823B05002



# AQUATOX FOR WINDOWS

## A MODULAR FATE AND EFFECTS MODEL FOR AQUATIC ECOSYSTEMS

## RELEASE 2.1

## ADDENDUM TO RELEASE 2 TECHNICAL DOCUMENTATION

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## TABLE OF CONTENTS

# 1 INTRODUCTION TO RELEASE 2.1

## Background

Nutrients (nitrogen and phosphorus) are leading causes of water quality impairment in the Nation's rivers, lakes and estuaries. To address this problem, states need the technical resources to establish nutrient criteria, adopt them into their water quality standards, and implement them in regulatory programs. Ecosystem models such as AQUATOX that mechanistically simulate nutrient dynamics can be one tool for deriving and implementing nutrient criteria.

To further assist in modeling nutrients AQUATOX has been significantly updated since EPA Release 2 was released. There have also been several enhancements related to toxicity, along with improvements to the user interface. This document is an addendum to the AQUATOX Release 2 Technical documentation (EPA-823-R-04-002, January 2004). The document describes changes in the model that distinguish Release 2.1 from Release 2.

## What's New

- The capability to model mean depth dynamically has been included.
- Various modifications to periphyton modeling, phytoplankton modeling, and a periphyton-phytoplankton linkage may be found in the section on biota.
- The capability to export Steinhaus similarity matrices has been added to provide a measure of community effects.
- The fraction of ammonia that is un-ionized is estimated and reported.
- Variable stoichiometry, new nutrient loading variables, new nutrient output variables, and strict mass balance of nutrients have all been added to AQUATOX since Release 2.
- pH may now be modeled dynamically as a function of a site's total alkalinity, carbon dioxide, and dissolved organic matter.
- Additional flexibility has been added to the modeling of toxic organic chemicals including new uptake and depuration modeling options and the ability to model toxicity based on external concentrations.
- Libraries now can be viewed in a "GridMode" spreadsheet form to facilitate comparison of chemical or organism parameters.
- The complete setup of a study, including state variable parameter values, loadings, and site constants, can be exported to a text file.
- The linkage to BASINS has been expanded to include a variety of phosphorus loadings. A revised User's Manual for the BASINS Extension to AQUATOX has been released that describes these changes. (EPA-823-B-05-001, October 2005)

# 3 PHYSICAL CHARACTERISTICS

***The following should be inserted before "Habitat Disaggregation" on p. 3-6.***

## Dynamic Mean Depth

AQUATOX normally uses an assumption of unchanging mean depth (i.e., mean over the site area). However, under some circumstances, and especially in the case of streams or rivers, the depth of the system can change considerably, which could result in a significantly different light climate for algae. For this reason, an option to import mean depth in meters has been added. A daily time-series of mean depth values may be imported into the software (using an interface found within the site screen by pressing the "Show Mean Depth Panel" button.) A time-series of mean depth values can be estimated given known water volumes or can be imported from a linked water hydrology model.

The user-input dynamic mean depth affects the following portions of AQUATOX:

- Light climate, see **(38);**
- Calculation of biotic volumes for sloughing calculations, see **(66);**
- Calculation of vertical dispersion for stratification calculations, *Thick* in equation **(18)**;
- Calculation of sedimentation for plants & detritus, *Thick* in **(135);**
- Oxygen reaeration, see **(158) .**
- Toxicant photolysis and volatilization, *Thick* in **(221)** and **(230)**

# 4 BIOTA

## 4.1 Algae

***(There have been minor refinements added to Algae Derivatives, and the following should replace equations 29 and 30 in the Release 2 Technical Documentation)***

$$\frac{dBiomass_{Phyto}}{dt} = Loading + Photosynthesis - Respiration - Excretion - Mortality - Predation \pm Sinking - Washout \pm TurbDiff + \frac{Slough}{3} \quad \textbf{(29)}$$

$$\frac{dBiomass_{Peri}}{dt} = Loading + Photosynthesis - Respiration - Excretion - Mortality - Predation + Sed_{Peri} \quad \textbf{(30)}$$

where:

| | | |
|---|---|---|
| *Slough* | = | Scour of Periphyton to Phytoplankton, see **(1a)**; |
| $Sed_{Peri}$ | = | Sedimentation of Phytoplankton to Periphyton, see **(7a).** |

***(See page 4-2 of Release 2 Technical Documenation for other terms and equations.)***

## Periphyton Code Changes

***The following should replace the text and equations on p 4-22 and 4-23, up to "Detrital Accumulation in Periphyton" on p. 4-23.***

Suboptimal light, nutrients, and temperature cause senescence of cells that bind the periphyton and keep them attached to the substrate. This effect is represented by a factor, *Suboptimal*, which is computed in modeling the effects of environmental conditions on photosynthesis. *Suboptimal* decreases the critical force necessary to cause sloughing. If the drag force exceeds the critical force for a given algal group modified by the *Suboptimal* factor and an adaptation factor, then sloughing occurs:

$$\text{If } DragForce > Suboptimal_{Org} \cdot FCrit_{Org} \cdot Adaptation$$
$$\text{then } Slough = Biomass \cdot FracSloughed$$
$$\text{else } Slough = 0 \qquad \textbf{(1a)}$$

where:

| | | |
|---|---|---|
| $Suboptimal_{Org}$ | = | factor for suboptimal nutrient, light, and temperature effect on senescence of given periphyton group (unitless); |
| $FCrit_{Org}$ | = | critical force necessary to dislodge given periphyton group (kg $m/s^2$); |
| *Adaptation* | = | factor to adjust for mean discharge of site compared to reference site (unitless); |
| *Slough* | = | biomass lost by sloughing ($g/m^3$); |
| *FracSloughed* | = | fraction of biomass lost at one time (97%, unitless). |

$$Suboptimal_{Org} = NutrLimit_{Org} \cdot LtLimit_{Org} \cdot TCorr_{Org} \cdot 20$$
$$\text{If } Suboptimal_{Org} > 1 \text{ then } Suboptimal_{Org} = 1 \qquad \textbf{(2a)}$$

where:

| | | |
|---|---|---|
| *NutrLimit* | = | nutrient limitation for given algal group (unitless) computed by AQUATOX, see **(47)**; |
| $LtLimit_{Org}$ | = | light limitation for given algal group (unitless) computed by AQUATOX, see **(33)**; and |
| *TCorr* | = | temperature limitation for a given algal group (unitless) computed by AQUATOX, see **(51)**; |
| 20 | = | factor to desensitize construct. |

The sloughing construct was tested and calibrated (U.S. E.P.A., 2001) with data from experiments with artificial and woodland streams in Tennessee (Rosemond, 1993, ). However, in modeling periphyton at several sites, it was observed that sloughing appears to be triggered at greatly differing mean velocities. The working hypothesis is that periphyton adapt to the ambient conditions of a particular channel. Therefore, a factor is included to adjust for the velocity of a given site compared to the reference site in Tennessee. It is still necessary to calibrate *FCrit* for each site to account for intangible differences in channel and flow conditions, analogous to the calibration of shear stress by sediment modelers, but the range of calibration needed is reduced by the *Adaptation* factor:

$$Adaptation = \frac{Vel^2}{0.006634} \qquad \textbf{(3a)}$$

where:

| | | |
|---|---|---|
| *Vel* | = | velocity for given site (m/s), see **(14)**; |
| 0.006634 | = | mean velocity$^2$ for reference experimental stream (m/s). |

***The following two sections should be added to the end of Section 4.1, on p. 4-24***

## Phytoplankton and Zooplankton Residence Time

Phytoplankton and zooplankton can quickly wash out of a short reach, but they may be able to grow over an extensive reach of a river, including its tributaries. Somehow the volume of water occupied by the phytoplankton needs to be taken into consideration. To solve this problem, AQUATOX takes into account the "Total Length" of the river being simulated, as opposed to the length of the river reach, or "SiteLength" so that phytoplankton and zooplankton production upstream can be estimated. This parameter can be directly entered on the Site Data screen or estimated based on watershed area based on Leopold et al. 1964.

$$TotLength = 1.609 \cdot 1.4 \cdot (WaterShed \cdot 0.386)^{0.6} \qquad \textbf{(4a)}$$

where:

| | | |
|---|---|---|
| *TotLength* | = | total river length (km); |
| *Watershed* | = | land surface area contributing to flow out of the reach (square km); |
| 1.609 | = | km per mile; |
| 0.386 | = | square miles per square km. |

If the total length or watershed area is entered as zero, the phytoplankton and zooplankton residence time equations are not used and Eqs. 63 and 105 of Release 2 are used to calculate washout. Otherwise, to simulate the inflow of plankton from upstream reaches plankton upstream loadings are estimated as follows:

$$Loading_{upstream} = Washout_{biota} - \left( \frac{Washout_{biota}}{TotLength / SiteLength} \right) \quad \textbf{(5a)}$$

where:

| | | |
|---|---|---|
| $Loading_{upstream}$ | = | loading of plankton due to upstream production (mg/L); |
| $Washout_{biota}$ | = | washout of plankton from the current reach (mg/L); |
| *TotLength* | = | total river length (km); |
| *SiteLength* | = | length of the modeled reach (km). |

An integral assumption in this approach is that upstream reaches being modeled have identical environmental conditions as the reach being modeled and that plankton production in each mile up-stream will be identical to plankton production in the given reach. Residence time for plankton within the total river length is estimated as follows:

$$t_{residence} = \frac{Volume}{Discharge} \left( \frac{TotLength}{SiteLength} \right) \quad \textbf{(6a)}$$

where:

| | | |
|---|---|---|
| $t_{residence}$ | = | residence time for floating biota within the total river length (d); |
| *Volume* | = | volume of modeled segment reach ($m^3$); see (2, Rel. 2); |
| *Discharge* | = | discharge of water from modeled reach ($m^3$/d); see Table 1, Rel. 2; |
| *TotLength* | = | total river length (km); |
| *SiteLength* | = | length of the modeled reach (km). |

## Periphyton-Phytoplankton Link

Periphyton may slough or be scoured, contributing to the suspended algae; this may be reflected in the chlorophyll *a* observed in the water column. Previously, AQUATOX assumed that sloughed periphyton became detritus. Periphyton may now be linked to a phytoplankton compartment so that chlorophyll *a* results reflect the results of periphyton sloughing. One-third of periphyton is assumed to become phytoplankton and two thirds is assumed to become suspended detritus in a sloughing event.

Additionally, when phytoplankton undergoes sedimentation it will now be incorporated into the linked periphyton layer if such a linkage exists. If multiple periphyton species are linked to a single phytoplankton species, biomass is distributed to periphyton weighted by the mass of each periphyton compartment.

$$Sed_{Periphyton\,A} = Sink_{Phyto} \frac{Mass_{Periphyton\,A}}{Mass_{All\,Linked\,Peri}} \quad \textbf{(7a)}$$

where:

| | | |
|---|---|---|
| $Sed_{Periphyton\ A}$ | = | sedimentation that goes to periphyton compartment A; |
| $Sink_{Phyto}$ | = | total sedimentation of linked phytoplankton compartment, see **(61, Rel.2)**; |
| $Mass_{Periphyton\ A}$ | = | mass of periphyton compartment A; |
| $Mass_{All\ Linked\ Peri}$ | = | mass of all periphyton compartments linked to the relevant phytoplankton compartment. |

If no linkage is present, settling phytoplankton are assumed to contribute to sedimented detritus.

## 4.4 Steinhaus Similarity Index

***This section should be added to page 4-45.***

Within the differences graph portion of the output interface, a user may now select to write a set of Steinhaus similarity indices in Microsoft Excel format. The Steinhaus index (Legendre and Legendre 1998) measures the concordance in values (usually numbers of individuals, but biomass in this application) between two samples for each species. A Steinhaus index of 1.0 indicates that all species have identical biomass in both simulations (i.e., the perturbed and control simulations); an index of 0.0 indicates a complete dissimilarity between the two simulations.

The equation for the Steinhaus index is as follows:

$$S = \frac{2 \cdot \sum_{i=1}^{n} \min\left(Biomass_{i\_control}, Biomass_{i\_perturbed}\right)}{\sum_{i=1}^{n} \left(Biomass_{i\_control} + Biomass_{i\_perturbed}\right)} \qquad \textbf{(8a)}$$

where:

| | | |
|---|---|---|
| $S$ | = | Steinhaus similarity index at time t; |
| $Biomass_{i\_control}$ | = | biomass of species i, control scenario at time t; |
| $Biomass_{i\_perturbed}$ | = | biomass of species i, perturbed scenario at time t. |

A time-series of indices is written for each day of the simulation representing the similarity on that date. Separate indices are written out for plants, all animals, invertebrates only, and fish only.

# 5 REMINERALIZATION

## 5.2 Nitrogen

***Replace Section 5.2 with the following section. Note: equations 138 and 139 have been removed as they are now replaced with the Remineralization calculation below (9a).***

Two nitrogen compartments, ammonia and nitrate, are modeled. Nitrite occurs in very low concentrations and is rapidly transformed through nitrification and denitrification (Wetzel, 1975); therefore, it is modeled with nitrate. Un-ionized ammonia ($NH_3$) is not modeled as a separate state variable but is estimated as a fraction of ammonia **(10a)**. Ammonia is assimilated by algae and macrophytes and is converted to nitrate as a result of nitrification:

$$\frac{dAmmonia}{dt} = Loading + Remineralization - Nitrify - Assimilation_{Ammonia} - Washout \pm TurbDiff \quad \textbf{(137)}$$

where:

| | | |
|---|---|---|
| d*Ammonia*/d*t* | = | change in concentration of ammonia with time (g/m$^3$·d); |
| *Loading* | = | loading of nutrient from inflow (g/m$^3$·d); |
| *Remineralization* | = | ammonia derived from detritus and biota (g/m$^3$·d), see **(9a)**; |
| *Nitrify* | = | nitrification (g/m$^3$·d), see **(144)**; |
| *Assimilation* | = | assimilation of nutrient by plants (g/m$^3$·d), see **(141)** and **(142)**; |
| *Washout* | = | loss of nutrient due to being carried downstream (g/m$^3$·d), see **(16)** |
| *TurbDiff* | = | depth-averaged turbulent diffusion between epilimnion and hypolimnion if stratified (g/m$^3$·d), see **(22)** and **(23)**. |

*Remineralization* includes all processes by which ammonia is produced from animal, plants, and detritus, including decomposition, excretion, and other processes required to maintain variable stoichiometry (see Table 2 on page 22):

$$\begin{aligned} Remineralization = {} & PhotoResp + DarkResp + AnimalResp + AnimalExcr \\ & + DetritalDecomp + AnimalPredation + NutrRelDefecation \\ & + NutrRelPlantSink + NutrRelMortality + NutrRelGameteLoss \\ & + NutrRelColonization + NutrRelPeriScour \end{aligned} \quad \textbf{(9a)}$$

where:

| | | |
|---|---|---|
| *PhotoResp* | = | algal excretion of ammonia due to photo respiration (g/m$^3$·d); |
| *DarkResp* | = | algal excretion of ammonia due to dark respiration (g/m$^3$·d); |

| | | |
|---|---|---|
| *AnimalResp* | = | excretion of ammonia due to animal respiration ($g/m^3 \cdot d$); |
| *AnimalExcr* | = | animal excretion of excess nutrients to ammonia to maintain constant org. to n ratio as required ($g/m^3 \cdot d$); |
| *DetritalDecomp* | = | nitrogen release due to detrital decomposition ($g/m^3 \cdot d$); |
| *AnimalPredation* | = | change in nitrogen content necessitated when an animal consumes prey with a different nutrient content ($g/m^3 \cdot d$); |
| *NutrRelDefecation* | = | ammonia released from animal defecation ($g/m^3 \cdot d$); |
| *NutrRelPlantSink* | = | ammonia balance from sinking of plants and conversion to detritus ($g/m^3 \cdot d$); |
| *NutrRelMortality* | = | ammonia balance from biota mortality and conversion to detritus ($g/m^3 \cdot d$); |
| *NutrRelGameteLoss* | = | ammonia balance from gamete loss and conversion to detritus ($g/m^3 \cdot d$); |
| *NutrRelColonization* | = | ammonia balance from colonization of refractory detritus into labile detritus ($g/m^3 \cdot d$); |
| *NutrRelPeriScour* | = | ammonia balance when periphyton is scoured and converted to phytoplankton and suspended detritus. ($g/m^3 \cdot d$); |

Nitrate is assimilated by plants and is converted to free nitrogen (and lost) through denitrification:

$$\frac{dNitrate}{dt} = Loading + Nitrify - Denitrify - Assim_{Nitrate} - Washout \pm TurbDiff \qquad \textbf{(140)}$$

where:

| | | |
|---|---|---|
| d*Nitrate*/d*t* | = | change in concentration of nitrate with time ($g/m^3 \cdot d$); |
| *Loading* | = | user entered loading of nitrate, including atmospheric deposition; |
| and | | |
| *Denitrify* | = | denitrification ($g/m^3 \cdot d$). |

Free nitrogen can be fixed by blue-green algae. Both nitrogen fixation and denitrification are subject to environmental controls and are difficult to model with any accuracy; therefore, the nitrogen cycle is represented with considerable uncertainty.

## Assimilation

Nitrogen compounds are assimilated by plants as a function of photosynthesis in the respective groups (Ambrose et al., 1991):

$$Assimilation_{Ammonia} = \Sigma_{Plant}(Photosynthesis_{Plant} \cdot Uptake_{Nitrogen} \cdot NH4Pref) \qquad \textbf{(141)}$$

$$Assimilation_{Nitrate} = \Sigma_{Plant}(Photosynthesis_{Plant} \cdot Uptake_{Nitrogen} \cdot (1 - NH4Pref)) \quad \textbf{(142)}$$

where:

| | | |
|---|---|---|
| *Assimilation* | = | assimilation rate for given nutrient ($g/m^3 \cdot d$); |
| *Photosynthesis* = | | rate of photosynthesis ($g/m^3 \cdot d$), see **(31)**; |
| $Uptake_{Nitrogen}$ | = | fraction of photosynthate that is nitrogen (unitless, 0.01975 if nitrogen-fixing, otherwise 0.079); |
| *NH4Pref* | = | ammonia preference factor (unitless). |

Only 23 percent of nitrate is nitrogen, but 78 percent of ammonia is nitrogen. This results in an apparent preference for ammonia. The preference factor is calculated with an equation developed by Thomann and Fitzpatrick (1982) and cited and used in WASP (Ambrose et al., 1991):

$$NH4Pref = \frac{N2NH4 \cdot Ammonia \cdot N2NO3 \cdot Nitrate}{(KN + N2NH4 \cdot Ammonia) \cdot (KN + N2NO3 \cdot Nitrate)} + \frac{N2NH4 \cdot Ammonia \cdot KN}{(N2NH4 \cdot Ammonia + N2NO3 \cdot Nitrate) \cdot (KN + N2NO3 \cdot Nitrate)} \quad \textbf{(143)}$$

where:

| | | |
|---|---|---|
| *N2NH4* | = | ratio of nitrogen to ammonia (0.78); |
| *N2NO3* | = | ratio of nitrogen to nitrate (0.23); |
| *KN* | = | half-saturation constant for nitrogen uptake ($g\ N/m^3$); |
| *Ammonia* | = | concentration of ammonia ($g/m^3$); and |
| *Nitrate* | = | concentration of nitrate ($g/m^3$). |

For algae other than blue-greens, *Uptake* is the Redfield (1958) ratio; although other ratios (cf. Harris, 1986) may be used by editing the parameter screen. At this time nitrogen-fixation by blue-greens is represented by using a smaller uptake ratio, thus "creating" nitrogen.

## Nitrification and Denitrification

Nitrification is the conversion of ammonia to nitrite and then to nitrate by nitrifying bacteria; it occurs primarily at the sediment-water interface (Effler et al., 1996). The maximum rate of nitrification, corrected for the area to volume ratio, is reduced by limitation factors for suboptimal dissolved oxygen and pH, similar to the way that decomposition is modeled, but using the more restrictive correction for suboptimal temperature used for plants and animals:

$$Nitrify = KNitri \cdot \frac{Area}{Volume} \cdot DOCorrection \cdot TCorr \cdot pHCorr \cdot Ammonia \qquad \textbf{(144)}$$

where:

| | | |
|---|---|---|
| *Nitrify* | = | nitrification rate ($g/m^3 \cdot d$); |
| *KNitri* | = | maximum rate of nitrification (m/d); |
| *Area* | = | area of site or segment ($m^2$); |
| *Volume* | = | volume of site or segment ($m^3$); see **(2)**; |
| *DOCorrection* | = | correction for anaerobic conditions (unitless) see **(131)**; |
| *TCorr* | = | correction for suboptimal temperature (unitless); see **(51)**; |
| *pHCorr* | = | correction for suboptimal pH (unitless), see **(133)**; and |
| *Ammonia* | = | concentration of ammonia ($g/m^3$). |

The nitrifying bacteria have narrow environmental optima; according to Bowie et al. (1985) they require aerobic conditions with a pH between 7 and 9.8, an optimal temperature of 30 , and minimum and maximum temperatures of 10 and 60 respectively (**Figure 60**, **Figure 61**).

**Figure 60**
Response to pH, Nitrification

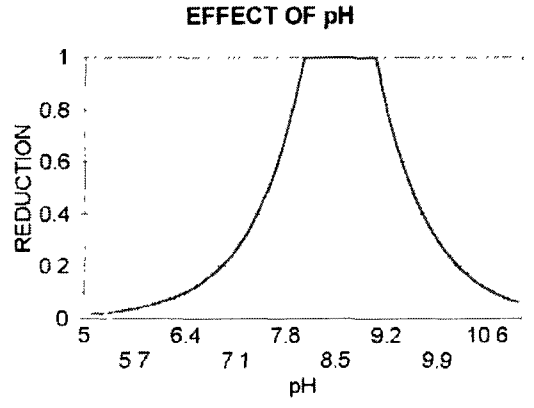
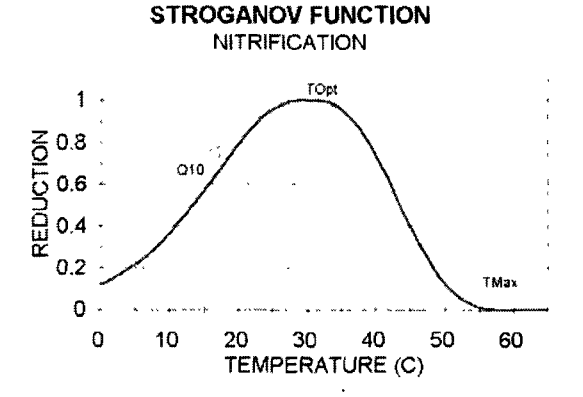



**Figure 61**
Response to Temperature, Nitrification




In contrast, denitrification (the conversion of nitrate and nitrite to free nitrogen) is an anaerobic process, so that *DOCorrection* enhances the process (Ambrose et al., 1991):

$$Denitrify = KDenitri \cdot (1 - DOCorrection) \cdot TCorr \cdot pHCorr \cdot Nitrate \qquad \textbf{(145)}$$

where:

| | | |
|---|---|---|
| *Denitrify* | = | denitrification rate ($g/m^3 \cdot d$); |
| *KDenitri* | = | maximum rate of denitrification (g ammonia/g nitrate); and |
| *Nitrate* | = | concentration of nitrate ($g/m^3$). |

Furthermore, it is accomplished by a large number of reducing bacteria under anaerobic conditions and with broad environmental tolerances (Bowie et al., 1985; **Figure 62**, **Figure 63**).

**Figure 60**
Response to pH, Denitrification

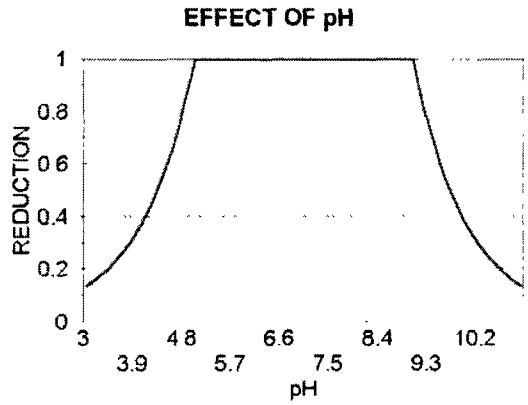
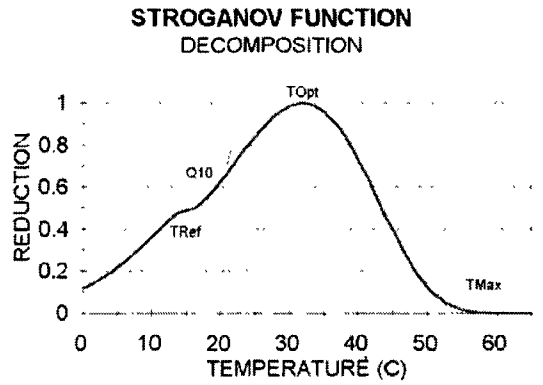



**Figure 61**
Response to Temperature, Denitrification




## Ionization of Ammonia

The un-ionized form of ammonia, $NH_3$, is toxic to invertebrates and fish. Therefore, it is often singled out as a water quality criterion. Un-ionized ammonia is in equilibrium with the ammonium ion, $NH_4^+$, and the proportion is determined by pH and temperature. Previous versions of AQUATOX did not differentiate the forms of ammonia. However, now that pH is a dynamic variable (see new section 5.7), it is useful to report $NH_3$ as well as total ammonia ($NH_3 + NH_4^+$).

The computation of the fraction of total ammonia that is un-ionized is relatively straightforward (Bowie et al. 1985):

$$FracNH3 = \frac{1}{1 + 10^{pkh - pH}} \quad \textbf{(10a)}$$

$$NH3 = FracNH3 \cdot Ammonia \quad \textbf{(11a)}$$

$$pkh = 0.09018 + \frac{2729.92}{TKelvin} \quad \textbf{(12a)}$$

where:

| | | |
|---|---|---|
| *FracNH3* | = | fraction of un-ionized ammonia (unitless); |
| *pkh* | = | hydrolysis constant; |
| *NH3* | = | un-ionized ammonia (mg/L); |
| *Ammonia* | = | total ammonia (mg/L); see (137, Rel. 2) |
| *TKelvin* | = | temperature (°K). |

The relative contributions of temperature and pH can be seen by graphing the fraction of un-ionized ammonia against each of those variables in simulations of Lake Onondaga (Figures 1 and

2). As inspection of the construct would suggest, un-ionized ammonia has a linear relationship to temperature and a logarithmic relationship to pH, which causes it to be sensitive to extremes in pH.

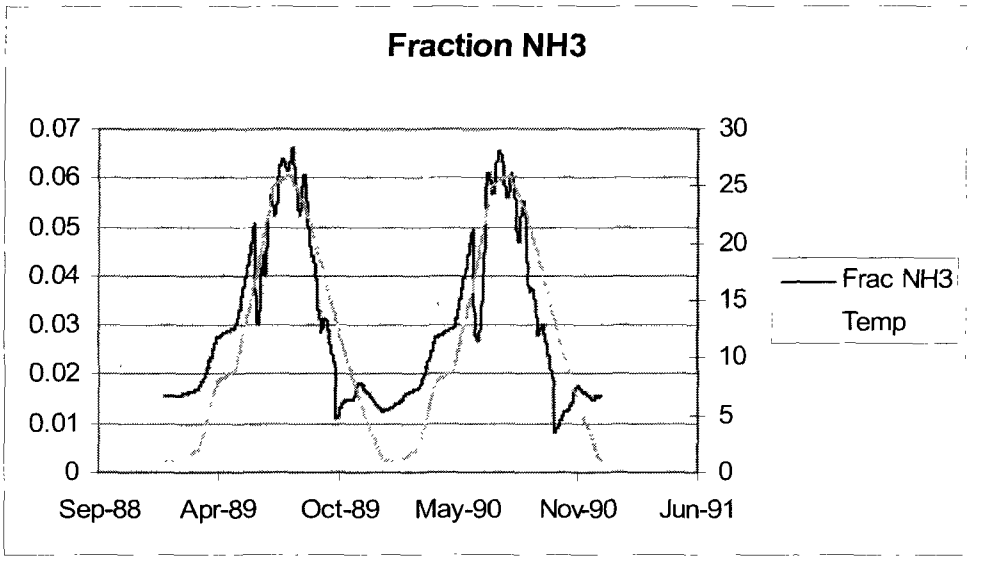



**Figure 1. Fraction of un-ionized ammonia roughly following temperature.**

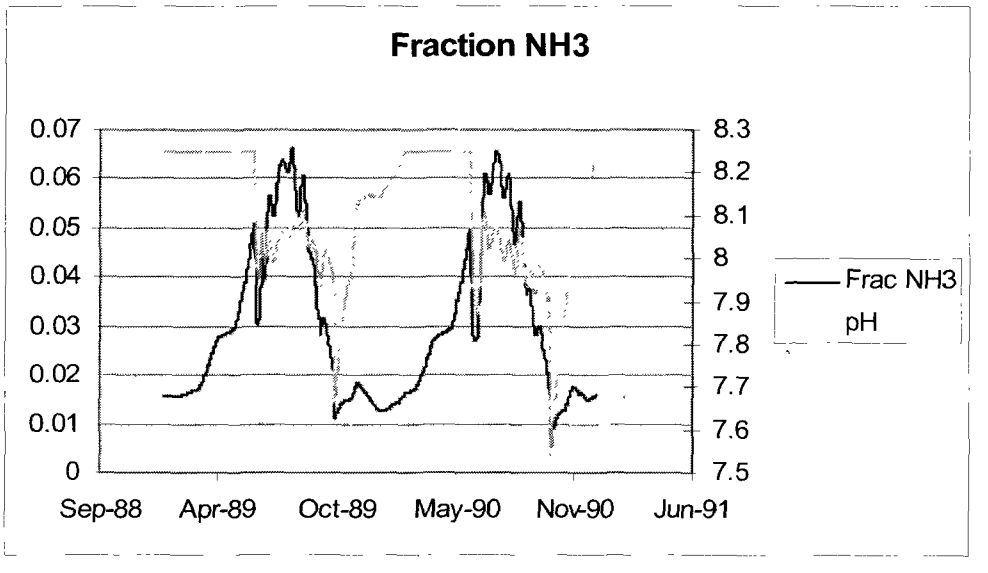



**Figure 2. Fraction of un-ionized ammonia affected by extreme values of pH.**

The construct was verified with the same set of data from Lake Onondaga as was used for the pH verification (Effler et al. 1996). It fits the observed data well (Figure 3).

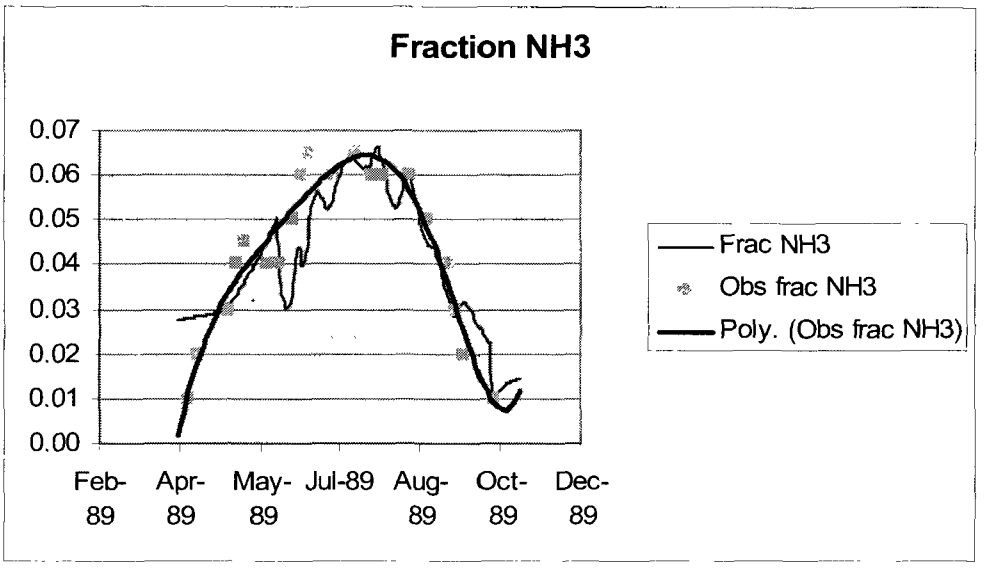



**Figure 3. Comparison of predicted and observed fraction of NH3 for Lake Onondaga, NY. Data from (Effler et al. 1996).**

## 5.3 Phosphorus

***Replace Section 5.2 with the following section. Note: equations 147 and 148 have been removed as they are now replaced with the Remineralization calculation below (13a).***

$$\frac{dPhosphate}{dt} = Loading + Remineralization - Assimilation_{Phosphate} - Washout \pm TurbDiff \quad \textbf{(146)}$$

where:

| | | |
|---|---|---|
| d*Phosphate*/d*t* | = | change in concentration of phosphate with time (g/m$^3$·d); |
| *Loading* | = | loading of nutrient from inflow (g/m$^3$·d); |
| *Remineralization* | = | phosphate derived from detritus and biota (g/m$^3$·d), see **(13a)**; |
| *Assimilation* | = | assimilation of nutrient by plants (g/m$^3$·d), see **(149)**; |
| *Washout* | = | loss of nutrient due to being carried downstream (g/m$^3$·d), see **(16)** |
| *TurbDiff* | = | depth-averaged turbulent diffusion between epilimnion and hypolimnion if stratified (g/m$^3$·d), see **(22)** and **(23)**. |

As was the case with ammonia, *Remineralization* includes all processes by which phosphate is produced from animal, plants, and detritus, including decomposition, excretion, and other processes required to maintain mass balance given variable stoichiometry (see Table 3 on page 24):

$$Remineralization = PhotoResp + DarkResp + AnimalResp + AnimalExcr + DetritalDecomp + AnimalPredation + NutrRelDefecation + NutrRelPlantSink + NutrRelMortality + NutrRelGameteLoss + NutrRelColonization + NutrRelPeriScour \quad \textbf{(13a)}$$

where:

| | | |
|---|---|---|
| *PhotoResp* | = | algal excretion of phosphate due to photo respiration ($g/m^3 \cdot d$); |
| *DarkResp* | = | algal excretion of phosphate due to dark respiration ($g/m^3 \cdot d$); |
| *AnimalResp* | = | excretion of phosphate due to animal respiration ($g/m^3 \cdot d$); |
| *AnimalExcr* | = | animal excretion of excess nutrients to phosphate to maintain constant org. to p ratio as required ($g/m^3 \cdot d$); |
| *DetritalDecomp* | = | phosphate release due to detrital decomposition ($g/m^3 \cdot d$); |
| *AnimalPredation* | = | change in phosphate content necessitated when an animal consumes prey with a different nutrient content ($g/m^3 \cdot d$); |
| *NutrRelDefecation* | = | phosphate released from animal defecation ($g/m^3 \cdot d$); |
| *NutrRelPlantSink* | = | phosphate balance from sinking of plants and conversion to detritus ($g/m^3 \cdot d$); |
| *NutrRelMortality* | = | phosphate balance from biota mortality and conversion to detritus ($g/m^3 \cdot d$); |
| *NutrRelGameteLoss* | = | phosphate balance from gamete loss and conversion to detritus ($g/m^3 \cdot d$); |
| *NutrRelColonization* | = | phosphate balance from colonization of refractory detritus into labile detritus ($g/m^3 \cdot d$); |
| *NutrRelPeriScour* | = | phosphate balance when periphyton is scoured and converted to phytoplankton and suspended detritus. ($g/m^3 \cdot d$); |

At this time AQUATOX models only phosphate available for plants; a correction factor in the loading screen allows the user to scale total phosphate loadings to available phosphate. A future enhancement could be to consider phosphate precipitated with calcium carbonate, which would better represent the dynamics of marl lakes; however, that process is ignored in the current version. A default value is provided for average atmospheric deposition, but this should be adjusted for site conditions. In particular, entrainment of dust from tilled fields and new highway construction can cause significant increases in phosphate loadings. As with nitrogen, the uptake parameter is the Redfield (1958) ratio; it may be edited if a different ratio is desired (cf. Harris, 1986).

## 5.4 Nutrient Mass Balance

***This section should be inserted on p. 5-17 as the new section 5.4. Current Sections 5.4 (Dissolved Oxygen) and 5.5 (Carbon Dioxide), should be renumbered as 5.5 and 5.6, respectively***

## Variable Stoichiometry

A notable simplification in AQUATOX has been the assumption of constant stoichiometry across trophic levels. However, in order to better model nutrients, the latest version of AQUATOX allows the ratios of elements in organic matter to vary considerably. This is accomplished by providing editable fields for N:organic matter and P:organic matter for each compartment. Furthermore, the wet to dry ratio is editable for all compartments; it had been hard-wired with a value of 5.

In order to maintain the specified ratios for each compartment, the model now explicitly accounts for processes that balance the ratios during transfers, such as excretion coupled with consumption and nutrient uptake coupled with colonization. Nutritional value is not automatically related to stoichiometry in the model, but it is implicit in default egestion values provided with various food sources. Table 1 shows the default stoichiometric values suggested for the model based on two references (Elser et al. 2000) (Sterner and Elser 2002).

**Table 1: Default Stochiometric Values in AQUATOX**

| Compartment | Frac. N (dry) | Frac. P (dry) | Reference |
|---|---|---|---|
| Refrac. detritus | 0.002 | 0.0002 | Sterner & Elser 2002 |
| Labile detritus | 0.059 | 0.007 | Same as phytoplankton |
| Phytoplankton | 0.059 | 0.007 | Sterner & Elser 2002 |
| Bl-greens | 0.059 | 0.007 | same as phytoplankton for now |
| Periphyton | 0.04 | 0.0044 | Sterner & Elser 2002 |
| Macrophytes | 0.018 | 0.002 | Sterner & Elser 2002 |
| Cladocerans | 0.09 | 0.014 | Sterner & Elser 2002 |
| Copepods | 0.09 | 0.006 | Sterner & Elser 2002 |
| Zoobenthos | 0.09 | 0.014 | same as cladocerans for now |
| Minnows | 0.097 | 0.0149 | Sterner 2000 |
| Shiner | 0.1 | 0.025 | Sterner 2000 |
| Perch | 0.1 | 0.031 | Sterner 2000 |
| Smelt | 0.1 | 0.016 | Sterner 2000 |
| Bluegill | 0.1 | 0.031 | same as perch for now |
| Trout | 0.1 | 0.031 | same as perch for now |
| Bass | 0.1 | 0.031 | same as perch for now |

## Nutrient Loading Variables

Often water quality data are given as total nitrogen and phosphorus. In order to improve agreement with monitoring data, AQUATOX can now accept both loadings and initial conditions as "Total N" and "Total P." This is made possible by accounting for the nitrogen and phosphorus contributed by suspended and dissolved detritus and phytoplankton and back-calculating the amount that must be available as freely dissolved nutrients. The precision of this conversion is aided by the model's variable stoichiometry. For nitrogen:

$$N_{Dissolved} = N_{Total} - N_{SuspendedDetritus} - N_{SuspendedPlants} \quad \textbf{(14a)}$$

where:

| | | |
|---|---|---|
| $N_{Dissolved}$ | = | bioavailable dissolved nitrogen (g/m$^3$ d); see (137 & 140, Rel. 2); |
| $N_{Total}$ | = | loadings of total nitrogen as input by the user (g/m$^3$ d); |
| $N_{SuspendedDetritus}$ | = | nitrogen in suspended detritus loadings (g/m$^3$ d); |
| $N_{SuspendedPlants}$ | = | nitrogen in suspended plant loadings (g/m$^3$ d). |

In acknowledgment of the way it is used in the model, the phosphorus state variable is now designated "Total Soluble P." Phosphorus that is not bioavailable (i.e. immobilized phosphorus/ acid soluble phosphorus) may be specified using the *FracAvail* parameter as shown here:

$$TSP = FracAvail\left(P_{Total} - P_{SuspendedDetritus} - P_{SuspendedPlants}\right) \quad \textbf{(15a)}$$

where:

| | | |
|---|---|---|
| $TSP$ | = | bioavailable phosphorus (g/m$^3$ d); see (146, Rel. 2); |
| $FracAvail$ | = | user input bioavailable fraction of phosphorus; |
| $P_{Total}$ | = | loadings of total phosphorus (g/m$^3$ d); |
| $P_{SuspendedDetritus}$ | = | phosphorus in suspended detritus loadings (g/m$^3$ d); |
| $P_{SuspendedPlants}$ | = | phosphorus in suspended plant loadings (g/m$^3$ d). |

## Nutrient Output Variables

In order to compare model results with monitoring data, total phosphorus, and total nitrogen are now calculated as output variables. This is accomplished by the reverse of the calculations for the loadings: the contributions of the nutrient in the freely dissolved state and tied up in phytoplankton and dissolved and particulate organic matter are calculated and summed.

Biochemical oxygen demand ($BOD_5$) is computed as the sum of the contributions from phytoplankton and labile dissolved and particulate organic matter using a conversion of 1.35 BOD/organic matter.

## Mass Balance of Nutrients

New variables for tracking mass balance and nutrient fate have been added to the output as detailed below. Phosphorus and Nitrogen now balance mass to machine accuracy. To maintain mass balance, nutrients are tracked through many interactions. The mass balance and nutrient fate tracking variables are:

Nutrient Tot. Mass: Total mass of nutrient in the system in kg
Nutrient Tot. Loss: Total loss of nutrient from system since simulation start, kg
Nutrient Tot. Washout: Total washout since simulation start, kg

Nutrient Wash, Dissolved: Washout in dissolved form since simulation start, kg
Nutrient Wash, Animals: Washout in animals since start, kg
Nutrient Wash, Detritus: Washout in detritus since start, kg
Nutrient Wash, Plants: Washout in plants since start, kg
Nutrient Loss EmergeI: Loss of nutrients in emerging insects since start, kg
Nutrient Loss Denitrif.: Denitrification since start, kg
Nutrient Burial: Burial of nutrients since start, kg
Nutrient Tot. Load: Total nutrient load since start, kg
Nutrient Load, Dissolved: Dissolved nutrient load since start, kg
Nutrient Load as Detritus: Nutrient load in detritus since start, kg
Nutrient Load as Biota: Nutrient load in biota since start, kg
Nutrient Root Uptake: Load of nutrients into sytem via macrophyte roots since start, kg
Nutrient MB Test: Mass balance test, total Mass + Loss – Load: Should stay constant
Nutrient Exposure: Exposure of buried nutrients
Nutrient Net Layer Sink: For stratified systems, sinking since start, kg
Nutrient Net TurbDiff: For stratified systems, Turbdiff since start, kg
Nutrient Net Layer Migr.: For stratified systems, migration since start, kg
Nutrient Total Net Layer: Net movement over layers, kg
Nutrient Mass Dissolved: Total mass of dissolved nutrient in system, kg
Nutrient Mass Detritus: Total mass of nutrient in detritus in system, kg
Nutrient Mass Animals: Total mass of nutrient in animals in system, kg
Nutrient Mass Plants: Total mass of nutrient in plants in system, kg

Please make careful note of the units presented in the list above. Load and loss terms are calculated in terms of "kg since the start of the simulation," total mass units are "kg at the current moment."

A simplified diagram of the nitrogen and phosphorus cycles can be found in Figures 4 and 5. A full accounting of the 18 nutrient linkages and all external loads and losses for nitrogen and phosphorus is also provided in Tables 2 and 3.

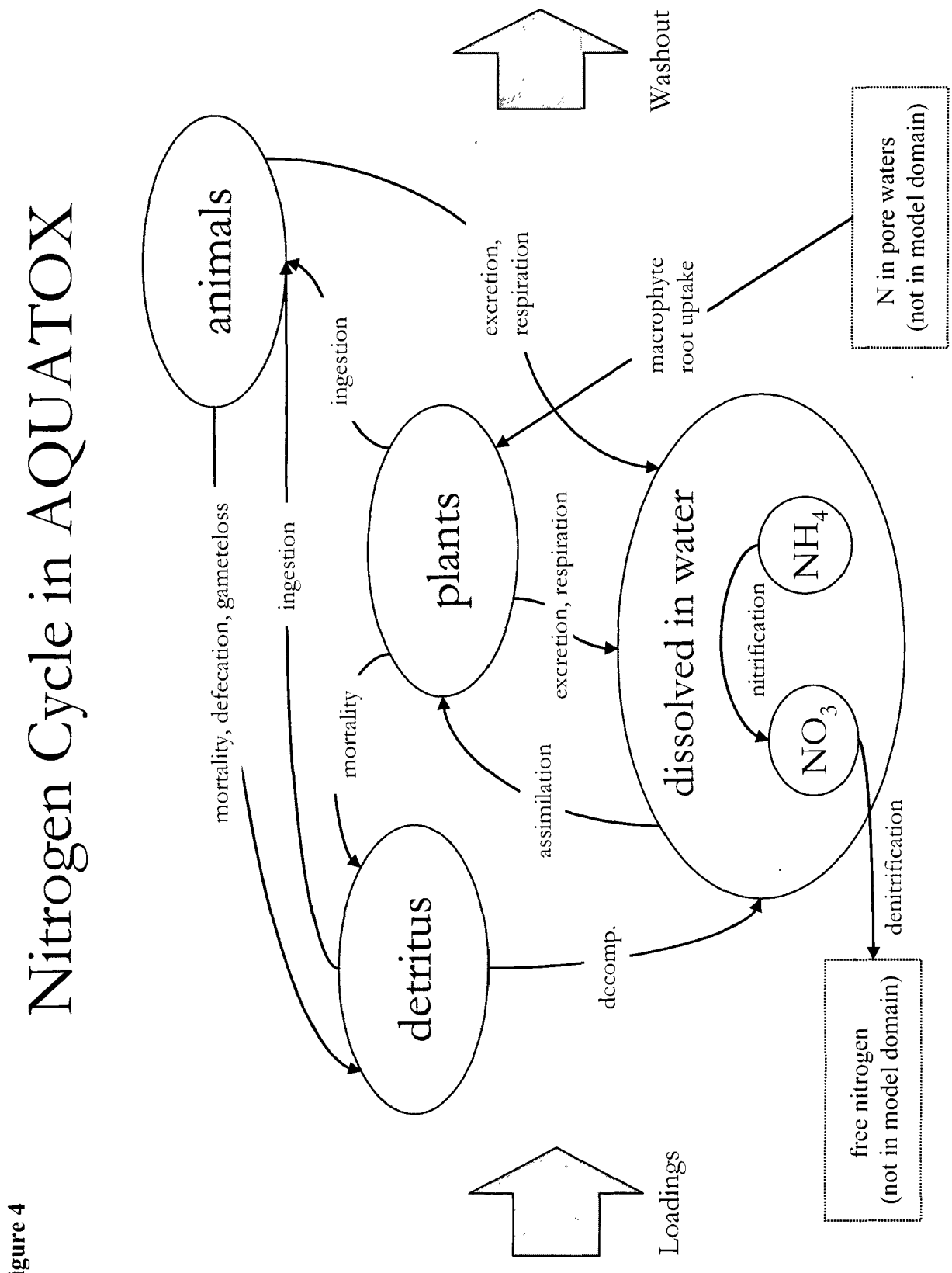

Nitrogen Cycle in AQUATOX
animals
plants
detritus
dissolved in water
$NH_4$
$NO_3$
Washout
Loadings
N in pore waters
(not in model domain)
free nitrogen
(not in model domain)
ingestion
mortality, defecation, gameteloss
ingestion
mortality
excretion,
respiration
excretion, respiration
assimilation
macrophyte
root uptake
nitrification
decomp.
denitrification

**Figure 4**

# Table 2

## Nitrogen Mass Balance: Accounting

| NO3 | link | | NH4 | link | | Detritus, Sed. Refractory | link | | Detritus, Sed. Labile | link | | Detritus, Dissolved | link | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Load | *external load* | | Load | *external load* | | Load | *external load* | | Load | *external load* | | Load | *external load* | |
| Nitrif | **from NH4** | a | Nitrif | **to NO3** | a | Defecation | **from animal** | e | Defecation | **from animal** | e | Decomp (labile) | **to NH4** | d |
| DeNitrif | *external loss* | | Assimil | **to plant** | b | Plant Sedmtn | **from plant** | f | Plant Sedmtn | **from plant** | f | Mortality | **from anim/plt** | k |
| NO3Assim | **to plant** | b | Excretion | **from anim/plt** | c,o | Colonz | **to SedLabDetr** | g | Colonz | **from SedRefrDetr** | g | Colonz | **DissRefr->PartLab** | g |
| Washout | *external loss* | | Respiration | **from anim/plt** | m,n | Predation | **to Animal** | h | Predation | **to Animal** | h | Excretion | **from anim/plt** | l |
| TurbDiff | *layer accountg* | | DetritalDecomp | **from LabileDetr** | d | Sedimentation | **from PartRefrDetr** | i | Decomp | **to NH4** | d | Washout | *external loss* | |
| | | | Washout | *external loss* | | Scour | **to PartRefrDetr** | j | Sedimentation | **from PartLabDetr** | i | TurbDiff | *layer accountg* | |
| | | | TurbDiff | *layer accountg* | | Burial | *external loss* | | Scour | **to PartLabDetr** | j | | | |
| | | | | | | Exposure | *external load* | | Burial | *external loss* | | | | |
| | | | | | | | | | Exposure | *external load* | | | | |

| Detritus, Particulate Refr. | link | | Detritus, Particulate Labile | link | | Algae | link | | Macrophytes | link | | Animals | link | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Load | *external load* | | Load | *external load* | | Load | *external load* | | Load | *external load* | | Load | *external load* | |
| mortality | **from anim/plt** | k | Decomp | **to NH4** | d | Photosyn | **from NO3, NH4** | b | Photosyn | *root uptake, external* | | Consumption | **from anim/plt** | h |
| Colonz | **to PartLabDetr** | g | mortality | **from anim/plt** | k | Respiration | **to NH4** | m | Respiration | **to NH4** | m | Defecation | **to sed detr** | e |
| Washout | *external loss* | | GamLoss | **from Animal** | q | Photo Resp | **to diss detr, NH4** | l,c | Photo Resp | **to diss detr, NH4** | l,c | Respiration | **to NH4 if req.** | n |
| Predation | **to Animal** | h | Colonz | **from Diss,PartRefr** | g | Mortality | **to Diss / Part Detr** | k | Mortality | **to Part Detr** | k | Excretion | **to NH4 if req.** | o |
| Sedimentation | **to SedRefrDetr** | i | Washout | *external loss* | | Predation | **to Animal** | h | Predation | **to animal** | h | TurbDiff | *layer accountg* | |
| Scour | **from SedRefrDetr** | j | Predation | **to Animal** | h | Washout | *external loss* | | Breakage | **to detr., as mort** | k | Predation | **to animal** | h |
| SinkToHyp | *layer accountg* | | Sedimentation | **to SedLabDetr** | i | Sedimntn (Sink) | **to Sed Detr** | f | | | | Mortality | **to Part Detr** | k |
| SinkFromEpi | *layer accountg* | | Scour | **from SedLabDetr** | j | TurbDiff | *layer accountg* | | | | | GameteLoss | **to PartLabDetr** | q |
| TurbDiff | *layer accountg* | | SinkToHypo | *layer accountg* | | SinkToHypo | *layer accountg* | | | | | Drift | *external loss* | |
| | | | SinkFromEpi | *layer accountg* | | SinkFromEpi | *layer accountg* | | | | | Entrain | *external loss* | |
| | | | TurbDiff | *layer accountg* | | Sloughing | **to detr., phytoplk** | r | | | | Promotion | **to animal** | p |
| | | | | | | ToxDislodge | **to detr., as mort** | k | | | | Recruit | **from animal** | p |
| | | | | | | | | | | | | *Emergel* | *external loss* | |
| | | | | | | | | | | | | Migration | *layer accountg* | |

Linkage Notes

a Denitrification from NH4 to NO3
b An appropriate quantity of NO3 and NH4 are taken into a plant as part of photosynthesis so that mass balance is maintained.
c When excretion & respiration takes place in plants and animals, all nitrogen lost goes directly to dissolved NH4.
d Labile detritus breaks down and the nutrient content is released as NH4
e *Defecation is split into sedimented-labile and sed-refr detritus . . Excess nitrogen is released as NH4*
f Plants sink and are split into sedimented-labile and sed-refr detritus (92-08) Excess nitrogen is released as NH4.
g Refractory detritus breaks down into labile detritus Any nitrogen imbalance is balanced using NH4 in water
h Animals eat plants and detritus Animal homeostasis (const org to n ratio) is managed through Respiration & Excretion.
i Suspended sediment sinks and joins bottom sediment Any change in N between phases is made up using dissolved NH4
j Bottom sediment is scoured up and joins suspended sediment Any change in N between phases is made up using dissolved NH4
k Animals and plants die and are divided up among suspended and dissolved detritus. Excess nitrogen is released as NH4
l Plants excrete organic matter to dissolved detritus. Excess Nitrogen is released as NH4
m Plant respiration, nutrients are released to NH4
n Animal respiration, nutrients are relased to NH4 to maintain animal constant org. to n ratio as required
o Animal excretion of excess nutrients to NH4 to maintain constant org to n ratio as required.
p If young and old age-classes have different ratios, a warning is raised Prom/Recr takes place outside derivatives so ratios must match.
q Through gameteloss, biomass is converted to Part Lab Detr Excess Nitrogen is released as NH4.
r 1/3 of periphyton sloughing goes to phytoplankton, 2/3 to detritus as mortality. Nutrients are balanced between compartments

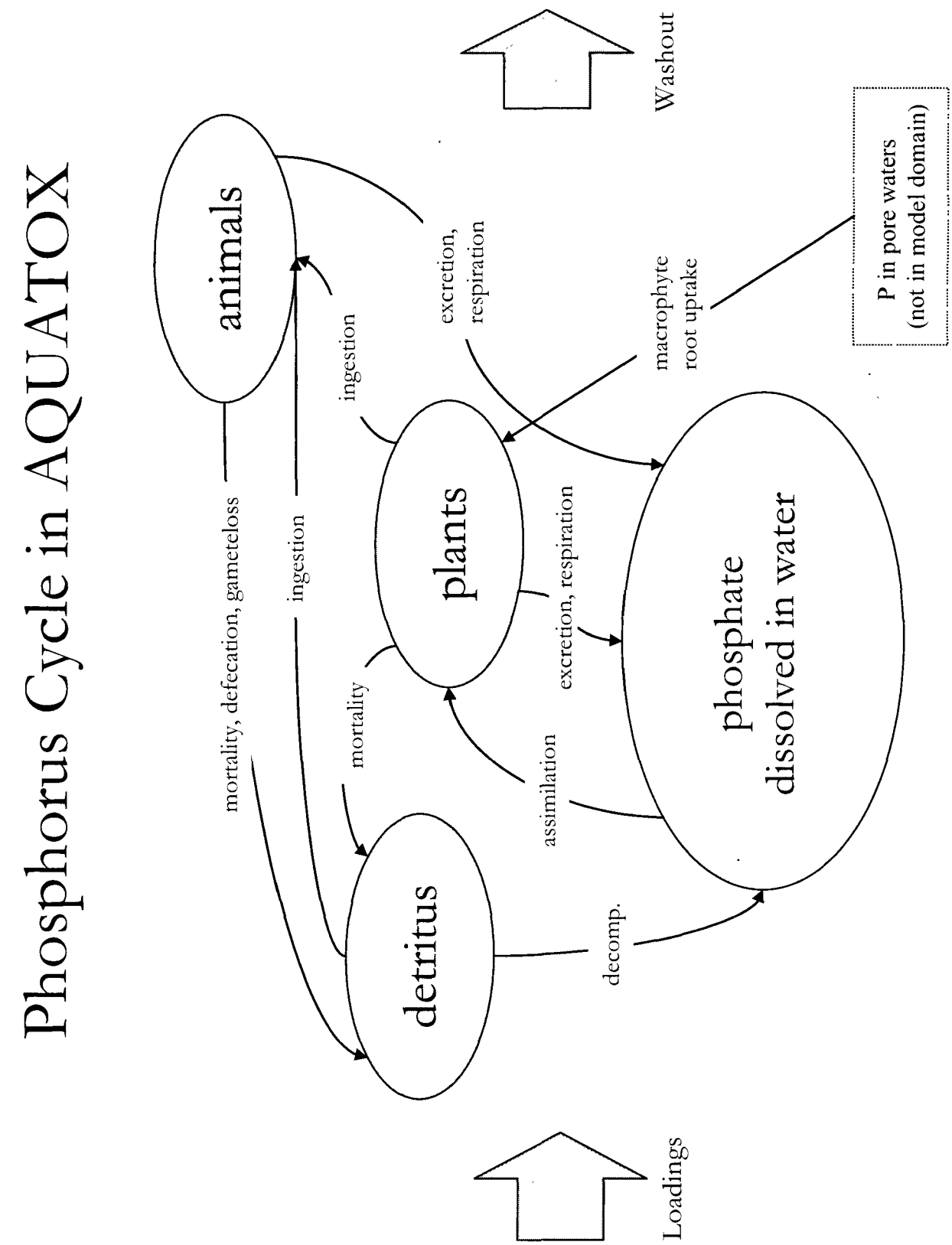

Phosphorus Cycle in AQUATOX
animals
plants
detritus
phosphate
dissolved in water
Loadings
Washout
P in pore waters
(not in model domain)
mortality, defecation, gameteloss
ingestion
ingestion
excretion,
respiration
macrophyte
root uptake
mortality
excretion, respiration
assimilation
decomp.

**Figure 5**

# Table 3

## Phosphorus Mass Balance: Accounting

| Total Soluble P | link | | Detritus, Sed. Refractory | link | | Detritus, Sed. Labile | link | | Detritus, Dissolved | link | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Load | *external load* | | Load | *external load* | | Load | *external load* | | Load | *external load* | |
| Assimilation | **to plant** | b | Defecation | **from animal** | e | Defecation | **from animal** | e | Decomp (labile) | **to TSP** | d |
| Excretion | **from anim/plt** | c,o | Plant Sedmtn | **from plant** | f | Plant Sedmtn | **from plant** | f | Mortality | **from anim/plt** | k |
| Respiration | **from anim/plt** | m,n | Colonz | **to SedLabDetr** | g | Colonz | **from SedRefrDetr** | g | Colonz | **DissRefr->PartLab** | g |
| DetritalDecomp | **from LabileDetr** | d | Predation | **to Animal** | h | Predation | **to Animal** | h | Excretion | **from anim/plt** | l |
| Washout | *external loss* | | Sedimentation | **from PartRefrDetr** | i | Decomp | **to TSP** | d | Washout | *external loss* | |
| TurbDiff | *layer accountg* | | Scour | **to PartRefrDetr** | j | Sedimentation | **from PartLabDetr** | i | TurbDiff | *layer accountg* | |
| | | | Burial | *external loss* | | Scour | **to PartLabDetr** | j | | | |
| | | | Exposure | *external load* | | Burial | *external loss* | | | | |
| | | | | | | Exposure | *external load* | | | | |

| Detritus, Particulate Refr. | link | | Detritus, Particulate | link | | Algae | link | | Macrophytes | link | | Animals | link | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Load | *external load* | | Load | *external load* | | Load | *external load* | | Load | *external load* | | Load | *external load* | |
| mortality | **from anim/plt** | k | Decomp | **to TSP** | d | Photosyn | **from TSP** | b | Photosyn | *root uptake, external* | | Consumption | **from anim/plt** | h |
| Colonz | **to PartLabDetr** | g | mortality | **from anim/plt** | k | Respiration | **to TSP** | m | Respiration | **to TSP** | m | Defecation | **to sed detr** | e |
| Washout | *external loss* | | GamLoss | **from Animal** | q | Photo Resp | **to diss detr, TSP** | l,c | Photo Resp | **to diss detr, TSP** | l,c | Respiration | **to TSP if req.** | n |
| Predation | **to Animal** | h | Colonz | **from Diss,PartRefr** | g | Mortality | **to Diss / Part Detr** | k | Mortality | **to Part Detr** | k | Excretion | **to TSP if req.** | l,o |
| Sedimentation | **to SedRefrDetr** | i | Washout | *external loss* | | Predation | **to Animal** | h | Predation | **to animal** | h | TurbDiff | *layer accountg* | |
| Scour | **from SedRefrDetr** | j | Predation | **to Animal** | h | Washout | *external loss* | | Breakage | **to detr., as mort** | k | Predation | **to animal** | h |
| SinkToHyp | *layer accountg* | | Sedimentation | **to SedLabDetr** | i | Sedimntn (Sink) | **to Sed Detr** | f | | | | Mortality | **to Part Detr** | k |
| SinkFromEpi | *layer accountg* | | Scour | **from SedLabDetr** | j | TurbDiff | *layer accountg* | | | | | GameteLoss | **to PartLabDetr** | q |
| TurbDiff | *layer accountg* | | SinkToHypo | *layer accountg* | | SinkToHypo | *layer accountg* | | | | | Drift | *external loss* | |
| | | | SinkFromEpi | *layer accountg* | | SinkFromEpi | *layer accountg* | | | | | Entrain | *external loss* | |
| | | | TurbDiff | *layer accountg* | | Sloughing | **to detr., phytopik** | r | | | | Promotion | **to animal** | p |
| | | | | | | ToxDislodge | **to detr , as mort** | k | | | | Recruit | **from animal** | p |
| | | | | | | | | | | | | Emergel | *external loss* | |
| | | | | | | | | | | | | Migration | *layer accountg* | |

Linkage Notes

- b An appropriate quantity of phosphorus is taken into a plant as part of photosynthesis so that mass balance is maintained
- c When excretion & respiration takes place in plants and animals (organic matter becomes DOM) additional P lost goes directly to dissolved P
- d Labile detritus breaks down and the nutrient content is released as dissolved P
- e Defecation is split into sedimented-labile and sed-refr detritus 50-50 Excess phosphorus is released as dissolved P
- f Plants sink and are split into sedimented-labile and sed-refr detritus (92-08) Excess phosphorus is released as dissolved P.
- g Refractory detritus breaks down into labile detritus Any P imbalance is balanced using dissolved P in water
- h Animals eat plants and detritus Animal homeostasis (const org to n ratio) is managed through Respiration & Excretion
- i Suspended sediment sinks and joins bottom sediment Any change in P between phases is made up using dissolved P
- j Bottom sediment is scoured up and joins suspended sediment Any change in P between phases is made up using dissolved P.
- k Animals and plants die and are divided up among suspended and dissolved detritus Excess phosphorus is released as dissolved P
- l Plants and animals excrete organic matter to dissolved detritus. Excess phosphorus is released as dissolved P.
- m Plant respiration, nutrients are released to dissolved phosphorus.
- n Animal respiration, nutrients are relased to dissolved P to maintain animal constant org to n ratio as required
- o Animal excretion of excess nutrients to P to maintain constant org to n ratio as required.
- p If young and old age-classes have different ratios, a warning is raised. Prom/Recr takes place outside derivatives so ratios must match
- q Through gameteloss, biomass is converted to Part Lab Detr Excess phosphorus is released as dissolved P
- r 1/3 of periphyton sloughing goes to phytoplankton, 2/3 to detritus as mortality Nutrients are balanced between compartments

There are instances in which nutrients can be moved to and from compartments that are not in the model domain. For example, when $NO_3$ undergoes denitrification and becomes free nitrogen the free nitrogen is no longer tracked within AQUATOX. An example of nutrients entering the model domain comes with the growth of macrophytes. Rooted macrophytes are not limited by a lack of nutrients in the water column as nutrients are derived from the sediment. Therefore, when photosynthesis of macrophytes produces growth, the nutrient content within the leaves of the macrophytes is assumed to originate from the pore waters of the sediments which is not modeled in this version of AQUATOX.

In some cases, when concentrations of nutrients in the water column drop to zero, perfect mass balance of nutrients will not be maintained. Nutrient to organic matter ratios within organisms do not vary over time, therefore transformation of organic matter (e.g. consumption, mortality, sloughing, and sedimentation) occasionally requires that a nutrient difference be made up from the water column. If there are no available nutrients in the water column, a slight loss of mass balance is possible.

The mass associated with each component can be plotted, as in Figure 6.

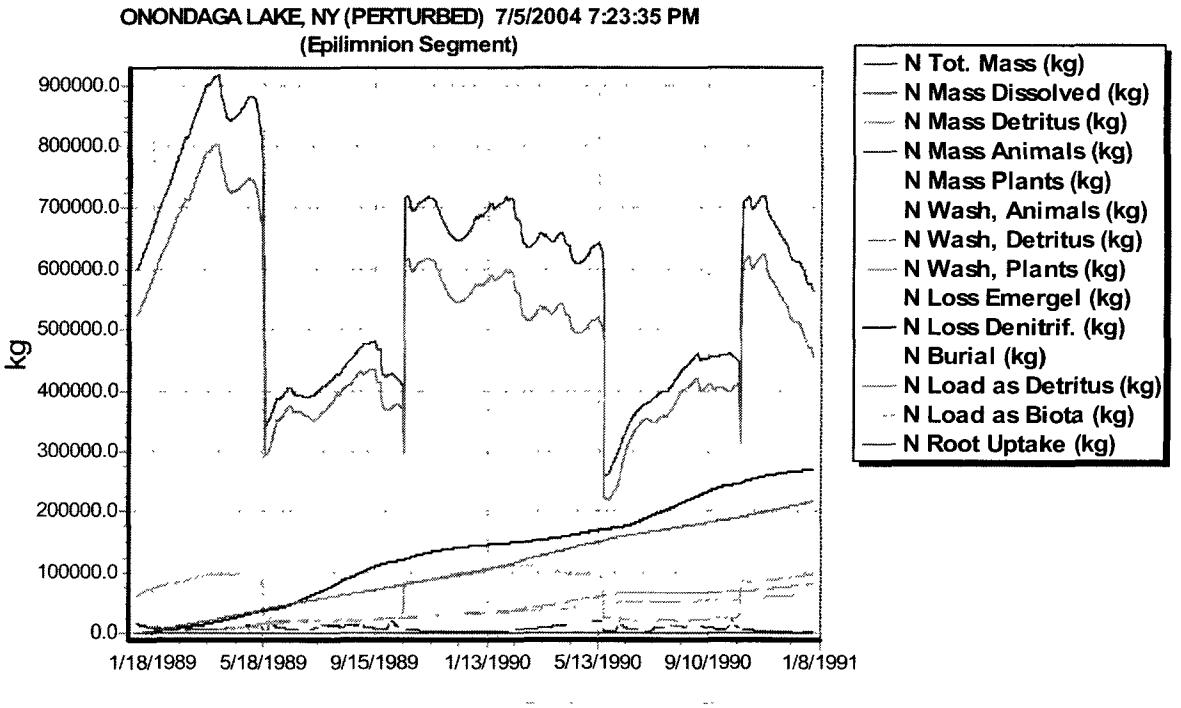



**Figure 6 Distribution of predicted mass of nitrogen in Lake Onondaga NY.**

## 5.7 Modeling Dynamic pH

***(add this section to the end of chapter 5)***

Dynamic pH is important in simulations for several reasons. As demonstrated in section 5.2, ionization of ammonia is sensitive to pH. Furthermore, hydrolysis of organic chemicals can be sensitive to pH. Both these relationships are modeled in AQUATOX. In addition, the viability of organisms and bioaccumulation and toxicity of organic chemicals can be dependent on pH; these relationships are not currently modeled by AQUATOX.

Many models follow the example of Stumm and Morgan (1996) and solve simultaneous equations for pH, alkalinity, and the complete carbonate-bicarbonate equilibrium system. However, this approach requires more data than are often available, and the iterative solution of the equations entails an additional computational burden—all for a precision that is unnecessary for ecosystem models. The alternative is to restrict the range of simulated pH to that of normal aquatic systems and to make simplifying assumptions that allow a semi-empirical computation of pH (Marmorek et al. 1996, Small and Sutton 1986). That is the approach taken for AQUATOX.

The computation is good for the pH range of 4 to 8.25, where the carbonate ion is negligible and can thus be ignored. The derivation is given by Small and Sutton (1986), with a correction for dissolved organic carbon (Marmorek et al. 1996). It incorporates a quadratic function of carbon dioxide; and it is a nonlinear function of mean alkalinity and the concentration of refractory dissolved organic carbon (humic and fulvic acids), by means of an inverse hyperbolic sine function:

$$pHCalc = A + B \cdot ArcSinH\left(\frac{Alkalinity - 5.1 \cdot DOC}{C}\right) \quad \textbf{(16a)}$$

where:

| | | |
|---|---|---|
| *pHCalc* | = | pH; |
| ArcSinH | = | inverse hyperbolic sine function; |
| *Alkalinity* | = | mean Gran alkalinity (µeq $CaCO_3$/L); |
| *DOC* | = | refractory dissolved organic carbon (mg/L); calc. from (114, 115, Rel 2); |
| 5.1 | = | average µeq of organic ions per mg of *DOC;* |

$A = -Log\sqrt{Alpha}$

$B = 1/\ln(10)$

$C = 2 \cdot \sqrt{Alpha}$

$Alpha = H2CO3^* \cdot CCO2 + pkw$

$H2CO3^* = 10^{-(6.57 - 0.0118\ T + 0.00012\ T\ T)\ 0.92}$

where:

| | | |
|---|---|---|
| *H2CO3** | = | first acidity constant; |
| *CCO2* | = | $CO_2$ expressed as µeq/L; see (164, Rel. 2); |
| *pkw* | = | ionization constant for water (1e-14); |
| *T* | = | temperature (°C); see (24, Rel. 2); |
| 0.92 | = | correction factor for dissolved $CO_2$ |

Calibration and verification of the construct used data from nine lakes and ponds in the National Eutrophication Survey (U.S. Environmental Protection Agency, 1977), two observations on Lake

Onondaga, NY, from before and after closure of a chlor-alkali plant (Effler et al., 1996), and one observation in a river (Figure 7). The correction factor for $CO_2$ was obtained by fitting the data to the unity line, but ignoring the two highest points because the construct does not predict pH above 8.25.

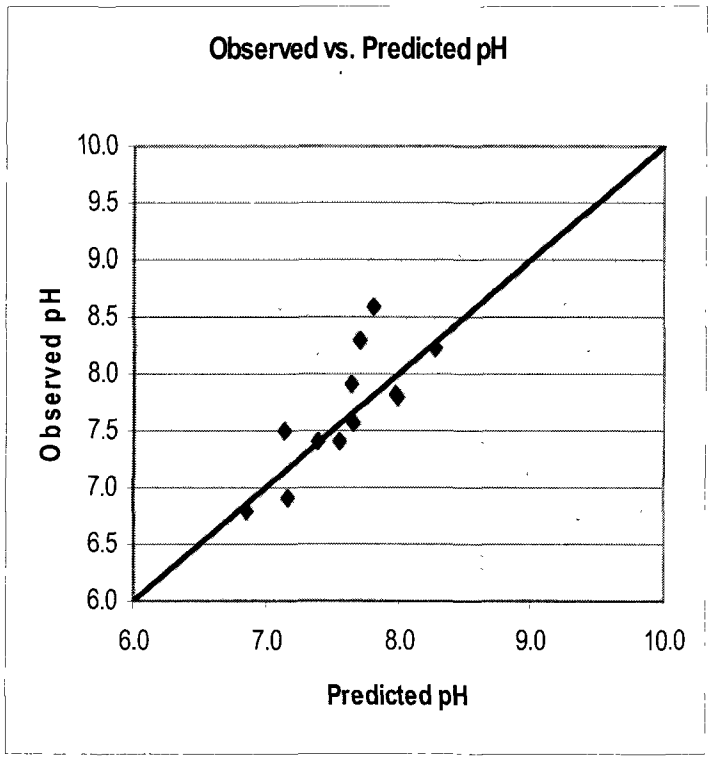



**Figure 7 Comparison of predicted and observed pHs from selected lakes.**

The construct also was verified using time-series data from Lake Onondaga, NY (Figure 8). The observed data were interpolated from the 2-m depth pH isopleths on a graph (Effler et al. 1996), introducing some uncertainty into the comparison.

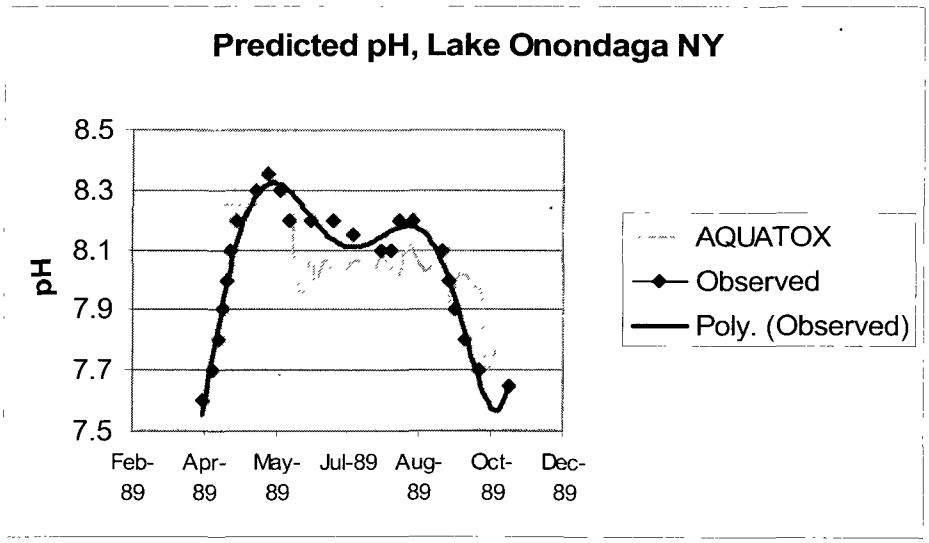



**Figure 8. Comparison of predicted and observed pH values for Lake Onondaga, NY. Data from (Effler et al. 1996).**

# 7 Toxic Organic Chemicals

## 7.6 Nonequilibrium Kinetics

***The following text and equation should replace Equation (251) on page 7-24 and the descriptive paragraph preceding it.***

Given the latest model formulations and testing, it is not necessary to normalize an uptake rate constant *(Diff)* based on competing uptake rates. The Runge-Kutta dufferential equation solver effectively removes any issues of excessive chemical uptake and toxicant mass balance is maintained at all times. Therefore:

$$Diff = 1.0 \qquad \textbf{(251)}$$

## 7.7 Alternative Uptake Model: Entering BCFs, K1, and K2

***The following should be added to the end of Chapter 7, on page 7-36.***

When performing bioaccumulation calculations, the default behavior of the AQUATOX model is to allow the user to enter elimination rate constants (K2) for all plants and animals for a particular organic chemical. K2 values may also be estimated based on the $LogK_{OW}$ of the chemical. Uptake in plants is a function of log $K_{OW}$ while gill uptake in animals is a function of respiration and chemical uptake efficiency. The AQUATOX default model works well for a wide variety of bioaccumulative organic chemicals, but some chemicals are subject to very rapid uptake and depuration are not effectively modeled using these relationships.

For this reason, an alternative uptake model is provided to the user. In the chemical toxicity record, the user may enter two of the three factors defining uptake (BCF, K1, K2) and the third factor is calculated using the below relationship:

$$BCF = \frac{K1}{K2} \qquad \textbf{(17a)}$$

where: $BCF$ = bioconcentration factor (L/kg dry);
$K1$ = uptake rate constant (L/kg dry day);
$K2$ = elimination rate constant (1/d).

Given these parameters, AQUATOX calculates uptake and depuration in plants and animals as kinetic processes.

$$Uptake = K1 \cdot ToxState \cdot Biomass \cdot 1e-6 \qquad \textbf{(18a)}$$

$$Depuration = K2 \cdot ToxState \tag{19a}$$

where: *Uptake* = uptake rate within organism (µg/L day);
*K1* = uptake rate constant (L/kg dry day);
*ToxState* = concentration of toxicant in organism in water (µg/L)
*Biomass* = concentration organism in water (mg/L)
1e-6 = (kg/mg)
*Depuration* = loss rate within organism (µg/L day);
*K2* = elimination rate constant (1/d).

Dietary uptake of chemicals by animals is not affected by this alternative parameterization.

## 7.8 Half Life Calculation Refinement DT50 & DT95

The half-life estimation capability with AQUATOX has been significantly upgraded since Release 2. AQUATOX now estimates time to 50% (half-lives, DT50s) and time to 95% chemical loss (DT95s) independently in bottom sediment and in the water column. Estimates are produced at each output time-step depending on the average loss rate during that time-step in that medium.

$$Loss_{Water} = \frac{Hydrolysis_{Water} + Photolysis + Microbial_{Water} + Washout + Volat. + Sorption}{Mass_{Water}} \tag{20a}$$

$$Loss_{Sed} = \frac{Microbial_{Sed} + Hydrolysis_{Sed} + Desorption}{Mass_{Sed}} \tag{21a}$$

where: $Loss_{Media}$ = loss rate within media (1/d);
$Hydrolysis_{Media}$ = hydrolysis rate in given media (µg/L d), see **(212**, Rel. 2**)**;
*Photolysis* = photolysis rate in the water column (µg/L d), see **(219**, Rel. 2**)**;
$Microbial_{Media}$ = rate of microbial metabolism in given media (µg/L d), see **(225**, Rel. 2**)**;
*Washout* = rate of toxicant washout from the water column (µg/L d); see **(16**, Rel. 2**)**
*Volat* = rate of chemical volatilization in the water column (µg/L d), see **(230**, Rel. 2**)**;
*Sorption* = sorption of toxicant to detritus, plants, and animals (µg/L d), see **(249**, Rel. 2**)**;
$Mass_{Media}$ = mass of chemical in the media (µg/L);
*Desorption* = desorption of toxicant from bottom sediment, see **(250**, Rel. 2**)**.

Loss rates are converted into time to 50% and 95% loss using the following formulae for first-order reactions:

$$DT50_{Media} = 0.693 / Loss_{Media} \quad \textbf{(22a)}$$

$$DT95_{Media} = 2.996 / Loss_{Media} \quad \textbf{(23a)}$$

where: $DT50_{Media}$ = time in which 50% of chemical will be lost at current loss rate (d);
$DT95_{Media}$ = time in which 95% of chemical will be lost at current loss rate (d);
$Loss_{Media}$ = loss rate within media (1/d);

***The following should be inserted at the end of Chapter 8, on p. 8-10***

# 8 ECOTOXICOLOGY

## 8.3 External Toxicity

Chemicals that are taken up very rapidly and those that have an external mode of toxicity, such as affecting the gills directly, are best simulated with an external toxicity construct. AQUATOX has an alternative computation for *CumFracKilled,* when calculating toxic effects based on external concentrations, using the two-parameter Weibull distribution as in Christiensen and Nyholm (1984):

$$CumFracKilled = 1 - \exp(-kz^{Eta}) \quad \textbf{(24a)}$$

where: $z$ = external concentration of toxicant (µg/L);
*CumFracKilled* = cumulative fraction of organisms killed for a given period of exposure (fraction/d);
$k$ and *Eta* = fitted parameters describing the dose response curve.

Rather than require the user to fit toxicological bioassay data to determine the parameters for $k$ and *Eta*, these parameters are derived to fit the LC50 and the slope of the cumulative mortality curve at the LC50 (in the manner of the RAMAS Ecotoxicology model, Spencer and Ferson, 1997):

$$k = \frac{-\ln(0.5)}{LC50^{Eta}} \quad \textbf{(25a)}$$

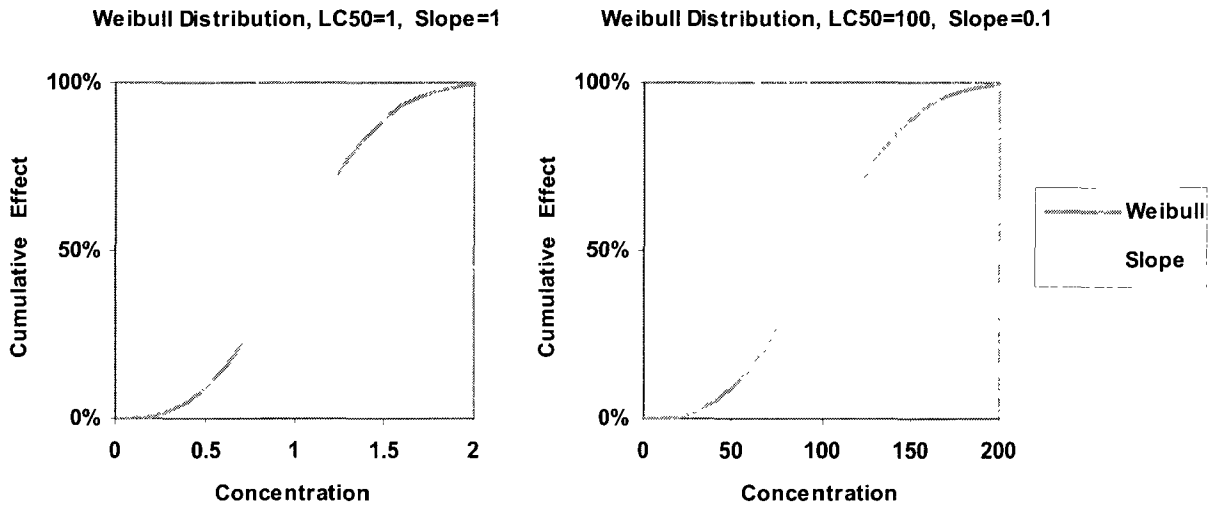
$$Eta = \frac{-2 \cdot LC50 \cdot slope}{\ln(0.5)} \quad \textbf{(26a)}$$

where: *slope* = slope of the cumulative mortality curve at LC50 (unitless).
LC50 = concentration where half of individuals are affected (µg/L).

AQUATOX assumes that each chemical's dose response curve has a distinct shape, relevant to all organisms modeled. In this manner, a single parameter describing the shape of the Weibull parameter can be entered in the chemical record rather than requiring the user to derive slope parameters for each organism modeled.

However, as shown below, the slope of the curve at the LC50 is both a function of the shape of the Weibull distribution and also the magnitude of the LC50 in question.

Figures 9 and 10 show two Weibull distributions with identical shapes, but with slopes that are significantly different due to the scales of the x axes:




**Figures 9 and 10: Weibull distributions with identical shapes, but with slopes that are significantly different due to the scales of the x axes**

For this reason, rather than have a user enter "the slope at LC50" into the chemical record, AQUATOX asks that the user enter a "slope factor" defined as "the slope at LC50 multiplied by LC50." In the above example, the user would enter a slope factor of 1.0 and then, given an LC50 of 1 or an LC50 of 100, the above two curves would be generated.

When modeling toxicity based on external concentrations, organisms are assumed to come to equilibrium with external concentrations (or the toxicity is assumed to be based on external effects to the organism).

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