f_{d1} = fraction dissolved in layer 1

f_{d2} = fraction dissolved in layer 2

f_{p1} = fraction particulate in layer 1

f_{p2} = fraction particulate in layer 2

$C_{T1}^{t+\Delta t}$ = total concentration in layer 1 at time t+Δt

$C_{T2}^{t+\Delta t}$ = total concentration in layer 2 at time t+Δt

C_{T2}^{t} = total concentration in layer 2 at time t

$C_{dO}^{t+\Delta t}$ = concentration in overlying water column

K_{L12} = mass transfer coefficient via diffusion

ω_{12} = particle mixing coefficient between layers 1 and 2

ω_2 = sedimentation velocity for layer 2

$J_{T1}^{t+\Delta t}$ = source term for total chemical in layer 1 at time t+Δt

$J_{T2}^{t+\Delta t}$ = source term for total chemical in layer 2 at time t+Δt

κ_1^2 = square of reaction velocity in layer 1

κ_2 = reaction velocity in layer 2

$\dot{H}_1^-$ = time derivative for H in layer 1 (*not used*)

$\dot{H}_1^+$ = time derivative for H in layer 1 (*not used*)

$\dot{H}_1$ = time derivative for H in layer 1 (*not used*)

$\dot{H}_2$ = time derivative for H in layer 2 (*not used*)

H_2 = thickness of layer 2

Δt = time step

The two equations and two unknowns can be written in the form

Equation 8

$$a_{11}x_1 + a_{12}x_2 = b_1$$

Equation 9

$$a_{21}x_1 + a_{22}x_2 = b_2$$

The equations are solved for the new concentrations ($C_{T1}^{t+\Delta t}$ and $C_{T2}^{t+\Delta t}$) using a matrix. The solution to this system of equations is (Chapra and Canale 1998) as follows:

$$x_1 = \frac{a_{22}b_1 - a_{12}b_2}{a_{11}a_{22} - a_{12}a_{21}}$$

$$x_2 = \frac{a_{11}b_2 - a_{21}b_1}{a_{11}a_{22} - a_{12}a_{21}}$$

where the elements of the matrix are:

Equation 10

$$a_{11} = -s\left(f_{d1}\right) - \omega_{12}\left(f_{p1}\right) - K_{L12}\left(f_{d1}\right) - \omega_2 - \frac{\kappa_1^2}{s}$$

Equation 11

$$a_{21} = +\omega_{12}\left(f_{p1}\right) + K_{L12}\left(f_{d1}\right) + \omega_2$$

Equation 12

$$a_{12} = +\omega_{12}\left(f_{p2}\right) + K_{L12}\left(f_{d2}\right)$$

Equation 13

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \kappa_2 - \omega_2 - \frac{H_2}{\Delta t}$$

Equation 14

$$b_1 = -J_{T1}^{t+\Delta t}$$

Equation 15

$$b_2 = -J_{T2}^{t+\Delta t} - \frac{H_2 C_{T2}^{t}}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 16

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \kappa_2 - \omega_2$$

Equation 17

$$b_2 = -J_{T2}^{t+\Delta t}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 18

$$f_{d,1} = \frac{1}{1+\pi_{C1} S_1}\,;\; f_{p,1} = \frac{\pi_{C1} S_1}{1+\pi_{C1} S_1}$$

$$f_{d,2} = \frac{\mathbf{1}}{\mathbf{1} + \boldsymbol{\pi}_{C2} S_2}\mathbf{;}\ f_{p,2} = \frac{\boldsymbol{\pi}_{C2} S_2}{\mathbf{1} + \boldsymbol{\pi}_{C2} S_2}$$

where

π_{C1} = partition coefficient for total chemical in layer 1

π_{C2} = partition coefficient for total chemical in layer 2

S1 = solids concentration in layer 1

S2 = solids concentration in layer 2

The equations are conveniently solved for the new concentrations ($C_{T1}^{t+\Delta t}$ and $C_{T2}^{t+\Delta t}$) using the matrix solution. Once the concentrations have been updated, the flux of the material to the overlying water column (J) can be computed from:

Equation 19

$$J = s\left(f_{d1} C_{T1}^{t+\Delta t} - C_{dO}^{t+\Delta t} \right)$$

The surface transfer rate (s) quantifies the mixing between layer 1 and the overlying water column, which can be related to sediment oxygen demand by (Di Toro 2001).

Equation 20

$$SOD = D \left. \frac{d[O_2]}{dz} \right|_{z=0} \approx D \frac{[O_2(0) - O_2(H_1)]}{H_1} = \frac{D}{H_1}[O_2(0)]$$

where

D = rate of oxygen diffusion

$O_2(0)$ = oxygen concentration of the overlying water, and

$O_2(H_1)$ = oxygen concentration at the depth H_1

assuming a straight line approximation of the derivative, so that the mass transfer coefficient ($K_{L,O2}$) may be estimated from (Di Toro 2001)

Equation 21

$$K_{L,O2} = \frac{D}{H_1} = \frac{SOD}{[O_2(o)]} = s$$

The reaction rate in the aerobic layer is formulated as a first order rate (K_1), where the term in the layer 1 equation is K_1H_1. The depth of the aerobic zone follows the definition of the surface mass transfer coefficient ($s=D/H_1$) so that $K_1H_1=K_1D_1/s$ so that

Equation 22

$$\boldsymbol{\kappa}_1 = \sqrt{DK_1}$$

and

Equation 23

$$K_1 H_1 = \frac{\boldsymbol{\kappa}_1^2}{s}$$

which is the term applied to the total chemical in the equation for layer 1 (Equation 6).

The rate of mixing of the sediment by macrobenthos (bioturbation, w_{12}) is estimated by an apparent particle diffusion coefficient (D_p), temperature corrected that varies with the biomass of the benthos. Assuming that the mass of the benthos is proportional to the labile carbon in the sediment ($C^t_{POC,1}$, or POC, in oxygen equivalents in layer 2 in G class 1),

Equation 24

$$w^*_{12} = D_P \frac{\Theta^{(T-20)}}{H_2/2} \frac{C^t_{POC,1}}{C_{POC,R}}$$

where w^*_{12} is a particle mixing coefficient that is further modified as discussed below and $C_{POC,R}$ is a reference POC concentration. Note that in the above equation and elsewhere, POC in the WASP code is in units of oxygen equivalents. Also note that the ICM code and Equation 13.1 of DiToro (2001) use H_2 in denominator, rather than $H_2/2$, so that the user should use caution in providing the appropriate value for D_p when comparing model codes or inputs.

An additional impact is that if anoxia occurs for periods of time, the benthic population is ultimately reduced or eliminated, so that bioturbuation is consequently reduced or eliminated. To include this effect, Di Toro (2001) computes the stress that low dissolved oxygen conditions (benthic stress, S) imposes on the population assuming that the stress accumulates as

Equation 25

$$\frac{\partial S}{\partial t} = -k_s S^{t+\Delta t} + \frac{K_{M,D_P}}{K_{M,D_P} + [O_2(0)]} \approx \frac{S^{t+\Delta t} - S^t}{\Delta t}$$

where

k_s = decay constant for benthic stress,

$K_{M,Dp}$ = particle mixing half-saturation concentration for oxygen

which can be solved for

Equation 26

$$S^{t+\Delta t} = \frac{S^t + \dfrac{K_{M,D_P}}{K_{M,D_P} + [O_2(\mathbf{0})]}\Delta t}{\mathbf{1} + k_s \Delta t}$$

As [O_2(0)] approaches zero, then (1-k_sS) approaches zero, so that the particle mixing coefficient is similarly reduced, as

Equation 27

$$w_{12} = w^*_{12}\left(\mathbf{1} - k_s S^{t+\Delta t}\right)$$

The stress is continued at the minimum value for the year to conform with the observation that once the benthic population has been reduced by low dissolved oxygen, it does not recover until the next year (Di Toro 2001).

The dissolved phase mixing coefficient between layers 1 and 2 (K_{L12}) is due to passive molecular diffusion that is enhanced by the action of organisms (bio-irrigation). The mixing coefficient is computed from (Equation 13.6, Di Torro 2001)

Equation 28

$$K_{L12} = \frac{D_D}{H_2 / \mathbf{2}} \Theta^{(T-\mathbf{20})}$$

where

D_D = pore-water diffusion coefficient

$K_{L,B}$ = ratio of bio-irrigation to bio-particle mixing.

Note that the ICM code uses H_2 in denominator, rather than H_2/2, so that the user should use caution in providing the appropriate value for D_D when comparing model codes or inputs. The sediment temperature is assumed equal to the temperature of the overlying water column.

The solution of the reaction and transfer equations comprises the bulk of the computations of the diagenesis model. Part of the complexity results from the relationship of the surface transfer coefficient (s) to the sediment oxygen demand (SOD) and dissolved oxygen concentration in the overlying water column {O_2(0); s=SOD/[O_2(0)]}. Since the SOD is a function of the computed ammonia, nitrate (denitrification), sulfide (salt water) or methane (fresh water) concentrations, an iterative solution is required for those constituents. The procedure for the solution is:

1. Start with an initial estimate of the SOD
2. Solve layer 1 and 2 equations for ammonia, nitrate, sulfide and methane
    a. Solve for the ammonia flux by establishing the chemical specific conditions

  b. Compute the oxygen consumed by nitrification (NCOD)
  c. Solve for the nitrate flux by establishing the chemical specific conditions
  d. Compute methane (fresh water) or sulfide (salt water) oxidation
    i. For salt water, compute sulfide reaction terms and compute SOD due to hydrogen sulfide
    ii. For fresh water, compute methane flux by establishing the chemical specific
      1. Compare computed and saturation concentrations and correct
      2. Calculate the CSOD due to methane
    a. Compute the total CSOD due to sulfides or methane
    b. Compute flux terms
    c. Compute the total SOD due to the sulfide or methane, adding term for NCOD
    d. Refine the estimate of SOD. A root finding method is used to make the new estimate
3. Go to step (2) if no convergence

Once the SOD is determined, then the layer 1 and 2 equations for phosphate and silica can be solved and the flux rates determined.

Computation of SOD and related reactions

As discussed above, the SOD is computed iteratively using a function Zbrent from Numerical Recipes, Press et al. (1992), which finds the root of a function without knowing the derivative. The SOD related terms are solved for each iteration, until convergence is attained. The computations require the solution of equations for ammonia, nitrate, nitrite, sulfide (salt water) or methane (fresh water) reactions, along with the carbonaceous and nitrogeneous SOD. The computation of each of these terms is briefly presented below.

Ammonia

The two-layer mass balance equations for ammonia are:

Layer 1

Equation 29

$$\mathbf{0} = -s\left(f_{d\mathbf{1}} C_{NH\mathbf{4}T,\mathbf{1}}^{t+\Delta t} - C_{NH\mathbf{4}T,O}^{t+\Delta t} \right) + \boldsymbol{\omega}_{\mathbf{12}} \left(f_{p\mathbf{2}} C_{NH\mathbf{4}T,\mathbf{2}}^{t+\Delta t} - f_{p\mathbf{1}} C_{NH\mathbf{4}T,\mathbf{1}}^{t+\Delta t} \right)$$
$$+K_{L\mathbf{12}} \left(f_{d\mathbf{2}} C_{NH\mathbf{4}T,\mathbf{2}}^{t+\Delta t} - f_{d\mathbf{1}} C_{NH\mathbf{4}T,\mathbf{1}}^{t+\Delta t} \right) - \boldsymbol{\omega}_{\mathbf{2}}\ C_{NH\mathbf{4}T,\mathbf{1}}^{t+\Delta t} - \frac{\boldsymbol{\kappa}_{NH\mathbf{4,1}}^{\mathbf{2}} \boldsymbol{\theta}^{T-\mathbf{20}}}{s} f_O f_{NH\mathbf{4}}\ f_{d\mathbf{1}} C_{NH\mathbf{4}T,\mathbf{1}}^{t+\Delta t}$$

Layer 2

Equation 30

$$\mathbf{0} = -\omega_{12}\left(f_{p2}C^{t+\Delta t}_{NH4T,2} - f_{p1}C^{t+\Delta t}_{NH4T,1}\right) - K_{L12}\left(f_{d2}C^{t+\Delta t}_{NH4T,2} - f_{d1}C^{t+\Delta t}_{NH4T,1}\right)$$

$$+\omega_2\left(C^{t+\Delta t}_{NH4T,1} - C^{t+\Delta t}_{NH4T,2}\right) - \frac{H_2 C^{t+\Delta t}_{NH4T,2}}{\Delta t} + J^{t+\Delta t}_{NH4T,2} + \frac{H_2 C^{t}_{NH4T,2}}{\Delta t}$$

where all terms have been previously defined, with the exception of two terms for the surface layer (f_{NH4}, f_O). Note that the primary difference between the general equations presented previously and the ammonia equations are that the square of the reaction velocity in layer 1 (nitrification) is applied only to the dissolved fraction and is modified by functions based on the oxygen and ammonia concentrations. Note also that there are two separate reaction velocities that may be specified for layer 1 in the diagenesis code ($\kappa_{NH4,1}$), for fresh and salt waters respectively, with the one used based on the salinity (SAL) of the overlying water column as compared to a salinity switch (input). In addition, the reaction velocity for layer 2 is zero. The source term for ammonia in layer 2 is equal to the flux from the diagenesis of PON.

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 31

$$a_{11} = -\left(f_{d1}\right)K_{L12} - \left(f_{p1}\right)\omega_{12} - \frac{\kappa^2_{NH4}\theta^{\mathrm{T-20}}}{s}\,\mathbf{f_O}\;\mathbf{f_{NH4}}\;f_{d1} - \left(f_{d1}\right)s - \omega_2$$

Equation 32

$$a_{21} = +\omega_{12}\left(f_{p1}\right) + K_{L12}\left(f_{d1}\right) + \omega_2$$

Equation 33

$$a_{12} = +\omega_{12}\left(f_{p2}\right) + K_{L12}\left(f_{d2}\right)$$

Equation 34

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2 - \frac{H_2}{\Delta t}$$

Equation 35

$$b_1 = -s\,C^{t+\Delta t}_{NH4T,O}$$

Equation 36

$$b_2 = -J^{t+\Delta t}_{NH4T,2} - \frac{H_2 C^{t}_{NH4T,2}}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 37

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_{2}$$

Equation 38

$$b_{2} = -J_{NH4T,2}^{t+\Delta t}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 39

$$f_{d1} = \frac{1}{1+\pi_{NH4}S_{1}};\ f_{p1} = \frac{\pi_{NH4}S_{1}}{1+\pi_{NH4}S_{1}}$$

$$f_{d2} = \frac{1}{1+\pi_{NH4}S_{2}};\ f_{p1} = \frac{\pi_{NH4}S_{2}}{1+\pi_{NH4}S_{2}}$$

where

π_{NH4} = partition coefficient for ammonia

S1 = solids concentration in layer 1

S2 = solids concentration in layer 2

The modification of the nitrification reaction for dissolved oxygen is computed from

Equation 40

$$f_{O} = \frac{O_{2,0}}{O_{2,0}+K_{NH4,O2}}$$

where

$O_{2,0}$ = dissolved oxygen concentration in the overlying water column, and

$K_{NH4,O2}$ = half-saturation concentration of dissolved oxygen in the nitrification reaction

The modification for ammonia concentrations is computed by

Equation 41

$$f_{NH4} = \frac{K_{NH4}}{C_{NH4,1}^{t}+K_{NH4}}$$

where

$C_{NH4,1}^{t}$ = ammonia concentration from the previous time step,

K_{NH4} = half-saturation concentration of ammonia in the nitrification reaction

Note that if K_{NH4} is specified in input, the f_{NH4} is computed as above. Otherwise $f_{NH4}=1$.

Once the ammonia concentrations have been updated, the flux to the water column is computed from:

Equation 42

$$J_{NH\mathbf{4}} = s\left(C_{NH\mathbf{4,1}}^{t+\Delta t} - C_{NH\mathbf{4,0}}\right)$$

where J_{NH4} is the flux to the water column.

In order to compute the oxygen consumption due to the oxidation of ammonia in the aerobic layer, the two-stage reaction can be represented by (Chapra 1997, Di Toro 2001)

Equation 43

$$NH_{\mathbf{4}}^{+} + \mathbf{1.5}O_{\mathbf{2}} \rightarrow \mathbf{2}H^{+} + NO_{\mathbf{2}}^{-} + H_{\mathbf{2}}O$$

so that the consumption of oxygen during the process can be represented by (Chapra 1997, Equation 23.3)

Equation 44

$$a_{no} = \frac{\mathbf{1.5(32)}}{\mathbf{14}} = \mathbf{3.43} \quad gO \quad gN^{-1}$$

Therefore the contribution of the oxidation of ammonia to SOD can be estimated from

Equation 45

$$NSOD_{NH_{\mathbf{4}}} = a_{no} \frac{\boldsymbol{\kappa}_{NH\mathbf{4,1}}^{\mathbf{2}} \boldsymbol{\theta}^{T-\mathbf{20}}}{s} f_O \, f_{NH\mathbf{4}} \; f_{d\mathbf{1}} C_{NH_{\mathbf{4}},\mathbf{1}}^{t+\Delta t}$$

Nitrite

The two-layer mass balance equations for nitrite are:

Layer 1

Equation 46

$$\mathbf{0} = -s\left(C_{NO\mathbf{2,1}}^{t+\Delta t} - C_{NO\mathbf{2},O}^{t+\Delta t}\right) + K_{L\mathbf{12}}\left(C_{NO\mathbf{2,2}}^{t+\Delta t} - C_{NO\mathbf{2,1}}^{t+\Delta t}\right) - \boldsymbol{\omega}_{\mathbf{2}} \; C_{NO\mathbf{2}T,\mathbf{1}}^{t+\Delta t}$$
$$-\frac{\boldsymbol{\kappa}_{N\mathbf{02,1}}^{\mathbf{2}} \boldsymbol{\theta}^{T-\mathbf{20}}}{s} f_O C_{NO\mathbf{2,1}}^{t+\Delta t} + \frac{\boldsymbol{\kappa}_{NH\mathbf{4,1}}^{\mathbf{2}} \boldsymbol{\theta}^{T-\mathbf{20}}}{s} f_O \, f_{NH\mathbf{4}} \; f_{d\mathbf{1}} C_{NH_{\mathbf{4}},\mathbf{1}}^{t+\Delta t}$$

Layer 2

Equation 47

$$\mathbf{0} = -K_{L\mathbf{12}}\left(C_{NO\mathbf{2,2}}^{t+\Delta t} - C_{NO\mathbf{2,1}}^{t+\Delta t}\right)$$
$$+\boldsymbol{\omega}_{\mathbf{2}}(C_{NO\mathbf{2,1}}^{t+\Delta t} - C_{NO\mathbf{2,2}}^{t+\Delta t}) - \frac{H_{\mathbf{2}} C_{NO\mathbf{2,2}}^{t+\Delta t}}{\Delta t} + \frac{H_{\mathbf{2}} C_{NO\mathbf{2,2}}^{t}}{\Delta t}$$

where all terms have been previously defined. Note that the primary difference between the general equations presented previously and the nitrite equations are that

- The reaction velocity for nitrite is modified by the dissolved oxygen concentration in the overlying water column (factor f_O)
- All nitrite is assumed dissolved, therefore the fraction particulate is zero and the rate of particle mixing zero
- The first-stage nitrification loss from layer one becomes a source term for nitrite
- The reaction velocity for layer 2 is zero.

Note also that unlike reaction rates for ammonia and nitrate-nitrogen, the reaction velocity for nitrite is assumed not to vary between fresh and salt water systems. Note also that this model assumes that the only reaction of NO_2 is nitrification to NO3. However, Wetzel (2001, pp. 217&513) indicates that denitrification occurs through NO_2. Any error is assumed small due to the typically small concentration of NO_2.

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 48

$$a_{11} = -K_{L12} - \frac{\boldsymbol{\kappa}^{2}_{NO2}\boldsymbol{\theta}^{\mathbf{T\text{-}20}}}{s}\mathbf{f_O} - s - \boldsymbol{\omega}_2$$

Equation 49

$$a_{21} = K_{L12} + \boldsymbol{\omega}_2$$

Equation 50

$$a_{12} = K_{L12}$$

Equation 51

$$a_{22} = -K_{L12} - \boldsymbol{\omega}_2 - \frac{H_2}{\Delta t}$$

Equation 52

$$b_1 = -s\,C^{t+\Delta t}_{NO2,O} - \frac{\boldsymbol{\kappa}^{2}_{NH4,1}\boldsymbol{\theta}^{T-20}}{s} f_O\, f_{NH4}\;\, f_{d1} C^{t+\Delta t}_{NH_4,1}$$

Equation 53

$$b_2 = -\frac{H_2 C^{t}_{NO2,2}}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 54

$$a_{22} = -K_{L12} - \omega_2$$

Equation 55

$$b_2 = 0$$

The modification of the second-stage nitrification reaction by dissolved oxygen is computed from

Equation 56

$$f_O = \frac{O_{2,0}}{O_{2,0} + K_{NO2,O2}}$$

where

$O_{2,0}$ = dissolved oxygen concentration in the overlying water column, and

$K_{NO2,O2}$ = half-saturation concentration of dissolved oxygen in the second-stage nitrification reaction

Once the nitrite-concentrations have been updated, the flux to the water column is computed from:

Equation 57

$$J_{NO2} = s\left(C_{NO2,1}^{t+\Delta t} - C_{NO2,0}\right)$$

where J_{NO2} is the nitrite flux to the water column. Note that in WASP, nitrite is not a state variable and the water column concentration is assumed to equal zero.

In order to compute the oxygen consumption due to the oxidation of ammonia in the aerobic layer, the second state of the nitrification reaction can be represented by (Chapra 1997)

Equation 58

$$NO_2^- + 0.5O_2 \rightarrow NO_3^-$$

so that the consumption of oxygen during the process can be represented by (Chapra 1997, Equation 23.4)

Equation 59

$$a_{no2} = \frac{0.5(32)}{14} = 1.14 \quad gO \quad gN^{-1}$$

Therefore the contribution of the oxidation of ammonia to SOD can be estimated from

Equation 60

$$NSOD_{NO2} = a_{no2}\frac{\kappa_{NO2,1}^2 \theta^{T-20}}{s} f_O C_{NO2,1}^{t+\Delta t}$$

Nitrate

The two-layer mass balance equations for nitrate are:

Layer 1

Equation 61

$$\mathbf{0} = -s\left(C_{NO\mathbf{3,1}}^{t+\Delta t} - C_{NO\mathbf{3},O}^{t+\Delta t}\right) + K_{L\mathbf{12}}\left(C_{NO\mathbf{3,2}}^{t+\Delta t} - C_{NO\mathbf{3,1}}^{t+\Delta t}\right) - \boldsymbol{\omega}_{\mathbf{2}}\, C_{NO\mathbf{3,1}}^{t+\Delta t} - \frac{\boldsymbol{\kappa}_{NO\mathbf{3,1}}^{\mathbf{2}}}{s} C_{NO\mathbf{3,1}}^{t+\Delta t}$$

$$+\frac{\boldsymbol{\kappa}_{N\mathbf{02,1}}^{\mathbf{2}}\boldsymbol{\theta}^{T-\mathbf{20}}}{s}\, f_O C_{NO\mathbf{2,1}}^{t+\Delta t}$$

Layer 2

Equation 62

$$\mathbf{0} = -K_{L\mathbf{12}}\left(C_{NO\mathbf{3,2}}^{t+\Delta t} - C_{NO\mathbf{3,1}}^{t+\Delta t}\right) + \boldsymbol{\omega}_{\mathbf{2}}\mathbf{(}C_{NO\mathbf{3,1}}^{t+\Delta t} - C_{NO\mathbf{3,2}}^{t+\Delta t}\mathbf{)} - \frac{H_{\mathbf{2}}C_{NO\mathbf{3,2}}^{t+\Delta t}}{\Delta t}$$

$$-\boldsymbol{\kappa}_{NO\mathbf{3,2}}C_{NO\mathbf{3,2}}^{t+\Delta t} + \frac{H_{\mathbf{2}}C_{NO\mathbf{3,2}}^{t}}{\Delta t}$$

where all terms have been previously defined. Note that the primary difference between the general and nitrate equations is that there is no sorption so the total and dissolved concentrations are equal. For nitrate, there is a reaction velocity due to denitrification for both layers 1 and 2. The second-stage nitrification rate becomes a source term for layer 1. Note also that there are two separate denitrification reaction velocities specified for each layer ($\kappa_{NO3,1}$ and $\kappa_{NO3,2}$), for fresh and salt waters with the one used based on the salinity (SAL) as compared to a salinity switch (SALTND, input).

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 63

$$a_{\mathbf{11}} = -K_{L\mathbf{12}} - \frac{\boldsymbol{\kappa}_{NO\mathbf{3,1}}^{\mathbf{2}}\boldsymbol{\theta}^{\mathbf{T\text{-}20}}}{s} - s - \boldsymbol{\omega}_{\mathbf{2}}$$

Equation 64

$$a_{\mathbf{21}} = K_{L\mathbf{12}} + \boldsymbol{\omega}_{\mathbf{2}}$$

Equation 65

$$a_{\mathbf{12}} = K_{L\mathbf{12}}$$

Equation 66

$$a_{\mathbf{22}} = -K_{L\mathbf{12}} - \boldsymbol{\kappa}_{NO\mathbf{3,2}}\boldsymbol{\theta}^{\mathbf{T\text{-}20}} - \boldsymbol{\omega}_{\mathbf{2}} - \frac{H_{\mathbf{2}}}{\Delta t}$$

Equation 67

$$b_1 = -s\, C_{NO3,O}^{t+\Delta t} - \frac{\kappa_{NO3,1}^{2}\theta^{T-20}}{s}\, f_O C_{NO2,1}^{t+\Delta t}$$

Equation 68

$$b_2 = -\frac{H_2 C_{NO3,2}^{t}}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 69

$$a_{22} = -K_{L12} - \kappa_{NO3,2}\theta^{\mathrm{T\text{-}20}} - \omega_2$$

Equation 70

$$b_2 = 0$$

Once the nitrate concentrations have been updated, the flux to the water column is computed from:

Equation 71

$$J_{NO3} = s\left(C_{NO3,1}^{t+\Delta t} - C_{NO3,0}\right)$$

where J_{NO3} is the flux to the water column.

The process of denitrfication requires a carbon source as indicated by (Di Toro 2001, Equation 9.16)

Equation 72

$$\frac{10}{8}CH_2O + H^+ + NO_3^- \rightarrow \frac{10}{8}CO_2 + \frac{1}{2}N_2 + \frac{7}{4}H_2O$$

so that the carbon to nitrogen stoichiometric coefficient (a_{cn}) is 1.071 gC gN^{-1}. The oxidation of methane in the aerobic zone may be represented by

Equation 73

$$\frac{1}{2}CH_4 + O_2 \rightarrow \frac{1}{2}CO_2 + H_2O$$

so the oxygen to carbon stoichiometric coefficient (a_{oc}) is 2.67 g O g C^{-1}.

If all of the carbon produced by the diagenesis reaction was converted to methane and fully oxidized, the maximum SOD that could be produced would be

Equation 74

$$J_{O_2,C} = J_{C,2}^{t+\Delta t}$$

where in WASP, J_c is in oxygen equivalents.

However, this maximum is reduced by the carbon utilized during denitrification, so that the maximum oxygen utilization becomes

Equation 75

$$J_{O_2,C} = J_{C,2}^{t+\Delta t} - a_{oc}a_{cn}\left[\frac{\kappa_{NO3,1}\Theta^{T-20}C_{NO3,1}^{t+\Delta t}}{s} + \kappa_{NO3,2}\Theta^{T-20}C_{NO3,2}^{t+\Delta t}\right]$$

where $a_{oc}a_{cn}$ is 2.857.

Sulfides

Note that sulfide reactions are only computed in the WASP model for salt water systems (salinity greater than a salt switch, SALTSW). The two-layer mass balance equations for sulfide are:

Layer 1

Equation 76

$$\mathbf{0} = -s\left(f_{d1}C_{H2S,1}^{t+\Delta t} - C_{H2S,O}^{t+\Delta t}\right) + \omega_{12}\left(f_{p2}C_{H2S,2}^{t+\Delta t} - f_{p1}C_{H2S,1}^{t+\Delta t}\right) + K_{L12}\left(f_{d2}C_{H2S,2}^{t+\Delta t} - f_{d1}C_{H2S,1}^{t+\Delta t}\right)$$

$$-\omega_2\, C_{H2S,1}^{t+\Delta t} - f_O\left[\frac{\kappa_{D,H2S,1}^2}{s}\, f_{d1} + \frac{\kappa_{P,H2S,1}^2}{s}\, f_{p1}\right]C_{H2S,1}^{t+\Delta t}$$

Layer 2

Equation 77

$$\mathbf{0} = -\omega_{12}\left(f_{p2}C_{H2S,2}^{t+\Delta t} - f_{p1}C_{H2S,1}^{t+\Delta t}\right) - K_{L12}\left(f_{d2}C_{H2S,2}^{t+\Delta t} - f_{d1}C_{H2S,1}^{t+\Delta t}\right) + \omega_2(C_{H2S,1}^{t+\Delta t} - C_{H2S,2}^{t+\Delta t})$$

$$-\frac{H_2C_{HS,2}^{t+\Delta t}}{\Delta t} + J_{HS,2}^{t+\Delta t} + \frac{H_2C_{HS,2}^{t}}{\Delta t}$$

where all terms have been previously defined. Note that the primary difference between the ammonia and sulfide equations is that there are separate reaction velocities in layer 1 for the dissolved and particulate forms.

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 78

$$a_{11} = -\left(f_{d1}\right)K_{L12} - \left(f_{p1}\right)\omega_{12} - \frac{\left(\kappa_{HS,D}^2\, f_{D,1} + \kappa_{HS,P}^2\, f_{P,1}\right)\theta^{\mathrm{T-20}}}{s}\,\mathbf{f_O} - \left(f_{d1}\right)s - \omega_2$$

Equation 79

$$a_{21} = +\omega_{12}\left(f_{p1}\right) + K_{L12}\left(f_{d1}\right) + \omega_2$$

Equation 80

$$a_{12} = +\omega_{12}\left(f_{p2}\right) + K_{L12}\left(f_{d2}\right)$$

Equation 81

$$a_{22} = -\boldsymbol{\omega}_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \boldsymbol{\omega}_2 - \frac{H_2}{\Delta t}$$

Equation 82

$$b_1 = \mathbf{0}$$

Equation 83

$$b_2 = -J_{OC} - \frac{H_2 C^{t}_{HS,2}}{\Delta t}$$

where the $J_{HS,2}$ flux (Equation 77) is expressed as an oxygen equivalent flux (J_{OC}) computed from Equation 75. For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 84

$$a_{22} = -\boldsymbol{\omega}_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \boldsymbol{\omega}_2$$

Equation 85

$$b_2 = -J_{OC}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 86

$$f_{d1} = \frac{\mathbf{1}}{\mathbf{1} + \boldsymbol{\pi}_{HS,1} S_1}\mathbf{;}\ f_{p1} = \frac{\boldsymbol{\pi}_{HS,1} S_1}{\mathbf{1} + \boldsymbol{\pi}_{HS,1} S_1}$$

$$f_{d2} = \frac{\mathbf{1}}{\mathbf{1} + \boldsymbol{\pi}_{HS,2} S_2}\mathbf{;}\ f_{p1} = \frac{\boldsymbol{\pi}_{HS,2} S_2}{\mathbf{1} + \boldsymbol{\pi}_{HS,2} S_2}$$

where

$\pi_{HS,1}$ = partition coefficient for sulfides in layer 1

$\pi_{HS,2}$ = partition coefficient for sulfides in layer 2

S1 = solids concentration in layer 1

S2 = solids concentration in layer 2

The dissolved oxygen correction to the surface reaction is computed from (with KMHSO2 being the half-saturation constant for sulfide reaction),

Equation 87

$$f_O = \frac{O_{2,0}}{K_{MHS,O2}}$$

The primary other difference is that partition coefficients are specified separately for the two layers, so that

Equation 88

$$f_{d,1} = \frac{1}{1+\pi_{H2S,1}S_1}; \; f_{p,1} = \frac{\pi_{H2S,1}S_1}{1+\pi_{H2S,1}S_1}$$

Equation 89

$$f_{d,2} = \frac{1}{1+\pi_{H2S,2}S_2}; \; f_{p,1} = \frac{\pi_{H2S,2}S_2}{1+\pi_{H2S,2}S_2}$$

where

$\pi_{H2S,1}$ = partition coefficient for sulfide in layer 1

$\pi_{H2S,2}$ = partition coefficient for sulfide in layer 2

S1 = solids concentration in layer 1

S2 = solids concentration in layer 2

There is no external source term for sulfides in layer 1. The source term for layer 2 is computed from the carbon diagenesis term (Equation 75), in oxygen equivalents and corrected for denitrification, since denitrification requires a carbon source and is a sink for carbon. Once the sulfide concentrations have been updated, the flux to the water column is computed from:

Equation 90

$$J_{H2S} = s \; f_{D1} C_{H2S,1}^{t+\Delta t}$$

where J_{H2S} is the flux to the water column. The SOD due to carbonaceous demand is then computed from

Equation 91

$$CSOD_{HS} = \frac{\left(\kappa_{HS,D}^{2} f_{D,1} + \kappa_{HS,P}^{2} f_{P,1}\right)\theta^{\mathrm{T-20}}}{s} \; \mathbf{f_O} \; C_{H2S,1}^{t+\Delta t}$$

Methane

In WASP, methane fluxes are only computed for freshwater systems (where the salinity (SAL) is less than a specified quantity (SALTSW). The first consideration in the computation of methane fluxes is that the maximum methane production, in oxygen equivalents, is related to the carbon diagenesis (J_{OC}), corrected for denitrification (Equation 75). Assuming complete oxidation, the maximum carbonaceous SOD that can be exerted is (Chapra 2000, DiToro 2001)

Equation 92

$$CSOD_{\mathbf{max}} = \sqrt{2K_{L12}C_S J_{O2}}$$

or (for computed $CSOD_{max} > J_{O2}$)

Equation 93

$$CSOD_{\mathbf{max}} = J_{O\mathbf{2}}$$

where K_{L12} was defined previously and C_s the saturation methane concentration, computed from (Di Toro 2001, Equation 10.51)

Equation 94

$$\mathbf{C_{CH4,SAT} = 100\left(1+\frac{H_O}{10}\right)1.024^{(20\text{-}T)}}$$

where H_o is the depth of the water column over the sediment. As indicated, if the computed $CSOD_{max}$ exceeds the available carbon flux (J_{OC} in oxygen equivalents and corrected for denitrification), then $CSOD_{max}$ is set equal to that flux ($CSOD_{max}=J_{OC}$).

The flux of dissolved methane at the sediment water interface can be computed from (Chapra 2000, Eq. 25.43; DiToro 2001 Eq. 10.32)

Equation 95

$$J_{out} = CSOD_{\mathbf{max}}\ Sech\boldsymbol{(}\lambda_c H_{\mathbf{1}}\boldsymbol{)}$$

where (Di Toro 2001, Equation 10.39)

Equation 96

$$\lambda_c H_{\mathbf{1}} = \frac{\kappa_{CH\mathbf{4,1}}\theta^{(T-\mathbf{20})/\mathbf{2}}}{s}\boldsymbol{)}$$

Note that the temperature correction in the above equation is reflected in the ICM code (Cerco and Cole 1995) and elsewhere. The the hyperbolic secant (Sech) is computed as

Equation 97

$$Sech\boldsymbol{(}x\boldsymbol{)} = \frac{\mathbf{2}}{e^{x}+e^{-x}}$$

Methane may be oxidized, producing sediment oxygen demand, or exchanged with the water column in either gaseous or dissolved form. The carbonaceous SOD can be computed from

Equation 98

$$CSOD_{CH\mathbf{4}} = CSOD_{\mathbf{max}}\boldsymbol{(}\mathbf{1}-Sech\boldsymbol{(}\lambda_c H_{\mathbf{1}}\boldsymbol{))}$$

and the fluxes of dissolved and gaseous methane can be computed from

Equation 99

$$J\boldsymbol{[}CH_{\mathbf{4}}\boldsymbol{(}aq\boldsymbol{)]} = CSOD_{\mathbf{max}} - CSOD_{CH\mathbf{4}}\boldsymbol{;} \quad J\boldsymbol{[}CH_{\mathbf{4}}\boldsymbol{(}g\boldsymbol{)]} = J_{OC} - J\boldsymbol{[}CH_{\mathbf{4}}\boldsymbol{(}aq\boldsymbol{)]} - CSOD_{CH\mathbf{4}}$$

SOD

Once the concentrations of materials affecting oxygen are computed, and the stoichiometric relationships described above applied, the SOD is computed from

Equation 100

$$SOD = CSOD_{HS} + CSOD_{NH\mathbf{4}} + CSOD_{NO\mathbf{2}}$$

for salt water systems or

Equation 101

$$SOD = CSOD_{CH\mathbf{4}} + CSOD_{NH\mathbf{4}} + CSOD_{NO\mathbf{2}}$$

for freshwater systems, where the oxygen demands due to sulfide (Equation 91), methane (Equation 98), and nitrification (Equation 45 and Equation 60) were defined previously.

Note that in the iterative solution for s, the SOD computed this computational step is compared to that from the previous iteration, and as discussed above, if it differs by more than a specified amount, a new value of s is computed and the solution iterated.

Computation of phosphate and silica

As discussed above, the SOD is computed iteratively in order to determine the value of s (the surface sediment transfer rate). Once completed, the concentrations of phosphate and ammonia, which do not affect SOD, are computed. The computations for phosphate and silica are similar to those described above and briefly presented below.

Silica

The two-layer mass balance equations for silica are:

Layer 1

Equation 102

$$\mathbf{0} = -s\left(f_{d\mathbf{1}} C_{Si,\mathbf{1}}^{t+\Delta t} - C_{Si,O}^{t+\Delta t} \right) + \boldsymbol{\omega}_{\mathbf{12}} \left(f_{p\mathbf{2}} C_{Si,\mathbf{2}}^{t+\Delta t} - f_{p\mathbf{1}} C_{Si,\mathbf{1}}^{t+\Delta t} \right)$$
$$+K_{L\mathbf{12}} \left(f_{d\mathbf{2}} C_{Si,\mathbf{2}}^{t+\Delta t} - f_{d\mathbf{1}} C_{Si,\mathbf{1}}^{t+\Delta t} \right) - \boldsymbol{\omega}_{\mathbf{2}}\ C_{Si,\mathbf{1}}^{t+\Delta t}$$

Layer 2

Equation 103

$$\mathbf{0} = -\boldsymbol{\omega}_{\mathbf{12}} \left(f_{p\mathbf{2}} C_{Si,\mathbf{2}}^{t+\Delta t} - f_{p\mathbf{1}} C_{Si,\mathbf{1}}^{t+\Delta t} \right) - K_{L\mathbf{12}} \left(f_{d\mathbf{2}} C_{Si,\mathbf{2}}^{t+\Delta t} - f_{d\mathbf{1}} C_{Si,\mathbf{1}}^{t+\Delta t} \right) + \boldsymbol{\omega}_{\mathbf{2}} \mathbf{(} C_{Si,\mathbf{1}}^{t+\Delta t} - C_{Si\mathbf{4,2}}^{t+\Delta t} \mathbf{)}$$
$$-\boldsymbol{\kappa}_{\mathbf{3}} C_{Si,\mathbf{2}}^{t+\Delta t} - \frac{H_{\mathbf{2}} C_{Si,\mathbf{2}}^{t+\Delta t}}{\boldsymbol{\Delta} t} + J_{Si,\mathbf{2}}^{t+\Delta t} + \frac{H_{\mathbf{2}} C_{Si,\mathbf{2}}^{t}}{\boldsymbol{\Delta} t}$$

where all terms have been previously defined. Note that the primary difference between the general equations presented previously and the silica equations are there are no silica source terms or reactions in the aerobic layer. In the anaerobic layer (layer 2), the reaction rate is applied only to the dissolved fraction.

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 104

$$a_{\mathbf{11}} = -\left(f_{d\mathbf{1}} \right) K_{L\mathbf{12}} - \left(f_{p\mathbf{1}} \right) \boldsymbol{\omega}_{\mathbf{12}} - \boldsymbol{\omega}_{\mathbf{2}}$$

Equation 105

$$a_{21} = +\omega_{12}\left(f_{p1}\right) + K_{L12}\left(f_{d1}\right) + \omega_2$$

Equation 106

$$a_{12} = +\omega_{12}\left(f_{p2}\right) + K_{L12}\left(f_{d2}\right)$$

Equation 107

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2 - \kappa_3 - \frac{H_2}{\Delta t}$$

Equation 108

$$b_1 = -s\, C_{Si,O}^{t+\Delta t}$$

Equation 109

$$b_2 = -J_{Si}^{t+\Delta t} - \frac{H_2 C_{Si,2}^{t}}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 110

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2 - \kappa_3$$

Equation 111

$$b_2 = -J_{Si,2}^{t+\Delta t}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 112

$$f_{d1} = \frac{1}{1+\pi_{Si,1}S_1};\ f_{p1} = \frac{\pi_{Si,1}S_1}{1+\pi_{Si,1}S_1}$$

$$f_{d2} = \frac{1}{1+\pi_{Si,2}S_2};\ f_{p1} = \frac{\pi_{Si,2}S_2}{1+\pi_{Si,2}S_2}$$

where

$\pi_{Si,1}$ = partition coefficient for Silica in layer 1

$\pi_{Si,1}$ = partition coefficient for Silica in layer 2

S1 = solids concentration in layer 1

S2 = solids concentration in layer 2

The partition coefficient in the anaerobic layer is set to an input value. For layer 1, the aerobic layer, if the oxygen concentration in the overlying water column exceeds a critical concentration (specified in input) then the partition coefficient is increased to represent the trapping of silica, or sorption onto iron oxyhydroxide. If the dissolved oxygen is below the critical value, then the sorption coefficient in layer 1 goes to zero as in (Di Toro 2001, Eq. 7.18)

Equation 113

$$\boldsymbol{\pi}_{Si,\mathbf{1}} = \boldsymbol{\pi}_{Si,\mathbf{2}}\left(\boldsymbol{\Delta\pi}_{Si,\mathbf{1}}\right) \; \mathit{for} \left[O_{\mathbf{2}}(\mathbf{0})\right] > \left[O_{\mathbf{2}}(\mathbf{0})\right]_{crit,Si}$$

and

Equation 114

$$\boldsymbol{\pi}_{Si,\mathbf{1}} = \boldsymbol{\pi}_{Si,\mathbf{2}}\left(\boldsymbol{\Delta\pi}_{Si,\mathbf{1}}\right)^{\beta_{Si}} \; \mathit{for} \left[O_{\mathbf{2}}(\mathbf{0})\right] \le \left[O_{\mathbf{2}}(\mathbf{0})\right]_{crit,Si}$$

$$\text{where } \boldsymbol{\beta}_{PO\mathbf{4}} = \frac{\left[O_{\mathbf{2}}(\mathbf{0})\right]}{\left[O_{\mathbf{2}}(\mathbf{0})\right]_{crit,PO\mathbf{4}}}$$

and $\Delta\pi_{Si}$ is a specified incremental change.

The expression for silica dissolution in the anaerobic layer, modified by the Michaelis-Menton dependency of the dissolution rate on particulate silica, is given by (Di Toro 2001, Eq. 7.16)

Equation 115

$$S_{Si} = k_{Si}\Theta^{(T-\mathbf{20})}\frac{P_{Si}}{P_{Si}+K_{m,PSi}}\left(C_{Si,sat} - f_{d,\mathbf{2}}C_{Si,\mathbf{2}}^{t+\Delta t}\right)$$

where

P_{Si}	= the biogenic silica diagenesis flux to which detrital silica was added
$K_{m,PSi}$	=half saturation constant (KMPSI)
k_{Si}	= rate of silica dissolution (KADSA from water quality model)

$C_{Si,sat}$ = saturation concentration for silica ($C_{SI,sat}$, an input value)

Based on Equation 115, the loss term (κ_3) and source term for the sediments ($J_{Si,\mathbf{2}}^{t+\Delta t}$) are then specified as

Equation 116

$$\boldsymbol{\kappa}_{\mathbf{3}} = k_{Si}\Theta^{(T-\mathbf{20})} f_{d,\mathbf{2}}\frac{P_{Si}}{P_{Si}+K_{m,PSi}}$$

and

Equation 117

$$J_{Si,\mathbf{2}}^{t+\Delta t} = k_{Si}\Theta^{(T-\mathbf{20})}\frac{P_{Si}}{P_{Si}+K_{m,PSi}}C_{Si,sat}$$

Once the silica concentrations have been updated, the flux to the water column is computed from:

Equation 118

$$J_{Si} = s\left(C_{Si,1}^{t+\Delta t} - C_{Si,0}\right)$$

where J_{Si} is the flux to the water column.

Phosphate

The two-layer mass balance equations for phosphate are:

Layer 1

Equation 119

$$\begin{aligned} 0 &= -s\left(f_{d1}C_{PO4,1}^{t+\Delta t} - C_{PO4,O}^{t+\Delta t} \right) + \omega_{12}\left(f_{p2}C_{PO4,2}^{t+\Delta t} - f_{p1}C_{PO4,1}^{t+\Delta t} \right) \\ &+ K_{L12}\left(f_{d2}C_{PO4,2}^{t+\Delta t} - f_{d1}C_{PO4,1}^{t+\Delta t} \right) - \omega_2 C_{PO4,1}^{t+\Delta t} \end{aligned}$$

Layer 2

Equation 120

$$\begin{aligned} 0 &= -\omega_{12}\left(f_{p2}C_{PO4,2}^{t+\Delta t} - f_{p1}C_{PO4,1}^{t+\Delta t} \right) - K_{L12}\left(f_{d2}C_{PO4,2}^{t+\Delta t} - f_{d1}C_{PO4,1}^{t+\Delta t} \right) + \omega_2 (C_{PO4,1}^{t+\Delta t} - C_{PO44,2}^{t+\Delta t}) \\ &- \frac{H_2 C_{PO4,2}^{t+\Delta t}}{\Delta t} + J_{PO4,2}^{t+\Delta t} + \frac{H_2 C_{PO4,2}^{t}}{\Delta t} \end{aligned}$$

where all terms have been previously defined. Note that the primary difference between the general equations presented previously and the phosphate equations are there are no reactions in either layer.

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 121

$$a_{11} = -\left(f_{d1} \right) K_{L12} - \left(f_{p1} \right) \omega_{12} - (f_{d1}) s - \omega_2$$

Equation 122

$$a_{21} = +\omega_{12}\left(f_{p1} \right) + K_{L12}\left(f_{d1} \right) + \omega_2$$

Equation 123

$$a_{12} = +\omega_{12}\left(f_{p2} \right) + K_{L12}\left(f_{d2} \right)$$

Equation 124

$$a_{22} = -\omega_{12}\left(f_{p2} \right) - K_{L12}\left(f_{d2} \right) - \omega_2 - \frac{H_2}{\Delta t}$$

Equation 125

$$b_1 = -s\, C_{PO4,O}^{t+\Delta t}$$

Equation 126

$$b_2 = -J_{PO4,2}^{t+\Delta t} - \frac{H_2 C_{PO4,2}^{t}}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 127

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2$$

Equation 128

$$b_2 = -J_{PO4,2}^{t+\Delta t}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 129

$$f_{d,1} = \frac{\mathbf{1}}{\mathbf{1} + \pi_{PO4,1} S_1}\,;\; f_{p,1} = \frac{\pi_{PO4,1} S_1}{\mathbf{1} + \pi_{PO4,1} S_1}$$

$$f_{d,2} = \frac{\mathbf{1}}{\mathbf{1} + \pi_{PO4,2} S_2}\,;\; f_{p,1} = \frac{\pi_{PO4,2} S_2}{\mathbf{1} + \pi_{PO4,2} S_2}$$

where

$\pi_{PO4,i}$ = partition coefficient for silica in layer i (PIE2)

S1 = solids concentration in layer 1 (M1)

S2 = solids concentration in layer 2 (M2)

The partition coefficient in the anaerobic layer is set to an input value. For layer 1, the aerobic layer, if the oxygen concentration in the overlying water column exceeds a critical concentration (O2CRIT, specified in input) then the partition coefficient is increased to represent the trapping of phosphates, or sorption onto iron oxyhydroxide. If the dissolved oxygen is below the critical value, then the sorption coefficient in layer 1 goes to zero as in (Di Toro 2001, Eq. 6.19)

Equation 130

$$\pi_{PO4,1} = \pi_{PO4,2}\left(\Delta\pi_{PO4,1}\right)\ for\ \left[O_2(\mathbf{0})\right] > \left[O_2(\mathbf{0})\right]_{crit}$$

and

$$\pi_{PO4,1} = \pi_{PO4,2}\left(\Delta\pi_{PO4,1}\right)^{\beta_{PO4}}\ for\ \left[O_2(\mathbf{0})\right] \le \left[O_2(\mathbf{0})\right]_{crit}$$

where $\boldsymbol{\beta}_{PO\mathbf{4}} = \frac{[O_2(\mathbf{0})]}{[O_2(\mathbf{0})]_{crit,PO\mathbf{4}}}$

and $\Delta\pi_{PO4}$ is a specified incremental change (which is set to either a freshwater or saltwater input value).

The source term for layer 2 is a result of the phosphate produced by sediment diagenesis to which is added the flux of inorganic phosphorus from the water column. Once the phosphate concentrations have been updated, the flux to the water column is computed from:

Equation 131

$$J_{PO\mathbf{4}} = s\left(C^{t+\Delta t}_{PO\mathbf{4},\mathbf{1}} - C_{PO\mathbf{4},\mathbf{0}}\right)$$

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