**EPA**

AQUATOX (RELEASE 3.2)

MODELING ENVIRONMENTAL FATE AND ECOLOGICAL EFFECTS IN AQUATIC ECOSYSTEMS

VOLUME 2: TECHNICAL DOCUMENTATION

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MODELING ENVIRONMENTAL FATE AND ECOLOGICAL EFFECTS IN AQUATIC ECOSYSTEMS

VOLUME 2: TECHNICAL DOCUMENTATION

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DISCLAIMER

This document describes the scientific and technical background of the aquatic ecosystem model AQUATOX, Release 3.2. Anticipated users of this document include persons who are interested in using the model, including but not limited to researchers and regulators. The model described in this document is not required, and the document does not change any legal requirements or impose legally binding requirements on EPA, states, tribes or the regulated community. This document has been approved for publication by the Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency. Mention of trade names, commercial products or organizations does not imply endorsement or recommendation for use.

ACKNOWLEDGMENTS

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PREFACE

The Clean Water Act- formally the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-50), and subsequent amendments in 1977, 1979, 1980, 1981, 1983, and 1987- calls for the identification, control, and prevention of pollution of the nation's waters. Data submitted by the States to the U.S. Environmental Protection Agency's WATERS (Watershed Assessment, Tracking & Environmental ResultS) database (http://www.epa.gov/waters/) indicate that a very high percentage of the Nations waters continue to be impaired. As of early 2009, of the waters that have been assessed, 44% of rivers and streams, 59% of lakes, reservoirs and ponds, and 35% of estuaries were impaired for one or more of their designated uses. The five most commonly reported causes of impairment in rivers and streams were: pathogens, sediment, nutrients, habitat alteration and organic enrichment/dissolved oxygen depletion. In lakes and reservoirs the five most common causes were mercury, nutrients, organic enrichment/dissolved oxygen depletion, metals, and turbidity. In estuaries the five most common causes were pathogens, mercury, organic enrichment/oxygen depletion, pesticides and toxic organics. Many waters are impaired for multiple uses, by multiple causes, from multiple sources.

New approaches and tools, including appropriate technical guidance documents, are needed to facilitate ecosystem analyses of watersheds as required by the Clean Water Act. In particular, there is a pressing need for refinement and release of an ecological risk methodology that addresses the direct, indirect, and synergistic effects of nutrients, metals, toxic organic chemicals, and non-chemical stressors on aquatic ecosystems, including streams, rivers, lakes, and estuaries.

The ecosystem model AQUATOX is one of the few general ecological risk models that represents the combined environmental fate and effects of toxic chemicals. The model also represents conventional pollutants, such as nutrients and sediments, and considers several trophic levels, including attached and planktonic algae, submerged aquatic vegetation, several types of invertebrates, and several types of fish. It has been implemented for experimental tanks, ponds and pond enclosures, streams, small rivers, linked river segments, lakes, reservoirs, linked reservoir segments, and estuaries.

1. INTRODUCTION

1.1 Overview

The AQUATOX model is an open-source[1] general ecological risk assessment model that represents the combined environmental fate and effects of conventional pollutants, such as nutrients and sediments, and toxic chemicals in aquatic ecosystems. It considers several trophic levels, including attached and planktonic algae and submerged aquatic vegetation, invertebrates, and forage, bottom-feeding, and game fish; it also represents associated organic toxicants (Figure 1). It can be implemented as a simple model (indeed, it has been used to simulate an abiotic flask) or as a truly complex food-web model. Often it is desirable to model a food web rather than a food chain, for example to examine the possibility of less tolerant organisms being replaced by more tolerant organisms as environmental perturbations occur. "Food web models provide a means for validation because they mechanistically describe the bioaccumulation process and ascribe causality to observed relationships between biota and sediment or water" (Connolly and Glaser 1998). The best way to accurately assess bioaccumulation is to use more complex models, but only if the data needs of the models can be met and there is sufficient time (Pelka 1998).

It has been implemented for experimental tanks, ponds and pond enclosures, streams, small rivers, linked river segments, lakes, reservoirs, linked reservoir segments, and estuaries. It is intended to be used to evaluate the likelihood of past, present, and future adverse effects from various stressors including potentially toxic organic chemicals, nutrients, organic wastes, sediments, and temperature. The stressors may be considered individually or together.

The fate portion of the model, which is applicable especially to organic toxicants, includes: partitioning among organisms, suspended and sedimented detritus, suspended and sedimented inorganic sediments, and water; volatilization; hydrolysis; photolysis; ionization; and microbial degradation. The effects portion of the model includes: sublethal and lethal toxicity to the various organisms modeled; and indirect effects such as release of grazing and predation pressure, increase in detritus and recycling of nutrients from killed organisms, dissolved oxygen sag due to increased decomposition, and loss of food base for animals.

AQUATOX represents the aquatic ecosystem by simulating the changing concentrations (in mg/L or g/m^3) of organisms, nutrients, chemicals, and sediments in a unit volume of water (Figure 1). As such, it differs from population models, which represent the changes in numbers of individuals. As O'Neill et al. (1986) stated, ecosystem models and population models are complementary; one cannot take the place of the other. Population models excel at modeling individual species at risk and modeling fishing pressure and other age/size-specific aspects; but recycling of nutrients, the combined fate and effects of toxic chemicals, and other interdependencies in the aquatic ecosystem are important aspects that AQUATOX represents and that cannot be addressed by a population model.

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[1] To download the AQUATOX Source code go to the "Help" menu and select "About" and click on the "Source Code" button.

Figure 1. Conceptual model of ecosystem represented by AQUATOX
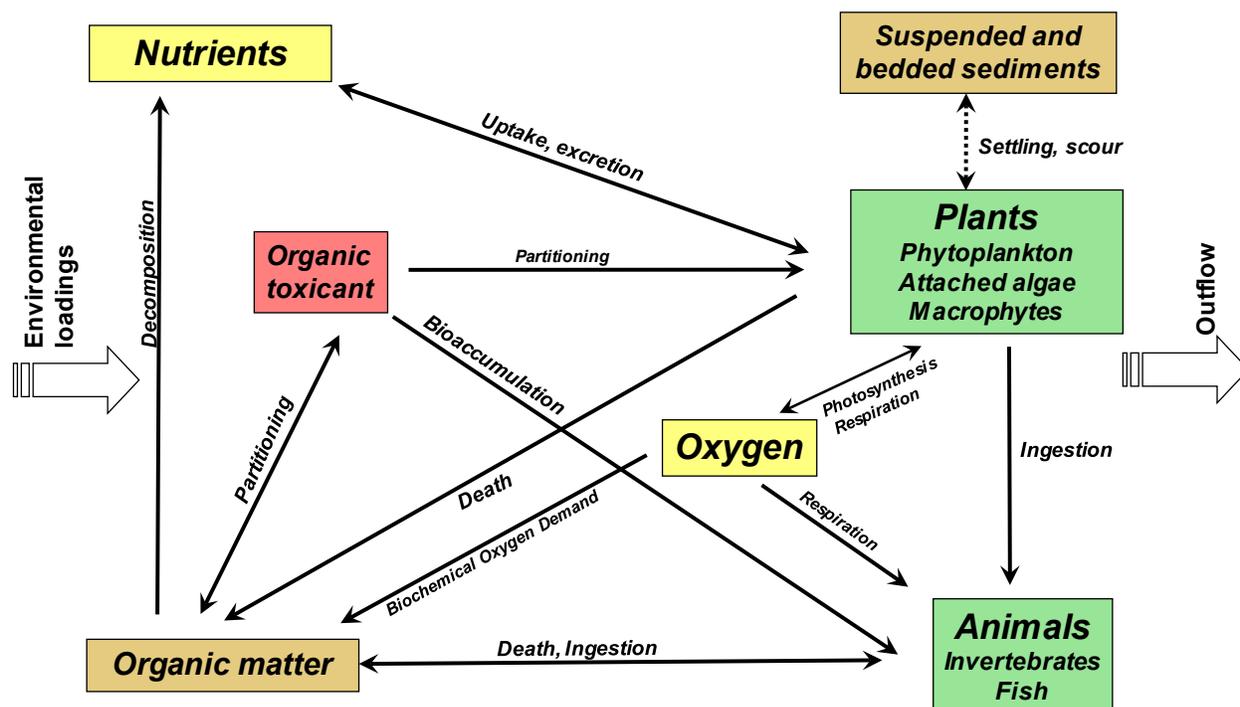
Any ecosystem model consists of multiple components requiring input data. These are the abiotic and biotic **state variables** or compartments being simulated (Figure 2). In AQUATOX the biotic state variables may represent trophic levels, guilds, and/or species. The model can represent a food web with both detrital- and algal-based trophic linkages. Closely related are **driving variables**, such as temperature, light, and nutrient loadings, which force the system to behave in certain ways. In AQUATOX state variables and driving variables are treated similarly in the code. This provides flexibility because external loadings of state variables, such as phytoplankton carried into a reach from upstream, may function as driving variables; and driving variables, such as temperature, could be treated as dynamic state variables in a future implementation. Constant, dynamic, and multiplicative loadings can be specified for atmospheric, point- and nonpoint sources. Loadings of pollutants can be turned off at the click of a button to obtain a **control** simulation for comparison with the **perturbed** simulation.

Figure 2. State variables in AQUATOX as implemented for Cahaba River, Alabama.
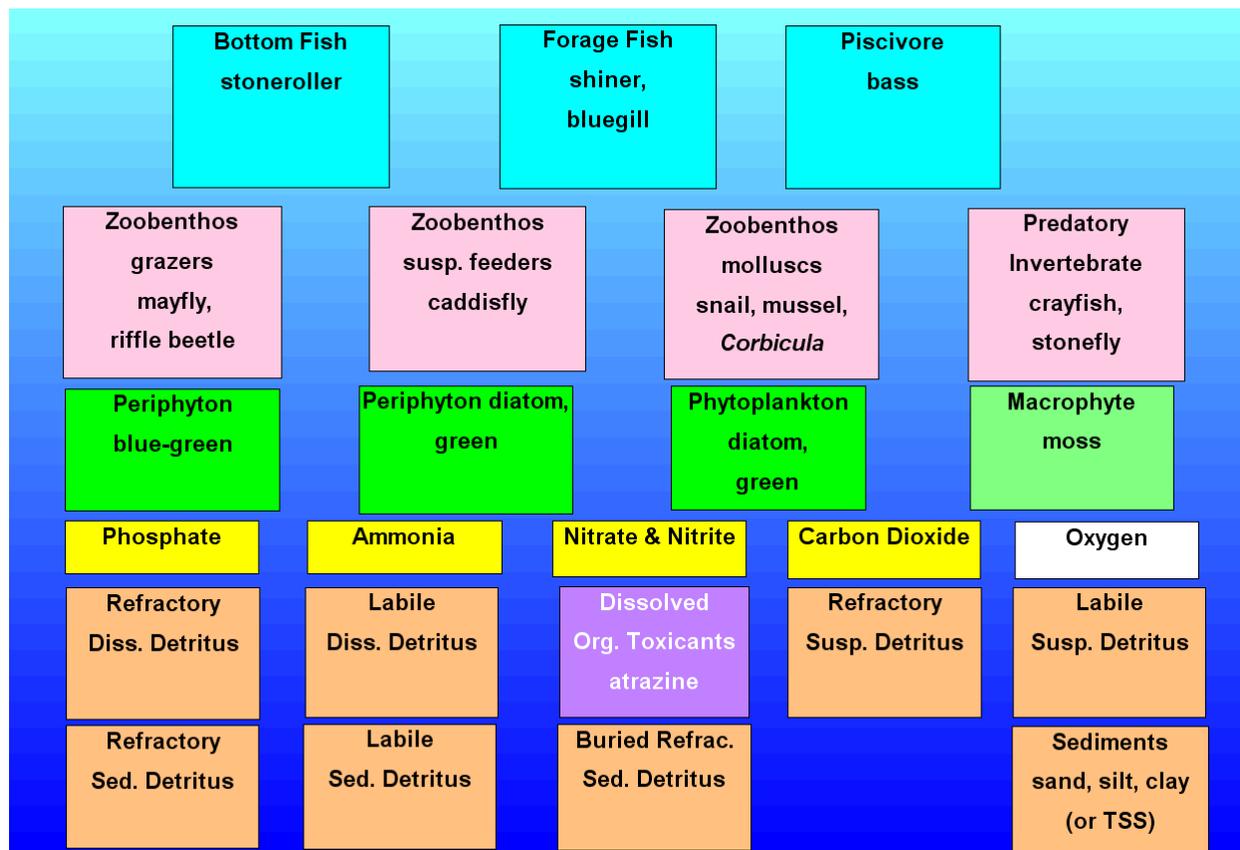
The model is written in object-oriented Pascal using the Delphi programming system for Windows. An object is a unit of computer code that can be duplicated; its characteristics and methods also can be inherited by higher-level objects. For example, the organism object, including variables such as the *LC50* (lethal concentration of a toxicant) and process functions such as respiration, is inherited by the plant object; that is enhanced by plant-specific variables and functions and is duplicated for four kinds of algae; and the plant object is inherited and modified slightly for macrophytes and moss. This modularity forms the basis for the remarkable flexibility of the model, including the ability to add and delete given state variables interactively.

AQUATOX utilizes **differential equations** to represent changing values of state variables, normally with a reporting time step of one day. These equations require starting values or **initial conditions** for the beginning of the simulation. If the first day of a simulation is changed, then the initial conditions may need to be changed. A simulation can begin with any date and may be for any length of time from a few days, corresponding to a microcosm experiment, to decades, corresponding to an extreme event followed by long-term recovery.

The **process equations** contain another class of input variables: the **parameters** or **coefficients** that allow the user to specify key process characteristics. For example, the maximum consumption rate is a critical parameter characterizing various consumers. AQUATOX is a

mechanistic model with many parameters; however, default values are available so that the analyst only has to be concerned with those parameters necessary for a specific risk analysis, such as characterization of a new chemical. In the pages that follow, differential equations for the state variables will be followed by process equations and parameter definitions.

Finally, the system being modeled is characterized by **site constants**, such as mean and maximum depths. At present one can model lakes, reservoirs, streams, small rivers, estuaries, and ponds- and even enclosures and tanks. The "Generalized Parameter" screen is used for all these site types, although some, such as the hypolimnion and estuary entries, obviously are not applicable to all. The temperature and light constants are used for simple forcing functions, blurring the distinctions between site constants and driving variables.

<div align="center">

Table 1. Model Overview Summary (also see Section 2.1)

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Category:	Summary:	Notes:
Reporting Time Step	Daily or Hourly	time-step over which equations are solved
Differentiation	Variable time-step Runge Kutta (with fixed time-step option)	smaller step sizes than the reporting time-step may be utilized to reduce relative error
Output Averaging	Variable	editable by user
Conceptual Approach	Kinetic; biomass model	no longer a fugacity option for chemicals; individual organisms are not modeled
Horizontal Spatial Resolution	Point model, or 1D and 2D with linked segments	modeled units can be a lake, river, reservoir, stream segment, estuary, or enclosure
Vertical Spatial Resolution	Vertically stratified water column when relevant	user-specified or model calculated dates of stratification
Sediment Bed	Multiple sediment bed options	active layer only, multi-layer sediments, sediment diagenesis submodels
Boundary Conditions	Inflows and outflows of all state variables (dissolved oxygen, nutrients, biota, detritus, and toxic organics)	water inflow, point sources, nonpoint sources, direct precipitation, separate tributary inputs
Ecological Complexity	Variable—user can model representative groups or individual species	can model abiotic conditions or single macrophyte species in a water tank up to dozens of plant and animal species in a complex river or reservoir system
Chemical Complexity	Zero to 20 organic chemicals	biotransformation to daughter products may be modeled
Mass Balance Tracking	For nutrients and chemicals	

1.2 Background

AQUATOX 3.2 is an update to AQUATOX Release 3 (see section 1.6 below for a list of updates in Release 3.2). AQUATOX Release 3 was the result of an effort to combine all of the various versions of AQUATOX into a single consolidated version. Models that were combined to produce Release 3 included:

- AQUATOX Multi-Segment version
- AQUATOX Estuarine Version

- AQUATOX PFA Model (Perfloroalkylated Surfactants)

Each of these versions is discussed in a separate section below.

AQUATOX is the latest in a long series of models, starting with the aquatic ecosystem model CLEAN (Park et al., 1974) and subsequently improved in consultation with numerous researchers at various European hydrobiological laboratories, resulting in the CLEANER series (Park et al., 1975, 1979, 1980; Park, 1978; Scavia and Park, 1976) and LAKETRACE (Collins and Park, 1989). The MACROPHYTE model, developed for the U.S. Army Corps of Engineers (Collins et al., 1985), provided additional capability for representing submersed aquatic vegetation. Another series started with the toxic fate model PEST, developed to complement CLEANER (Park et al., 1980, 1982), and continued with the TOXTRACE model (Park, 1984) and the spreadsheet equilibrium fugacity PART model. AQUATOX combined algorithms from these models with ecotoxicological constructs; and additional code was written as required for a truly integrative fate and effects model (Park, 1990, 1993). The model was then restructured and linked to Microsoft Windows interfaces to provide greater flexibility, capacity for additional compartments, and user friendliness (Park et al., 1995). The current version has been improved with the addition of constructs for sublethal effects and uncertainty analysis, making it a powerful tool for probabilistic risk assessment.

This technical documentation is intended to provide verification of individual constructs or mathematical and programming formulations used within AQUATOX. The scientific basis of the constructs reflects empirical and theoretical support; precedence in the open literature and in widely used models is noted. Units are given to confirm the dimensional analysis. The mathematical formulations have been programmed and graphed in spreadsheets and the results have been evaluated in terms of behavior consistent with our understanding of ecosystem response; many of those graphs are given in the following documentation. The variable names in the documentation correspond to those used in the program so that the mathematical formulations and code can be compared, and the computer code has been checked for consistency with those formulations.   Much of this has been done as part of the continuing process of internal review. Releases 2 and 3 of the AQUATOX model and documentation have undergone successful peer reviews by external panels convened by the U.S. Environmental Protection Agency.   Release 3 has also been described in the peer-reviewed literature (Park et al. 2008).

Release 3 has significant additional capabilities compared to Release 2.2:

- The full source code is now available. To download the open-source codebase use the "Source Code" button in the model's "About" window.
- Link to WEB-ICE (Interspecies Correlation Estimates) database and graphics
- Sediment diagenesis based on the Di Toro model
- Optional hourly time step with diel oxygen, light, and photosynthesis;
- Low oxygen effects
- Toxicity due to ammonia
- Suspended and bedded sediment effects on organisms; % embeddedness

- Calcium carbonate precipitation and removal of phosphorus
- Adaptive light limitation for plants
- Linked periphyton and phytoplankton compartments
- Conversions for many units in input screens
- User-specified seasonally varying thermocline depth
- User-specified reaeration constant in addition to alternative estimation procedures
- Improved CBOD to organic matter estimation
- Estuarine reaeration incorporating salinity
- Sensitivity analysis with tornado diagrams
- Correlation of variables in uncertainty analysis
- Sediment oxygen demand (SOD) output
- Enhanced graphics including log plot, duration and exceedance graphs, and threshold analysis
- Option to export all graphs to Microsoft Word
- Output of statistics for all graphed model results
- Output of trophic state indices and ecosystem bioenergetics such as gross primary productivity and community respiration
- Integrated user's manual and context-sensitive help files

1.3 The Multi-Segment Version

The AQUATOX Multi-Segment version was developed and applied for the EPA Office of Water in support of the Modeling Study of PCB Contamination in the Housatonic River. Capabilities introduced with this version include the linkage of individual AQUATOX segments into a single simulation. Segments can be linked together in a manner that allows feedback into the upstream segment or a one-way "cascade" linkage can be created. More information about the physical characteristics of linked segments may be found in Section 3.8 of this document.

Additionally, a sediment submodel was added to the AQUATOX model to enable tracing the passage of toxicants within a multi-layered sediment bed. Specifications for this multi-layer sediment model may be found in section 6.2 of this document.

1.4 The Estuarine Submodel

The Risk Assessment Division (RAD), EPA Office of Pollution Prevention and Toxics, is responsible for assessing the human health and ecological risks of new and existing chemicals that are regulated under the Toxic Substances Control Act (TSCA). RAD has partially funded AQUATOX from its initial conceptualization. Many of the industrial chemicals regulated under TSCA are discharged into estuarine environments.

Therefore, AQUATOX's capabilities were enhanced by adding salinity and other components (including shore birds) that would be needed to simulate an estuarine environment. The estuarine version of AQUATOX is intended to be an exploratory model for evaluating the possible fate and effects of toxic chemicals and other pollutants in estuarine ecosystems. The model is not intended to represent detailed, spatially varying site-specific conditions, but rather to be used in representing the potential behavior of chemicals under average conditions. Therefore, it is best used as a screening-level model applicable to data-poor evaluations in estuarine ecosystems.

Complete documentation for the AQUATOX estuarine submodel may be found in Chapter 10 of this document.

1.5 The PFA Submodel

The bioaccumulation and effects of a group of chemicals known as perfluorinated surfactants has been of recent interest. There are two major types of perfluorinated surfactants: perfluoro-alkanesulfonates and perfluorocarboxylates. The perfluorinated compounds of interest as bioaccumulators are the perfluorinated acids (PFAs). Perfluoroctane sulfonate (PFOS) belongs to the sulfonate group and perfluorooctanoic acid (PFOA) belongs to the carboxylate group. These persistent chemicals have been found in humans, fish, birds, and marine and terrestrial mammals throughout the world. PFOS has an especially high bioconcentration factor in fish. The principal focus was on PFOS because of its prevalence and the availability of data. Because both chemical classes contain high- and low-chain homologs, AQUATOX will be useful in estimating the fate and effects of a wide range of molecular weight components where actual data are not available for every homolog.

Complete documentation for the AQUATOX Perfloroalkylated Surfactants model may be found in Section 8.13 of this document.

1.6 AQUATOX Release 3.2 Overview

Additional capabilities are available in Release 3.2 as compared to Release 3.   Some highlights follow:

- Addition of sediment-diagenesis "steady-state" mode to significantly increase model speed;
- Modification of denitrification code in order to simplify calibration and to achieve alignment with other models;
- Enabled importation of equilibrium CO_2 concentrations to enable linkage to CO2SYS and similar models;
- New CBOD to organic matter conversion relying on percent-refractory detritus input; Input and output BOD is clarified to be "carbonaceous" BOD.
- Floating plants refinements
  - Added floating option for plants other than cyanobacteria (formerly known as "blue-green algae)

- • Converted the averaging depth for floating plants to the top three meters to more closely correspond to monitoring data
- • Floating plants now explicitly move from the hypolimnion to the epilimnion when a system is stratified.
- • Modifications to PFA (perfluoroalkylated surfactants) model to increase flexibility:
  - • Uptake rates (K1s) and elimination rates (K2s) are visible and editable for animals and plants
  - • New interface to estimate animal K1s and K2s as a function of chain length
  - • Improved gill-uptake equation for invertebrates.
- • Bioaccumulation and toxicity modeling improvements:
  - • Optional alternative elimination-rate estimation for animals based on Barber (2003) ;
  - • Updated ICE (toxicity regressions), based on new EPA models released in February 2010 and improved AQUATOX ICE interface;
  - • Addition of output of K1, K2, and BCF estimates.
- • Improved sensitivity and uncertainty analyses
  - • "Output to CSV" option for uncertainty runs so that complete results for every iteration may be examined;
  - • Option for non-random sampling for "statistical sensitivity analyses";
  - • A "reverse tornado" diagram (effects diagram) that shows the effects of each parameter change on the overall simulation;
  - • Nominal range sensitivity analysis has been added for linked segment applications.
- • Database Improvements
  - • AQUATOX database search functions dramatically improved.
  - • "Scientific Name" field added to Animal and Plant databases.
- • Interface and Data Input Improvements
  - • Software and software installer is 64-bit OS compatible;
  - • Added an option in the "Setup" screen to trigger nitrogen fixation based on the N to P ratio.
  - • Addition of output variables to clarify whether photosynthesis is sub-optimal due to high-light or low-light conditions.
  - • Time-varying evaporation option in the "Site" screen with linkage from the "Water Volume" screen
  - • Grid mode within a study so that all animal, plant, and chemical parameters in a study can be examined, edited, and then exported to Excel
  - • Added capability to input time-series loads of organisms based on fish stocking
  - • Updated HSPF WDM file linkage to be more generally applicable (does not require use of WinHSPF).
  - • Enabled hourly loadings for the following variables: all nutrients, CO_2, Oxygen, Inorganic suspended sediments (sand/silt/clay), TSS, Light, Organic Matter

- "Graph Setup" window now enabled for linked-mode graphics.
- Other minor interface improvements.

Documentation for each of these enhancements may be found in this technical documentation volume or in the User's Manual.

Release 3.1 plus Update

In 2014, EPA Release 3.1 plus was released with several additions to the model. Most importantly, the option to model nutrient limitation in plants based on internal rather than external nutrients was added. The internal concentration of P and N in each plant is tracked with a separate state variable (See *Internal Nutrients* in section 4.1 of this document). This allows for luxury uptake of nutrients during high-nutrient periods and expenditure of nutrient stores during lower-nutrient periods. Concentrations of internal nutrients and derivative rates may be output from these new state variables as well as the nutrient-to-organism ratio for each plant. Internal-nutrient simulations maintain nutrient mass balance throughout.

Other enhancements are listed below:

- The capability to load and save observed data sets to a file, to move these data from one study to another, was added to the interface.
- Improving the use of cached loading and saving of data has significantly optimized loading and saving of large "aps" or "als" files.
- In non-estuary segments, the sinking of plants and suspended detritus is now affected by salinity and the density of water when relevant.
- New outputs are produced for net-primary productivity, pelagic-invertebrate biomass, benthic- invertebrate biomass, and fish biomass.
- The default line-thickness on graphs is now 2 pixels to improve visibility.
- The maximum respiration rate and maximum consumption rate fields are now auto-calculated when allometric consumption or allometric respiration models are utilized. This helps to ensure parameters are producing a reasonable allometric model.
- Low-light limitation and high-light limitation (part of plant "rates" outputs) now show 1.0 if they are not the limiting factor, which is more intuitive than 0.0.
- "Gameteloss" is limited so that it is not allowed to exceed the total percent gametes of the organism.
- Moving waters (rivers and streams) are not predicted to ice over until their average water temperature drops below 0 degrees centigrade.
- A macrophyte mortality calculation bug was fixed; the model was not adding the "mortality coefficient" effect properly
- A few other minor interface glitches have been fixed to improve model usability.

Release 3.2 Update

In 2017, EPA Release 3.2 was produced. This version replaces the obsolete paradox database management system (used in previous versions) with SQLite databases.   In addition, the model now can write all model inputs and outputs in ASCII format by saving files with a "*.txt" extension. This allows users to view and change model inputs without using the graphical user interface. Another model upgrade is a command-line version, which allows users to execute and manipulate the model using a DOS command prompt. For information about how to use each of these updates, please see the Release 3.2 *User's Manual*.

In addition to the interface changes discussed above, changes were made to the model to represent the "nearshore marine environment" as discussed here.

Nearshore Marine Environment

AQUATOX Release 3.2 was designed to extend the existing AQUATOX estuarine version to include improved capabilities for situations encountered in the nearshore marine environment. Several changes were required to model food webs in the marine environment. The most notable updates include:

- Additional equations to model the physical complexity of oyster reefs and the marsh-edge environment;
- The capability to model size-classes of oysters and crabs within the model
- New invertebrate-modeling capabilities including allometric bioenergetics equations and burrowing refuge from predation; and,
- As discussed in Chapter 4, to better represent marine-biology conventions, the guilds used by AQUATOX to characterize these state variables were reorganized.

Differences from Release 3.1 plus

Most model simulations created in Release 3.1 and Release 3.1 plus produce identical or nearly-identical results in Release 3.2. A few differences are visible in some studies, however. Nutrient quantities may be slightly different because of a change in the animal-respiration equation **(100)**. This can have some ripple effects, especially in systems with long retention times.   Other changes to the process code that could affect model results follow:

- The BCF equation **(1)** has been changed to take into account metabolism of organic chemicals.
- A bug was fixed when the user has selected the "Calculate BCF" option **Alternative Uptake Mode**. The wrong equation was being used to calculate BCF in this seldom-used model option. See section 8.8 for more information.
- Carrying capacity was not utilized as a parameter for benthic invertebrates previously, but now is considered a hard cap based on habitat limitations. See equation **(109b).**

1.7 Comparison with Other Models

The following comparison is taken from Park et al. (2008):

The model is perhaps the most comprehensive aquatic ecosystem simulation model available, as can be seen by comparison with other representative dynamic models being used for risk assessment (Table 2). All the models, with the exception of QSim and CASM, are public domain. The closest to AQUATOX in terms of scope is the family of CATS models developed by Traas and others (Traas et al., 1996; Traas et al., 1998; Traas et al., 2001); these ecotoxicology models have simple representations of growth and are not as suitable as AQUATOX for detailed analyses of eutrophication effects. CASM (DeAngelis et al., 1989; Bartell et al., 1999) is similar to CATS, with simplified growth terms, but it lacks a toxicant fate component. QUAL2K (Chapra et al., 2007) and WASP (Di Toro et al., 1983; Wool et al., 2004) are water quality models that share many functions with AQUATOX, including benthic algae (Martin et al., 2006); WASP also models fate of toxicants. The hydraulic and water quality models EFDC (Tetra Tech Inc., 2002) and HEM3D (Park et al., 1995a) are often combined; EFDC has also been used to provide the flow field for linked segments in AQUATOX, resulting in a similar representation. AQUATOX, QUAL2K, WASP, and EFDC include the sediment diagenesis model for remineralization (Di Toro, 2001). WASP and the bioaccumulation model QEAFdChn (Quantitative Environmental Analysis, 2001) have been combined in the Green Bay Mass Balance (GBMB) study (U.S. Environmental Protection Agency, 1989), which Koelmans et al. (2001) considered to be more accurate for portraying bioaccumulation than AQUATOX. However, GBMB does not include an ecotoxicology component. BASS (Barber, 2001) is a very detailed bioaccumulation and ecotoxicology model; it provides better resolution than AQUATOX in modeling single species, but so far it has only been applied to fish and does not include ecosystem dynamics. The German model QSim (Schöl et al., 1999; Schöl et al., 2002; see also Rode et al., 2007) has detailed ecosystem functions and has been applied in studying impacts of both eutrophication and hydraulics on river ecosystems. Similar to AQUATOX, it has been used to analyze relationships between plankton and mussels and impacts of oxygen depletion. Further comparison of models can be found in a book by Pastorok et al. (2002).

Table 2.   Comparison of AQUATOX with other representative dynamic models used for risk assessment (Park et al. 2008).

State variables and processes	AQUATOX	CATS	CASM	Qual2K	WASP7	EFDC-HEM3D	QEAFdChn	BASS	QSim
Nutrients	X	X	X	X	X	X			X
Sediment diagenesis	X			X	X	X			
Detritus	X	X	X	X	X	X			X
Dissolved oxygen	X		X	X	X	X			X
DO effects on biota	X								X
pH	X			X					X
NH₄ toxicity	X								
Sand/silt/clay	X				X	X			
Sediment effects	X								
Hydraulics						X			X
Heat budget				X	X	X			X
Salinity	X				X	X			
Phytoplankton	X	X	X	X	X	X			X
Periphyton	X	X	X	X	X				X
Macrophytes	X	X	X						X
Zooplankton	X	X	X						X
Zoobenthos	X	X	X						X
Fish	X	X	X					X	X
Bacteria			X						X
Pathogens				X		X			
Organic toxicant fate	X	X			X			X	
Organic toxicants in									
Sediments	X	X			X	X			
Stratified sediments	X				X	X			
Phytoplankton	X	X							
Periphyton	X	X							
Macrophytes	X	X							
Zooplankton	X	X					X		
Zoobenthos	X	X					X		
Fish	X	X					X	X	
Birds or other animals	X	X							
Ecotoxicity	X	X	X					X	
Linked segments	X			X	X	X	X		X

1.8 Intended Application of AQUATOX

AQUATOX is intended to be used at any one of several levels of application. Like any model, it is best used as one of several tools in a weight-of-evidence approach. The level of required precision, rigor, data requirements and user effort depend upon the goals of the modeling exercise and the potential consequences of the model results.

Perhaps its most widespread use is as a screening-level model requiring few changes to default studies and parameters. In fact, it was originally developed as an evaluative model to assess the fate and effects of pesticides and industrial organic chemicals in representative or "canonical" environments; these include ponds and pond enclosures, experimental streams, and a representative estuary. It is especially useful in taking the place of expensive, labor-intensive mesocosm tests. It has been calibrated and validated with data from pond enclosures, experimental streams, and a polluted harbor. In one early application, AQUATOX was driven with predicted pesticide runoff into a farm pond adjacent to a corn field using the field model PRZM. Also, with little effort the model can provide insights into the potential impacts of invasive species and the possible effects of control measures, such as pesticide application, on the aquatic ecosystem.

In recent years AQUATOX has been applied as part of the process of developing water quality

targets for nutrients, and comparing model-derived values with regional criteria developed empirically. This application has involved setting up the model and calibrating with available data for rivers and reservoirs receiving nutrients from wastewater treatment plants, agricultural runoff, and background "natural" loadings. It has been our experience that this entails a substantial level of effort, especially if the system is spatially heterogeneous, which then requires application of linked segments. A certain amount of site-specific biotic, water quality and flow data is required, as well as pollutant loading data, for calibration. However, once the model is set up and calibrated for a site, it is relatively easy to represent a series of loading scenarios and determine threshold nutrient levels for deleterious impacts such as nuisance algal blooms and anoxia. This process is facilitated by the fact that the model has been calibrated across nutrient, turbidity, and discharge gradients, resulting in robust parameter sets that span these conditions. This is important because the intent of setting water quality targets is to model ecological communities under *changing* conditions as a result of environmental management decisions; this would give better assurance that the sometimes costly nutrient reduction actions would render the desired environmental result.

The most intensive, time-consuming application of AQUATOX is in environmental remediation projects, such as SUPERFUND. Because of the likely litigation and the potential for costly remediation, this level of application requires site-specific calibration and validation using quality-assured data collected specifically for the model. In dynamic systems, linkage to an equally well calibrated and validated hydrodynamic model is essential to represent, for example, burial and exhumation of contaminated sediments. Several of the more powerful features of the model, such as the linked segments and IPX layered-sediment submodel, were developed for this type of application. Unfortunately, the one remediation application performed by the model developers cannot be published because of continuing litigation.

2. SIMULATION MODELING

2.1 Temporal and Spatial Resolution and Numerical Stability

AQUATOX Release 3 is designed to be a general, realistic model of the fate and effects of pollutants in aquatic ecosystems. In order to be fast, easy to use, and verifiable, it was originally designed with the simplest spatial and temporal resolutions consistent with this objective. Release 3 may still be run as a non-dimensional point model. However, unlike previous versions of AQUATOX, in Release 3 spatial segments may be linked together to form a two- or three-dimensional model if a more complicated spatial resolution is desired.

> **Simulation Modeling: Simplifying Assumptions**
>
> - Each modeled segment is well-mixed
> - Model is run with a daily or hourly maximum time-step.
> - Results are trapezoidally integrated

The model generally represents average daily conditions for a well-mixed aquatic system. Each segment in a multi-dimensional run is also assumed to be well-mixed in each time-step. AQUATOX also represents one-dimensional vertical epilimnetic and hypolimnetic conditions for those systems that exhibit stratification on a seasonal basis. Multi-segment systems also can be set up with vertical stratification.   Furthermore, the effects of run, riffle, and pool environments can be represented for streams. Results may be plotted in the AQUATOX output screen with the capability to import observed data to examine against model predictions.

While the model is generally run with a daily maximum time-step, the temporal resolution of the model can also be reduced to an hourly maximum time-step. This capability was added so that AQUATOX can represent diel oxygen. See sections 3.6 and 5.5 for more information on how this choice of hourly time-step affects AQUATOX equations. The reporting step can be as long as several years or as short as one hour; results are integrated to obtain the desired reporting time period.

According to Ford and Thornton (1979), a one-dimensional model is appropriate for reservoirs that are between 0.5 and 10 km in length; if larger, then a two-dimensional model disaggregated along the long axis is indicated. The one-dimensional assumption is also appropriate for many lakes (Stefan and Fang, 1994). Similarly, one can consider a single reach or stretch of river at a time.

Usually the reporting time step is one day, but numerical instability is avoided by allowing the step size of the integration to vary to achieve a predetermined accuracy in the solution. (This is a numerical approach, and the step size is not directly related to the temporal scale of the ecosystem simulation.) AQUATOX uses a very efficient fourth- and fifth-order Runge-Kutta integration routine with adaptive step size to solve the differential equations (Press et al., 1986, 1992). The routine uses the fifth-order solution to determine the error associated with the fourth-order solution; it decreases the step size (often to 15 minutes or less) when rapid changes occur and increases the step size when there are slow changes, such as in winter. However, the step size is constrained to a maximum of one day (or one hour in hourly simulations) so that short-term pollutant loadings are always detected. The reporting step, on the other hand, can be as

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long as several years or as short as one hour; results are integrated to obtain the desired reporting time period.

As an alternative, the user may specify an exact step size that is used thoughout the simulation. This is similar to the way that many models solve the differential equations. The disadvantage is that the accuracy of the solution may not be maintained. However, it is useful under some circumstances and is discussed more fully later in this section.

The temporal and spatial resolution is in keeping with the generality and realism of the model (see Park and Collins, 1982). Careful consideration has been given to the hierarchical nature of the system. Hierarchy theory tells us that models should have resolutions appropriate to the objectives; phenomena with temporal and spatial scales that are significantly longer than those of interest should be treated as constants, and phenomena with much smaller temporal and spatial scales should be treated as steady-state properties or parameters (Figure 3; also see O'Neill et al., 1986). AQUATOX uses a longer time step than dynamic hydrologic models that are concerned with representing short-term phenomena such as storm hydrographs, and it uses a shorter time step than fate models that may be concerned only with long-term patterns such as bioaccumulation in large fish.

Figure 3. Position of ecosystem models such as AQUATOX in the spatial-temporal hierarchy of models.
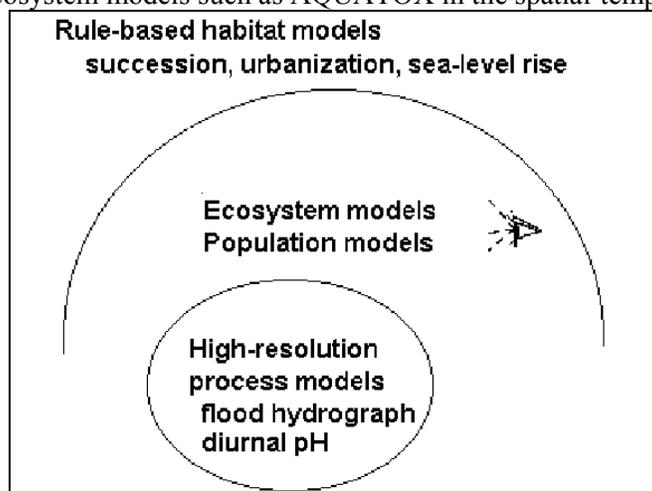
Changing the permissible relative error (the difference between the fourth- and fifth-order solutions) of the simulation can affect the results. The model allows the user to set the relative error, usually between 0.005 and 0.01. Comparison of output shows that up to a point a smaller error can yield a marked improvement in the simulation, although execution time is longer. For example, simulations of two pulsed doses of chlorpyrifos in a pond exhibit a spread in the first pulse of about 0.6 µg/L dissolved toxicant between the simulation with 0.001 relative error and the simulation with 0.05 relative error (Figure 4); this is probably due in part to differences in the timing of the reporting step. However, if we examine the dissolved oxygen levels, which combine the effects of photosynthesis, decomposition, and reaeration, we find that there are pronounced differences over the entire simulation period. The simulations with 0.001 and 0.01 relative error give almost exactly the same results, suggesting that the more efficient 0.01 relative error should be used; the simulation with 0.05 relative error exhibits instability in the oxygen

simulation; and the simulation with 0.1 error gives quite different values for dissolved oxygen (Figure 5). The observed mean daily maximum dissolved oxygen for that period was 9.2 mg/L (U.S. Environmental Protection Agency, 1988), which corresponds most closely with the results of simulation with 0.001 and 0.01 relative error.

Figure 4. Pond with chlorpyrifos in dissolved phase.
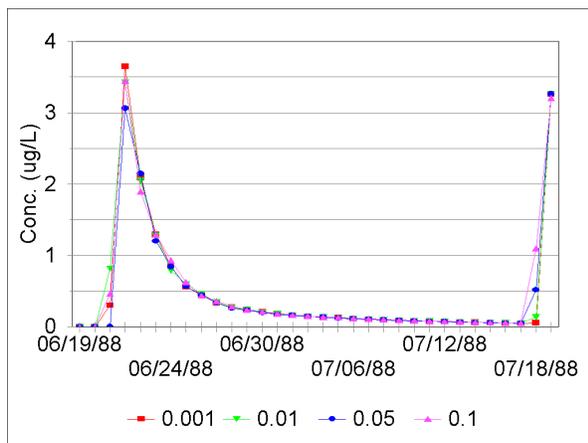
Figure 5. Same as Figure 4 with Dissolved Oxygen.
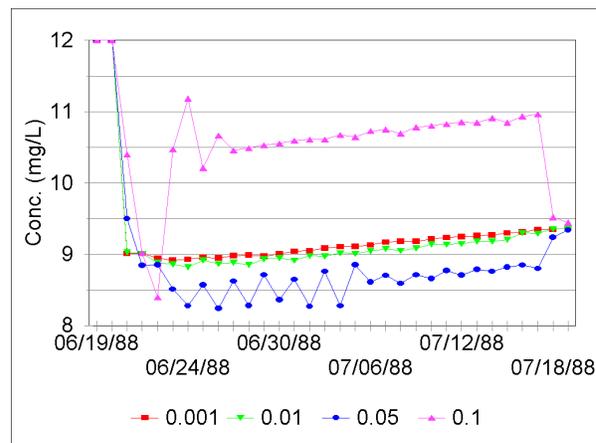
A common use of AQUATOX is to determine the impact of a perturbation in a perturbed simulation when compared with a control simulation. For example, the model is often run with and without a potentially toxic organic chemical, and a percent difference graph is plotted showing how the two simulations differ. Of particular interest is whether there are likely to be significant differences in state variables or other environmental indices at very low concentrations of the chemical. Because a simulation with the toxicant may require a decrease in step size to capture the dynamics of the fate of the toxicant as opposed to a simulation without the toxicant, there may be a mismatch in the step sizes of the two simulations, and the simulations may differ solely on the basis of the difference in numerical resolution. Although decreasing the relative error may decrease the mismatch, there may still be a difference that prevents determination of the "no effects" level of the chemical.

In the example that follows, toxicity of PFOS has been turned off by setting all LC50 and EC50 parameter values to 0. In Figure 6 the default variable step size option has been used with a very small relative error. In Figure 7 the simulation is the same except the constant step size option has been used, and it is readily apparent that there is no difference between the perturbed and control runs.

Figure 6. Percent differences in fish biomass between perturbed simulation with PFOS (toxicity turned off) and control simulation without PFOS, using variable step size (relative error = 0.0001). The differences are purely artifacts of the numerical method.
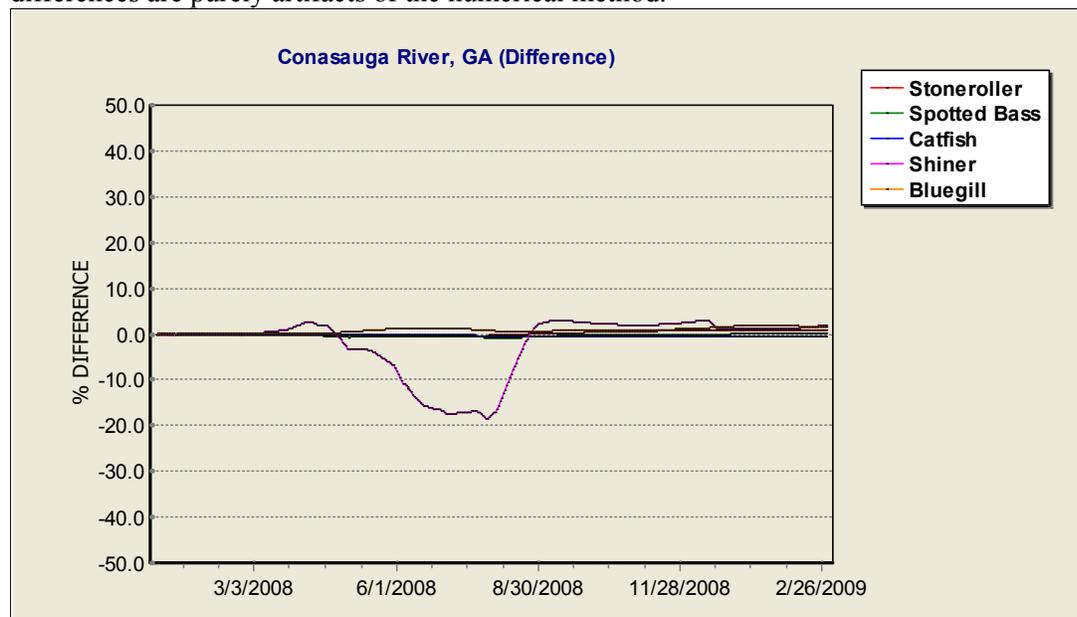
Figure 7. There is no difference in fish biomass between perturbed simulation with PFOS (toxicity turned off) and control simulation without PFOS using a constant step size (0.1 day).
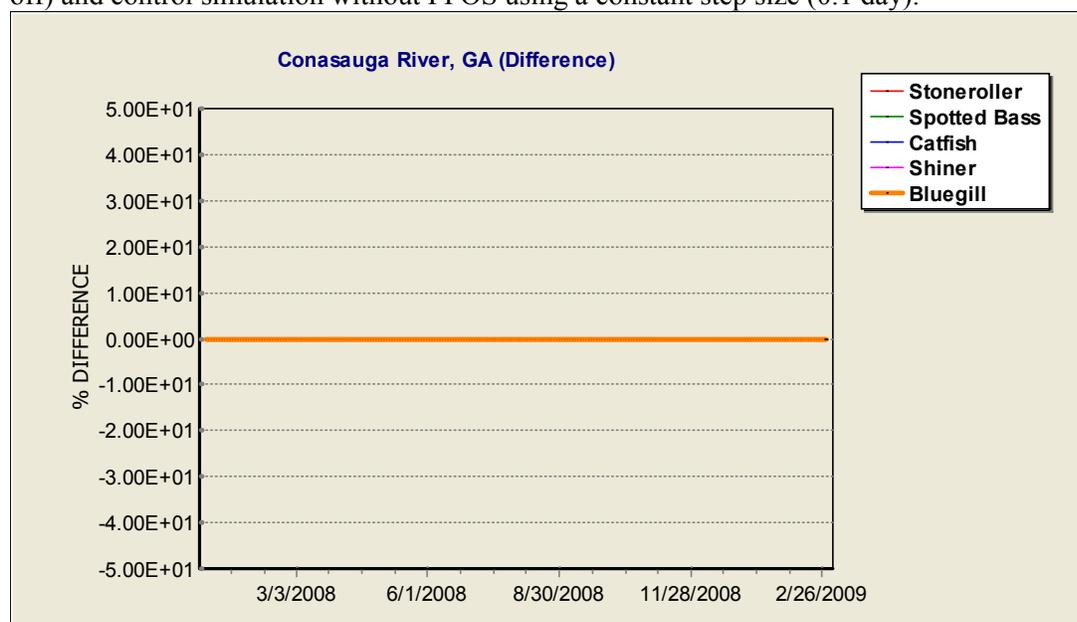
2.2 Results Reporting

The AQUATOX results reporting time step may be set to any desired frequency, from a fraction of an hour to multiple years. The Runge-Kutta differential equations solver produces a series of results of variable frequency; this frequency may be either greater than or less than the reporting time-step.   To standardize AQUATOX output, the user has two options, the trapezoidal

integration of results (default) or the output of "instantaneous" concentrations. Using either of these options, AQUATOX will produce output with time-stamps that match the reporting time-step precisely.

When instantaneous concentrations are requested (in the model's setup screen) AQUATOX returns output precisely at the requested reporting time-step through linear interpolation of the nearest Runge-Kutta results that occur before and after the relevant reporting time-step.

When results are trapezoidally integrated, AQUATOX calculates results by summing all of the trapezoids that can be produced by linear interpolation between Runge-Kutta results and dividing by the results-reporting step-size to get an average result over the reporting step. In Figure 8, for example, the areas of the four shaded trapezoids are summed together and this sum is divided by the results reporting step to achieve an average result over that reporting step. When trapezoidal integration is selected, AQUATOX output is time-stamped at the end of the interval over which the integration is taking place. For example, if a user selects a 366.25 day time-step, the results at the end of the first year will be reflective of all time-steps calculated within that year.

Figure 8. An example of trapezoidal integration.
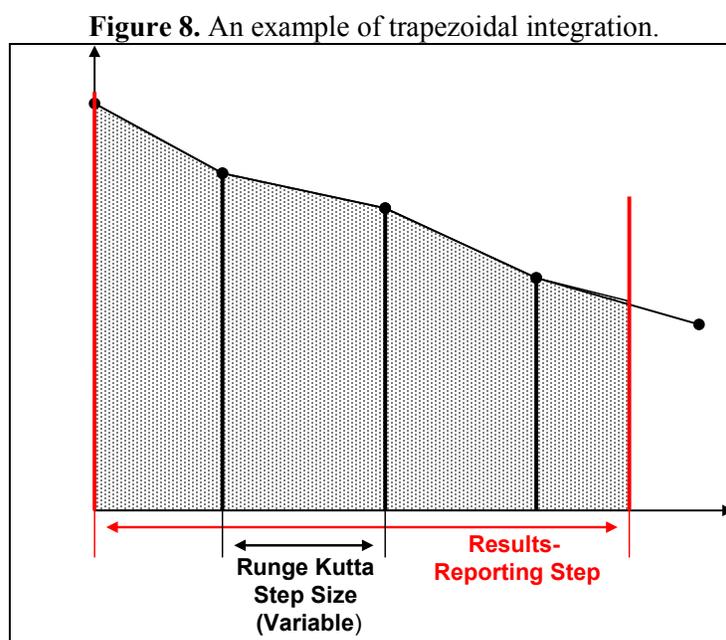
Results may be plotted in the AQUATOX output screen including the capability to import observed data to examine against model predictions.

2.3 Input Data

AQUATOX accepts several forms of input data, a partial list of which follows:

- Point-estimate parameters describing animals, plants, chemicals, sites, and remineralization. Default values for these parameters are generally available from included databases (called "libraries"). The full list of these parameters, their units, and

their manner of reference in the interface, this document, and the source code may be found in Appendix B of this document.

- Time series (or constant values) for nutrient-inflow, organic matter-inflow, and gas-inflow loadings.
- Time series for inorganic sediments in water, water volume variables, and the pH, light, and temperature climates.
- Time series of chemical inflow loadings and initial conditions.
- A feeding preference matrix must be specified to describe the food web in the simulation.
- Additional parameters may be required depending on which submodels are included (e.g. additional sediment diagenesis parameters.)
- Nearly all point-estimate parameters may be represented by distributions when the model is run in uncertainty mode (see section 2.5).

For more discussion of AQUATOX data requirements please see the "Data Requirements" section in the AQUATOX Users Manual (or in the context sensitive help files included with the model software). Furthermore, a *Technical Note on Data Requirements* is available.

For time-series loadings, when a value is input for every day of a simulation, AQUATOX will read the relevant value on each day. If missing values are encountered by the model, a linear interpolation will be performed between the surrounding dates. If the AQUATOX simulation time includes dates before or after the input time-series the model assumes an annual cycle and tries to calculate the appropriate input value accordingly.   Please see the "Important Note about Dynamic Loadings" in the AQUATOX Users Manual (integrated help-file) for a complete description of this process.

2.4 Sensitivity Analysis

"Sensitivity" refers to the variation in output of a mathematical model with respect to changes in the values of the model inputs (Saltelli 2001). It provides a ranking of the model input assumptions with respect to their relative contribution to model output variability or uncertainty (U.S. Environmental Protection Agency 1997).

AQUATOX includes a built-in nominal range sensitivity analysis (Frey and Patil 2001), which may be used to examine the sensitivity of multiple model outputs to multiple model parameters. The user first selects which model parameters to

Simplifying Assumptions:
- Parameters are treated as independent
- Feeding preference matrices are not included
- Sensitivity is compared for the last step of the simulation
Caution
- 10% change is appropriate, a large change can exceed reasonable values and give misleading results

vary and which output variables to track. The model iteratively steps through each of the parameters and varies them by a given percent in the positive and negative direction and saves model results in an Excel file.

A *sensitivity statistic* may then be calculated such that when a 10% change in the parameter results in a 10% change in the model result, the sensitivity is calculated as 100%.

$$Sensitivity = \frac{\left|Result_{Pos} - Result_{Baseline}\right| + \left|Result_{Neg} - Result_{Baseline}\right|}{2 \cdot \left|Result_{Baseline}\right|} \cdot \frac{100}{PctChanged}$$

where:

Sensitivity	=	normalized sensitivity statistic (%);
Result$_{Scenario}$	=	averaged AQUATOX result for a given endpoint given a positive change in the input parameter, a negative change in the input parameter or no change in the input parameter (baseline)
PctChanged	=	percent that the input parameter is modified in the positive and negative directions.

Sensitivity is computed for the last time step of the simulation, so one usually sets the reporting time step to encompass a year or the entire period of the simulation. For each output variable tracked, model parameters may be sorted on the average sensitivity (for the positive and negative tests) and plotted on a bar chart. The end result is referred to as a "Tornado Diagram." Tornado diagrams may automatically be produced within the AQUATOX output window (Figure 9). When interpreting a tornado diagram, the vertical line at the middle of the diagram represents the deterministic model result. Red lines represent model results when the given parameter is reduced by the user-input percentage while blue lines represent a positive change in the parameter. An "effects diagram" that illustrates the effects of a single parameter change on all tracked outputs can also be created. See the User's Manual (or context-sensitive help) for more information on how to create and interpret these types of output.

When sensitivity analysis is run on a multi-segment model, the user must choose either parameters that are relevant to all segments (e.g. animal or plant parameters) or individual segments (e.g. state-variable initial conditions, or the segment's physical characteristics). The segment for which the parameter is relevant may be selected in the sensitivity analysis setup window (see the User's Manual for more information) Any number of global or segment-specific parameters may be selected for a single sensitivity-analysis; output files will be written for each segment in the simulation.

Figure 9. An example tornado diagram showing calculated sensitivity statistic.

Sensitivity of Chironomid (g/m2 dry) to a 20% change in the 15 most sensitive (tested) parameters

220% - Site: Ave. Epilimnetic Temperature (deg C)
163% - Chironomid: Maximum Temperature (deg. C)
142% - Site: Epi Temp. Range (deg C)
137% - Peri, Green: Max Photosynthetic Rate (1/d)
115% - Temp: Multiply Loading by
102% - Sphaerid: Maximum Temperature (deg. C)
87.2% - Peri, Green: Optimal Temperature (deg. C)
74.8% - Chironomid: Respiration Rate: (1 / d)
68.7% - Mayfly (Baetis: Respiration Rate: (1 / d)
66.7% - Water Vol: Initial Condition (cu.m)
54.2% - Shiner: Optimal Temperature (deg. C)
42.1% - Phyt, Blue-Gre: Max Photosynthetic Rate (1/d)
33.8% - Mayfly (Baetis: Max Consumption (g / g day)
27.9% - Largemouth Ba2: Maximum Temperature (deg. C)
27.2% - Peri High-Nut : Maximum Temperature (deg. C)

Chironomid (g/m2 dry)

2.5 Uncertainty Analysis

There are numerous sources of uncertainty and variation in natural systems. These include: site characteristics such as water depth, which may vary seasonally and from site to site; environmental loadings such as water flow, temperature, and light, which may have a stochastic component; and critical biotic parameters such as maximum photosynthetic and consumption rates, which vary among experiments and representative organisms.

In addition, there are sources of uncertainty and variation with regard to pollutants, including: pollutant loadings from runoff, point sources, and atmospheric deposition, which may vary stochastically from day to day and year to year; physico-chemical characteristics such as octanol-water partition coefficients and Henry Law constants that cannot be measured easily; chemodynamic parameters such as microbial degradation, photolysis, and hydrolysis rates, which may be subject to both measurement errors and indeterminate environmental controls.

Increasingly, environmental analysts and decision makers are requiring probabilistic modeling approaches so that they can consider the implications of uncertainty in the analyses. AQUATOX

Uncertainty Analysis: Strengths

- Use of Latin hypercube sampling is more efficient than brute-force Monte Carlo analysis
- Nearly all variables and parameters may be represented as distributions
- Variables can be correlated

Simplifying Assumptions:

- Feeding preference matrices are not included
- Modeled correlations cannot be perfect (e.g. 1.0) due to limitations of the Iman & Conover method

provides this capability by allowing the user to specify the types of distributions and key statistics for almost all input variables. Depending on the specific variable and the amount of available information, any one of several distributions may be most appropriate. A lognormal distribution is the default for environmental and pollutant loadings. In the uncertainty analysis, the distributions for constant loadings are sampled daily, providing day-to-day variation within the limits of the distribution, reflecting the stochastic nature of such loadings. A useful tool in testing scenarios is the multiplicative loading factor, which can be applied to all loads. Distributions for dynamic loadings may employ multiplicative factors that are sampled once each iteration (Figure 10). Normally the multiplicative factor for a loading is set to 1, but, as seen in the example, under extreme conditions the loading may be ten times as great. In this way the user could represent unexpected conditions such as pesticides being applied inadvertently just before each large storm of the season. Loadings usually exhibit a lognormal distribution, and that is suggested in these applications, unless there is information to the contrary. Figure 11 exhibits the result of such a loading distribution.

Figure 10. Distribution screen for point-source loading of toxicant in water.
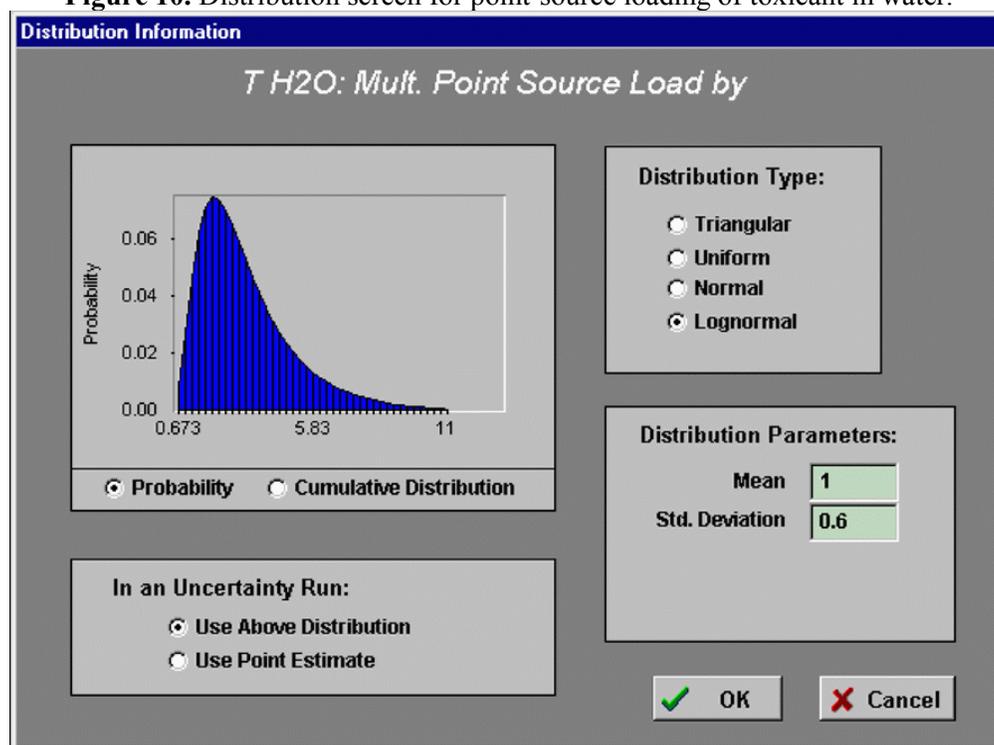
Choice of distribution: A sequence of increasingly informative distributions should be considered for most parameters. If only two values are known and nothing more can be assumed, the two values may be used as minimum and maximum values for a uniform distribution (Figure 12); this is often used for parameters where only two values are known. If minimal information is available but there is reason to accept a particular value as most likely, perhaps based on calibration, then a triangular distribution may be most suitable (Figure 13). Note that the minimum and maximum values for the distribution are constraints that have zero probability of occurrence. If additional data are available indicating both a central tendency and spread of response, such as parameters for well-studied processes, then a normal distribution

may be most appropriate (Figure 14). The result of applying such a distribution in a simulation of Onondaga Lake, New York, is shown in Figure 15, where simulated benthic feeding affects decomposition and subsequently the predicted hypolimnetic anoxia. Most distributions are truncated at zero because negative values would have no meaning (Log Kow is one exception).

Figure 11. Sensitivity of bass (g/m2) to variations in loadings of dieldrin in Coralville Lake, Iowa.
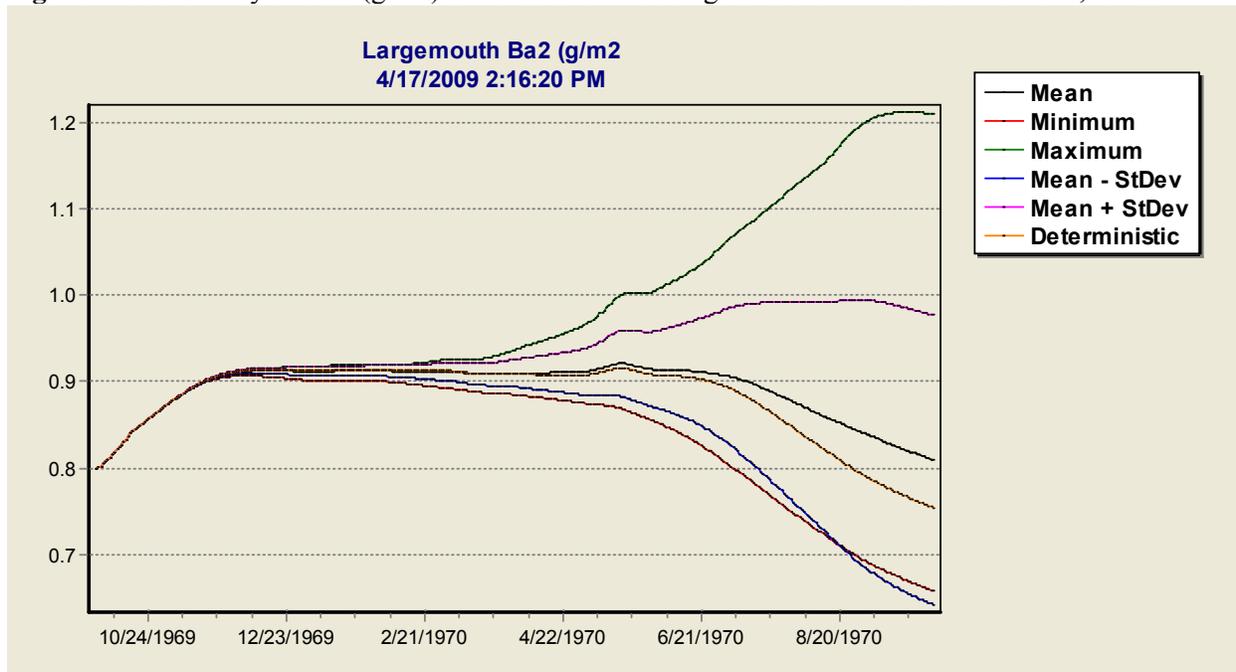
Figure 12. Uniform distribution for Henry's Law constant for esfenvalerate.
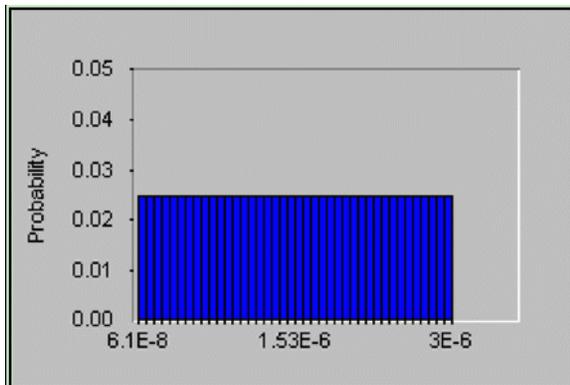
Figure 13. Triangular distribution for maximum consumption rate for bass.
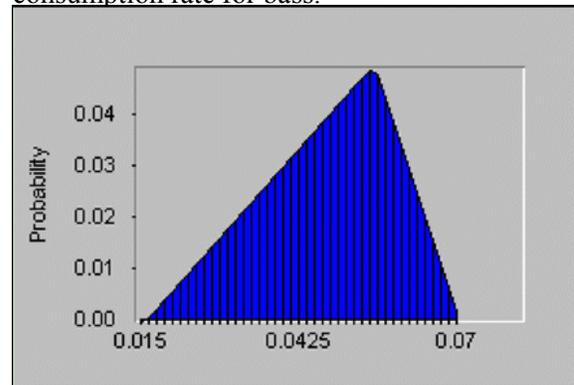
Figure 14. Normal distribution for maximum consumption rate for
the detritivorous invertebrate *Tubifex.*
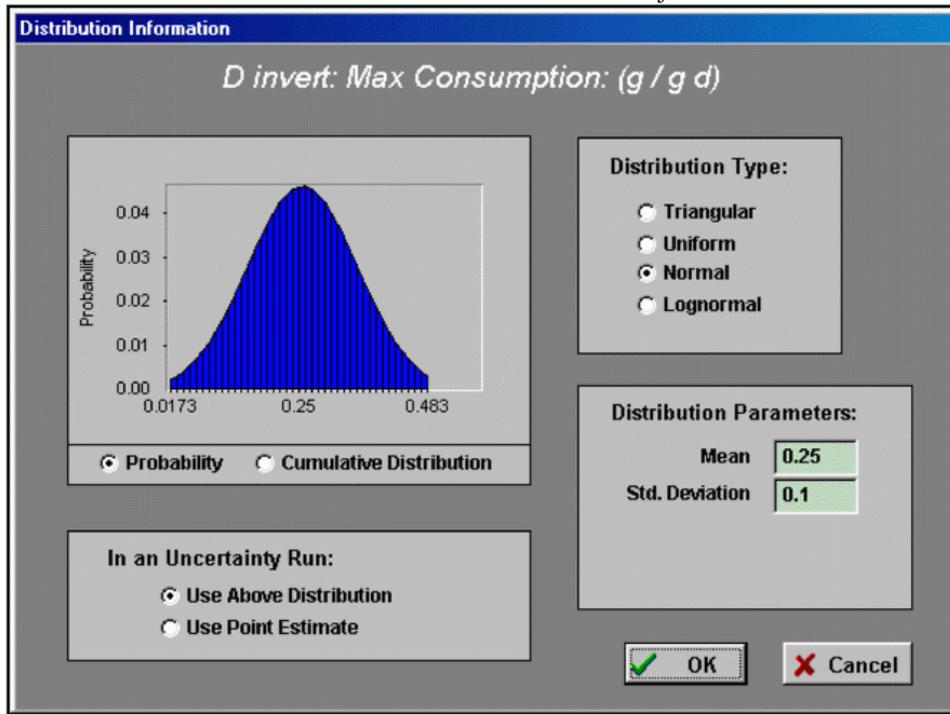
Figure 15. Sensitivity of hypolimnetic oxygen in Lake Onondaga to
variations in maximum consumption rates of detritivores.
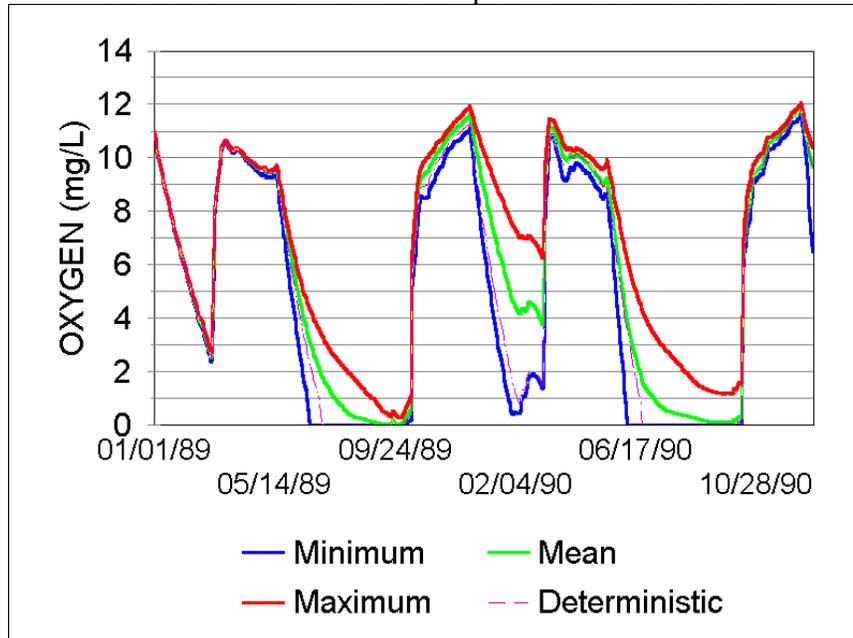
Efficient sampling from the distributions is obtained with the Latin hypercube method (McKay et al., 1979; Palisade Corporation, 1991). Depending on how many iterations are chosen for the analysis, each cumulative distribution is subdivided into that many equal segments. Then a

uniform random value is chosen *within* each segment and used in one of the subsequent simulation runs. For example, the distribution shown in Figure 14 can be sampled as shown in Figure 16.   This method is particularly advantageous because all regions of the distribution, including the tails, are sampled.   A non-random seed can be used for the random number generator, causing the same sequence of numbers to be picked in successive applications; this is useful if you want to be able to duplicate the results exactly.   The default is twenty iterations, meaning that twenty simulations will be performed with sampled input values; this should be considered the minimum number to provide any reliability. The optimal number can be determined experimentally by noting the number required to obtain convergence of mean response values for key state variables; in other words, at what point do additional iterations not result in significant changes in the results? As many variables may be represented by distributions as desired.   Correlations may be imposed using the method of Iman and Conover (1982). By varying one parameter at a time the sensitivity of the model to individual parameters can be determined in a more rigorous way than nominal range sensitivity offers.   This is done for key parameters in the following documentation.

Figure 16.   Latin hypercube sampling of a cumulative distribution with a mean of 25 and standard deviation of 8 divided into 5 intervals.
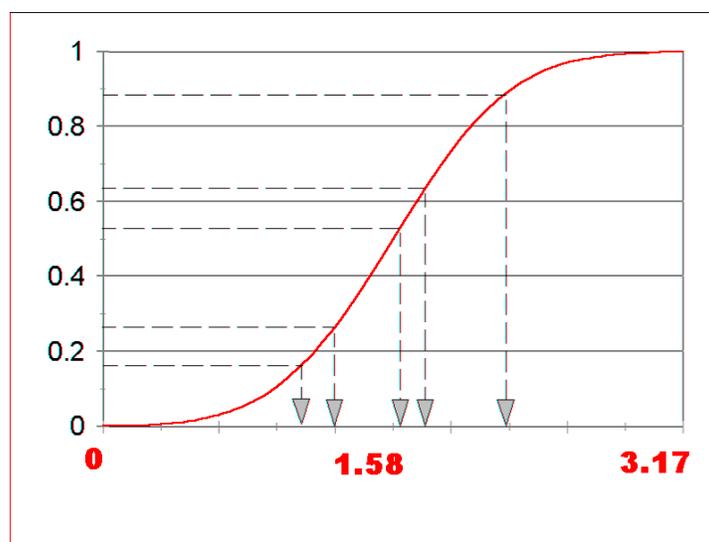
An alternate way of presenting uncertainty is by means of a biomass risk graph, which plots the probability that biomass will be reduced by a given percentage by the end of the simulation (Mauriello and Park 2002). In practice, AQUATOX compares the end value with the initial condition for each state variable, expressing the result as a percent decline:

$$Decline = \left(1 - \frac{EndVal}{StartVal} \right) \cdot 100 \qquad (2)$$

where:

Decline	=	percent decline in biomass for a given state variable (%);
EndVal	=	value at the end of the simulation for a given state variable (units depend on state variable);

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StartVal = initial condition for given state variable.

The results from each iteration are sorted and plotted in a cumulative distribution so that the probability that a particular percent decline will be exceeded can be evaluated (Figure 17). Note that there are ten points in this example, one for each iteration as the consecutive segments of the distribution are sampled.

Figure 17. Risk to bass from dieldrin in Coralville Reservoir, Iowa.
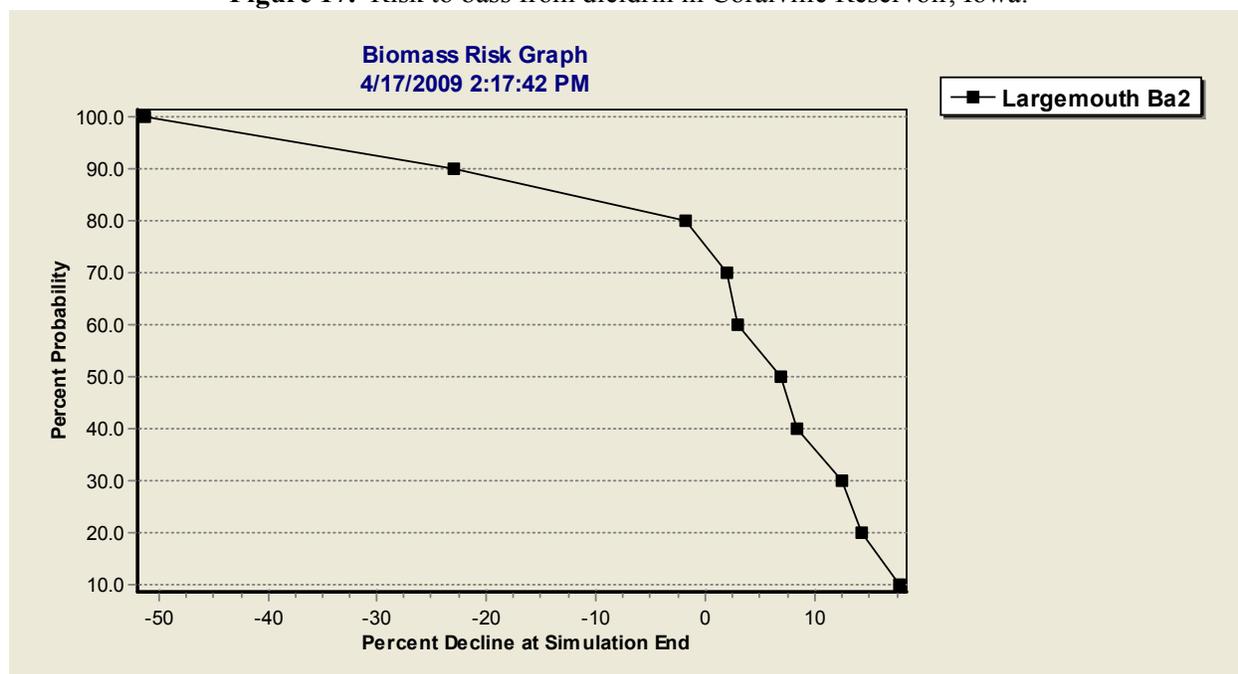
Uncertainty analysis can also be used to perform statistical sensitivity analysis, which is much more powerful than the screening-level nominal range sensitivity analysis. Parameters are tested one at a time using the most appropriate distribution of observed parameter values. The time-varying and mean coefficient of variation can be calculated in an exported Excel file using the mean and standard deviation results for a particular endpoint. Examples will be published in a separate report.

2.6 Calibration and Validation

Rykiel (1996) defines calibration as "the estimation and adjustment of model parameters and constants to improve the agreement between model output and a data set" while "validation is a demonstration that a model within its domain of applicability possesses a satisfactory range of accuracy consistent with the intended application of the model." A related process is verification, which is "a subjective assessment of the behavior of the model" (Jørgensen 1986). The terms are used in those ways in our applications of AQUATOX.

Endpoints for comparison of model results and data should utilize available data for various ecosystem components, preferably covering nutrients, dissolved oxygen, and different trophic

levels, and toxic organics if they are being modeled. Although AQUATOX models a complete food web, often the only biotic data available are chlorophyll *a* values. The model converts biomass predictions to chlorophyll *a* values to facilitate comparison. Likewise, Secchi depth is computed from the overall extinction coefficient for comparison with observed data. Verification should consider process rates to confirm that the results were obtained for the correct reasons (Wlosinski and Collins 1985). Rate information that can be assessed for reasonableness and compared with observations includes sediment oxygen demand (SOD), the fluxes of phosphorus, nitrogen, and dissolved oxygen, and all biotic process rates. These can be presented in tabular and graphical form in AQUATOX.

There are several measures of model performance that can be used for both calibrations and validations (Bartell et al. 1992, Schnoor 1996). The primary difficulty is in comparing general model behavior over long periods to observed data from a few points in time with poorly defined sample variability. Recognizing that evaluation is limited by the quantity and quality of data, stringent measures of goodness of fit are often inappropriate; therefore, we follow a weight-of-evidence approach with a sequence of increasingly rigorous tests to evaluate performance and build confidence in the model results:

- Reasonable behavior as demonstrated by time plots of key variables—is the model behavior reasonable based on general experience? Are the end conditions similar to the initial conditions? This is highly subjective, but when observed data are lacking or are sparse and restricted to short time periods it provides a limited reality check (Figure 18, Figure 19).

- Visual inspections of data points compared to model plots—do the observations and predictions exhibit a reasonable concordance of values (Figure 20, Figure 21)? Visual inspection can also take into consideration if there is concordance given a slight shift in time.

- Do model curves fall within the error bands of observed data (Figure 22)? Alternatively, if there are limited replicates, how do the model curves compare with the spread of observed data?

- Do point observations fall within predicted model bounds obtained through uncertainty analysis? This has the limitation of being dependent on the precision of the model; the greater the model uncertainty, the greater the possibility of the data being encompassed by the error bounds (Figure 23).

- Regression of paired data and model results—does the model produce results that are free of systematic bias? What is the correlation (R^2)? See Figure 24, which corresponds to the results shown in Figure 20.

- Overlap between data and model distributions based on relative bias (rB) in combination with the ratio of variances (F)—how much overlap is there (Figure 25)? Relative bias is a robust measure of how well central tendencies of predicted and observed results correspond; a value of 0 indicates that the means are the same (Bartell et al. 1992). The F test is the ratio of the variance of the model and the variance of the data. A value of 1 indicates that the variances are the same.

- Do the observed and predicted values differ significantly based on their cumulative distributions (Figure 26)? The Kolmogorov-Smirnov statistic, a non-parametric test, can be used; however, the two datasets should represent the same time periods (for example, one should not compare predicted values over a year with observed values taken only during spring and summer).

Figure 18. Predicted biomass patterns for animals in a hypothetical farm pond in Missouri.
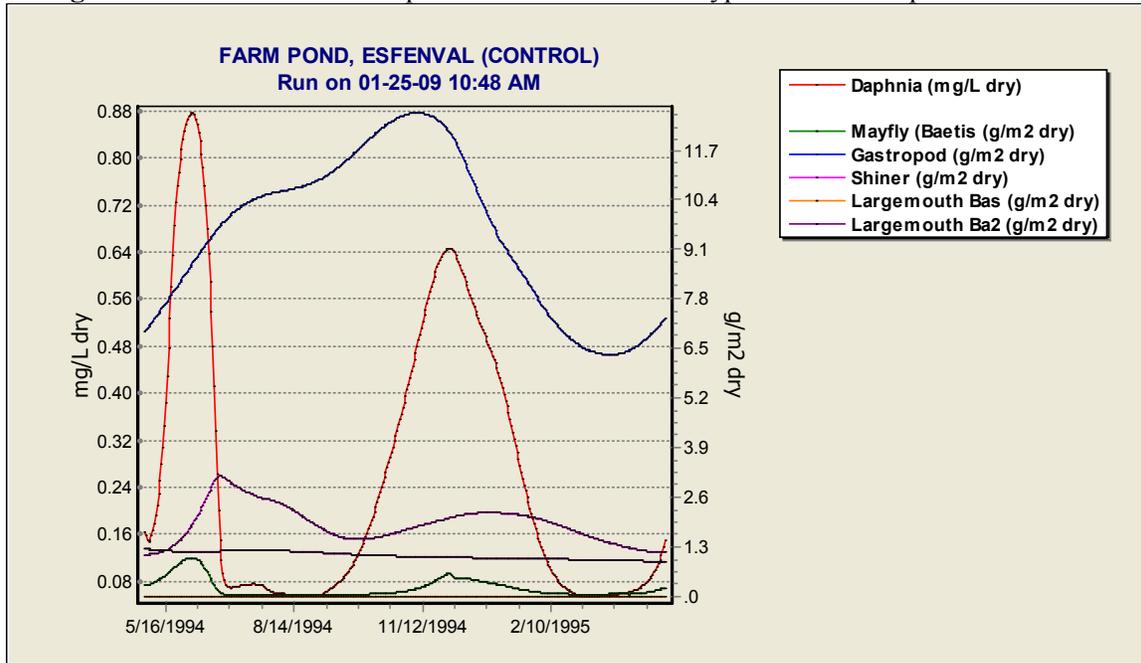
Figure 19. Sediment oxygen demand predicted for Lake Onondaga, using Di Toro sediment diagenesis option; this is an example of using rates for a reality check.
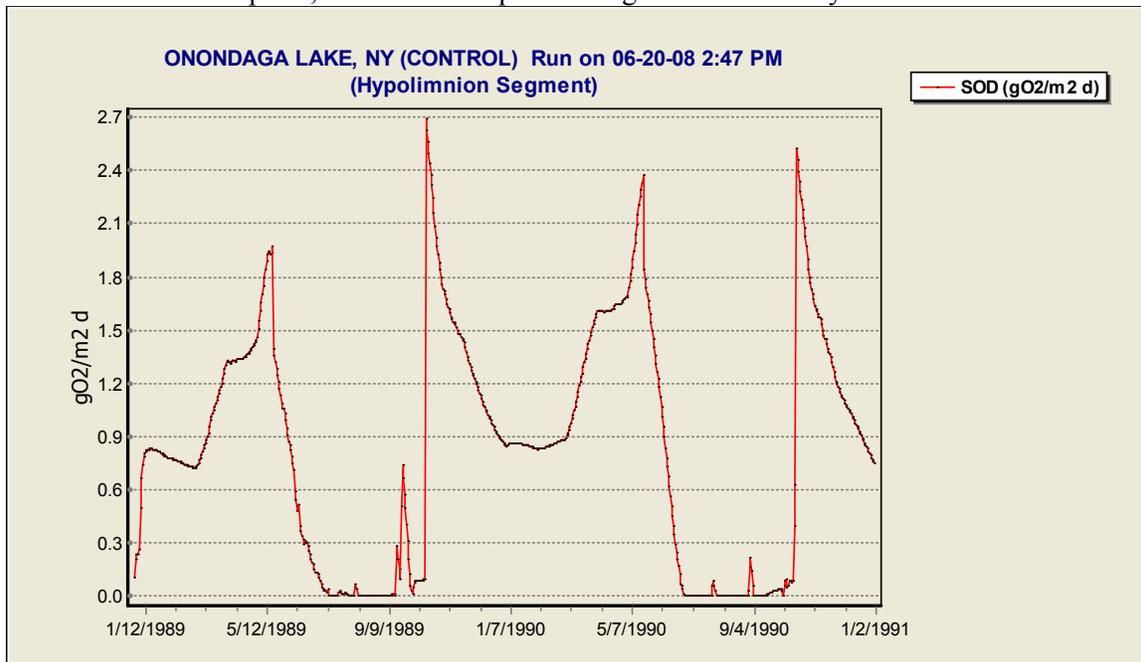
Figure 20. Comparison of predicted and observed (Oliver and Niemi 1988) PCB congener bioaccumulation factors in Lake Ontario lake trout.
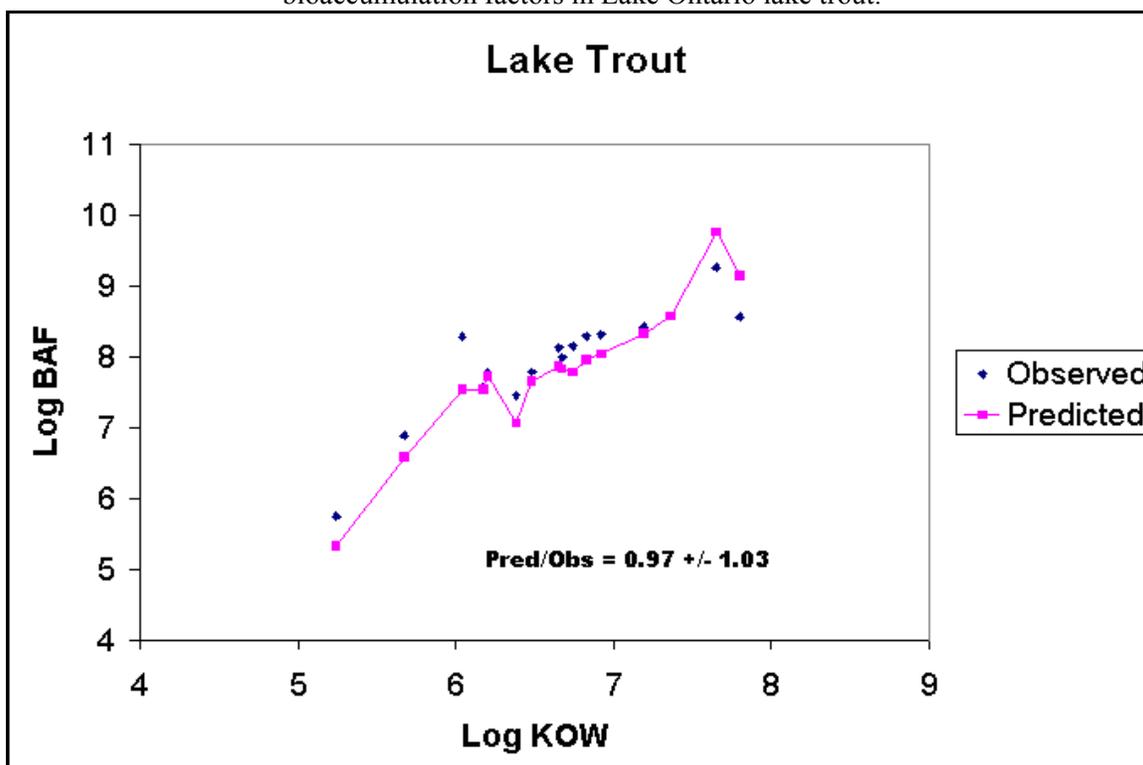
Figure 21. Predicted biomass and observed numbers of chironomid larvae in a Duluth, Minnesota, pond dosed with 6 μg/L chlorpyrifos.
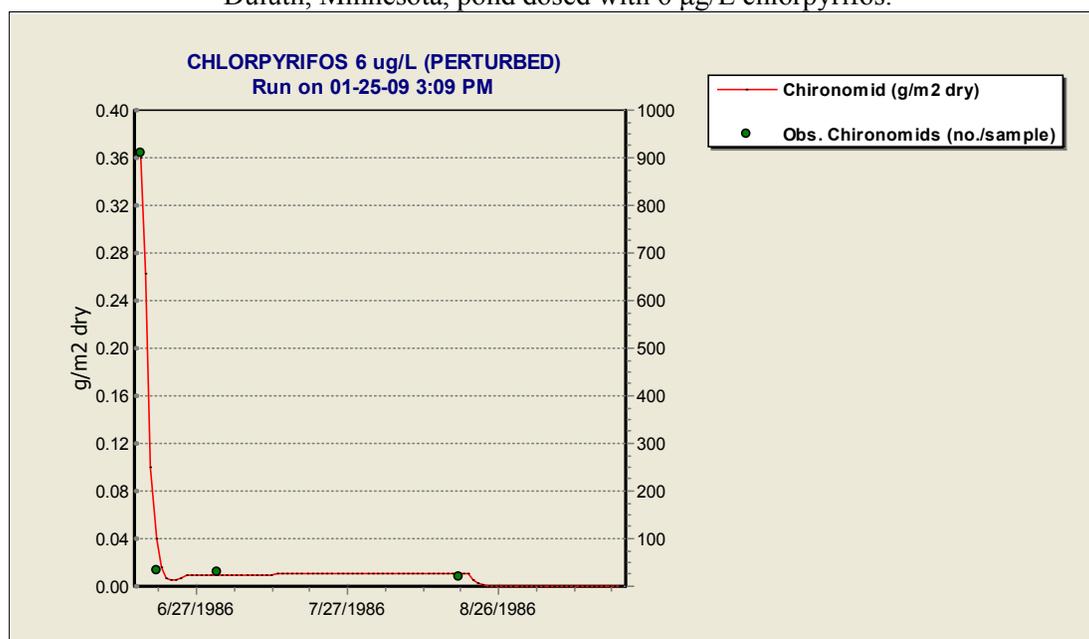
Figure 22. Predicted and observed benthic chlorophyll a in Cahaba River, Alabama; bars indicate one standard deviation in observed data.
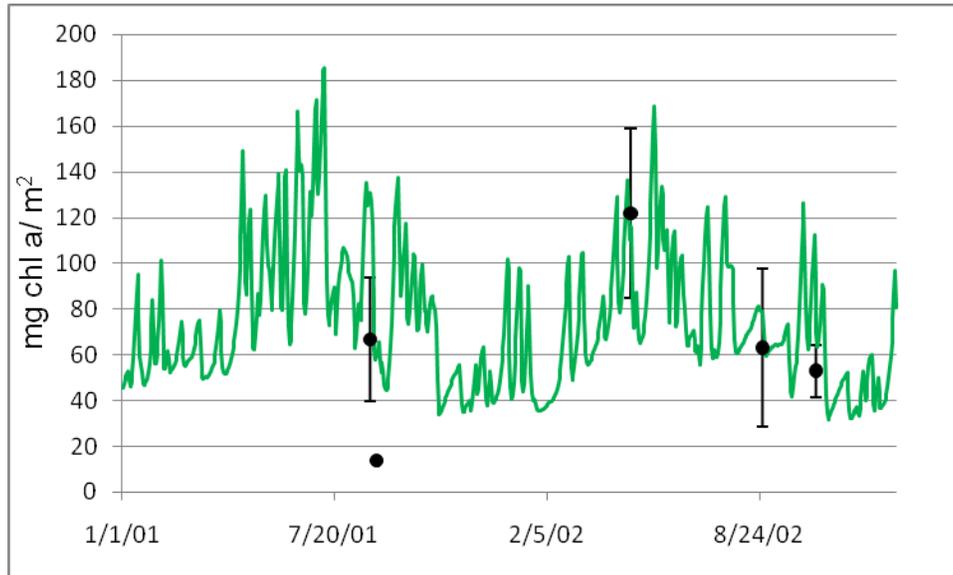
Figure 23. Visual comparison of the envelope of model uncertainty, using two standard deviations for each of the nutrient loading distributions, with the observed data for chlorophyll *a* in Lake Onondaga, NY.
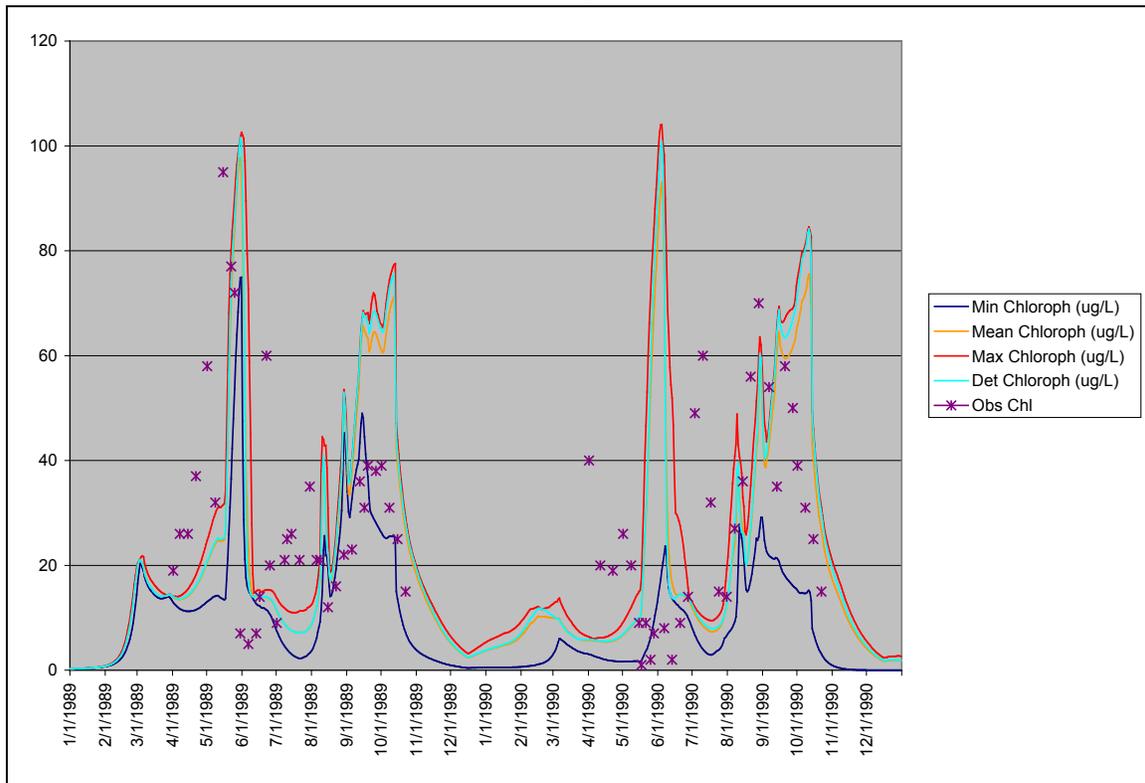
Figure 24. Regression shows that the correlation between predicted and observed (Oliver and Niemi 1988) PCB congener bioaccumulation factors in Lake Ontario trout may be very good, but the slope indicates that there is systematic bias in the relationship. See Figure 20 for another presentation of these same results.
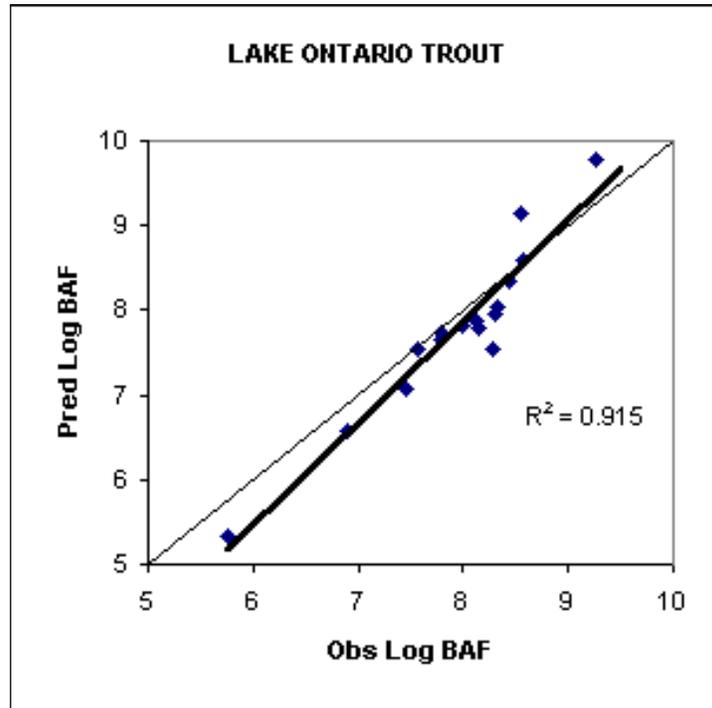
Figure 25. Relative bias and F test to compare means and variances of observed data and predicted results with AQUATOX. The isopleths correspond to the probability that the distributions of predicted and observed, as defined by the combination of the rB and F statistics, are similar. The isopleths assume normal distributions.
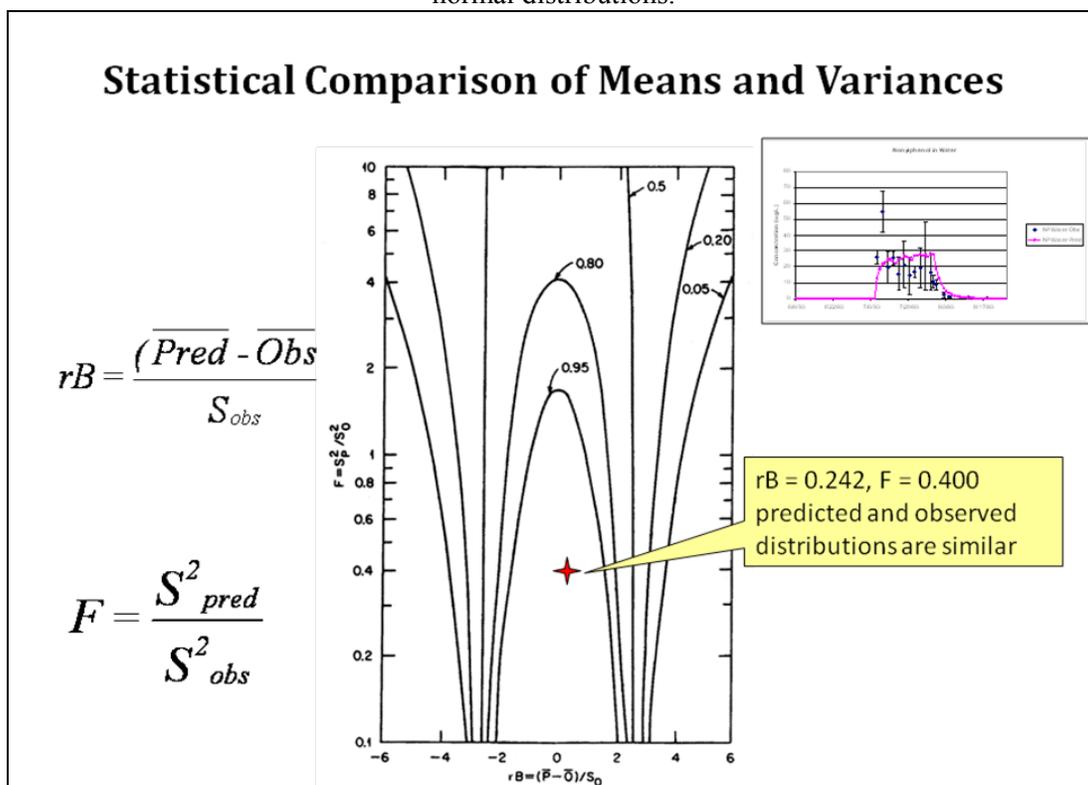
Figure 26. **Comparison of predicted and observed chlorophyll *a* in Lake Onondaga, New York (U.S. Environmental Protection Agency 2000). The Kolmogorov-Smirnov p statistic = 0.319, indicat**es **that the distributions are not significantly different.**
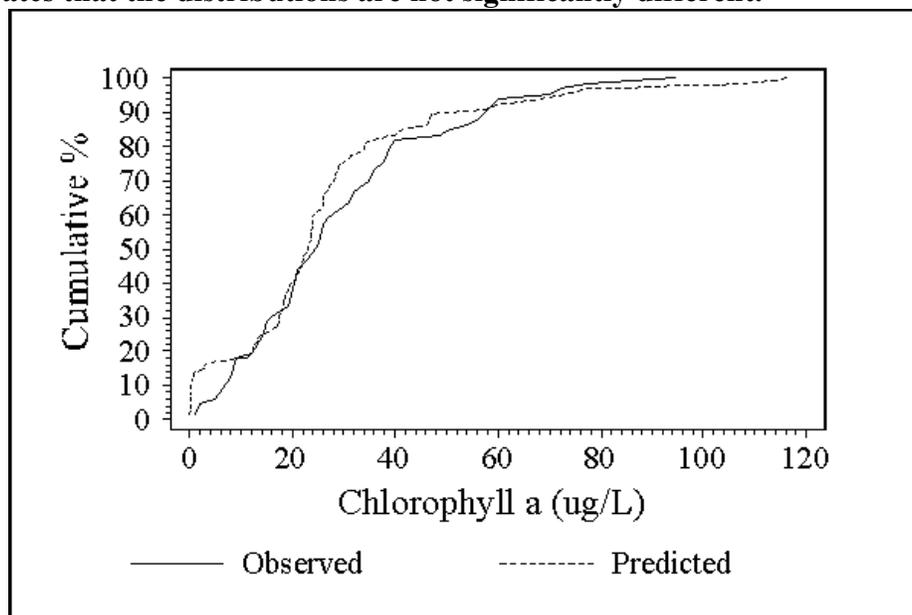
Data are often too sparse for adequate calibration at a given site. However, AQUATOX can be calibrated simultaneously across sites using an expanded state variable list representative of a range of conditions and using the same parameter set. In this way the observed biotic data can be pooled and the resulting state variable and parameter sets, being applicable to diverse sites, are assured to be robust. This is an approach that we have used on the Cahaba River, Alabama (Park et al. 2002); on three dissimilar rivers in Minnesota (Park et al. 2005); and on 13 diverse reaches on the Lower Boise River Idaho (CH2M HILL et al. 2008). The Minnesota rivers application is discussed below.

Time series of driving variables for the Minnesota rivers were obtained from several sources with varying degrees of resolution and reliability. Results of watershed simulations with HSPF (Hydrologic Simulation Program- Fortran, a watershed loading model) were linked to AQUATOX, providing boundary conditions (site constants and drivers) for the Blue Earth and Crow Wing Rivers (Donigian et al. 2005). HSPF was not run for the Rum River; however, a U.S. Geological Survey (USGS) gage is located at the sample site and both daily discharge and sporadic water quality data were available from the USGS Web pages (search on "National Water Information System"). AQUATOX interpolates between points, and this feature was used to compute daily time series of nutrient concentrations from USGS National Water Information System (NWIS) observed data. Total suspended solids (TSS) are critical because the daily light climate for algae is affected. Therefore, we derived a significant relationship by regressing TSS against ln-scaled discharge and used that to generate a daily time series for the Rum River (Figure 27).

Figure 27. TSS at Rum River: a) linear regression against daily flow at gage; b) resulting simulated daily time series (line), and observed values (symbols).
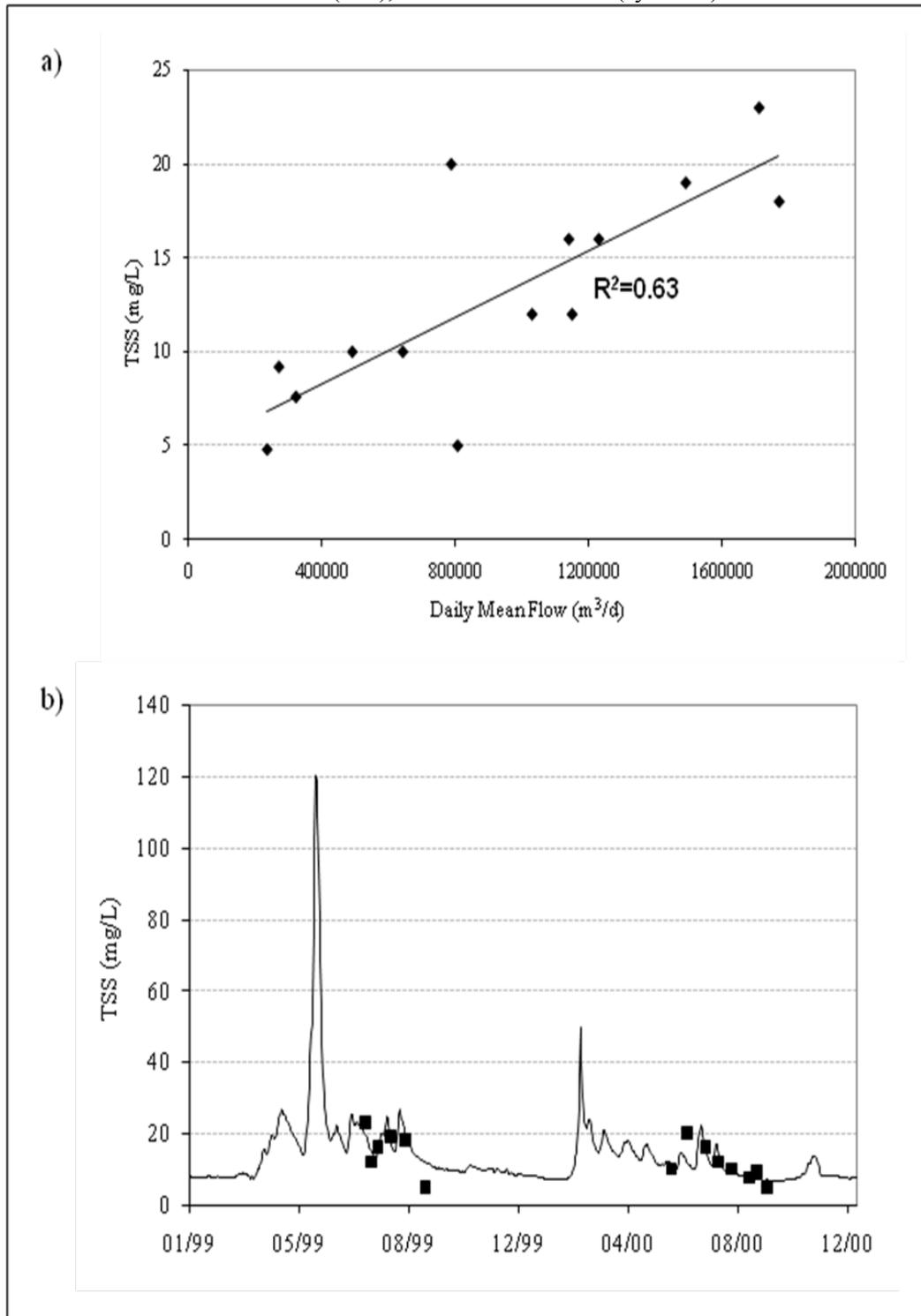
After calibration we evaluated the efficacy of generating daily time series for TN using a regression of TN on discharge. The relationship is statistically significant and yielded a more realistic time series than the interpolation with sparse data that we had used (Figure 28).

However, calculation of the different limitations on photosynthesis indicates that N is not limiting in the Rum River (Figure 29), so we kept the simpler approach and did not repeat the calibration (see section 4.1 for an explanation of the reduction factor as an expression of nutrient limitation) . TP did not exhibit a statistically significant trend with discharge ($R^2 = 0.124$) so the simple interpolation was also kept.

Figure 28. TN at Rum River site: a) ln-linear regression against daily flow at gage; b) interpolated TN observations (red) and time series (black) estimated from discharge regression.
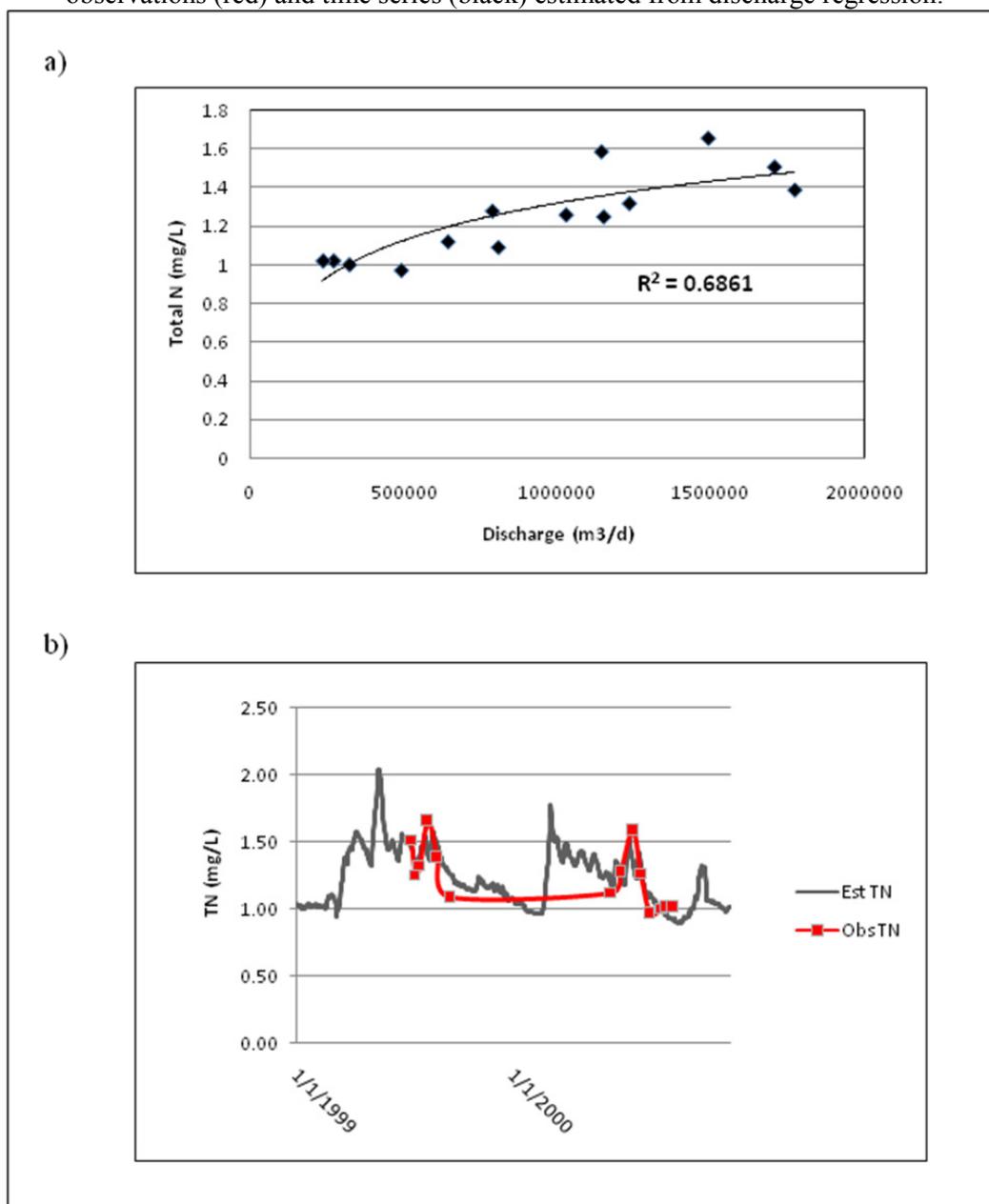
Figure 29. Predicted nutrient limitations for the dominant algal group in the Rum River. Note that N is not limiting.
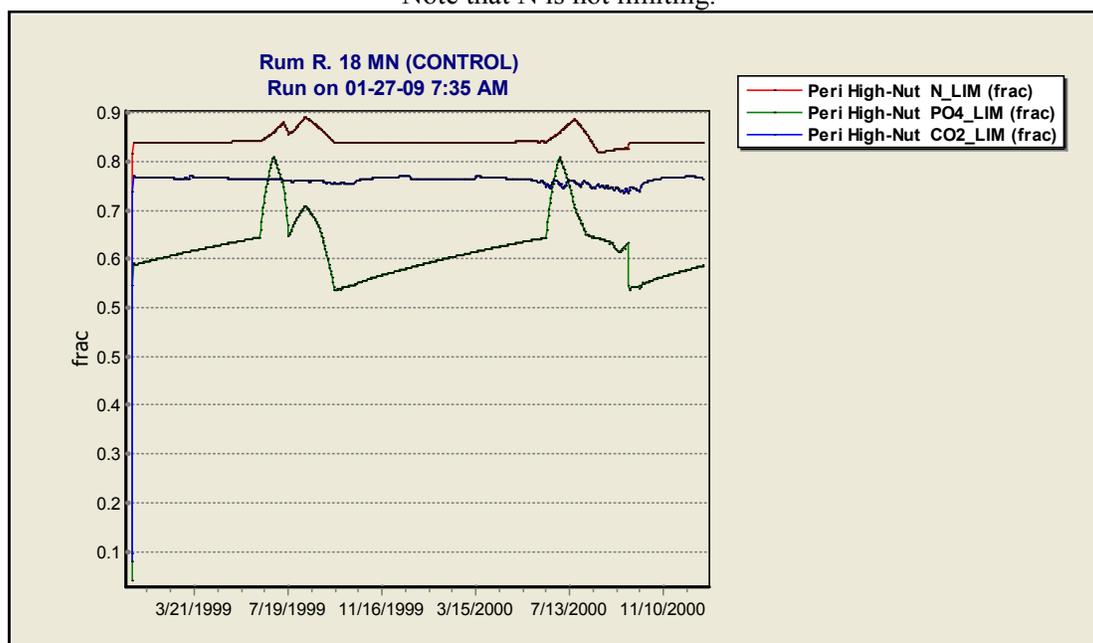
In almost all cases parameter values were chosen from ranges reported in the literature (for example, Le Cren and Lowe-McConnell 1980, Collins and Wlosinski 1983, Horne and Goldman 1994, Jorgensen et al. 2000, Wetzel 2001). However, because these often are broad ranges and the model is very sensitive to some parameters, iterative calibration was necessary for a subset of parameters in AQUATOX. Conversely, some parameters have well established values and default values were used with confidence. A few parameters such as extinction coefficients and critical force for sloughing of periphyton are poorly defined or are unique to the AQUATOX formulations and were treated as "free" parameters subject to broad calibration. For example, some periphyton species are able to migrate vertically through the periphyton mat, and others have open growth forms; therefore, they could be assigned extinction coefficient values without regard to the physics of light transmission through biomass fixed in space. As noted earlier, sensitivity analysis can help determine how much attention needs to be paid to individual parameters. Sensitivity analysis of five diverse studies has shown that the model is sensitive to optimal temperature (*TOpt*) for algae and fish, maximum photosynthesis (*PMax*) for algae, % lost in periphytic sloughing, and log octanol-water partition coefficient (*KOW*). It is advisable to perform sensitivity analysis when the initial calibration is complete in order to identify parameters and driving variables requiring additional attention. Although not used in this application, if modeling a toxic chemical, there are several published sources (for example, Lyman et al. 1982, Verscheuren 1983, Schwarzenbach et al. 1993), and there are a couple excellent online references, including the US EPA ECOTOX site and the USDA ARS Pesticide Properties Database, which can be found with an Internet search engine.

Calibration of AQUATOX for the Minnesota rivers used observed chlorophyll *a* as the primary target for obtaining best fits. Because there were only five to eight sestonic chlorophyll *a* observations in each of the two target years and only one benthic chlorophyll *a* observation at

each location, calibration adequacy was evaluated subjectively, based on generally expected behavior (*e.g.* blooms occurring during summer) and approximate concordance with observed values (in terms of both magnitude and timing), as determined through graphical comparisons of model output and data (Figure 30).

The central tendencies are similar for predicted and observed distributions for all three sites, as shown by the relative bias (Figure 31). Despite the fluctuations in predicted chlorophyll *a*, the predicted and observed variances are similar for the Crow Wing River and Rum River simulations. Predicted periphyton sloughing events played a major role in determining the timing of chlorophyll *a* peaks in both simulations. The variance in predicted values is too high in the Blue Earth River simulation, where summer peak concentrations in 1999 appear to be overestimated by a factor of about two. The reason for this is not known, but may be related to inherent uncertainties in the simulated flow and TSS values, the sparseness of water chemistry sampling data, and/or limitations of model algorithms. Given the wide range in degree of enrichment among these three rivers, and the fact that the model was calibrated against all three data sets using a single set of parameters, a two-fold error during one period of the Blue Earth River simulation seems to be acceptable. The combined probability that the Blue Earth River predictions and observations have the same distribution, based on both central tendency and dispersion, is greater than 0.8. For the purpose of this analysis, we judged the calibration to be adequate for the three rivers.

Figure 30. Observed (symbols) and calibrated AQUATOX simulations (lines) of chlorophyll *a* in three Minnesota rivers: a) Blue Earth at mile 54, b) Rum at mile 18, c) Crow Wing at mile 72. Note the order-of-magnitude range in scale among the figures.
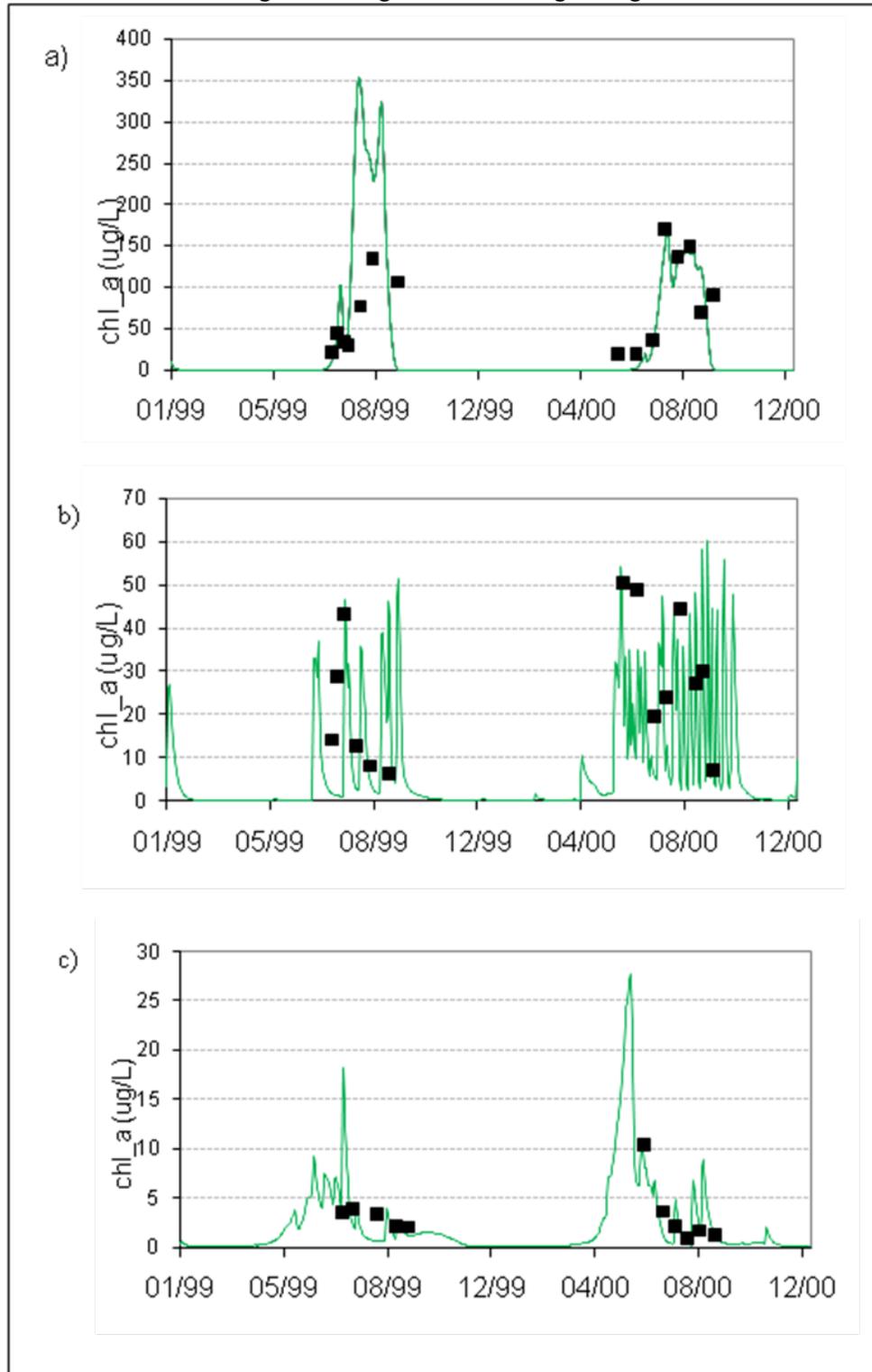
Figure 31. Overlap between model and data distributions based on relative bias and ratio of variances, F; 1 = Blue Earth River, 2 = Crow Wing River, 3 = Rum River. Isopleths indicate the probability that the predicted and observed distributions are the same, assuming normality**.**
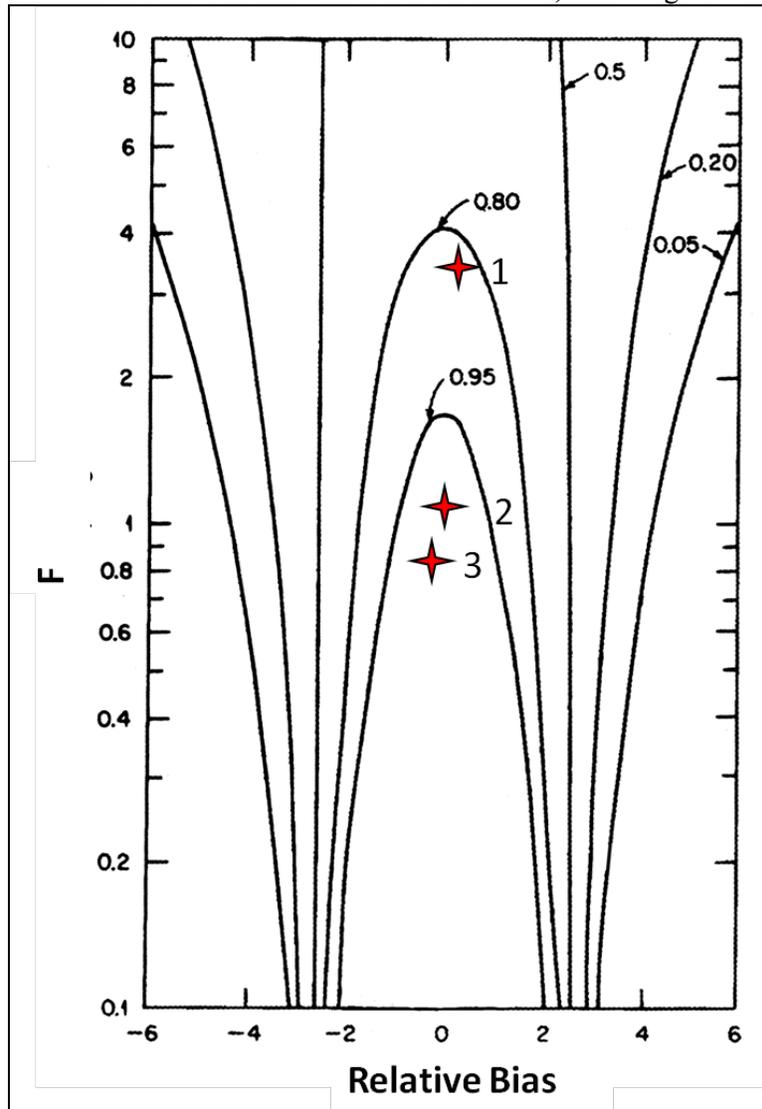
The calibrated algal model was also applied to three dissimilar sites on the Lower Boise River, Idaho, without modification from the Minnesota calibration.   This provided additional verification of the generality of the parameter set. The three sites cover a broad range of nutrient and turbidity conditions over 90 km. Eckert is a low-nutrient, clear-water site upstream of Boise; Middleton receives wastewater treatment effluent and is a nutrient-enriched, clear-water site; and Parma is a nutrient-enriched, turbid site impacted by irrigation return flow from agricultural areas. Although the model overestimated periphyton at the Eckert site, the fit of the initial application (Figure 32) provided an excellent basis for further river-specific calibration.

Figure 32. Predicted (line) and observed (symbols) benthic chlorophyll a (a) at Eckert Road, (b) near Middleton, (c) near Parma, Lower Boise River, Idaho, using Minnesota parameter set.
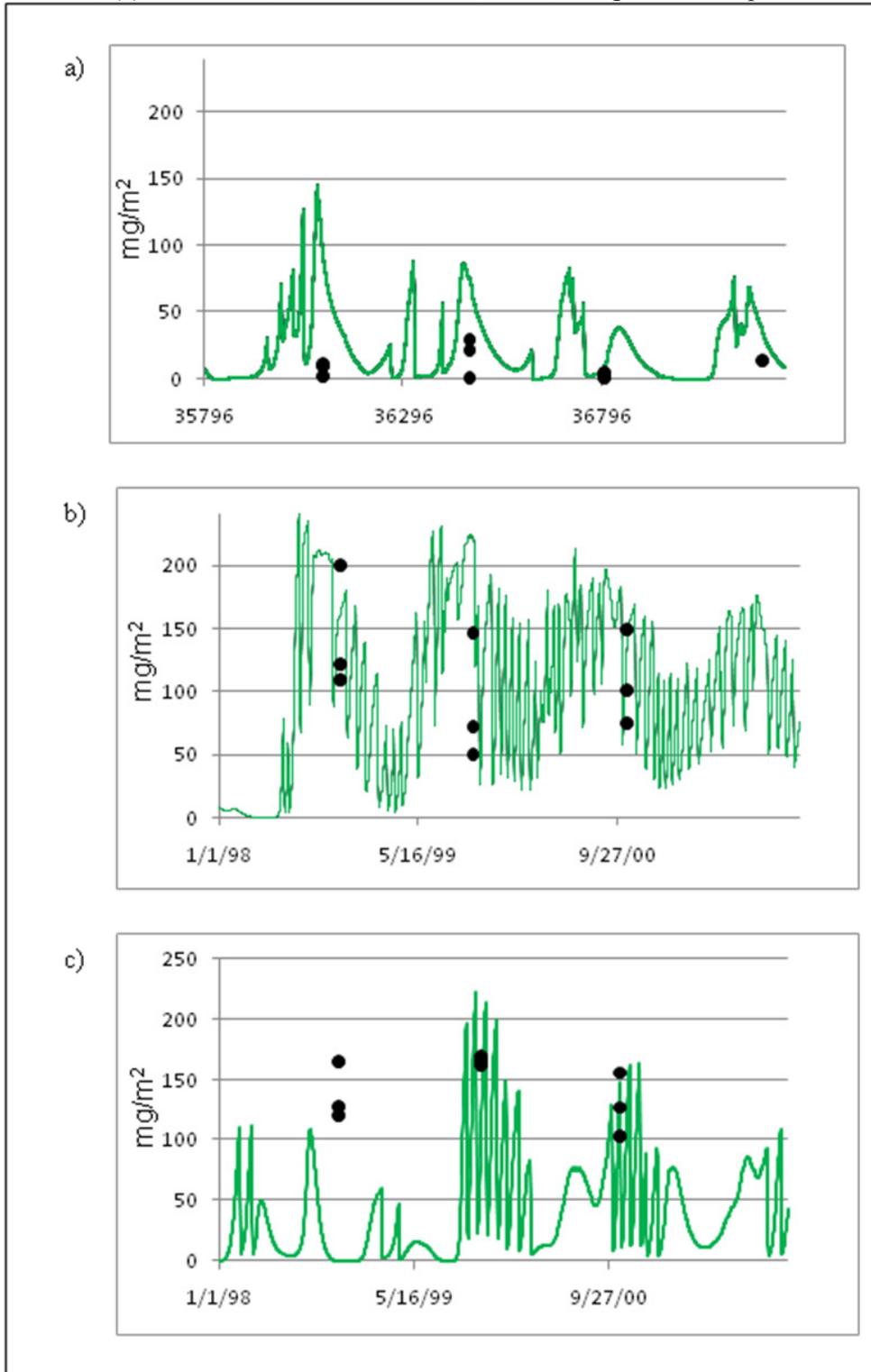
As a limited validation, the calibrated model was applied to a site on the Cahaba River south of Birmingham, Alabama, with modifications to only two parameters, critical force for periphyton scouring and optimal temperature for algae. The Crow Wing and Rum Rivers have cobbles and boulders and are more sensitive to higher current velocities than the bedrock outcrops in the Cahaba River. Not only is the bedrock stable, it also provides abundant crevices and lee sides that are protected refuges for periphyton. For these reasons greater water velocity is expected to be required to initiate periphyton scour in the Cahaba River than in the Crow Wing and Rum Rivers, thus the critical force (Fcrit) for scour of periphyton was more than doubled in the Cahaba River simulation. Also, between Minnesota and Alabama one would expect different local ecotypes in resident algal species, with differing adaptations to temperature. Based on professional judgment, the optimum temperature values (Topt) for green algae and cyanobacteria were therefore increased by 5°C to 31°C and 32°C respectively. The resulting fit to observed data (Figure 22) was good. Furthermore, the fish and zoobenthos fits were acceptable (Figure 33, see also Figure 70). Note that the bluegill are predicted to exhibit ammonia toxicity in 2001, an observation made possible by viewing biotic process rates. (Within rates graphs, animal mortality rates may be broken down into their various constituents, see **(112)**).

Figure 33. Predicted and observed fish in Cahaba River, Alabama; predicted shiner mean biomass = 0.6 g/m^2 compared to observed 0.5 g/m^2.
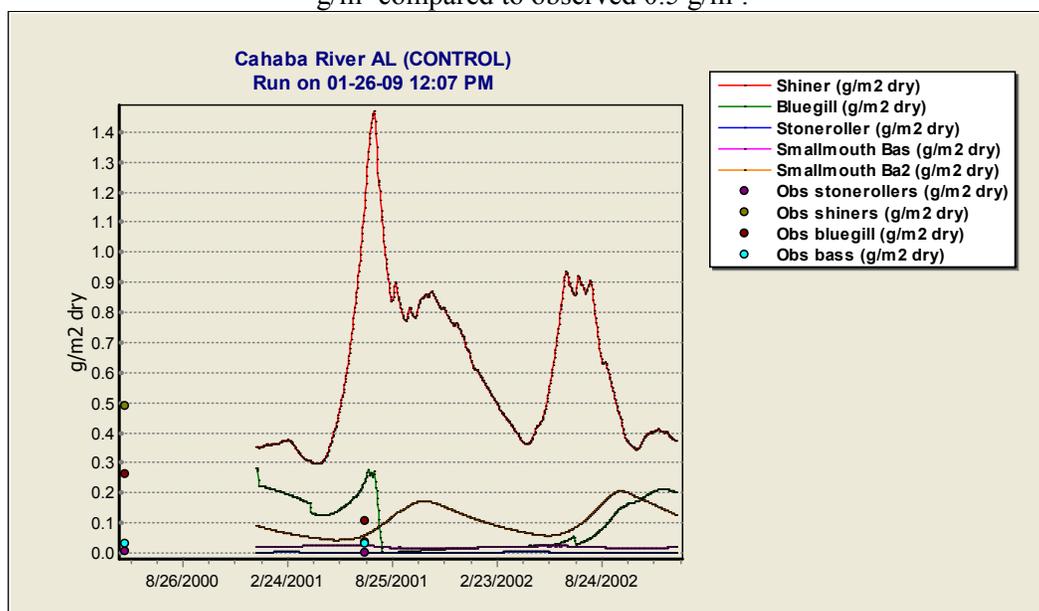
In another validation, published PCB data from New Bedford Harbor, Massachusetts, were used to verify the generality of the estuarine ecosystem bioaccumulation model. The observed concentrations of total PCBs in the water and bottom sediments in the Massachusetts site were set as constant values in a simulation of Galveston Bay, Texas. The predicted PCB concentrations in the various biotic compartments at the end of the simulation were then compared to the observed means and standard deviations in New Bedford Harbor (Figure 34). Considering that the sites and some of the species were different, the concordance in values provides a validation of the model for assessing bioaccumulation of chemicals in a "canonical" or representative estuarine environment.

Figure 34. Predicted and observed concentrations of PCBs in selected animals based on ecosystem calibration for Galveston Bay, Texas and exposure data (Connolly 1991) for New Bedford Harbor, Massachusetts.
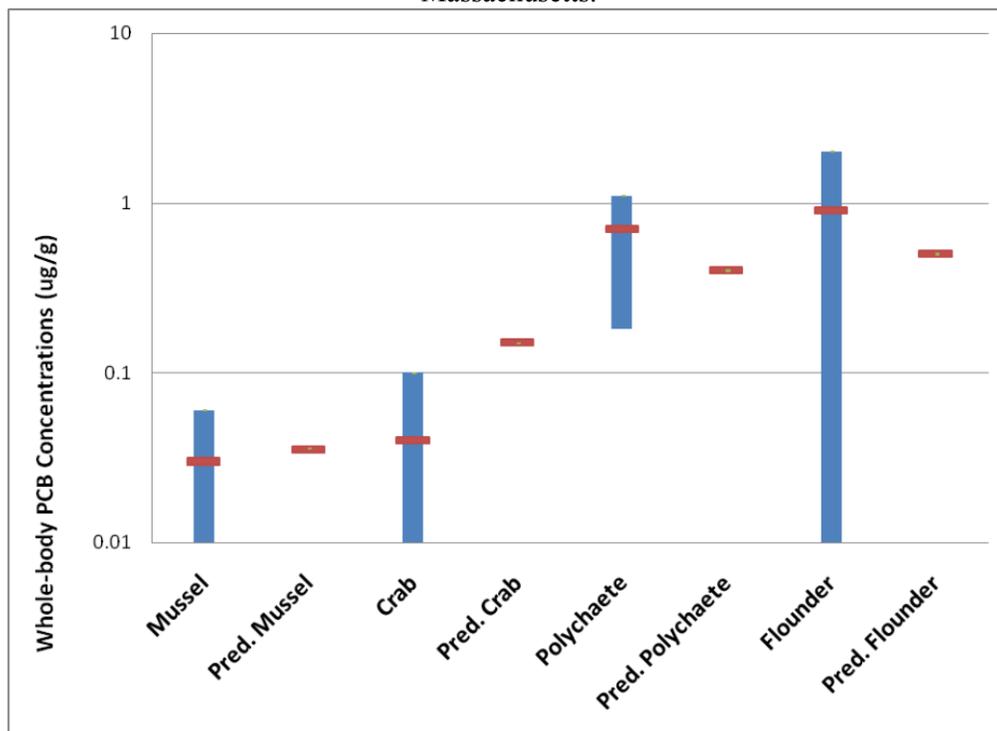
A third example of a validation is shown in Figure 21, which provides a visual comparison of predicted biomass and observed numbers per sample of chironomid larvae with dosing by an insecticide. No calibration was performed for either the fate or toxicity of the chemical.

3. PHYSICAL CHARACTERISTICS

3.1 Morphometry

Volume

Volume is a state variable and can be computed in several ways depending on availability of data and the site dynamics. It is important for computing the dilution or concentration of pollutants, nutrients, and organisms; it may be constant, but usually it is time varying. In the model, ponds, lakes, and reservoirs are treated differently than streams, especially with respect to computing volumes. The change in volume of ponds, lakes, and reservoirs is computed as:

> **Morphometry: Simplifying Assumptions**
>
> - Base flow equation assumes a rectangular channel
> - Site shapes are represented by idealized geometrical approximations
> - Mean Depth may be held constant or user varying depth may be imported

$$\frac{dVolume}{dt} = Inflow - Discharge - Evap \tag{3}$$

where:

$dVolume/dt$	=	derivative for volume of water (m3/d),
$Inflow$	=	inflow of water into waterbody (m3/d),
$Discharge$	=	discharge of water from waterbody (m3/d), and
$Evap$	=	evaporation (m3/d), see **(3)**.

AQUATOX cannot successfully run if the volume of water in a site falls to zero. To avoid this condition, if the site's water volume falls below a minimum value (which is defined as a fraction of the initial condition using the parameter "Minimum Volume Frac." from the "Site" screen), all differentiation of state variables is suspended (except for the water volume derivative) until the water volume again moves above the minimum value. Differentiation of all state variables then resumes.

A time series of evaporation may be entered in the "Site" screen in units of cubic meters per day. Otherwise, evaporation is converted from an annual value for the site to a daily value using the simple relationship:

$$Evap = \frac{MeanEvap}{365} \cdot 0.0254 \cdot Area \tag{4}$$

where:

$Evap$	=	mean daily evaporation (m^3/d)
$MeanEvap$	=	mean annual evaporation (in/yr),
365	=	days per year (d/yr),
0.0254	=	conversion from inches to meters (m/in), and
$Area$	=	area of the waterbody (m2).

The user is given several options for computing volume including keeping the volume constant; making the volume a dynamic function of inflow, discharge, and evaporation; using a time series of known values; and, for flowing waters, computing volume as a function of the Manning's equation. Depending on the method, inflow and discharge are varied, as indicated in Table 3. As shown in equation **(2)**, an evaporation term is present in each of these volume calculation options. In order to keep the volume constant, given a known inflow loading, evaporation must be subtracted from discharge. This will reduce the quantity of state variables that wash out of the system. In the dynamic formulation, evaporation is part of the differential equation, but neither inflow nor discharge is a function of evaporation as they are both entered by the user. When setting the volume of a water body to a known value, evaporation must again be subtracted from discharge for the volume solution to be correct. Finally, when using the Manning's volume equation, given a known discharge loading, the effects of evaporation must be added to the inflow loading so that the proper Manning's volume is achieved. (This could increase the amount of inflow loadings of toxicants and sediments to the system, although not significantly.)

Table 3. Computation of Volume, Inflow, and Discharge

Method	Inflow	Discharge
Constant	*InflowLoad*	*InflowLoad - Evap*
Dynamic	*InflowLoad*	*DischargeLoad*
Known values	*InflowLoad*	*InflowLoad - Evap + (State - KnownVals)/dt*
Manning	*ManningVol - State/dt + Discharge + Evap*	*DischargeLoad*

The variables are defined as:

$InflowLoad$ = user-supplied inflow loading (m^3/d);
$DischargeLoad$ = user-supplied discharge loading (m^3/d);
$State$ = computed state variable value for volume (m^3);
$KnownVals$ = time series of known values of volume (m^3);
dt = incremental time in simulation (d); and
$ManningVol$ = volume of stream reach (m^3), see **(4)**.

Figure 35 illustrates time-varying volumes and inflow loadings specified by the user and discharge computed by the model for a run-of-the-river reservoir. Note that significant drops in volume occur with operational releases, usually in the spring, for flood control purposes.

Figure 35. Volume, inflow, and discharge for a 4-year period
in Coralville Reservoir, Iowa.
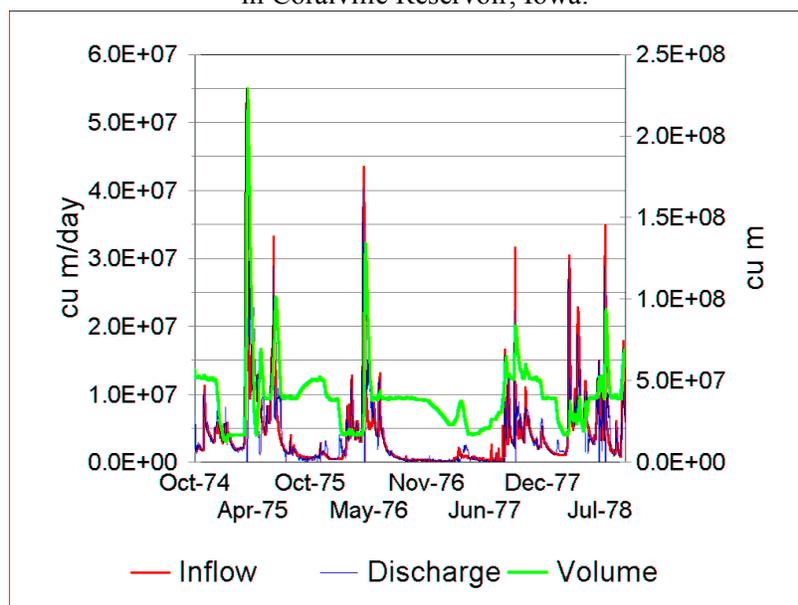
The time-varying volume of water in a stream channel is computed as:

$$ManningVol = Y \cdot CLength \cdot Width \tag{5}$$

where:

Y	=	dynamic mean depth (m), see **(5)**;
$CLength$	=	length of reach (m); and
$Width$	=	width of channel (m).

In streams the depth of water and flow rate are key variables in computing the transport, scour, and deposition of sediments. Time-varying water depth is a function of the flow rate, channel roughness, slope, and channel width using Manning's equation (Gregory, 1973), which is rearranged to yield:

$$Y = \left(\frac{Q \cdot Manning}{\sqrt{Slope \cdot Width}} \right)^{3/5} \tag{6}$$

where:

Q	=	flow rate (m^3/s);
$Manning$	=	Manning's roughness coefficient (s/$m^{1/3}$);
$Slope$	=	slope of channel (m/m); and
$Width$	=	channel width (m).

The Manning's roughness coefficient is an important parameter representing frictional loss, but it is not subject to direct measurement. The user can choose among the following stream types:

- concrete channel (with a default Manning's coefficient of 0.020);
- dredged channel, such as ditches and channelized streams (default coefficient of 0.030); and
- natural channel (default coefficient of 0.040).

These generalities are based on Chow's (1959) tabulated values as given by Hoggan (1989). The user may also enter a value for the coefficient.

In the absence of inflow data, the flow rate is computed from the initial mean water depth, assuming a rectangular channel and using a rearrangement of Manning's equation:

$$QBase = \frac{IDepth^{5/3} \cdot \sqrt{Slope} \cdot Width}{Manning} \tag{7}$$

where:

QBase	=	base flow (m³/s); and
Idepth	=	mean depth as given in site record (m).

The dynamic flow rate is calculated from the inflow loading by converting from m³/d to m³/s:

$$Q = \frac{Inflow}{86400} \tag{8}$$

where:

Q	=	flow rate (m³/s); and
Inflow	=	water discharged into channel from upstream (m³/d).

Bathymetric Approximations

The depth distribution of a water body is important because it determines the areas and volumes subject to mixing and light penetration. The shapes of ponds, lakes, reservoirs, and streams are represented in the model by idealized geometrical approximations, following the topological treatment of Junge (1966; see also Straškraba and Gnauck, 1985).   The shape parameter *P* (Junge, 1966) characterizes the site, with a shape that is indicated by the ratio of mean to maximum depth.:

$$P = 6.0 \cdot \frac{ZMean}{ZMax} - 3.0 \tag{9}$$

Where:

ZMean	=	mean depth (m);
ZMax	=	maximum depth (m); and
P	=	characterizing parameter for shape (unitless); P is constrained between -1.0 and 1.0

Shallow constructed ponds and ditches may be approximated by an ellipsoid where *Z/ZMax* = 0.6 and *P* = 0.6. Reservoirs and rivers generally are extreme elliptic sinusoids with values of *P*

constrained to -1.0. Lakes may be either elliptic sinusoids, with *P* between 0.0 and -1.0, or elliptic hyperboloids with *P* between 0.0 and 1.0. Not all water bodies fit the elliptic shapes, but the model generally is not sensitive to the deviations.

Based on these relationships, fractions of volumes and areas can be determined for any given depth (Junge, 1966). The *AreaFrac* function returns the fraction of surface area that is at depth *Z* given *Zmax* and *P*, which defines the morphometry of the water body. For example, if the water body were an inverted cone, when horizontal slices were made through the cone looking down from the top one could see both the surface area and the water/sediment boundary where the slice was made. This would look like a circle within a circle, or a donut (Figure 36). *AreaFrac* calculates the fraction that is the donut (not the donut hole). To get the donut hole, 1 - *AreaFrac* is used.

$$AreaFrac = (1 - P) \cdot \frac{Z}{ZMax} + P \cdot \left(\frac{Z}{ZMax}\right)^2 \qquad (10)$$

$$VolFrac = \frac{6.0 \cdot \frac{Z}{ZMax} - 3.0 \cdot (1.0 - P) \cdot \left(\frac{Z}{ZMax}\right)^2 - 2.0 \cdot P \cdot \left(\frac{Z}{ZMax}\right)^3}{3.0 + P} \qquad (11)$$

where:

AreaFrac	=	fraction of area of site above given depth (unitless);
VolFrac	=	fraction of volume of site above given depth (unitless); and
Z	=	depth of interest (m).

For example, the fraction of the volume that is epilimnion can be computed by setting depth *Z* to the mixing depth. Furthermore, by setting *Z* to the depth of the euphotic zone, where primary production exceeds respiration, the fraction of the area available for colonization by macrophytes and periphyton can be computed:

$$FracLit = (1 - P) \cdot \frac{ZEuphotic}{ZMax} + P \cdot \left(\frac{ZEuphotic}{ZMax}\right)^2 \qquad (12)$$

A relatively deep, flat-bottomed basin would have a small littoral area and a large sublittoral area (Figure 36).

Figure 36.
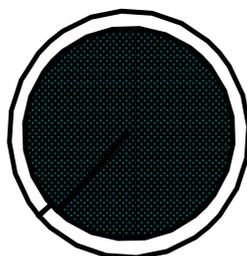
If the site is an artificial enclosure then the available area is increased accordingly:

$$FracLittoral = FracLit \cdot \frac{Area + EnclWallArea}{Area}$$

otherwise   **(13)**

$$FracLittoral = FracLit$$

where:

FracLittoral	=	fraction of site area that is within the euphotic zone (unitless);
ZEuphotic	=	depth of the euphotic zone, is assumed to be 1% of surface light and calculated as 4.605/*Extinct* (m) see **(40)**;
Area	=	site area (m^2); and
EnclWallArea	=	area of experimental enclosure's walls (m^2).

Figure 37. Area as a function of depth   **Figure 38.** Volume as a function of depth
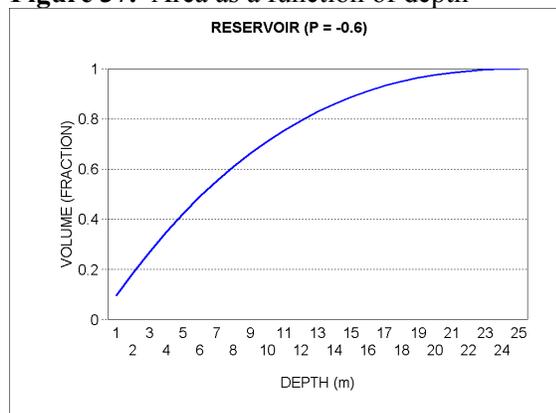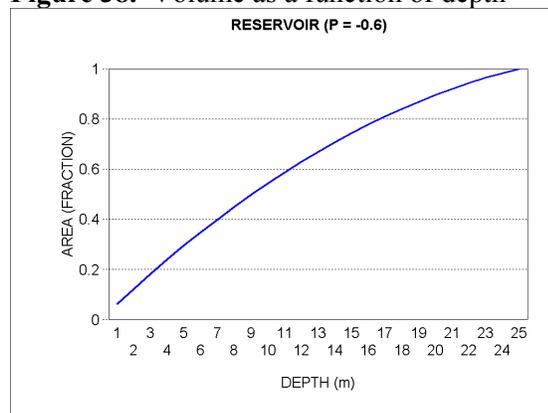
If a user wishes to model a simpler system, the bathymetric approximations may be bypassed in favor of a more rudimentary set of assumptions via an option in the "site data" screen.

When the user chooses not to "use bathymetry"

- the system is assumed to have vertical walls;
- the system is assumed to have a constant area as a function of depth;
- the system's depth may be calculated at any time as water volume divided by surface area.

This option may be useful when linking data from other models to AQUATOX as the horizontal spatial domain of AQUATOX remains unchanged over time. However, a system will not undergo dynamic stratification based on water temperature unless the more complex bathymetric approximations are utilized (**(8)** to **(11)**).

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 and reservoirs, the depth of the system can change considerably over time, 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 **(43)**;
- Calculation of biotic volumes for sloughing calculations, see **(74)**;
- Calculation of vertical dispersion for stratification calculations, *Thick* in equation **(18)**;
- Calculation of sedimentation for plants & detritus, *Thick* in **(165)**;
- Oxygen reaeration, see **(190)**;
- Toxicant photolysis and volatilization, *Thick* in **(320)** and **(331).**

Habitat Disaggregation

Riverine environments are seldom homogeneous. Organisms often exhibit definite preferences for habitats. Therefore, when modeling streams or rivers, animal and plant habitats are broken down into three categories: "riffle," "run," and "pool."   The combination of these three habitat categories make up 100% of the available habitat within a riverine simulation. The preferred percentage of each organism that resides within these three habitat types can be set within the animal or plant data. Within the *site* data, the percentage of the river that is composed of each of these three habitat categories also can be set. It should be noted that the habitat percentages are considered constant over time, and thus would not capture significant changes in channel morphology and habitat distribution due to major flooding events.

These habitats affect the simulations in two ways: as limitations on photosynthesis and consumption and as weighting factors for water velocity (see 3.2 Velocity). Each animal and plant is exposed to a weighted average water velocity depending on its location within the three habitats. This weighted velocity affects all velocity-mediated processes including entrainment of invertebrates and fish, breakage of macrophytes and scour of periphyton. The reaeration of the system also is affected by the habitat-weighted velocities.

Limitations on photosynthesis and consumption are calculated depending on a species' preferences for habitats and the available habitats within the water body. If the species preference for a particular habitat is equal to zero then the portion of the water body that contains that particular habitat limits the amount of consumption or photosynthesis accordingly.

$$HabitatLimit = \sum Preference_{habitat>0} \left(\frac{Percent_{habitat}}{100} \right) \tag{14}$$

where:

$HabitatLimit_{Species}$	=	fraction of site available to organism (unitless), used to limit ingestion, see **(91)**, and photosynthesis, see **(35)**, **(85)**;
$Preference_{habitat}$	=	preference of animal or plant for the habitat in question (percentage); and
$Percent_{habitat}$	=	percentage of site composed of the habitat in question (percentage).

It is important to note that the initial condition for an animal that is entered in g/m^2 is an indication of the total mass of the animal over the total surface area of the river. Because of this, density data for various benthic organisms, which is generally collected in a specific habitat type, cannot be used as input to AQUATOX until these values have been converted to represent the entire surface area. This is especially true in modeling habitats; for example, an animal could have a high density within riffles, but riffles might only constitute a small portion of the entire system.

3.2 Velocity

If the user has site-specific velocity data, this may be entered on the "site data" screen in units of cm/s. Otherwise, velocity is calculated as a simple function of flow and cross-sectional area:

$$Velocity = \frac{AvgFlow}{XSecArea} \cdot \frac{1}{86400} \cdot 100 \tag{15}$$

where

Velocity	=	velocity (cm/s),
AvgFlow	=	average flow over the reach (m^3/d),
XSecArea	=	cross sectional area (m^2),
86400	=	s/d, and
100	=	cm/m.

$$AvgFlow = \frac{Inflow + Discharge}{2} \tag{16}$$

where:

Inflow	=	flow into the reach (m^3/d);
Discharge	=	flow out of the reach (m^3/d).

It is assumed that this is the velocity for the run of the stream (user entered velocities are also assumed to pertain to the run of the screen). No distinction is made in terms of vertical differences in velocity in the stream. Following the approach and values used in the DSAMMt model (Caupp et al. 1995), the riffle velocity is obtained by using a conversion factor that is

dependent on the discharge.   Unlike the DSAMMt model, pools also are modeled, so a conversion factor is used to obtain the pool velocity as well (Table 4).

Table 4. Factors relating velocities to those of the average reach.

Flows (Q = discharge)	Run Velocity	Riffle Velocity	Pool Velocity
Q < 2.59e5 m^3/d	1.0	1.6	0.36
2.59e5 m^3/d < Q < 5.18e5 m^3/d	1.0	1.3	0.46
5.18e5 m^3/d < Q < 7.77e5 m^3/d	1.0	1.1	0.56
Q > 7.77e5 m^3/d	1.0	1.0	0.66

Figure 39. Predicted velocities in an Ohio stream according to habitat.
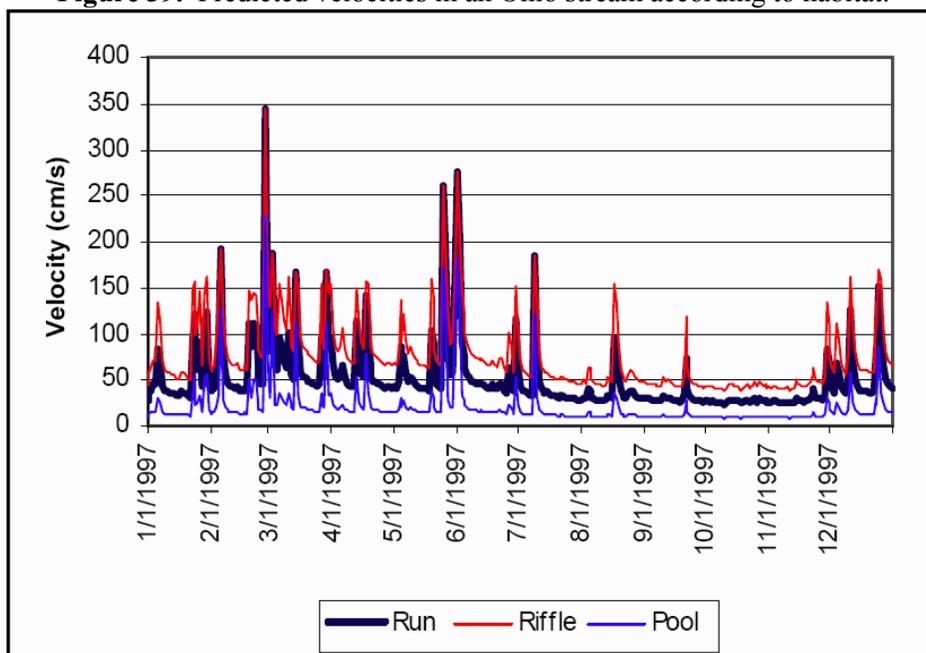
3.3 Washout

Transport out of the system, or washout, is an important loss term for nutrients, floating organisms, and dissolved toxicants in reservoirs and streams.   Although it is considered separately for several state variables, the process is a general function of discharge:

$$Washout = \frac{Discharge}{Volume} \cdot State \qquad (17)$$

where:

Washout	=	loss due to being carried downstream (g/m^3 ·d), and
State	=	concentration of dissolved or floating state variable (g/m^3).

3.4 Stratification and Mixing

Thermal stratification is handled in the simplest form consistent with the goals of forecasting the effects of nutrients and toxicants.   Lakes and reservoirs are considered in the model to have two vertical zones: epilimnion and hypolimnion (Figure 40); the metalimnion zone that separates these is ignored.   Instead, the thermocline, or plane of maximum temperature change, is taken as the separator; this is also known as the mixing depth (Hanna, 1990). Dividing the lake into two vertical zones follows the treatment of Imboden (1973), Park et al. (1974), and Straškraba and Gnauck (1983). The onset of stratification is considered to occur when the mean water temperature exceeds 4 deg. and the difference in temperature between the epilimnion and hypolimnion

> **Stratification: Simplifying Assumptions**
>
> - Two vertical zones modeled; metalimnion is ignored
> - Flowing waters are assumed not to stratify
> - Stratification occurs when vertical temperature difference exceeds three degrees
> - Winter stratification is not modeled
> - Thermocline occurs at constant depth except when user enters time series
> - Wind action is implicit in vertical dispersion calculations

exceeds 3 deg.. Overturn occurs when the temperature of the epilimnion is less than 3 deg., usually in the fall. Winter stratification is not modeled, unless manually input. For simplicity, the thermocline is generally assumed to occur at a constant depth. Alternatively, a user-specified time-varying thermocline depth may be specified, see the section on modeling reservoirs below.

Figure 40. Thermal stratification in a lake; terms defined in text
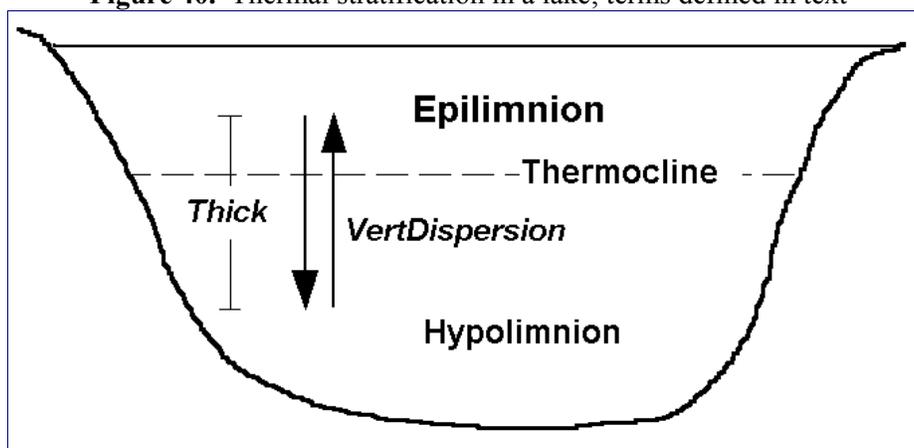
There are numerous empirical models relating thermocline depth to lake characteristics. AQUATOX uses an equation by Hanna (1990), based on the maximum effective length (or fetch). The dataset includes 167 mostly temperate lakes with maximum effective lengths of 172 to 108,000 m and ranging in altitude from 10 to 1897 m. The equation has a coefficient of determination $r^2 = 0.850$, meaning that 85 percent of the sum of squares is explained by the regression. Its curvilinear nature is shown in Figure 41, and it is computed as (Hanna, 1990):

$$\log(MaxZMix) = 0.336 \cdot \log(Length) - 0.245 \qquad \textbf{(18)}$$

where:

MaxZMix	=	maximum mixing depth under stratified conditions (thermocline depth) for lake (m); and
Length	=	maximum effective length for wave setup (m, converted from user-supplied km).

Figure 41. Mixing depth as a function of fetch
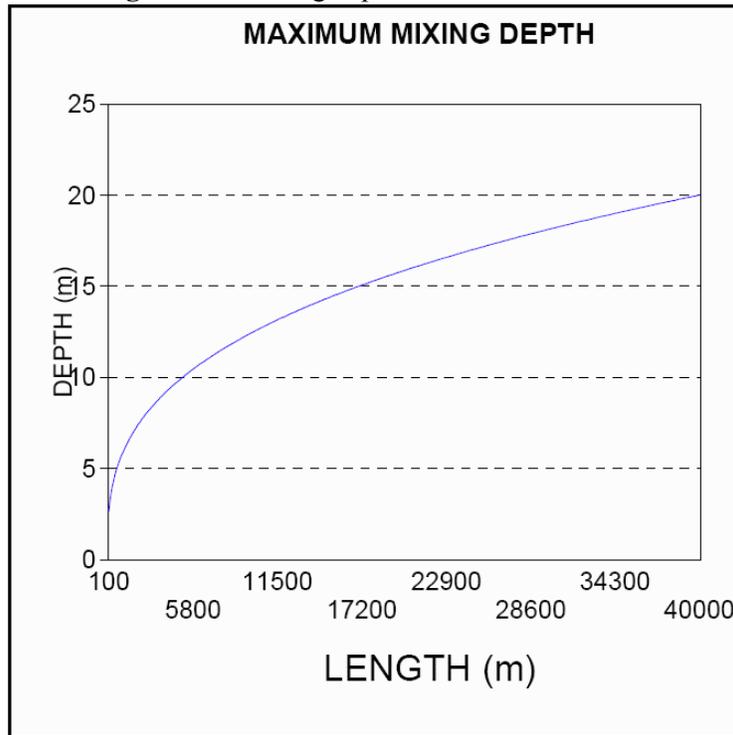
Wind action is implicit in this formulation. Wind has been modeled explicitly by Baca and Arnett (1976, quoted by Bowie et al., 1985), but their approach requires calibration to individual sites, and it is not used here.

Vertical dispersion for bulk mixing is modeled as a function of the time-varying hypolimnetic and epilimnetic temperatures, following the treatment of Thomann and Mueller (1987, p. 203; see also Chapra and Reckhow, 1983, p. 152; Figure 42):

$$VertDispersion = Thick \cdot \left(\frac{HypVolume}{ThermoclArea \cdot Deltat} \cdot \frac{T_{hypo}^{t-1} - T_{hypo}^{t+1}}{T_{epi}^{t} - T_{hypo}^{t}} \right) \qquad \textbf{(19)}$$

where:

VertDispersion	=	vertical dispersion coefficient (m^2/d);
Thick	=	distance between the centroid of the epilimnion and the centroid of the hypolimnion, effectively the mean depth (m);

53

HypVolume	=	volume of the hypolimnion (m^3);
ThermoclArea	=	area of the thermocline (m^2);
Deltat	=	time step (d);
T_{hypo}^{t-1}, T_{hypo}^{t+1}	=	temperature of hypolimnion one time step before and one time step after present time (deg. C); and
T_{epi}^{t}, T_{hypo}^{t}	=	temperature of epilimnion and hypolimnion at present time (deg.C).

Stratification can break down temporarily as a result of high throughflow. This is represented in the model by making the vertical dispersion coefficient between the layers a function of discharge for sites with retention times of less than or equal to 180 days (Figure 43), rather than temperature differences as in equation 11, based on observations by Straškraba (1973) for a Czech reservoir:

$$VertDispersion = 1.37 \cdot 10^4 \cdot Retention^{-2.269} \tag{20}$$

and:

$$Retention = \frac{Volume}{TotDischarge} \tag{21}$$

where:

Retention	=	retention time (d);
Volume	=	volume of site (m^3); and
TotDischarge	=	total discharge (m^3/d).

Figure 42. Vertical dispersion as a function of temperature differences
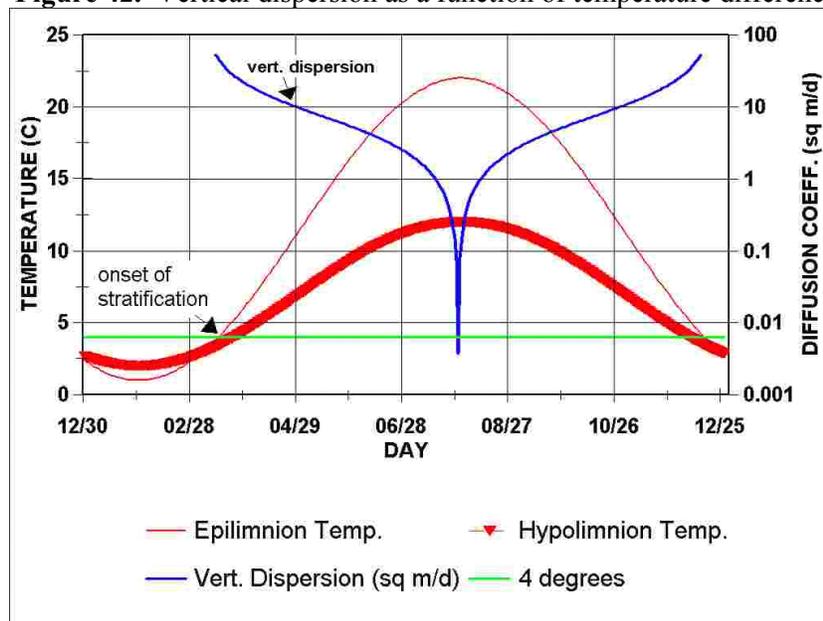
Figure 43. Vertical dispersion as a function of retention time
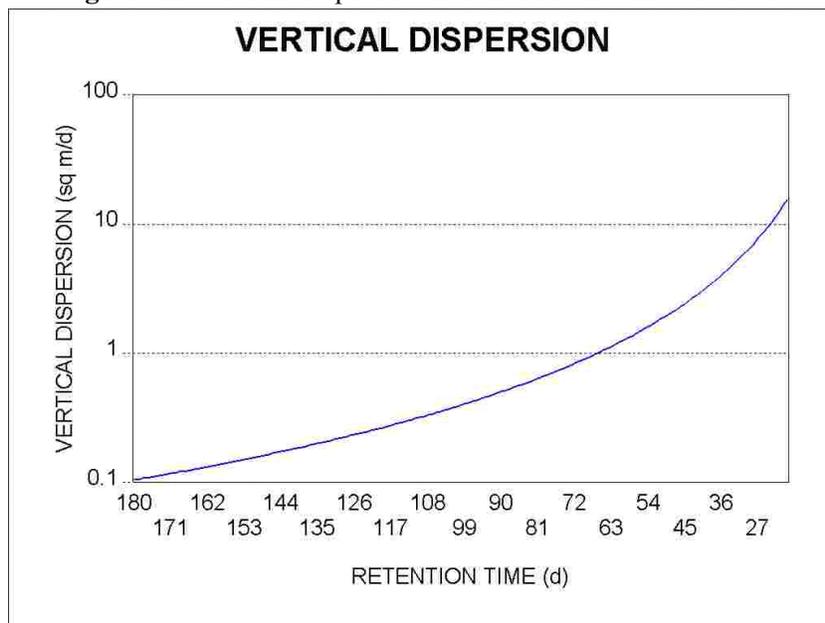
The bulk vertical mixing coefficient is computed using site characteristics and the time-varying vertical dispersion (Thomann and Mueller, 1987):

$$BulkMixCoeff = \frac{VertDispersion \cdot ThermoclArea}{Thick} \qquad (22)$$

where:

$BulkMixCoeff$ =	bulk vertical mixing coefficient (m^3/d),
$ThermoclArea$ =	area of thermocline (m^2).

Turbulent diffusion of biota and other material between epilimnion and hypolimnion is computed separately for each segment for each time step while there is stratification:

$$TurbDiff_{epi} = \frac{BulkMixCoeff}{Volume_{epi}} \cdot (Conc_{compartment, hypo} - Conc_{compartment, epi}) \qquad (23)$$

$$TurbDiff_{hypo} = \frac{BulkMixCoeff}{Volume_{hypo}} \cdot (Conc_{compartment, epi} - Conc_{compartment, hypo}) \qquad (24)$$

where:

$TurbDiff$	=	turbulent diffusion for a given zone ($g/m^3 \cdot$d);
$Volume$	=	volume of given segment (m^3); and
$Conc$	=	concentration of given compartment in given zone (g/m^3).

The effects of stratification, mixing due to high throughflow, and overturn are well illustrated by the pattern of dissolved oxygen levels in the hypolimnion of Lake Nockamixon, a eutrophic reservoir in Pennsylvania (Figure 44).

Figure 44. Stratification and mixing in Lake Nockamixon, Pennsylvania as shown by hypolimnetic dissolved oxygen
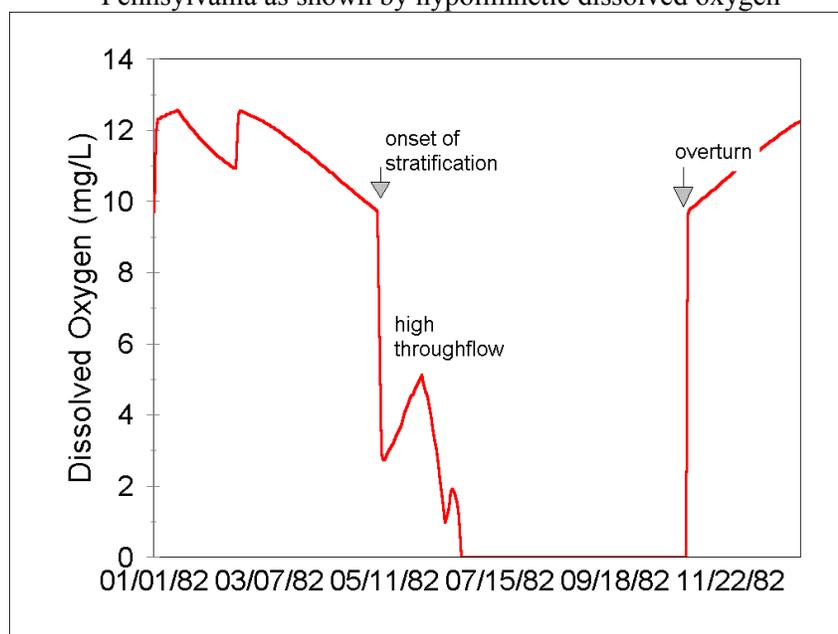
Modeling Reservoirs and Stratification Options

Stratification assumptions and equations based on lake characteristics may not be appropriate for modeling reservoirs. Moreover, a lake may have a unique morphometry or chemical composition that renders inappropriate the equations presented above. For this reason, a "stratification options" screen is available (through the "site" screen or "water-volume" screen) that allows a user to specify the following characteristics of a stratified system:

- a constant or time-varying thermocline depth;
- options as to how to route inflow and outflow water; and
- the timing of stratification.

Water volumes for each segment are calculated as a function of the overall system volume and the thermocline depth (see **(10)**). Because of this, if a time-varying thermocline depth is specified, water from one segment must usually be transferred into the other segment, along with the state variables within that water. In this manner, specifying a time-varying thermocline depth has the potential to promote mixing between layers. Alternatively, using the linked-mode model, two stratified segments may be specified with water volumes that are calculated independently from the thermocline depth; see section 3.8 for more details about stratification in linked-mode.

By default, AQUATOX routes inflow and outflow to and from both segments as weighted by volume. For example, if the hypolimnion has twice as much volume as the epilimnion, twice as

much inflow water will be routed to the hypolimnion as to the epilimnion (and twice as much outflow water will be routed from the hypolimnion). The user has the option to route all inflow and outflow waters to and from either segment. In this case, all of the nutrients, chemicals, and other loadings within the inflow water will be routed directly to the specified segment and will not be transferred to the other segment except through turbulent diffusion or overturn. Atmospheric and point-source loadings are assumed to be routed to the epilimnion in all cases (unless a linked-mode model is used in which case more flexibility is present).

Additionally, if a user has information about the timing of stratification, this may be specified on the "stratification-options" entry screen. This can be used to specify winter stratification, for example, or precise periods of stratification for each year modeled. If only one year of stratification dates are entered and multiple years are modeled, all years are assumed to stratify and overturn on the dates specified in the user input (regardless of the year specified).

3.5 Temperature

Temperature is an important controlling factor in the model. Virtually all processes are temperature-dependent. They include stratification; biotic processes such as decomposition, photosynthesis, consumption, respiration, reproduction, and mortality; and chemical fate processes such as microbial degradation, volatilization, hydrolysis, and bioaccumulation. On the other hand, temperature rarely fluctuates rapidly in aquatic systems. Default water temperature loadings for the epilimnion and hypolimnion are represented through a simple sine approximation for seasonal variations (Ward, 1963) based on user-supplied observed means and ranges (Figure 45):

$$Temperature = TempMean + (-1.0 \cdot \frac{TempRange}{2}$$
$$\cdot (\sin(0.0174533 \cdot (0.987 \cdot (Day + PhaseShift) - 30))))]$$

(25)

where:

$Temperature$	=	average daily water temperature (deg. C);
$TempMean$	=	mean annual temperature (deg. C);
$TempRange$	=	annual temperature range (deg. C),
Day	=	day of year (d); and
$PhaseShift$	=	time lag in heating (= 90 d).

Observed temperature loadings should be entered if responses to short-term variations are of interest. This is especially important if the timing of the onset of stratification is critical, because stratification is a function of the difference in hypolimnetic and epilimnetic temperatures (see Figure 42). It also is important in streams subject to releases from reservoirs and other point-source temperature impacts.

3.6 Light

Light is important as the controlling factor for photosynthesis and photolysis. The default incident light function formulated for AQUATOX is a variation on the temperature equation, but without the lag term:

<table>
<tr><td>

Light: Simplifying Assumptions

- Ice cover is assumed when the average water temperature drops below 3 degrees centigrade.
- Photoperiod is approximated by Julian date (day of year)
- Average daily light is the program default, although hourly light may be simulated

</td></tr>
</table>

$$Solar = LightMean + \frac{LightRange}{2} \cdot \sin(0.0174533 \cdot Day - 1.76) \cdot Frac_{Light}$$

(26)

$$Frac_{Light} = 1.0 - 0.98(Canopy)$$

where:

Solar	=	average daily incident light intensity (ly/d);
LightMean	=	mean annual light intensity (ly/d);
LightRange	=	annual range in light intensity (ly/d);
Day	=	day of year (d, adjusted for hemisphere);
Frac $_{Light}$	=	fraction of site that is shaded; and
Canopy	=	user input fraction of site that is tree shaded.

The derived values are given as average light intensity in Langleys per day (Ly/d = 10 kcal/m^2·d). An observed time-series of light also can be supplied by the user; this is especially important if the effects of daily weather conditions are of interest. For standing water, if the average water temperature drops below 3 deg.C, the model assumes the presence of ice cover and decreases transmitted light to 15% of incident radiation. (This has changed from 33% in Release 2.2.) This reduction, due to the reflectivity and transmissivity of ice and snow, is an average of widely varying values summarized by Wetzel (2001). New to Release 3.2, for moving water (streams and rivers), the average water temperature must drop below 0 deg. C before ice cover is assumed. For estuaries, average water temperature must fall below -1.8 deg.C before the model assumes ice cover due to the influence of salinity.

Shade can be an important limitation to light, especially in riparian systems. A user input "fraction of site subject to shade from a canopy" parameter can be entered either as a constant or as a time-series within the "Site" input screen. This parameter can be left as zero for no shading effects on light. Transmission of light through a riparian (stream-side) canopy is a combination of diffuse and direct transmission (Canham et al. 1990). The average of four forest types from closed hemlock to open spruce (and cypress) forests is 2% of incident radiation (Canham et al. 1990). Detailed studies in a Midwestern mixed deciduous forest confirm this value for the summer months, although transmission increased to 40% in winter (Oliphant et al. 2006). A

value of 2% transmission for a closed canopy is used in AQUATOX. If the density of canopy varies during the year, then a time-series should be provided, keeping in mind that the 2% transmission will still apply to the fraction of canopy that is indicated.

Photoperiod is an integral part of the photosynthesis formulation. It is approximated using the Julian date following the approach of Stewart (1975) (Figure 46):

$$Photoperiod = \frac{12 + A \cdot \cos\left(380 \cdot \frac{Day}{365} + 248\right)}{24} \tag{27}$$

where:

Photoperiod	=	fraction of the day with daylight (unitless); converted from hours by dividing by 24;
A	=	hours of daylight minus 12 (d); and
Day	=	day of year (d, converted to radians).

A is the difference between the number of hours of daylight at the summer solstice at a given latitude and the vernal equinox, and is given by a linear regression developed by Groden (1977):

$$A = 0.1414 \cdot Latitude - Sign \cdot 2.413 \tag{28}$$

where:

Latitude	=	latitude (deg., decimal), negative in southern hemisphere; and
Sign	=	1.0 in northern hemisphere, -1.0 in southern hemisphere.

Figure 45. Annual Temperature
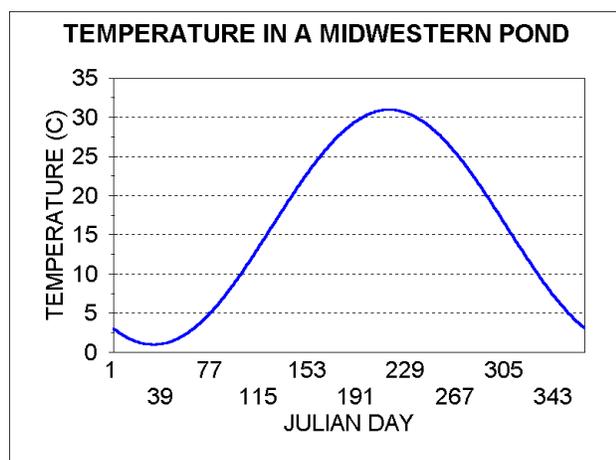
Figure 46. Photoperiod as a Function of Date
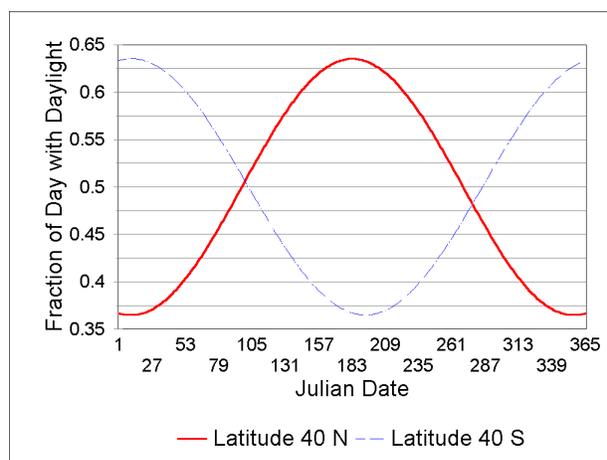
Hourly Light

When the model is run with an hourly time-step, solar radiation is calculated as variable during the course of each day. The following equation is used to distribute the average daily incident light intensity over the portion of the day with daylight hours.

$$Solar_{hourly} = \frac{\pi}{2} \cdot \frac{Solar_{daily}}{Photoperiod}$$

$$\cdot \sin\left(\pi \cdot \frac{FracDayPassed - \dfrac{1\text{-}Photoperiod}{2}}{Photoperiod}\right) \cdot Frac_{Light} \qquad \textbf{(29)}$$

where:

$Solar_{hourly}$	=	solar radiation at the given time-step (ly/d);
$Solar_{daily}$	=	average daily incident light intensity (ly/d), see **(25);**
$Photoperiod$	=	fraction of the day with daylight (unitless); see **(26);**
$FracDayPassed$	=	fraction of the day that has passed (unitless)
$Frac_{Light}$	=	fraction of site that is un-shaded, (frac., 1.0-user input shade);

A user may enter a constant or time-series shade variable in the site window ("Fraction of Site that is Shaded"). When this input is utilized then the $Frac_{Light}$ variable is calculated.

Figure 47: Average light per day is distributed during daylight hours
in a semi-sinusoidal pattern based on photoperiod.
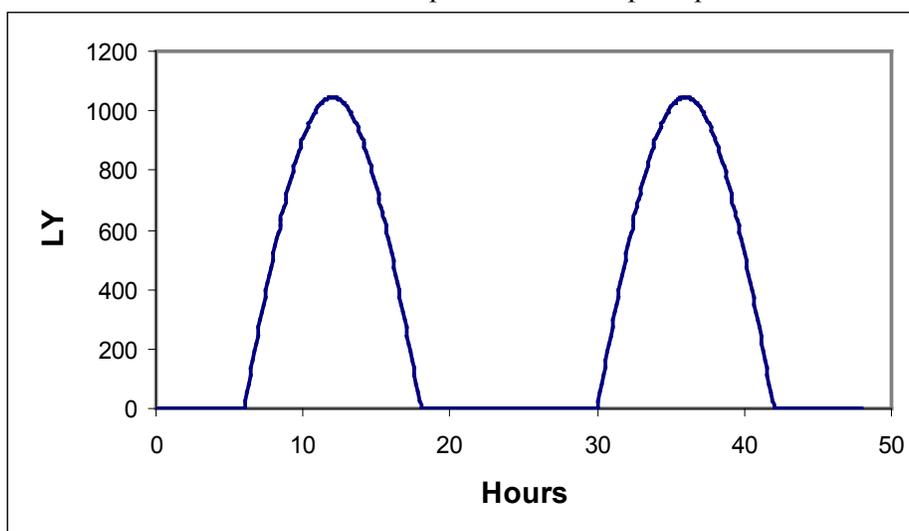
3.7 Wind

Wind is an important driving variable because it determines the stability of blue-green algal blooms, affects reaeration or oxygen exchange, and controls volatilization of some organic chemicals. Wind also can affect the depth of stratification for estuaries. Wind is usually measured at meteorological stations at a height of 10 m and is expressed

> **Wind: Simplifying Assumptions**
>
> - If site data are not available a Fourier series is used to represent wind loadings

as m/s. If site data are not available, default variable wind speeds are represented through a Fourier series of sine and cosine terms; the mean and twelve additional harmonics seem to effectively capture the variation (Figure 48):

$$Wind = CosCoeff_0 + \Sigma \left(CosCoeff_n \cdot Cos\left(\frac{Freq_n \cdot 2\pi \cdot Day}{365} \right) + SinCoeff_0 \cdot Sin\left(\frac{Freq_n \cdot 2\pi \cdot Day}{365} \right) \right) \textbf{(30)}$$

where:

Wind	=	wind speed; amplitude of the Fourier series (m/s);
CosCoeff$_0$	=	cosine coefficient for the 0-order harmonic, which is the mean wind speed (default = 3 m/s);
CosCoeff$_n$	=	cosine coefficient for the nth-order harmonic;
Day	=	day of year (d);
SinCoeff$_n$	=	sine coefficient for the nth-order harmonic;
Freq$_n$	=	selected frequency for the nth- order harmonic.

This default loading is based on an annual cycle of data taken from the Buffalo, NY airport. Therefore, it has a 365-day repeat, representative of seasonal variations in wind. Frequencies were selected to ensure that the standard deviation of the Fourier series and the data were closely matched. The frequency of wind-speeds of less than three meters per second were also precisely matched to observed data as well as the periodicity of wind-events. The Fourier approach is quite useful because the mean can be specified by the user and the variability will be imposed by the function.

If ice cover is predicted, wind is set to 0. A user also may input a site-specific time series, which may be important where the timing of a cyanobacteria bloom or reaeration is of interest.

Figure 48. Default wind loadings for Onondaga Lake with mean = 4.17 m/s.
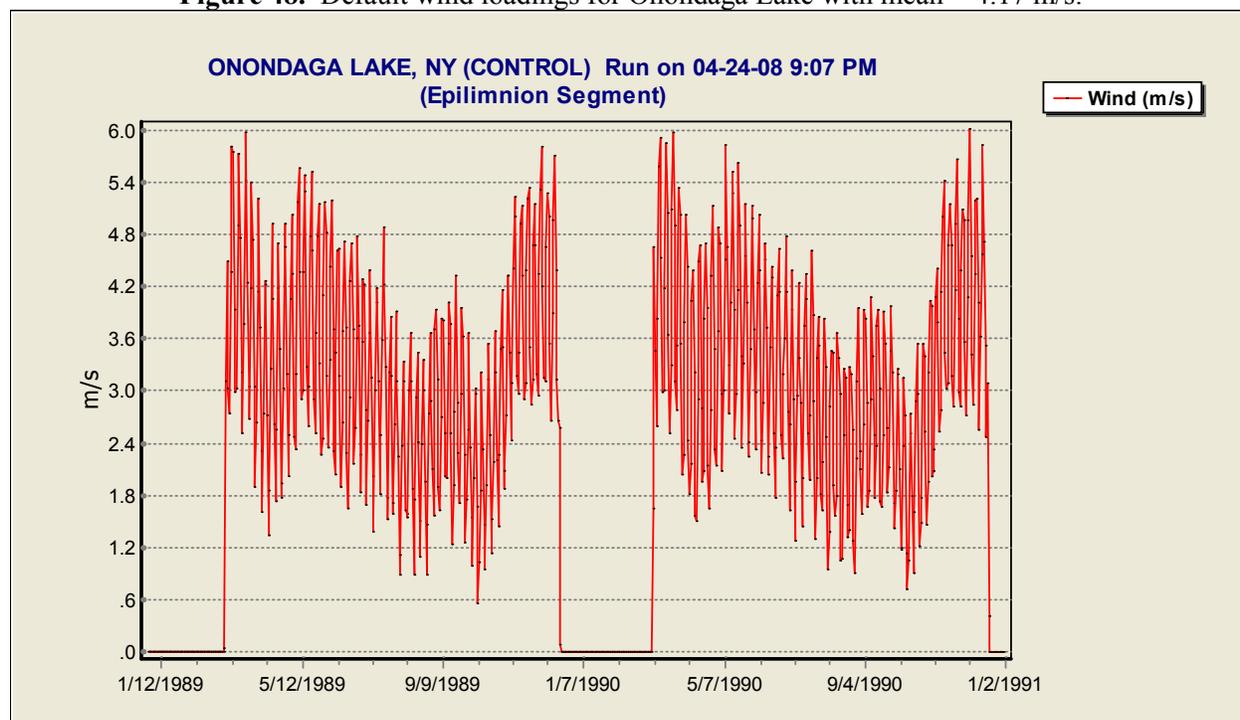
3.8 Multi-Segment Model

AQUATOX Release 3 includes the capability to link AQUATOX segments together, tracking the flow of water and the passage of state variables from segment to segment. Some general guidelines for using this model follow:

- All linked segments must have an identical set of state variables. (State variables that do not occur in one segment may be set to zero there.)
- Parameters pertaining to animal, plant, and chemical state variables (i.e. "underlying data") are considered global to the entire linked system. If the user changes one of these parameters in one segment, this parameter changes within all segments.
- On the other hand, "site" parameters, initial conditions, and boundary conditions are unique to each segment.
- State variables can pass from segment to segment through active upstream and downstream migration, passive drift, diffusion, and bedload.
- Mass balance of all state variables is maintained throughout a multi-segment simulation.

> **Multi-Segment Model: Simplifying Assumptions**
>
> - All linked segments have an identical set of state variables
> - Each segment is well mixed
> - Linkages between segments may be unidirectional or bidirectional
> - Dynamic stratification does not apply; stratified pairs of segments must be specified by the user

There are two types of linkages that may be specified between individual segments, "cascade links" and "feedback links." A cascade link is unidirectional; there is no potential for water or

state variable flow back upstream. Segments that are linked together by cascade linkages are solved separately from one another moving from upstream to downstream. This is particularly useful when modeling faster flowing rivers and streams.

A feedback link allows for water or state variables to flow in both directions. For bookkeeping purposes, water flows are required to be unidirectional (i.e. entered water flows over a feedback link must not be negative). However, two feedback links may be specified simultaneously (in opposite directions) to allow for bidirectional water flows. Feedback links may also be subject to diffusion; a diffusion coefficient, characteristic length, and cross section must be entered for diffusion to be calculated, see **(32)**. Segments that are linked together by feedback links are solved simultaneously. There may only be one contiguous set of segments linked together by feedback linkages within a simulation (i.e. the model will not solve a "feedback" set of segments followed by downstream cascade segments followed by more feedback segments below that.)

Figure 49 gives an example of a simulation in which cascade segments and feedback segments are both included. In this case, AQUATOX solves the simulation from the top down, solving each segment 1-4, 6, and 6b individually before moving on to solve the feedback segments simultaneously. Finally, segments 11-14 are be solved individually using the results from the simultaneous segment run.

Figure 49: An example of feedback and cascade segments linked together**.**
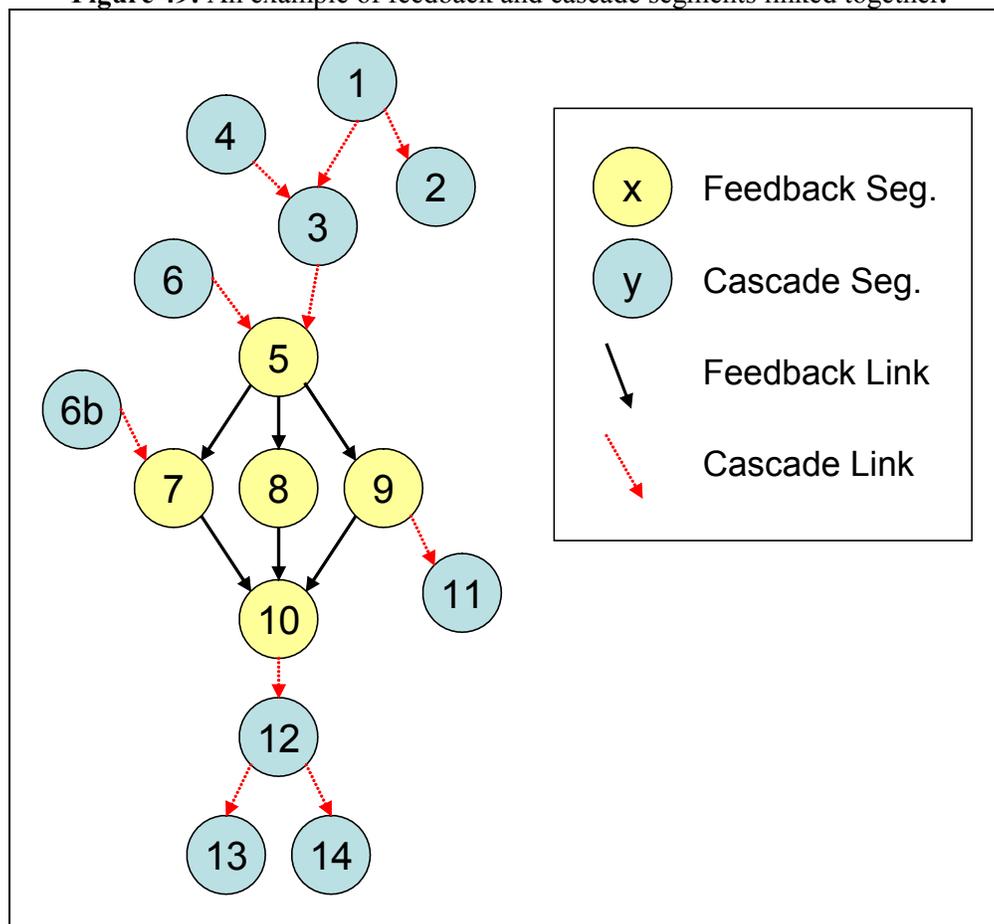
Stratification and the Multi-Segment Model

Dynamic stratification as described in section 3.4 does not apply to the multi-segment model. Instead, a user may specify two linked segments as a stratified pair. In this case, the segments must be linked together with a feedback linkage. A "stratification" screen within each segment's main interface allows a user to specify whether a segment is part of a stratified pair and, if so, whether it is the epilimnion or the hypolimnion segment.

When two segments are set up as stratified together, the thermocline area is defined by the user-entered cross section between. Annual cycles of stratification and overturn may be specified using the time varying water flows and dispersion coefficients. As was the case in the dynamic stratification model, fish automatically migrate to the epilimnion in the case of hypoxia in the lower segment. Sinking phytoplankton and suspended detritus in the epilimnion segment fall into the designated hypolimnion segment. The light climate of the bottom segment is limited to that light which penetrates the segment defined as the epilimnion.

When the linked system has enough specified throughflow between the epilimnion and hypolimnion segment, it is considered to be "well mixed." This is defined as when the average daily water flow between segments is greater than 30% of the total water volume in both segments. In this case, fish are assumed to have an equal preference to both segments and they migrate to equality in a biomass basis. (This allows fish to return to the hypolimnion if it had earlier been vacated due to anoxia.) Another implication of a well-mixed stratified system (in linked mode) is that a weighted average of light climate is used when calculating plant productivity. The calculation of *LightLimit* for plants **(38)** is based on a thickness-weighted average of algal biomass and sediment throughout the entire thickness of the system. This prevents unreasonable model results due to the light climate in a very thin epilimnion, for example. Because the system is well-mixed, suspended algae should instead be subject to the light climate throughout the water column.

State Variable Movement in the Multi-Segment Model

To maintain mass balance, all state variables that are subject to washout or passive drift are also added to any downstream linked segments. The calculation for this process is as follows:

$$Washin = \sum_{upstream\ links} \frac{Washout_{Upstream} \cdot Volume_{Upstream} \cdot FracWash_{ThisLink}}{Volume_{Downstream\ Segment}} \quad \textbf{(31)}$$

In the case of toxicants that are absorbed to or contained within a drifting state variable, the following equation is used:

$$Washin_{ToxCarrier} = \sum_{upstream\ links} \frac{Washout_{Carrier} \cdot PPB_{Carrier} \cdot 1e6 \cdot Volume_{Upstream} \cdot FracWash_{ThisLink}}{Volume_{Dowstream\ Segment}} \quad \textbf{(32)}$$

where:

$Washin$ =   inflow load from upstream segment (unit/$L_{downstream} \cdot$ d);

$Washout_{Upstream}$ =   washout from upstream segment (unit/$L_{upstream} \cdot$ d), see **(16)**;

$Volume_{Segment}$ =   volume of given segment (m^3);

$FracWash_{ThisLink}$ =   fraction of upstream segment's outflow that goes to this particular downstream segment (unitless);

$Washin_{ToxCarrier}$ =   inflow load of toxicant sorbed to a carrier from an upstream segment ($\mu g/L_{downstream} \cdot$ d);

$Washout_{Carrier}$ =   washout of toxicant carrier from upstream (mg/$L_{upstream} \cdot$ d);

$PPB_{Carrier}$ =   concentration of toxicant in carrier upstream ($\mu g/kg$), see **(310)**;

1e-6   =   units conversion (kg/mg)

This *Washin* term is added to all derivatives for state variables that are suspended in the water column and subject to drift or "washout."

Dissolved state variables are subject to diffusion across feedback links.

$$Diffusion_{\,ThisSeg} = \frac{DiffCoeff \cdot Area}{CharLength}\left(Conc_{OtherSeg} - Conc_{ThisSeg}\right) \qquad \textbf{(33)}$$

where:

$Diffusion_{ThisSeg}$ = gain of state variable due to diffusive transport over the feedback link between two segments, (unit/d);

$DiffCoeff$ =   dispersion coefficient of feedback link, (m^2 /d);

$Area$ =   surface area of the feedback link (m^2);

$CharLength$ =   characteristic mixing length of the feedback link, (m);

$Conc_{Segment}$ =   concentration of state variable in the relevant segment, (unit/m^3);

3.9 "Marine" Site Type

A "marine" site type has been added to the AQUATOX list of site types, bringing the full list to "pond," "lake," "stream," "reservoir," "enclosure," "estuary," and "marine." The marine site type was required because the "estuary" site type includes assumptions of salt-wedge stratification that are not always appropriate for the nearshore marine environment (for more information about the estuarine submodel, please see chapter 10.

If a "marine" site type has been selected the following characteristics of a simulation apply:
- Salinity must be included as a state variable;
- Nitrification and denitrification are not assumed limited by dissolved oxygen (i.e. *DO Correction* is set to 1.0 in Equation **(174)** is and to 0.0 in equation **(175)**)
- Reaeration is calculated using the AQUATOX estuarine reaeration code that takes into account salinity, wind effects, and water velocity (see equation **(445)**)

- Stratified segments are labeled "upper" and "lower" rather than "epilimnion" and "hypolimnion."
- The temperature at which water is assumed to freeze is calculated using Equation (1) below from UNESCO (1983).

$$T_f = -0.0575 \cdot S + 1.710523 \cdot 10^{-3} \cdot S^{\frac{3}{2}} - 2.154996 \cdot 10^{-4} \cdot S^2 \qquad \textbf{(23b)}$$

where:

T_f =   freezing temperature of saline water (deg C); and
S =   salinity (ppt).

4. BIOTA

The biota consists of two main groups, plants and animals; each is represented by a set of process-level equations. In turn, plants are differentiated into algae and macrophytes, represented by slight variations in the differential equations. Algae may be either phytoplankton or periphyton. Phytoplankton are subject to sinking and

> **Biota: Simplifying Assumptions**
>
> - Biomass is simulated but not numbers of individual organisms
> - Responses are simulated as averages for the entire group

washout, while periphyton are subject to substrate limitation and scour by currents. Bryophytes and freely-floating macrophytes are modeled as special classes of macrophytes, limited by nutrients in the water column. These differences are treated at the process level in the equations (Table 5). All are subject to habitat availability, but to differing degrees.

Table 5. Significant Differentiating Processes for Plants

Plant Type	Nutrient Lim.	Current Lim.	Light Lim.	Sinking	Washout	Sloughing	Breakage	Habitat
Phytoplankton	❑		❑	❑	❑			❑
Periphyton	❑	❑	❑			❑		❑
Benthic Macrophytes			❑				❑	❑
Rooted-Floating Macrophytes							❑	❑
Free-Floating Macrophytes	❑				❑		❑	❑
Bryophytes	❑		❑				❑	❑

Animals are subdivided into invertebrates and fish; the invertebrates may be "plankton invertebrates," "nekton invertebrates," "benthic insects," or other "benthic invertebrates." These groups are represented by different parameter values and by variations in the equations. Insects are subject to emergence and therefore are lost from the system, but benthic invertebrates are not. Fish may be represented by both juveniles and adults, which are connected by promotion. One fish species can be designated as multi-year with up to 15 age classes connected by promotion. Differences are shown in Table 6.

In addition to the directly-modeled animal categories above, a bioaccumulative endpoint such as bald eagle, dolphin, or mink that feeds on aquatic compartments can be simulated. This compartment is defined by feeding preferences, biomagnification factor, and clearance rate (see section 4.4).

Table 6. Significant Differentiating Processes for Animals

Animal Type	Washout	Drift	Scour Entrainment	Emergence	Promotion/ Recruitment	Multi-year
Plankton Invert.	❑					
Nekton Invert.		❑	❑		*	
Benthic Invert.		❑	❑		*	
Benthic Insect		❑	❑	❑		
Fish			❑		❑	❑

* Oysters or size-class predatory invertebrates.

Guild Organization

To better generalize the aquatic ecosystem and to represent marine-biology conventions, the guilds used by AQUATOX to characterize animals have been reorganized in this version. Specifically, "shredders" have been renamed to "deposit feeders" and the "grazer" compartment has been split into "suspended feeders" and "deposit feeders." The animal compartments available for food web modeling are as follows:

Guild Name	Number of Compartments
Suspension Feeders	6
Deposit Feeders	3
Veliger	2
Spat	2
Clams/Adult Oysters	4
Snails	2
Small Predatory Invert.	2
Predatory Invertebrate	4
Small Forage Fish	2
Large Forage Fish	2
Small Bottom Fish	2
Large Bottom Fish	2
Small Game Fish	4
Large Game Fish	4
Age-Class Fish	15

Anti-Extinction Code

Plants or animals with non-zero initial conditions are assumed to be "seeded" in the case that their biomass drops to zero. This allows for species recovery in the aftermath of a physical or

chemical shock to a system.   Each time a plant or animal has a biomass that falls to below 1×10^{-10} mg/L that organism is re-seeded with a loading of 1×10^{-7} mg/L.

4.1 Algae

Plants: Simplifying Assumptions

- Photosynthesis is modeled as a maximum observed rate multiplied by reduction factors. The reduction factors are assumed to be independent of one another.
- There are two options for modeling nutrient effects on plants. Intracellular storage of nutrients may be modeled as a new option to Release 3.2; otherwise constant stoichiometry within species is assumed and nutrient limitation is calculated as a function of nutrients in the water column.
- For each individual nutrient, saturation kinetics is assumed
- Algae exhibit a nonlinear, adaptive response to temperature changes
- Low temperatures are assumed not to affect algal mortality
- The ratio between biovolume and biomass is assumed to be constant for a given growth form
- Constant chlorophyll a to biomass ratios are assumed within algae groups

Phytoplankton-specific
- Phytoplankton other than cyanobacteria are assumed to be mixed throughout the well-mixed layer unless specified as "surface floating."
- In the event of ice cover, all phytoplankton will occur in the top 2 m
- Sinking of phytoplankton is modeled as a function of physiological state
- Phytoplankton are subject to downstream drift as a simple function of discharge
- To model phytoplankton (and zooplankton) residence time, an implicit assumption may be made that upstream reaches included in the *"Total River Length"* have identical environmental conditions as the reach being modeled

Cyanobacteria-specific
- By default cyanobacteria are specified as "surface floating" in which case they are assumed to be located in the top 0.1 m unless limited by lack of nutrients or sufficient wind occurs in which case they are located within the top 3 m. This default assumption (that cyanobacteria float) can be changed by the user.
- The averaging depth for "surface floating" plants is three meters to more closely correspond to monitoring data.
- Cyanobacteria are not severely limited by nitrogen due to facultative nitrogen fixation (if N less than ½ KN)

Periphyton-specific
- Periphyton are limited by slow currents that do not replenish nutrients and carry away senescent biomass
- Periphyton are assumed to adapt to the ambient conditions of a particular channel
- Periphyton are defined as including associated detritus; non-living biomass is modeled implicitly

Macrophyte-specific
- Macrophytes occupy the littoral zone
- Rooted macrophytes and benthic macrophytes are not limited by nutrients but are assumed to take up necessary nutrients from bottom sediments (located outside the AQUATOX domain)
- Rooted floating macrophytes are differentiated from benthic macrophytes in that rooted-floating macrophytes are assumed to occur near the surface and are not limited by low light
- Non-rooted, floating macrophytes are limited by nutrients but not by low light. These macrophytes can wash out of a system.
- Bryophytes are limited by nutrients, can tolerate low light, and contain a high percentage of refractory material

The change in algal biomass—expressed as g/m^3 for phytoplankton, but as g/m^2 for periphyton—is a function of the loading (especially phytoplankton from upstream), photosynthesis, respiration, excretion or photorespiration, nonpredatory mortality, grazing or predatory mortality, sloughing, and washout. As noted above, phytoplankton also are subject to sinking. If the system is stratified, turbulent diffusion also affects the biomass of phytoplankton.

$$\frac{dBiomass_{Phyto}}{dt} = Loading + Photosynthesis - Respiration - Excretion$$
$$- Mortality - Predation \pm Sinking \pm Floating \qquad \textbf{(34)}$$
$$- Washout + Washin \pm TurbDiff + Diffusion_{Seg} + \frac{Slough}{3}$$

$$\frac{dBiomass_{Peri}}{dt} = Loading + Photosynthesis - Respiration - Excretion$$
$$\qquad \textbf{(35)}$$
$$- Mortality - Predation + Sed_{Peri} - Slough$$

where:

$dBiomass/dt$	=	change in biomass of phytoplankton and periphyton with respect to time (g/m^3·d and g/m^2·d);
$Loading$	=	boundary-condition loading of algal group (g/m^3·d and g/m^2·d);
$Photosynthesis$	=	rate of photosynthesis (g/m^3·d and g/m^2·d), see **(35)**;
$Respiration$	=	respiratory loss (g/m^3·d and g/m^2·d), see **(63)**;
$Excretion$	=	excretion or photorespiration (g/m^3·d and g/m^2·d), see **(64)**;
$Mortality$	=	nonpredatory mortality (g/m^3·d and g/m^2·d), see **(66)**;
$Predation$	=	herbivory (g/m^3·d and g/m^2·d), see **(99)**;
$Washout$	=	loss due to being carried downstream (g/m^3·d), see **(129)**;
$Washin$	=	loadings from upstream segments (linked segment version only, g/m^3·d), see **(30)**;
$Sinking$	=	loss or gain due to sinking between layers and sedimentation to bottom (g/m^3·d), see **(69)**;
$Floating$	=	loss from the hypolimnion or gain to the epilimnion due to the floatation of "surface-floating" phytoplankton. 100% of "surface-floating" phytoplankton that arrive in the hypolimnion through loadings or water flows are set to immediately float.
$TurbDiff$	=	turbulent diffusion (g/m^3·d), see **(22)** and **(23)**;
$Diffusion_{Seg}$	=	gain or loss due to diffusive transport over the feedback link between two segments, (g/m^3·d), see **(32)**;
$Slough$	=	Scour loss of Periphyton or addition to linked Phytoplankton, see **(75)**; and
Sed_{Peri}	=	Sedimentation of Phytoplankton to Periphyton, see **(83).**

Figure 50 and Figure 51 are examples of the predicted changes in biomass and the processes that contribute to these changes in a eutrophic lake. Note that photosynthesis and predation dominate the diatom rates, with respiration much less important during the growing season.

Figure 50. Predicted algal biomass in Lake Onondaga, New York
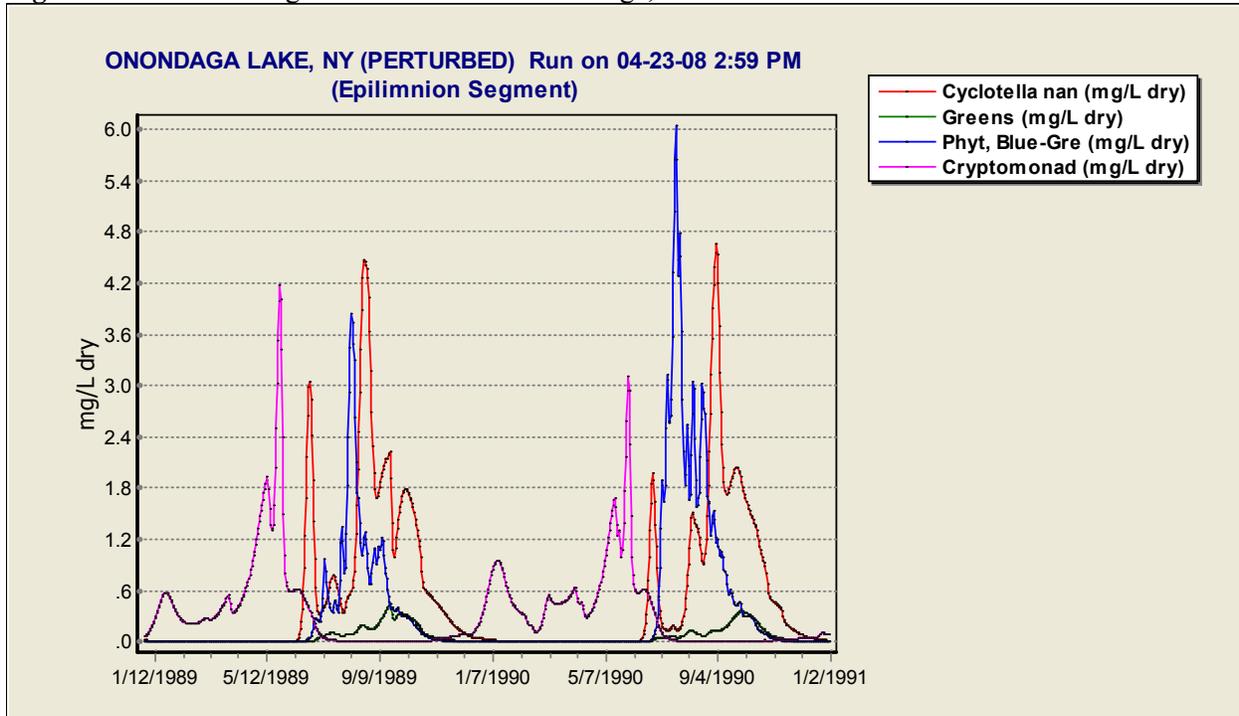
Figure 51. Predicted process rates for diatoms in Lake Onondaga, New York
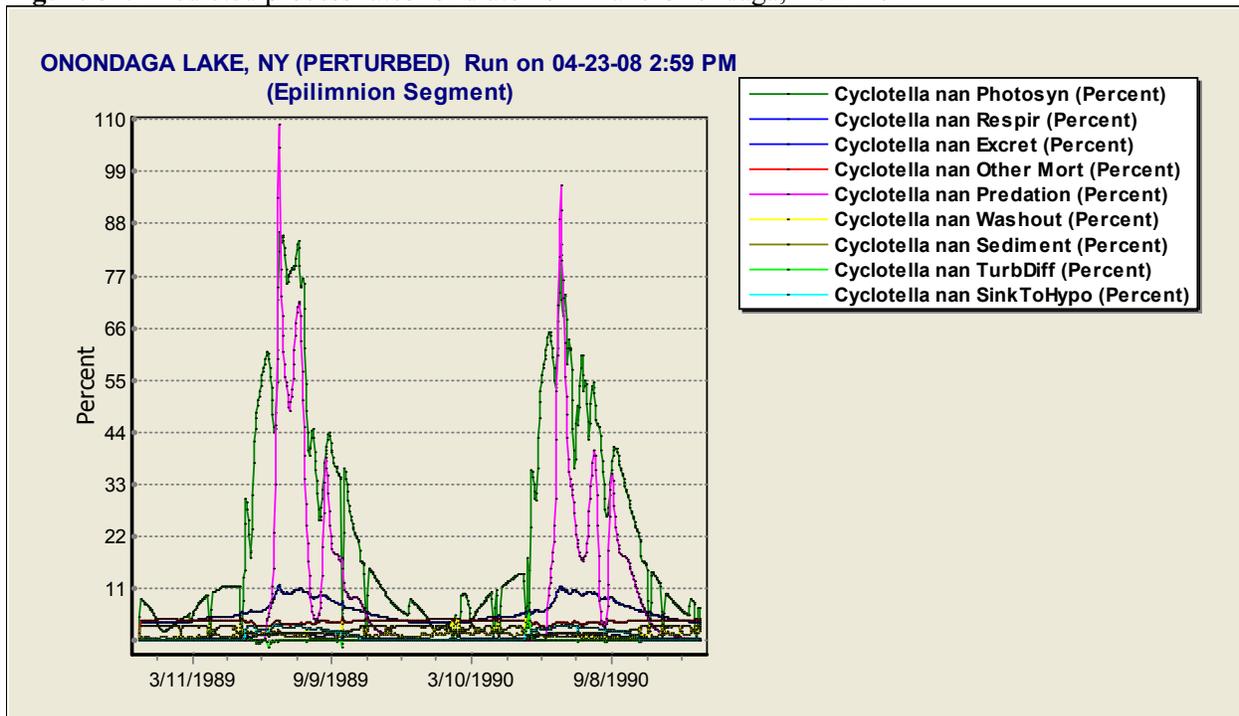
Photosynthesis is modeled as a maximum observed rate multiplied by reduction factors for the effects of toxicants, habitat, and suboptimal light, temperature, current, and nutrients:

$$Photosynthesis = PMax \cdot PProdLimit \cdot Biomass \cdot HabitatLimit \cdot SaltEffect \qquad \textbf{(36)}$$

The limitation of primary production in phytoplankton is:

$$PProdLimit = LtLimit \cdot NutrLimit \cdot TCorr \cdot FracPhoto \qquad \textbf{(37)}$$

Periphyton have an additional limitation based on available substrate, which includes the littoral bottom and the available surfaces of macrophytes. The macrophyte surface area conversion is based on the observation of 24 m^2 periphyton/m^2 bottom (Wetzel, 1996) and assumes that the observation was made with 200 g/m^3 macrophytes.

$$PProdLimit = \ LtLimit \cdot NutrLimit \cdot VLimit \cdot TCorr \cdot FracPhoto$$
$$\cdot (\ FracLittoral + SurfAreaConv \cdot Biomass_{Macrophytes}\ ) \qquad \textbf{(38)}$$

where:

$Pmax$	=	maximum photosynthetic rate (1/d);
$LtLimit$	=	light limitation (unitless), see **(38)**;
$NutrLimit$	=	nutrient limitation (unitless), see **(55)** and **(55b)** ;
$Vlimit$	=	current limitation for periphyton (unitless), see **(56)**;
$TCorr$	=	limitation due to suboptimal temperature (unitless), see **(59)**;
$HabitatLimit$	=	in streams, habitat limitation based on plant habitat preferences (unitless), see **(13)**.
$SaltEffect$	=	effect of salinity on photosynthesis (unitless);
$FracPhoto$	=	reduction factor for effect of toxicant on photosynthesis (unitless), see **(421)**;
$FracLittoral$	=	fraction of area that is within euphotic zone (unitless) see **(11)**;
$SurfAreaConv$	=	surface area conversion for periphyton growing on macrophytes (0.12 m^2/g);
$Biomass_{Macro}$	=	total biomass of macrophytes in system (g/m^2); and
$Biomass_{Peri}$	=	biomass of periphytic algae (g/m^2).

Under optimal conditions, a reduction factor has a value of 1; otherwise, it has a fractional value. Use of a multiplicative construct implies that the factors are independent. Several authors (for example, Collins, 1980; Straškraba and Gnauck, 1983) have shown that there are interactions among the factors. However, we feel the data are insufficient to generalize to all algae; therefore, the simpler multiplicative construct is used, as in many other models (Chen and Orlob, 1975; Lehman et al., 1975; Jørgensen, 1976; Di Toro et al., 1977; Kremer and Nixon, 1978; Park et al., 1985; Ambrose et al., 1991). Default parameter values for the various processes are taken primarily from compilations (for example, Jørgensen, 1979; Collins and Wlosinski, 1983; Bowie et al., 1985); they may be modified as needed.

Light Limitation

Because it is required for photosynthesis, light is a very important limiting variable. It is especially important in controlling competition among plants with differing light requirements. Similar to many other models (for example, Di Toro et al., 1971; Park et al., 1974, 1975, 1979, 1980; Lehman et al., 1975; Canale et al., 1975, 1976; Thomann et al., 1975, 1979; Scavia et al., 1976; Bierman et al., 1980; O'Connor et al., 1981), AQUATOX uses the Steele (1962) formulation for light limitation. Light is specified as average daily radiation. The average radiation is multiplied by the photoperiod, or the fraction of the day with sunlight, based on a simplification of Steele's (1962) equation proposed by Di Toro et al. (1971). The equation is slightly different when the model is run with a daily versus an hourly time-step:

$$LtLimit_{Daily} = 0.85 \cdot \frac{e \cdot Photoperiod \cdot (LtAtDepth_{Daily} - LtAtTop_{Daily}) \cdot PeriphytExt}{Extinct \cdot (Depth_{Bottom} - Depth_{Top})} \quad \textbf{(39)}$$

$$LtLimit_{Hourly} = \frac{e \cdot (LtAtDepth_{Hourly} - LtAtTop_{Hourly}) \cdot PeriphytExt}{Extinct \cdot (Depth_{Bottom} - Depth_{Top})} \quad \textbf{(40)}$$

where:

$LtLimit_{TimeStep}$	=	light limitation (unitless);
e	=	the base of natural logarithms (2.71828, unitless);
$Photoperiod$	=	fraction of day with daylight (unitless), see **(26)**;
$Extinct$	=	total light extinction (1/m), see **(40)**, **(41)**;
$Depth_{Bottom}$	=	maximum depth or depth of bottom of layer if stratified (m); if periphyton or macrophyte then limited to euphotic depth;
$Depth_{Top}$	=	depth of top of layer (m);
$LtAtTop$	=	limitation of algal growth due to light, (unitless) see **(44)**, **(45)**;
$LtAtDepth$	=	limitation due to insufficient light, (unitless), see **(43)**;
$PeriphytExt$	=	extinction due to periphyton; only affects periphyton and macrophytes (unitless), see **(42)**.

Because the equation overestimates by 15 percent the cumulative effect of light limitation over a 24-hour day, a correction factor of 0.85 is applied to the daily formulation (Kremer and Nixon, 1978). When AQUATOX is run with an hourly time-step, the correction factor of 0.85 is not relevant, nor the inclusion of photoperiod.

Light limitation does not apply to free-floating macrophytes as these are assumed to be located at the surface of the water.

Even when the model is run with an hourly time-step, two algal equations utilize the daily light limit equation **(38)** as most appropriate. First, when calculating algal mortality, the stress factor for suboptimal light and nutrients **(68)** is expecting the input of daily light limitation (i.e. the plants do not all die each night). Secondly, when calculating the sloughing of benthic algae **(75)**

the calculation of suboptimal light is calibrated to daily light limitation, not the instantaneous absence or presence of light (i.e. sloughing is not more likely to occur when it is dark).

Extinction of light is based on several additive terms: the baseline extinction coefficient for water (which may include suspended sediment if it is not modeled explicitly), the so-called "self-shading" of plants, attenuation due to suspended particulate organic matter (POM) and inorganic sediment, and attenuation due to dissolved organic matter (DOM):

$$Extinct = WaterExtinction + PhytoExtinction + ECoeffDOM \cdot DOM$$
$$+ ECoeffPOM \cdot \Sigma PartDetr + ECoeffSed \cdot InorgSed$$

(41)

where:

WaterExtinction	=	user-supplied extinction due to water (1/m);
PhytoExtinction	=	user-supplied extinction due to phytoplankton and macrophytes (1/m), see **(41)**, **(42)**;
ECoeffDOM	=	attenuation coefficient for dissolved detritus $1/(m \cdot g/m^3)$;
DOM	=	concentration of dissolved organic matter (g/m^3), see **(143)** and **(144)**;
ECoeffPOM	=	attenuation coefficient for particulate detritus $1/(m \cdot g/m^3)$;
PartDetr	=	concentration of particulate detritus (g/m^3), see **(141)** and **(142)**;
ECoeffSed	=	attenuation coefficient for suspended inorganic sediment $1/(m \cdot g/m^3)$; and
InorgSed	=	concentration of total suspended inorganic sediment (g/m^3), see **(244)**.

For computational reasons, the value of *Extinct* is constrained between 5^{-19} and 25. Self-shading by phytoplankton, periphyton, and macrophytes is a function of the biomass and attenuation coefficient for each group. Extinction by periphyton is computed differently because it is not depth-dependent but rather pertains to the growing surface:
and

$$PhytoExtinction = \sum_{alga} (ECoeffPhyto_{alga} \cdot Biomass_{alga})$$

(42)

$$PeriPhytExt = e^{\sum_{peri} (- ECoeffPhyto_{peri} \cdot Biomass_{peri})}$$

(43)

where:

EcoeffPhyto_{alga}	=	attenuation coefficient for given phytoplankton or macrophyte $(1/m\text{-}g/m^3)$,
EcoeffPhyto_{peri}	=	attenuation coefficient for given periphyton $(1/m\text{-}g/m^2)$,
Biomass	=	concentration of given plant $(g/m^3$ or $g/m^2)$, and

The light limitation at depth is computed by:

$$LtAtDepth_{TimeStep} = e^{\left(-\frac{Light_{TimeStep} \cdot e^{-Extinct_{Epi} \cdot DepthTop}}{LightSat \cdot LightCorr} \cdot e^{-Extinct_{VSeg} \cdot DepthBottom} \right)} \qquad \textbf{(44)}$$

Light limitation at the surface of the water body is computed by:

$$LtAtTop_{TimeStep} = e^{-\frac{Light_{TimeStep}}{LightSat \cdot LightCorr}} \qquad \textbf{(45)}$$

and light limitation at the top of the hypolimnion is computed by:

$$LtAtTop_{TimeStep} = e^{-\frac{Light_{TimeStep}}{LightSat \cdot LightCorr} \cdot e^{-Extinct_{Epi} \cdot DepthTop}} \qquad \textbf{(46)}$$

where:

LtAtTop	=	limitation of algal growth due to light, (unitless multiplier, *0 being no limitation, 1 being 100% limitation*)
LtAtDepth	=	limitation due to insufficient light, (unitless, see *LtAtTop*)
Extinct	=	overall extinction of light in relevant vertical segment (1/m), **(40)**
Light$_{TimeStep}$	=	photosynthetically active radiation (ly/d), **(46)**;
LightCorr	=	Correction factor, 1.0 for a daily time-step, 1.25 for an hourly time-step. *LightSat* is increased by 25% to account for instantaneous solar radiation as opposed to daily averages;
LightSat	=	light saturation level for photosynthesis (ly/d).

Phytoplankton not specified as "surface floating" are assumed to be mixed throughout the well mixed layer, although subject to sinking. However, healthy cyanobacteria (and some other algal species) tend to float. Therefore, if the phytoplankton is specified as "surface floating" and the nutrient limitation is greater than 0.25 (Equation **(55)**) and the wind is less than 3 m/s then *DepthBottom* for surface floating algae is set to 0.1 m to account for buoyancy. Otherwise it is set to 3 m to represent downward transport by Langmuir circulation. When calculating self-shading for surface-floating algae the model accounts for more intense self shading in the upper layer of the water column due to the floating concentration of algae there. The *Extinct* term in equation **(43)** is multiplied by the segment thickness and divided by the thickness over which the floating algae occur so that the more intense self-shading effects of these algae concentrated at the top of the system are properly accounted for. Rather than average the biomass of "surface floating" plants over the entire water column, the biomass is normalized to the top 3 m to more closely correspond with monitoring data.

Under the ice, all phytoplankton are represented as occurring in the top 2 m (cf. LeCren and Lowe-McConnell, 1980). As discussed in Section 3.6, light is decreased to 15% of incident radiation if ice cover is predicted. Approximately half the incident solar radiation is photosynthetically active (Edmondson, 1956):

$$Light_{TimeStep} = Solar_{TimeStep} \cdot 0.5 \qquad \textbf{(47)}$$

where:

      $Solar_{TimeStep}$ = daily light intensity on a daily **(25)** or hourly **(28)** basis (ly/d).

The light-limitation function represents both limitation for suboptimal light intensity and photoinhibition at high light intensities (Figure 52). When considered over the course of the year, photoinhibition can occur in very clear, shallow systems during summer mid-day hours (Figure 54), but it often is not a factor when considered over 24 hours (Figure 55).

To help understand the occurrence of photoinhibition as opposed to insufficient light, two new output "photosynthetic limitation variables" are available—"LowLt_LIM" and "HighLt_LIM." These output variables are same as the overall light limitation factor (Lt_LIM) but are modified to indicate photoinhibition as opposed to insufficient light. When low-light limitation causes light conditions to be sub-optimal then the "high-light limitation" is set to zero. When photoinhibition is occurring then the "low-light limitation" is set to zero. To determine this difference AQUATOX differentiates the equations used to produce the curves in Figures 50 and 51 (see **(38)** and **(39)**) and and determines whether the current light is greater than or less than the maximum value.

It is also worth noting that in simulations with a one-day time step, the light limitation factor (Lt_LIM) represents a *daily* light limitation and is therefore subject to the photoperiod. In other words, if the sun is shining only 50% of the day, the maximum the LtLimit can be is 0.5. This is because Lt_LIM is a limitation on the maximum daily photosynthesis rate for a plant which would be based on 24-hours of light exposure.

The extinction coefficient for pure water varies considerably in the photosynthetically-active 400-700 nm range (Wetzel, 1975, p. 55); a value of 0.016 (1/m) correspond to the extinction of green light. In many models dissolved organic matter and suspended sediment are not considered separately, so a much larger extinction coefficient is used for "water" than in AQUATOX. The attenuation coefficients have units of $1/m\text{-}(g/m^3)$ because they represent the amount of extinction caused by a given concentration (**Table 7**).

Table 7. Light Extinction and Attenuation Coefficients

WaterExtinction	0.02 1/m	Wetzel, 1975
ECoeffPhyto$_{diatom}$	0.14 $1/m\text{-}(g/m^3)$	calibrated
ECoeffPhyto$_{blue\text{-}green}$	0.099 $1/m\text{-}(g/m^3)$	Megard et al., 1979 (calc.)
ECoeffDOM	0.03 $1/m\text{-}(g/m^3)$	Effler et al., 1985 (calc.)
ECoeffPOM	0.12 $1/m\text{-}(g/m^3)$	Verduin, 1982
ECoeffSed	0.17 $1/m\text{-}(g/m^3)$	Straškraba and Gnauck, 1985

All coefficients may be user-supplied in the plant or site underlying data.

Figure 52. Instantaneous Light Response Function

Figure 53. Daily Light Response Function

Diatoms in 0.5-m Deep Pond

Diatoms in 0.5-m Deep Pond

Figure 54. Mid-day Light Limitation
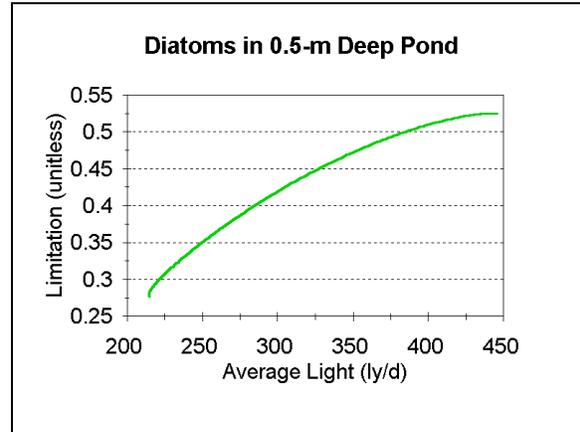
Figure 55. Daily Light Limitation

Diatoms in 0.5-m Deep Pond

Diatoms in 0.5-m Deep Pond
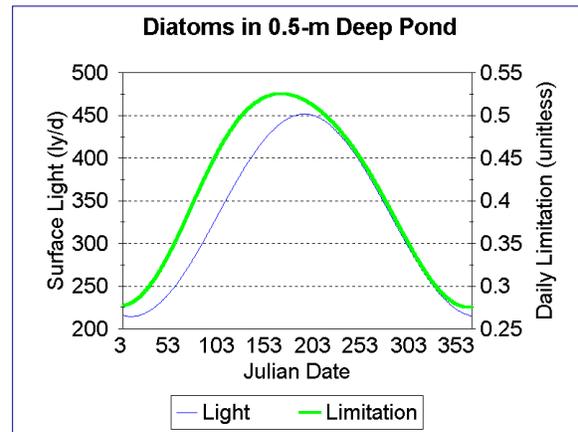
The Secchi depth, the depth at which a Secchi disk disappears from view, is a commonly used indication of turbidity. It is computed as (Straškraba and Gnauck, 1985):

$$Secchi = \frac{1.2}{Extinction} \tag{48}$$

where:

      Secchi   =   Secchi depth (m).

This relationship also could be used to back-calculate an overall Extinction coefficient if only the Secchi depth is known for a site.

It should be noted that although Secchi depth can be computed for the hypolimnion segment, based on the suspended material, it is a relatively meaningless value for the hypolimnion and generally should be ignored. Light extinction in the hypolimnion is calculated based on the light that has first filtered through the epilimnion as shown in equation **(45)**.

As a verification of the extinction computations, the calculated and observed Secchi depths were compared for Lake George, New York. The Secchi depth is estimated to be 8.3 m in Lake George, based on site data for the various components (Figure 56). This compares favorably with observed values of 7.5 to 11 (Clifford, 1982).

Figure 56. Contributions to light extinction in Lake George NY.
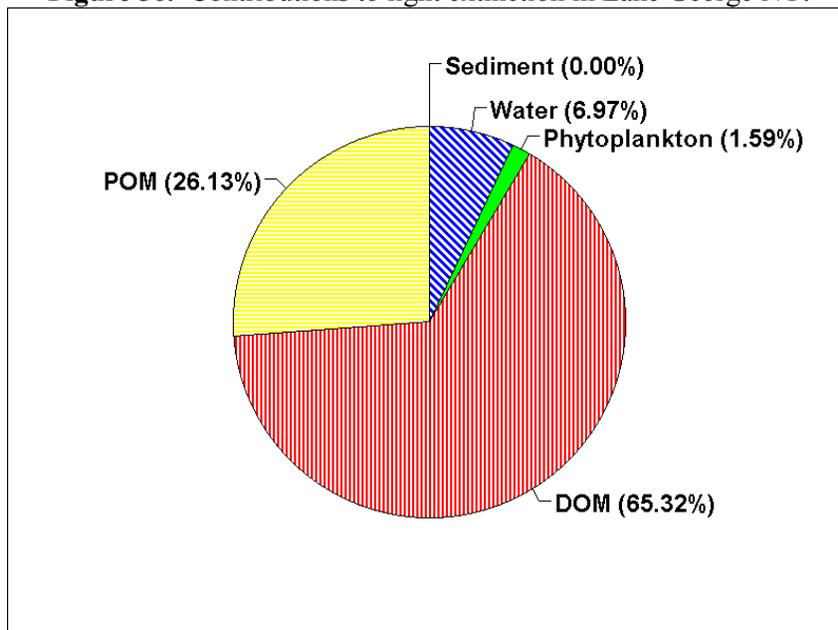
Adaptive Light

Saturating light can be specified as a constant for each plant taxonomic group (classic AQUATOX approach) or it can be adaptive based on Kremer and Nixon (1978) and similar to the approach used in EFDC. The adaptive light saturation is the weighted average of photosynthetically active solar radiation (PAR) at the optimal depth for growth of a given plant group, using an approximation based on the user-specified light saturation and site solar radiation and turbidity at the beginning of the simulation:

$$LightSatCalc = 0.7(LightHist_1) + 0.2(LightHist_2) + 0.1(LightHist_3) \qquad \textbf{(49)}$$

$$LightHist_n = PAR \cdot e^{(-Extinct \cdot ZOpt_{Plant})} \qquad \textbf{(50)}$$

where:

$LightSatCalc$	=	adaptive light saturation (Ly/d)
$LightHist_n$	=	photosynthetically active radiation at optimum depth for plant growth n days prior to simulation date (Ly/d)
PAR	=	photosynthetically active radiation, $Solar$ * 0.5 (Ly/d)
$Solar$	=	incident solar radiation (Ly/d)
$Extinct$	=	total light extinction computed dynamically **(40).**

If the *LightSatCalc* is greater or less than the user-entered maximum and minimum light saturation coefficients ("Plant underlying data" screen) then the *LightSatCalc* is set to the user-entered maximum or minimum. This *LightSatCalc* variable is then used in the *LtAtDepth* and *LtAtTop* calculations **(43)-(45)**.

$$ZOpt_{Plant} = \frac{\ln(LightSat / MaxDailyLight)}{-Extinct_{Init.Cond}} \qquad \textbf{(51)}$$

where:

$ZOpt_{Plant}$ =   optimum depth for a given plant (a constant approximated at the beginning of the simulation in meters);

LightSat   =   user entered light saturation coefficient (Ly/d);

MaxDailyLight =   maximum daily-averaged incident solar radiation for one calendar year forward from the start date (Ly/d);

$Extinct_{InitCond}$ =   initial condition total light extinction (unitless);

Nutrient Limitation

There are several ways that nutrient limitation has been represented in models. Algae are capable of taking up and storing sufficient nutrients to carry them through several generations, and models have been developed to represent this. However, if the timing of algal blooms is not critical, intracellular storage of nutrients can be ignored, constant stoichiometry can be assumed, and the model is much simpler. Therefore, based on the efficacy of this simplifying assumption, nutrient limitation by external nutrient concentrations has traditionally been used in AQUATOX, as in many other models (for example, Chen, 1970; Parker, 1972; Lassen and Nielsen, 1972; Larsen et al., 1974; Park et al., 1974; Chen and Orlob, 1975; Patten et al., 1975; Environmental Laboratory, 1982; Ambrose et al., 1991). New to Release 3.1 and beyond, internal nutrient concentrations may be modeled in AQUATOX; see the section on internal nutrients below.

When modeling nutrient limitations with external nutrients, for an individual nutrient, saturation kinetics is assumed, using the Michaelis-Menten or Monod equation (Figure 57); this approach is founded on numerous studies (cf. Hutchinson, 1967):

$$PLimit = \frac{Phosphorus}{Phosphorus + KP} \qquad \textbf{(52)}$$

$$NLimit = \frac{Nitrogen}{Nitrogen + KN} \qquad \textbf{(53)}$$

$$CLimit = \frac{Carbon}{Carbon + KCO2} \qquad \textbf{(54)}$$

where:

PLimit   =   limitation due to phosphorus (unitless);

Phosphorus   =   available soluble phosphorus (gP/m^3);
KP   =   half-saturation constant for phosphorus (gP/m^3);
NLimit   =   limitation due to nitrogen (unitless);
Nitrogen   =   available soluble nitrogen (gN/m^3);
KN   =   half-saturation constant for nitrogen (gN/m^3);
CLimit   =   limitation due to inorganic carbon (unitless);
Carbon   =   available dissolved inorganic carbon (gC/m^3); and
KCO2   =   half-saturation constant for carbon (gC/m^3).

Figure 57. Nutrient limitation
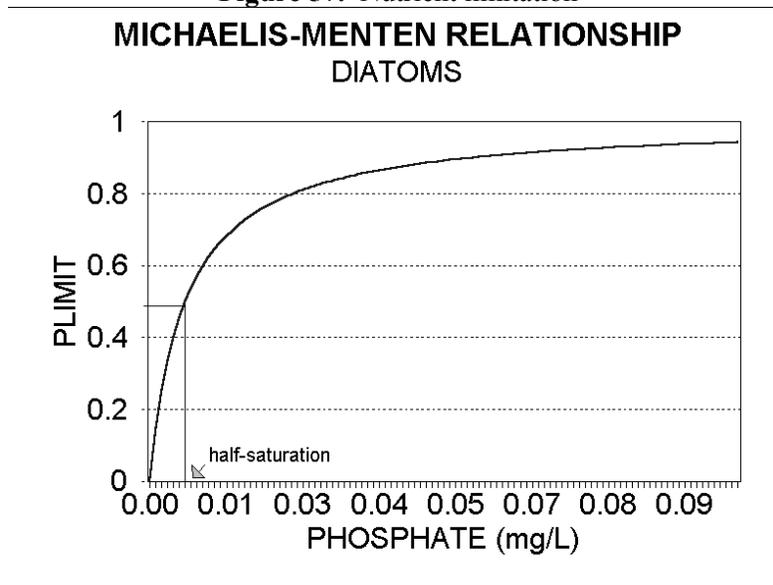
Nitrogen fixation in cyanobacteria is handled by setting *NLimit* to 1.0 if *Nitrogen* is less than half the *KN* value. Otherwise, it is assumed that nitrogen fixation is not operable, and *NLimit* is computed as for the other algae. AQUATOX also provides an option to trigger nitrogen fixation as a function of an input parameter, the ratio of inorganic N to inorganic P, which may be selected and specified in the "Study Setup" screen. When the ratio falls below the threshold, nitrogen fixation is assumed to occur; the default threshold N:P is 7. When internal nutrients are modeled, uptake of nitrogen is set to its maximum rate due to nitrogen fixation when the internal nutrient concentration falls below half of its *internal* half saturation coefficient. See **(55b)** and **(55f)** below.

Concentrations must be expressed in terms of the chemical element. Because carbon dioxide is computed internally, the concentration of carbon is corrected for the molar weight of the element:

$$Carbon = C2CO2 \cdot CO2 \tag{55}$$

where:
C2CO2   =   ratio of carbon to carbon dioxide (0.27); and
CO$_2$ =   inorganic carbon (g/m^3).

When modeling with internal or external nutrients, AQUATOX uses the minimum limiting

nutrient, whereby the Michaelis-Menten equation is evaluated for each nutrient, and the factor for the nutrient that is most limiting at a particular time is used. This is the approach used in many similar models (for example, Larsen et al., 1973; Baca and Arnett, 1976; Scavia et al., 1976; Smith, 1978; Bierman et al., 1980; Park et al., 1980; Johanson et al., 1980; Grenney and Kraszewski, 1981; Ambrose et al., 1991). The overall nutrient limitation is calculated as follows:

$$NutrLimit = \min(PLimit, NLimit, CLimit) \tag{56}$$

where:

> $NutrLimit$ = reduction due to limiting nutrient (unitless).

Alternative formulations used in other models include multiplicative and harmonic-mean constructs, but the minimum limiting nutrient construct is well-founded in laboratory studies with individual species.

Internal Nutrients Model

It is well known that many algae are able to take up nutrients even when not required for growth—so-called "luxury uptake." MS.CLEANER, a precursor to AQUATOX, used internal nutrients (Collins 1980), but this approach was not used in the original AQUATOX because of memory limitations at the time. The present version of AQUATOX has the option of modeling internal nutrients based on the approach of QUAL2K (Chapra et al. 2007) and WASP7 (Ambrose et al. 2006, Martin et al. 2006). When internal nutrients are specified, *NLimit* and *PLimit* are calculated as a function of the internal nutrient concentration in plants, with nitrogen fixation by cyanobacteria being a special case:

$$NLimit = 1 - \frac{Min\_N\_Ratio}{N\_Ratio}$$

$$\tag{55b}$$

$$PLimit = 1 - \frac{Min\_P\_Ratio}{P\_Ratio}$$

If the plant is cyanobacteria and

$$N\_Ratio < (0.5 \cdot NHalfSat_{Internal}) \text{ then } NLimit = 1.0.$$

where:

> N_Ratio or P_Ratio = internal nutrient concentration over biomass, (g/g AFDW);
> $NHalfSat_{Internal}$ = half-saturation constant for intracellular N (mg/mg AFDW);
> Min_N/P_Ratio = N_Ratio or P_Ratio at which growth ceases, a user-input ratio, (g/g AFDW);

Internal nutrients are calculated with independent derivatives for each relevant plant as follows

$$\frac{d\ Nutrient_{Phytoplankton}}{dt} = Loading + Uptake - Mortality - Respiration - Excretion$$
$$- \sum_{Pred} Predation_{Pred,\ Alga} \pm Sink \pm Floating - Washout \qquad \textbf{(55c)}$$
$$+ Washin \pm TurbDiff \pm Diffusion_{Seg} + Slough/3$$

$$\frac{d\ Nutrient_{Periphyton}}{dt} = Loading + Uptake - Mortality - Respiration - Excretion$$
$$\qquad \textbf{(55d)}$$
$$- \sum_{Pred} Predation_{Pred,\ Alga} + Sedimentation_{Phytoplankton} - Slough$$

where:

$Nutrient_{Alga}$	=	concentration of nutrient within plant compartment, (µg/L);
$N2O$	=	nutrient to organism ratio, (µg nutrient/mg organism);
$Loading$	=	external loadings · $N2O$; assumes external loadings have same stoichiometry as current biomass, (µg/L d);
$Uptake$	=	uptake of nutrients from the water column, see **(55e)** and **(55g)**, (µg/L d);
$Mortality$	=	mortality of algal biomass · $N2O$ (µg/L d);
$Predation$	=	predation of algal biomass · $N2O$ (µg/L d);
$Sinking\ Loss$	=	sinking loss of algal biomass · $N2O$ (µg/L d);
$Sinking\ Gain$	=	sinking gain of algal biomass · $N2O_{Other\ Segment}$ (µg/L d);
$Floating\ Loss$	=	floating loss of algal biomass · $N2O$ (µg/L d);
$Floating\ Gain$	=	floating gain of algal biomass · $N2O_{Other\ Segment}$ (µg/L d);
$Washout$	=	washout of algal biomass · $N2O$ (µg/L d);
$Washin$	=	gain from upstream segment of algal biomass, $Washout_{Other\ Segment} \cdot N2O_{Other\ Segment}$ (µg/L d);
$TurbDiff\ Loss$	=	turbulent diffusion loss of algal biomass · $N2O$ (µg/L d);
$TurbDiff\ Gain$	=	turbulent diffusion gain of biomass · $N2O_{Other\ Segment}$ (µg/L d);
$Diffusion$	=	$diffusion_{Linked\ Segment} \cdot N2O_{Linked\ Segment}$ (µg/L d);
$Slough$	=	sloughing loss of periphyton biomass · $N2O_{periphyton}$ (µg/L d);
$Sedimentation$	=	sedimentation of phytoplankton biomass · $N2O$ (µg/L d);
$Respiration$	=	dark respiration of algal biomass · $N2O$ (µg/L d);
$Excretion$	=	photo respiration of algal biomass · $N2O$ (µg/L d);

AQUATOX displays internal nutrients in plants as a concentration associated with overlying water (µg/L), and as nutrient-to-organism ratios of grams of nutrient per gram of AFDW organic matter.

Uptake of nutrients is modeled as follows:

$$PhytoUpN = MaxNUptake \cdot biomass \cdot 1e3 \cdot$$

$$\left(\frac{ammonia + nitrate}{NHalfSat + ammonia + nitrate} \right) \left(\frac{NHalfSat_{Internal}}{NHalfSat_{Internal} + (NRatio - MinNRatio)} \right) \quad \textbf{(55e)}$$

If the plant is cyanobacteria and is fixing nitrogen then uptake is assumed to occur at the maximum rate.

$$PhytoUpN = MaxNUptake \cdot biomass \cdot 1e3 \quad \textbf{(55f)}$$

Uptake of phosphorus is modeled with a similar formulation used for the uptake of nitrogen:

$$PhytoUpP = MaxPUptake \cdot biomass \cdot 1e3 \cdot$$

$$\left(\frac{TSP}{PHalfSat + TSP} \right) \left(\frac{PHalfSat_{Internal}}{PHalfSat_{Internal} + (PhosRatio - MinPRatio)} \right) \quad \textbf{(55g)}$$

where:

$PhytoUpNutrient$	=	uptake of internal nutrients (µg of nutrient/L d);
$MaxNutrientUptake$	=	the maximum uptake rate for the nutrient (mg/mg AFDW·d);
$NutrientHalfSat$	=	half-saturation constant for external nutrient (µg nutrient/L);
$NutrientHalfSat_{Internal}$	=	half-saturation constant for intracellular nutrient (mg/mg AFDW);
$biomass$	=	algal biomass (mg/L); and
$1e3$	=	units conversion (µg/mg).

Some additional observations about the internal nutrients option follow:

- While the internal-nutrient model allows stoichiometry of plants to vary over time, animal and suspended-organic-matter stoichiometry remain constant in the model at this time.
- The internal-nutrient model is not utilized for benthic or rooted macrophytes, which are assumed to get nutrients from sediments and are not assumed to have nutrient limitation for that reason.
- Boundary-condition loadings of plants are assumed to have the same nutrient characteristics as plants currently in the water body.

Current Limitation

Because they are fixed in space, periphyton also are limited by slow currents that do not replenish nutrients and carry away senescent biomass. Based on the work of McIntire (1973) and Colby and McIntire (1978), a factor relating photosynthesis to current velocity is used for periphyton:

$$VLimit = min(1, RedStillWater + \frac{VelCoeff \cdot Velocity}{1 + VelCoeff \cdot Velocity})$$ **(57)**

where:

VLimit	=	limitation or enhancement due to current velocity (unitless);
RedStillWater	=	user-entered reduction in photosynthesis in absence of current (unitless);
VelCoeff	=	empirical proportionality coefficient for velocity (0.057, unitless); and
Velocity	=	flow rate (converted to m/s), see **(14)**.

VLimit has a minimum value for photosynthesis in the absence of currents and increases asymptotically to a maximum value for optimal current velocity (Figure 58). In high currents scour can limit periphyton; see **(75)**. The value of *RedStillWater* depends on the circumstances under which the maximum photosynthesis rate was measured; if *PMax* was measured in still water then *RedStillWater* = 1, otherwise a value of 0.2 is appropriate (Colby and McIntire, 1978).

Figure 58. Effect of current velocity on periphyton photosynthesis.
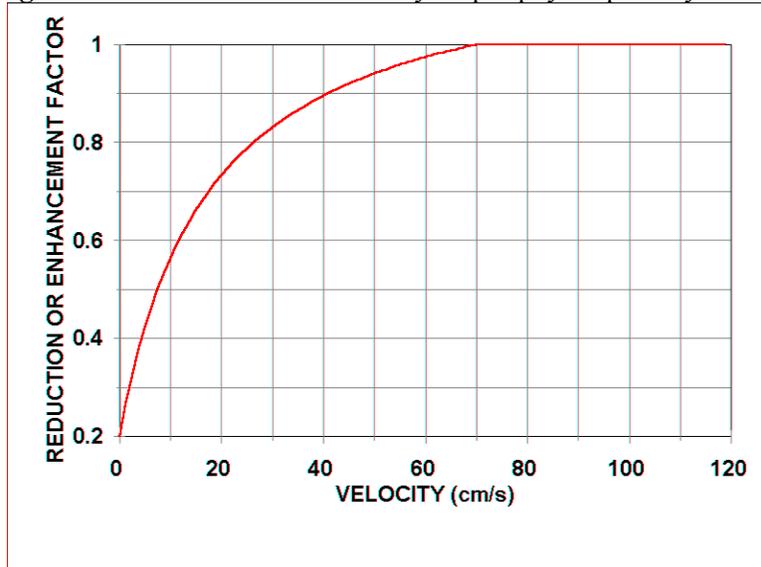
Adjustment for Suboptimal Temperature

AQUATOX uses a general but complex formulation to represent the effects of temperature. All organisms exhibit a nonlinear, adaptive response to temperature changes (the so-called Stroganov function). Process rates other than algal respiration increase as the ambient temperature increases until the optimal temperature for the organism is reached; beyond that optimum, process rates decrease until the lethal temperature is reached. This effect is represented by a complex algorithm developed by O'Neill et al. (1972) and modified slightly for application to aquatic systems (Park et al., 1974). An intermediate variable *VT* is computed first; it is the ratio of the difference between the maximum temperature at which a process will occur and the ambient temperature over the difference between the maximum temperature and the optimal temperature for the process:

$$VT = \frac{(TMax + Acclimation) - Temperature}{(TMax + Acclimation) - (TOpt + Acclimation)}$$

(58)

where:

Temperature	=	ambient water temperature (deg. C);
TMax	=	maximum temperature at which process will occur (deg. C);
TOpt	=	optimal temperature for process to occur (deg. C); and
Acclimation	=	temperature acclimation (deg. C), as described below.

Acclimation to both increasing and decreasing temperature is accounted for with a modification developed by Kitchell et al. (1972):

$$Acclimation = XM \cdot [1 - e^{(-KT \cdot ABS(Temperature - TRef))}]$$

(59)

where:

XM	=	maximum acclimation allowed (2.0 deg. C);
KT	=	coefficient for decreasing acclimation as temperature approaches T_{ref} (value is 0.5 and unitless);
ABS	=	function to obtain absolute value; and
TRef	=	"adaptation" temperature below which there is no acclimation (deg. C).

The mathematical sign of the variable *Acclimation* is negative if the ambient temperature is below the temperature at which there is no acclimation; otherwise, it is positive.

If the variable *VT* is less than zero, in other words, if the ambient temperature exceeds (*TMax* + *Acclimation*), then the suboptimal factor for temperature is set equal to zero and the process stops. Otherwise, the suboptimal factor for temperature is calculated as (Park et al., 1974):

$$TCorr = VT^{XT} \cdot e^{(XT \cdot (1-VT))}$$

(60)

where:

$$XT = \frac{WT^2 \cdot (1 + \sqrt{1 + 40/YT}\ )^2}{400} \qquad\qquad \textbf{(61)}$$

where:

$$WT = \ln(Q10) \cdot ((TMax + Acclimation) - (TOpt + Acclimation)) \qquad\qquad \textbf{(62)}$$

and,

$$YT = \ln(Q10) \cdot ((TMax + Acclimation) - (TOpt + Acclimation) + 2) \qquad\qquad \textbf{(63)}$$

where:

    Q10   =   slope or rate of change per 10°C temperature change (unitless).

This well-founded, robust algorithm for *TCorr* is used in AQUATOX to obtain reduction factors for suboptimal temperatures for all biologic processes in animals and plants, with the exception of decomposition and plant respiration. By varying the parameters, organisms with both narrow and broad temperature tolerances can be represented (Figure 59**,** Figure 60).

Figure 59. Temperature response of cyanobacteria   **Figure 60.** Temperature response of diatoms
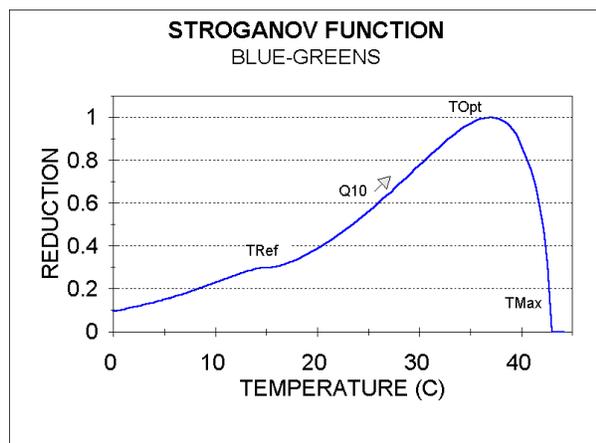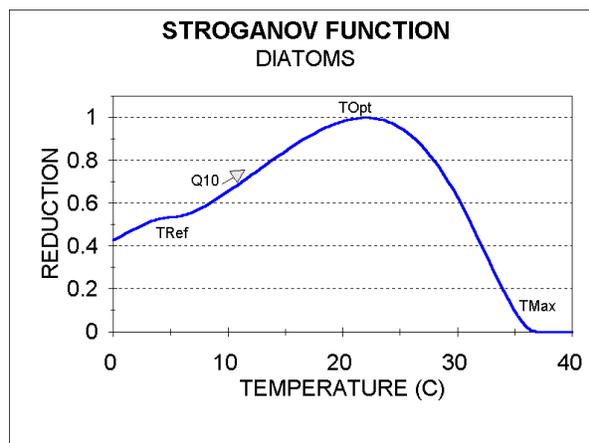
Algal Respiration

Endogenous or dark respiration is the metabolic process whereby oxygen is taken up by plants for the production of energy for maintenance and carbon dioxide is released (Collins and Wlosinski, 1983). Although it is normally a small loss rate for the organisms, it has been shown to be exponential with temperature (Aruga, 1965). Riley (1963, see also Groden, 1977) derived an equation representing this relationship. Based on data presented by Collins (1980), maximum respiration is constrained to 60% of photosynthesis. Laboratory experiments in support of the CLEANER model confirmed the empirical relationship and provided additional evidence of the correct parameter values (Collins, 1980), as demonstrated by Figure 61:

$$Respiration = Resp20 \cdot 1.045^{(Temperature-20)} \cdot Biomass \qquad \textbf{(64)}$$

where:

Respiration	=	dark respiration (g/m^3·d);
Resp20	=	user input respiration rate at 20°C (g/g·d);
1.045	=	exponential temperature coefficient (/°C);
Temperature	=	ambient water temperature (°C); and
Biomass	=	plant biomass (g/m^3).

This construct also applies to macrophytes.

Figure 61. Respiration (Data From Collins, 1980)
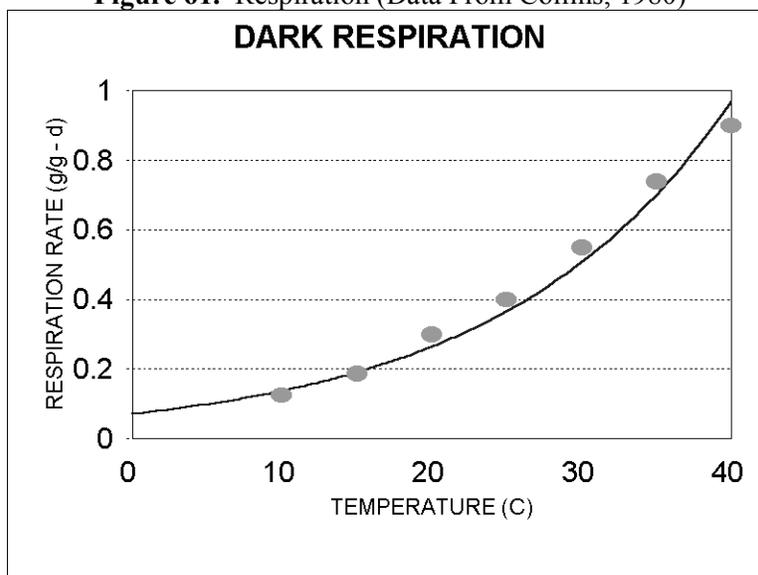
Photorespiration

Algal excretion, also referred to as photorespiration, is the release of photosynthate (dissolved organic material) that occurs in the presence of light. Environmental conditions that inhibit cell division but still allow photoassimilation result in release of organic compounds. This is especially true for both low and high levels of light (Fogg et al., 1965; Watt, 1966; Nalewajko, 1966; Collins, 1980). AQUATOX uses an equation modified from one by Desormeau (1978) that is the inverse of the light limitation:

$$Excretion = KResp \cdot LightStress \cdot Photosynthesis \qquad (65)$$

where:

Excretion	=	release of photosynthate (g/m3·d);
KResp	=	coefficient of proportionality between excretion and photosynthesis at optimal light levels (unitless); and
Photosynthesis =		photosynthesis (g/m3·d), see **(35)**,

and where:

$$LightStress = 1 - LtLimit \qquad (66)$$

where:

LtLimit	=	light limitation for a given plant (unitless), see **(38)**.

Excretion is a continuous function (Figure 62) and has a tendency to overestimate excretion slightly at light levels close to light saturation where experimental evidence suggests a constant relationship (Collins, 1980). The construct for photorespiration also applies to macrophytes.

Figure 62. *Excretion* as a fraction of photosynthesis
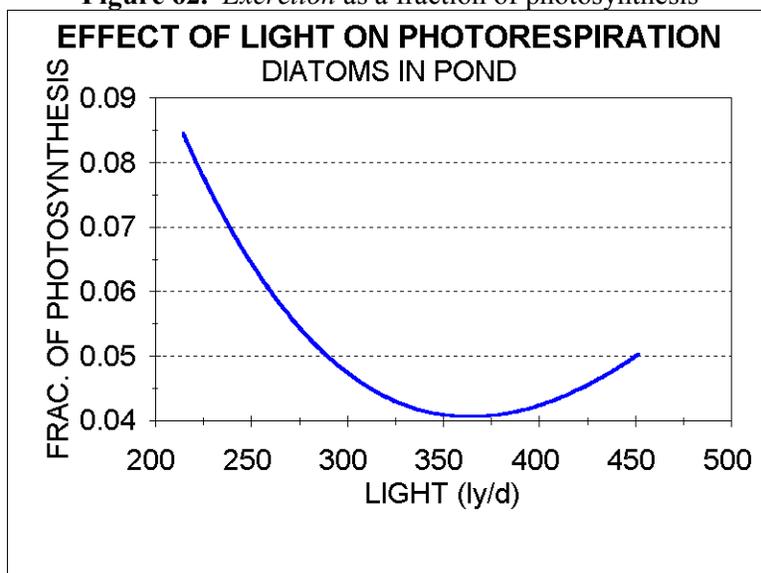
Algal Mortality

Nonpredatory algal mortality can occur as a response to toxic chemicals (discussed in **Chapter 8**) and as a response to unfavorable environmental conditions. Phytoplankton under stress may suffer greatly increased mortality due to autolysis and parasitism (Harris, 1986). Therefore, most phytoplankton decay occurs in the water column rather than in the sediments (DePinto, 1979). The rapid remineralization of nutrients in the water column may result in a succession of blooms (Harris, 1986). Sudden changes in the abiotic environment may cause the algal population to crash; stressful changes include nutrient depletion, unfavorable temperature, and damage by light (LeCren and Lowe-McConnell, 1980). These are represented by a mortality term in AQUATOX that includes toxicity, high temperature (Scavia and Park, 1976), and combined nutrient and light limitation (Collins and Park, 1989):

$$Mortality = (KMort + ExcessT + Stress) \cdot Biomass + Poisoned \qquad (67)$$

where:

Mortality	=	nonpredatory mortality (g/m^3·d);
Poisoned	=	mortality rate due to toxicant (g/m^3·d), see **(417)**;
KMort	=	intrinsic mortality rate (g/g·d); and
Biomass	=	plant biomass (g/m^3),

and where:

$$ExcessT = \frac{e^{(Temperature - TMax)}}{2} \qquad (68)$$

and:

$$Stress = 1 - e^{-EMort \cdot (1 - (NutrLimit \cdot LtLimit))} \qquad (69)$$

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where:

ExcessT	=	factor for high temperatures (g/g·d);
TMax	=	maximum temperature tolerated (° C);
Stress	=	factor for suboptimal light and nutrients (g/g·d),
Emort	=	approximate maximum fraction killed per day with total limitation (g/g·d);
NutrLimit	=	reduction due to limiting nutrient (unitless), see **(55)**
LtLimit	=	light limitation (unitless), see **(38)**.

Exponential functions are used so that increasing stress leads to rapid increases in mortality, especially with high temperature where mortality is 50% per day at the *TMax* (Figure 61), and, to a much lesser degree, with suboptimal nutrients and light (Figure 64). This simulated process is responsible in part for maintaining realistically high levels of detritus in the simulated water body. Low temperatures are assumed not to affect algal mortality.

Figure 63. Mortality due to high temperatures
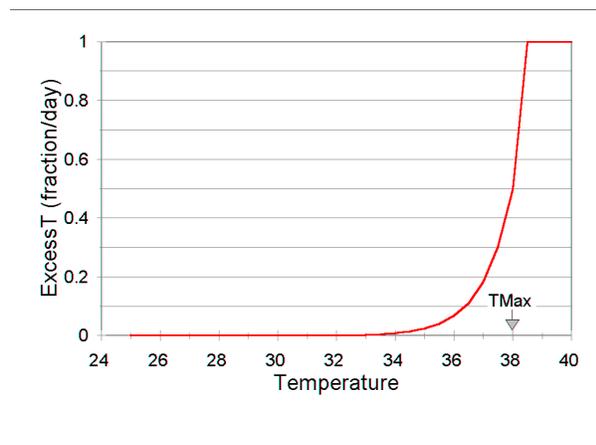
Figure 64. Mortality due to light limitation
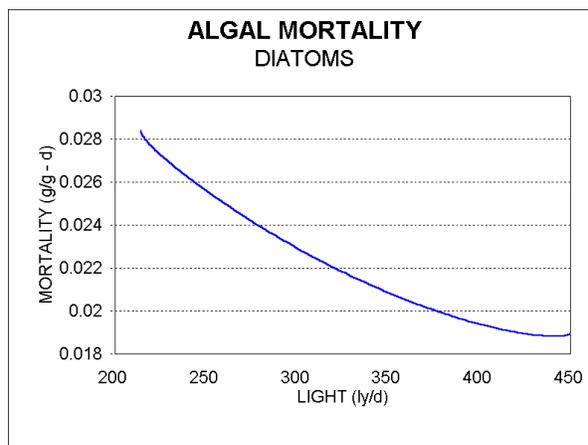
Sinking

Sinking of phytoplankton, either between layers or to the bottom sediments, is modeled as a function of physiological state, similar to mortality. Phytoplankton that are not stressed are considered to sink at given rates, which are based on field observations and implicitly account for the effects of averaged water movements (cf. Scavia, 1980). Sinking also is represented as being impeded by turbulence associated with higher discharge (but only when discharge exceeds mean discharge):

$$Sink = \frac{KSed}{Depth} \cdot \frac{MeanDischarge}{Discharge} \cdot SedAccel \cdot DensityFactor \cdot Biomass \qquad (70)$$

where:

Sink	=	phytoplankton loss due to settling (g/m^3·d);

KSed   =   intrinsic settling rate (m/d);
Depth   =   depth of water or, if stratified, thickness of layer (m);
MeanDischarge   =   mean annual discharge (m^3/d);
Discharge   =   daily discharge (m^3/d), see Table 3;
DensityFactor   =   if salinity is modeled, correction factor for water densities based on
                                  salinity and temperature, see **(442)**; and
Biomass   =   phytoplankton biomass (g/m^3).

The model is able to mimic high sedimentation loss associated with the crashes of phytoplankton blooms, as discussed by Harris (1986). As the phytoplankton are stressed by toxicants and suboptimal light, nutrients, and temperature, the model computes an exponential increase in sinking (Figure 65), as observed by Smayda (1974), and formulated by Collins and Park (1989):

$$SedAccel = e^{ESed \bullet (1 - LtLimit \bullet NutrLimit \bullet TCorr \bullet FracPhoto)} \tag{71}$$

where:

SedAccel   =   increase in sinking due to physiological stress (unitless);
ESed   =   exponential settling coefficient (unitless);
LtLimit   =   light limitation (unitless), see **(38)**;
NutrLimit   =   nutrient limitation (unitless), see **(55)**; and
FracPhoto   =   reduction factor for effect of toxicant on photosynthesis (unitless),
                                   see **(421)**;
TCorr   =   temperature limitation (unitless), see **(59)**.

Figure 65. Sinking as a function of nutrient stress

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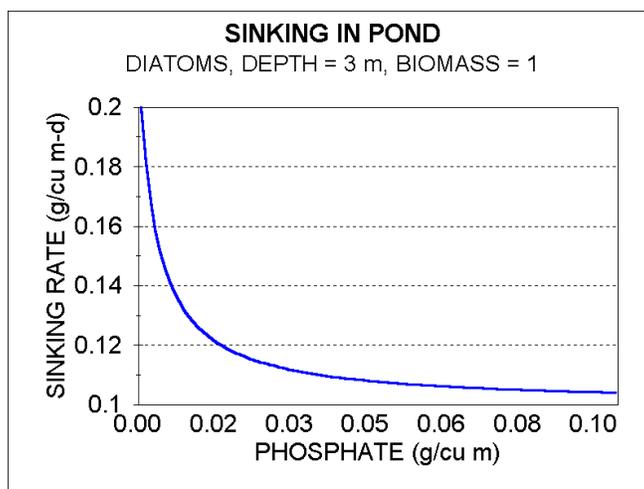
Washout and Sloughing

Phytoplankton are subject to downstream drift. In streams and in lakes and reservoirs with low retention times this may be a significant factor in reducing or even precluding phytoplankton populations (LeCren and Lowe-McConnell, 1980). The process is modeled as a simple function of discharge:

$$Washout_{phytoplankton} = \frac{Discharge}{Volume} \cdot Biomass \qquad\qquad (72)$$

where:

$Washout_{phytoplankton}$	=	loss due to downstream drift ($g/m^3 \cdot d$),
$Discharge$	=	daily discharge (m^3/d);
$Volume$	=	volume of site (m^3); and
$Biomass$	=	biomass of phytoplankton (g/m^3).

Periphyton often exhibit a pattern of buildup and then a sharp decline in biomass due to sloughing. Based on extensive experimental data from Walker Branch, Tennessee (Rosemond, 1993), a complex sloughing formulation, extending the approach of Asaeda and Son (2000), was implemented. This function was able to represent a wide range of conditions better (Figure 66 and Figure 67).

$$Washout_{periphyton} = Slough + Dislodge_{Peri,Tox} \qquad\qquad (73)$$

where:

$Washout_{Periphyton}$	=	loss due to sloughing ($g/m^3 \cdot d$);
$Slough$	=	loss due to natural causes ($g/m^3 \cdot d$), see **(75)**; and
$Dislodge_{peri, Tox}$	=	loss due to toxicant-induced sloughing ($g/m^3 \cdot d$), see **(427)**.

Figure 66. Comparison of predicted biomass of periphyton, constituent algae, and observed biomass of periphyton (Rosemond, 1993) in Walker Branch, Tennessee, with addition of both N and P and removal of grazers in Spring, 1989.
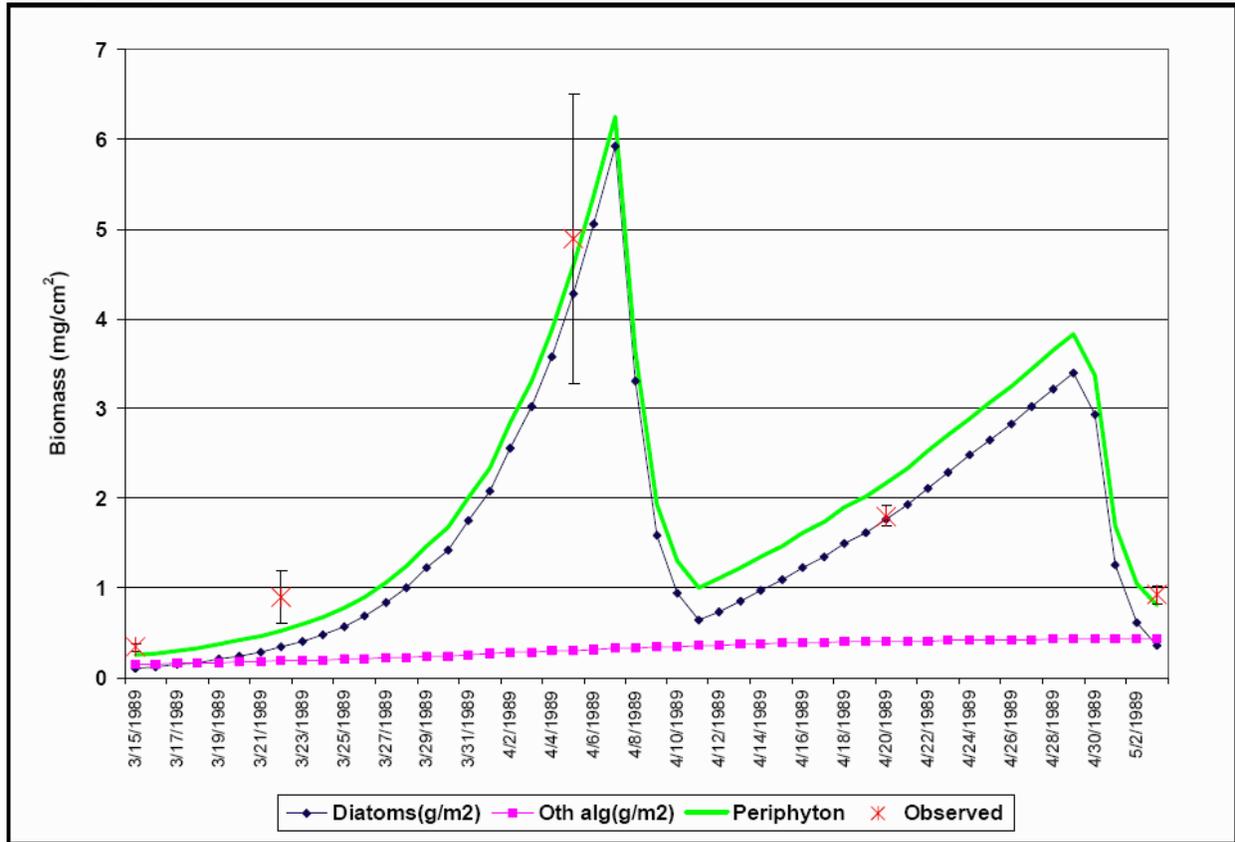
Figure 67. Predicted rates for diatoms in Walker Branch, Tennessee, with addition of both N and P and removal of grazers in Spring, 1989. Note the importance of periodic sloughing. Rates expressed as g/m^2 d.
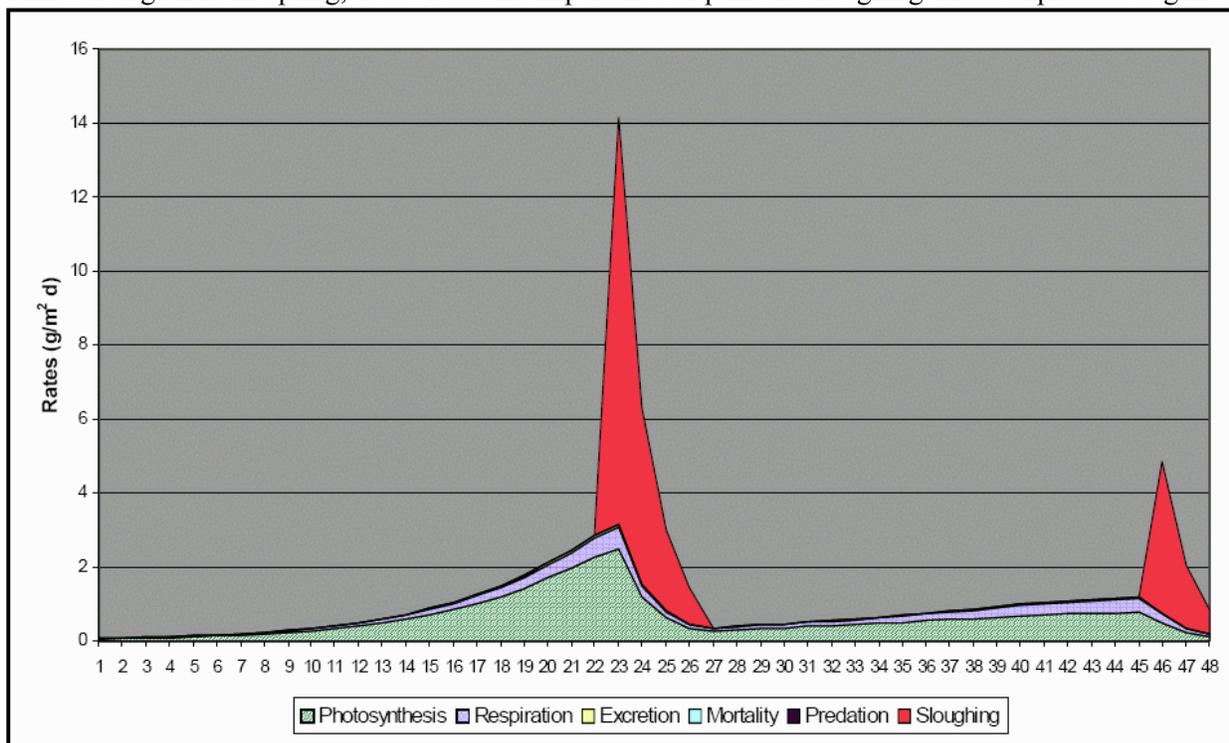
Natural sloughing is a function of senescence due to suboptimal conditions and the drag force of currents acting on exposed biomass. Drag increases as both biomass and velocity increase:

$$DragForce = Rho \cdot DragCoeff \cdot Vel^2 \cdot (BioVol \cdot UnitArea)^{2/3} \cdot 1E\text{-}6 \qquad \textbf{(74)}$$

where:

DragForce	=	drag force (kg m/s^2);
Rho	=	density of water (kg/m^3);
DragCoeff	=	drag coefficient (2.53E-4, unitless);
Vel	=	velocity (converted to m/s) see **(14)**;
BioVol	=	biovolume of algae (mm^3/mm^2);
UnitArea	=	unit area (mm^2);
1E-6	=	conversion factor (m^2/mm^2).

Biovolume is not modeled directly by AQUATOX, so a simplifying assumption is that the empirical relationship between biomass and biovolume is constant for a given growth form, based on observed data from Rosemond (1993):

$$Biovol_{Dia} = \frac{Biomass}{2.08\,\text{E-}9} \cdot ZMean$$

$$Biovol_{Fil} = \frac{Biomass}{8.57\text{E-}9} \cdot ZMean$$

(75)

where:

$Biovol_{Dia}$	=	biovolume of non-filamentous algae (mm^3/mm^2);
$Biovol_{Fil}$	=	biovolume of filamentous algae (mm^3/mm^2);
$Biomass$	=	biomass of given algal group (g/m^2);
$ZMean$	=	mean depth (m).

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:

If $DragForce > Suboptimal_{Org} \cdot FCrit_{Org} \cdot Adaptation$

then $Slough = Biomass \cdot FracSloughed$

else $Slough = 0$

(76)

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, editable.

$$Suboptimal_{Org} = NutrLimit_{Org} \cdot LtLimit_{Org} \cdot TCorr_{Org} \cdot 20$$

If $Suboptimal_{Org} > 1$ then $Suboptimal_{Org} = 1$

(77)

where:

$NutrLimit$	=	nutrient limitation for given algal group (unitless) computed by AQUATOX; see **(55)**;
$LtLimit_{Org}$	=	light limitation for given algal group (unitless) computed by AQUATOX; see **(38)**; and
$TCorr$	=	temperature limitation for a given algal group (unitless) computed by AQUATOX; see **(59)**.
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, Figure 66). 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 mean discharge 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:

$$Adaptation = \frac{Vel^2}{0.006634}$$

(78)

where:

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

Detrital Accumulation in Periphyton

In phytoplankton, mortality results in immediate production of detritus, and that transfer is modeled. However, for purposes of modeling, periphyton are defined as including associated detritus. The accumulation of non-living biomass is modeled implicitly by not simulating mortality due to suboptimal conditions. Rather, in the simulation biomass builds up, causing increased self-shading, which in turn makes the periphyton more vulnerable to sudden loss due to sloughing. The fact that part of the biomass is non-living is ignored as a simplification of the model.

Chlorophyll *a*

Chlorophyll *a* is not simulated directly. However, because chlorophyll *a* is commonly measured in aquatic systems and because water quality managers are accustomed to thinking of it as an index of water quality, the model converts phytoplankton biomass estimates into approximate values for chlorophyll *a*. The ratio of carbon to chlorophyll *a* exhibits a wide range of values depending on the nutrient status of the algae (Harris, 1986); cyanobacteria often have higher values (cf. Megard et al., 1979). Conversion factors between phytoplankton and chlorophyll *a* are now editable on a species by species basis within each plants "underlying data." In the absence of species-specific data, AQUATOX uses default values of 45 μgC/μg chlorophyll *a* for cyanobacteria and a value of 28 for other phytoplankton as reported in the documentation for WASP (Ambrose et al., 1991). The values are more representative for blooms than for static conditions, but managers are usually most interested in the maxima. Results are presented as total chlorophyll *a* in μg/L; therefore, the computation is:

$$ChlA = \sum \left(\frac{Biomass_{Phytoplankton} \cdot CToOrg}{CToChla_{Phytoplankton}} \right) \cdot 1000 \qquad \textbf{(79)}$$

where:

ChlA	=	estimated biomass as chlorophyll *a* (μg/L);
Biomass	=	biomass of given alga (mg/L);
CToOrg	=	ratio of carbon to biomass (0.526, unitless);
*CToChl*a	=	ratio of carbon to chlorophyll a (g carbon/g chl *a*); and
1000	=	conversion factor for mg to μg (unitless).

Periphytic chlorophyll *a* is computed as a conversion from the ash-free dry weight (AFDW) of periphyton; because periphyton can collect inorganic sediments, it is important to measure and model it as AFDW. The conversion factor is based on the observed average ratio of chlorophyll *a* to AFDW for the Cahaba River near Birmingham, Alabama (unpub. data) and also based on data published in Biggs (1996)and Rosemond (1993).

$$Perichlor = AFDW \cdot 5.0 \qquad \textbf{(80)}$$

where:

PeriChlor	=	periphytic chlorophyll *a* (mg/m^2);
AFDW	=	ash free dry weight (g/m^2).

Moss chlorophyll *a* is output for all plants designated with the plant type "Bryophytes." In this case, ash free dry weight is multiplied by 8.91 to get the estimate of chlorophyll *a* in mg/m^2 (Stream Bryophyte Group, 1999, p. 160). Total benthic chlorophyll *a* is also output in units of mg/m^2 (the sum of periphyton and moss chlorophyll *a*).

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 from the watershed area based on Leopold et al. (1964).

$$TotLength = 1.609 \cdot 1.4 \cdot (WaterShed \cdot 0.386)^{0.6} \qquad \textbf{(81)}$$

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 Enhanced Phytoplankton Retention is not chosen (or the total length or watershed area is entered as zero,) the phytoplankton and zooplankton residence time equations are not used and Equations **(71)** and **(129)** are used to calculate washout. In this case, the phytoplankton residence time is equal to the retention time of the system.

Otherwise, to simulate the inflow of plankton from upstream reaches plankton upstream loadings are estimated as follows:

$$Loading_{upstream} = Washout_{biota} - \left(\frac{Washout_{biota}}{TotLength \, / \, SiteLength} \right) \tag{82}$$

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 included in the total river length 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:

$$t_{residence} = \frac{Volume}{Discharge} \left(\frac{TotLength}{SiteLength} \right) \tag{83}$$

where:

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

Periphyton-Phytoplankton Link

Periphyton may slough or be physically scoured, contributing to the suspended (sestonic) algae; this may be reflected in the chlorophyll *a* observed in the water column. Periphyton may be linked to a phytoplankton compartment so that sestonic chlorophyll *a* reflects 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. The default is linkage to detritus with a warning.

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. (A single periphyton compartment cannot be linked to multiple phytoplankton compartments.)

$$Sed_{Periphyton\,A} = Sink_{Phyto}\,\frac{Mass_{Periphyton\,A}}{Mass_{All\,Linked\,Peri}} \tag{84}$$

where:

$Sed_{Periphyton\,A}$ = sedimentation that goes to periphyton compartment A;
$Sink_{Phyto}$ = total sedimentation of linked phytoplankton compartment, see **(69)**;
$Mass_{Periphyton\,A}$ = 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.

4.2 Macrophytes

Submersed aquatic vegetation or macrophytes can be an important component of shallow aquatic ecosystems. It is not unusual for the majority of the biomass in an ecosystem to be in the form of macrophytes during the growing season.   Seasonal macrophyte growth, death, and decomposition can affect nutrient cycling, and detritus and oxygen concentrations. By forming dense cover, they can modify habitat and provide protection from predation for invertebrates and smaller fish (Howick et al., 1993); this function is represented in AQUATOX (see Figure 73). Macrophytes also provide direct and indirect food sources for many species of waterfowl, including swans, ducks, and coots (Jupp and Spence, 1977b).

AQUATOX represents rooted macrophytes as occupying the littoral zone, that area of the bottom surface that occurs within the euphotic zone (see **(11)** for computation). Similar to periphyton, the macrophyte compartment has units of g/m^2. In nature, macrophytes can be greatly reduced if phytoplankton blooms or higher levels of detritus increase the turbidity of the water (cf. Jupp and Spence, 1977a).   Because the depth of the euphotic zone is computed as a function of the extinction coefficient (*ZEuphotic = 4.605/Extinct*), the area predicted to be occupied by macrophytes can increase or decrease depending on the clarity of the water.

The macrophyte equations are based on submodels developed for the International Biological Program (Titus et al., 1972; Park et al., 1974) and CLEANER models (Park et al., 1980) and for the Corps of Engineers' CE-QUAL-R1 model (Collins et al., 1985):

$$\frac{dBiomass}{dt} = Loading + Photosynthesis - Respiration - Excretion$$

$$- Mortality - Predation - Breakage \tag{85}$$

$$+ Washout_{FreeFloat} - Washin_{FreeFloat}$$

and:

$$Photosynthesis = PMax \cdot LtLimit \cdot TCorr \cdot Biomass \cdot FracLittoral$$

$$\cdot NutrLimit \cdot FracPhoto \cdot HabitatLimit \tag{86}$$

where:

dBiomass/dt	=	change in biomass with respect to time (g/m^2·d);
Loading	=	loading of macrophyte, usually used as a "seed" (g/m^2·d);
Photosynthesis	=	rate of photosynthesis (g/m^2·d);
Respiration	=	respiratory loss (g/m^2·d), see **(63)**;
Excretion	=	excretion or photorespiration(g/m^2·d), see **(64)**;
Mortality	=	nonpredatory mortality (g/m^2·d), see **(87)**;
Predation	=	herbivory (g/m^2·d), see **(99)**;
Breakage	=	loss due to breakage (g/m^2·d), see **(88)**;
PMax	=	maximum photosynthetic rate (1/d);
LtLimit	=	light limitation (unitless), see **(38)**;
TCorr	=	correction for suboptimal temperature (unitless), see **(59)**;
HabitatLimit	=	in streams, habitat limitation based on plant habitat preferences (unitless), see **(13)**;
FracLittoral	=	fraction of bottom that is in the euphotic zone (unitless) see **(11)**;
NutrLimit	=	nutrient limitation for bryophytes or freely-floating macrophytes (unitless), see **(55)**;
FracPhoto	=	reduction factor for effect of toxicant on photosynthesis (unitless), see **(421)**;
Washout$_{FreeFloat}$	=	washout of freely floating macrophytes, see **(86)**; and
Washin$_{FreeFloat}$	=	loadings from linked upstream segments (g/m^3·d), see **(30)**;

They share many of the constructs with the algal submodel described above. Temperature limitation is modeled similarly, but with different parameter values. Light limitation also is handled similarly, using the Steele (1962) formulation; the application of this equation has been verified with laboratory data (Collins et al., 1985). Periphyton are epiphytic in the presence of macrophytes; by growing on the leaves they contribute to the light extinction for the macrophytes (Sand-Jensen, 1977). Extinction due to periphyton biomass is computed in AQUATOX, by inclusion in *LtLimit*. For rooted macrophytes, nutrient limitation is not modeled at this time because macrophytes can obtain most of their nutrients from bottom sediments (Bristow and Whitcombe, 1971; Nichols and Keeney, 1976; Barko and Smart, 1980). Bryophytes and freely floating macrophytes assimilate nutrients from water and are subject to nutrient limitation.

Release 3 includes free-floating macrophytes. These macrophytes are assumed to be floating at the upper layer of the water column and therefore are not subject to light limitation. Furthermore, free-floating macrophytes are not subject to the *FracLittoral* limitation to macrophyte photosynthesis **(85)**. On the other hand the washing of macrophytes out of the system is affected by the carrying capacity for the species:

$$Washout_{freefloat} = \left(1 - \frac{KCap/ZMean - State}{KCap/ZMean}\right) \cdot \frac{Discharge}{Volume} \cdot State \qquad \textbf{(87)}$$

where:

$Washout_{freefloat}$	=	loss due to being carried downstream (g/m^3·d),
$State$	=	concentration of dissolved or floating state variable (g/m^3),
$KCap$	=	carrying capacity (g/m^2);
$ZMean$	=	mean depth from site underyling data (m);
$Discharge$	=	discharge (m^3/d), see Table 3; and
$Volume$	=	volume of site (m^3), see **(2)**;

Simulation of macrophyte respiration and excretion utilize the same equations as algae; excretion in rooted macrophytes results in "nutrient pumping" because the nutrients are assumed to come from the sediments but are excreted to the water column[2]. Non-predatory mortality is modeled similarly to algae as a function of suboptimal temperature (but not light). However, mortality is a function of low as well as high temperatures, and winter die-back is represented as a result of this control; the response is the inverse of the temperature limitation (Figure 68):

$$Mortality = [KMort + Poisoned + (1 - e^{-EMort \bullet (1 - TCorr)})] \cdot Biomass \qquad \textbf{(88)}$$

where:

$KMort$	=	intrinsic mortality rate (g/g·d);
$Poisoned$	=	mortality rate due to toxicant (g/g·d) **(417)**, and
$EMort$	=	maximum mortality due to suboptimal temperature (g/g·d).

Sloughing of dead leaves can be a significant loss (LeCren and Lowe-McConnell, 1980); it is simulated as an implicit result of mortality (Figure 68).

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[2] Because nutrients are not usually explicitly modeled in bottom sediments, macrophyte root uptake can result in loss of mass balance, particularly in shallow ponds. The optional sediment diagenesis model *does* include nutrients but linkage to macrophytes through root uptake has not yet been specified and implemented. However, the total mass of nutrients taken into the water column through macrophyte uptake can be tracked as a model output (N and P "Root Uptake" in kg).

Figure 68. Mortality as a function of temperature
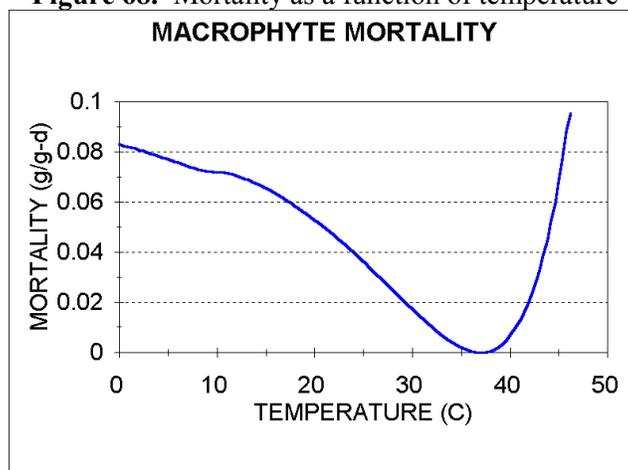
Macrophytes are subject to breakage due to higher water velocities; this breakage of live material is different from the sloughing of dead leaves. Although breakage is a function of shoot length and growth form as well as currents (Bartell et al., 2000; Hudon et al., 2000), a simpler construct was developed for AQUATOX (Figure 69):

$$Breakage = \frac{Velocity - VelMax}{Gradual \cdot UnitTime} \cdot Biomass \qquad (89)$$

where:

Breakage	=	macrophyte breakage (g/m^2 ·d);
Velocity	=	current velocity (cm/s) see **(14)**;
VelMax	=	velocity at which total breakage occurs (cm/s);
Gradual	=	velocity scaling factor (20 cm/s);
UnitTime	=	unit time for simulation (1 d);
Biomass	=	macrophyte biomass (g/m^2).

Figure 69. Breakage of macrophytes as a function of current velocity; *VelMax* set to 300 cm/s.
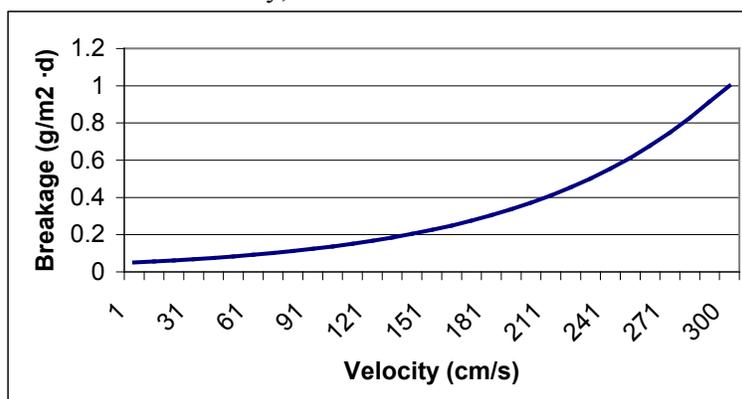
The *Breakage* formulation also applies to freely floating macrophytes and may be considered entrainment in periods of high flow. As such, *VelMax* should be set to a relatively high value for these organisms.

Bryophytes (mosses and liverworts) are a special class of macrophytes that attach to hard substrates, are stimulated by and take up nutrients directly from the water, are resistant to breakage, and decompose very slowly (Stream Bryophyte Group, 1999). Nutrient limitation is enabled when the "Bryophytes" plant type is selected, just as it is for algae. The model assumes that when a bryophyte breaks or dies the result is 75% particulate and 25% dissolved refractory detritus; in contrast, other macrophytes are assumed to yield 62% labile detritus. All other differences between bryophytes and other macrophytes in AQUATOX are based on differences in parameter values. These include low saturating light levels, low optimum temperature, very low mortality rates, moderate resistance to breakage, and resistance to herbivory (Arscott et al., 1998; Stream Bryophyte Group, 1999). Because in the field it is difficult to separate bryophyte chlorophyll from that of periphyton, it is computed so that the two can be combined and related to field values:

$$MossChlor = \Sigma\left(BryoConv \cdot Biomass_{Bryo}\right) \qquad \textbf{(90)}$$

where:

$MossChlor$	=	bryophytic chlorophyll a (mg/m^2);
$BryoConv$	=	conversion from bryophyte AFDW to chlorophyll a (8.9 mg/m^2: g/m^2);
$Biomass_{Bryo}$	=	biomass of given bryophyte (AFDW in g/m^2).

Currents and wave agitation can both stimulate and retard macrophyte growth. These effects will be modeled in a future version. Similar to the effect on periphyton, water movement can stimulate photosynthesis in macrophytes (Westlake, 1967); the same function could be used for macrophytes as for periphyton, although with different parameter values. Jupp and Spence (1977b) have shown that wave agitation can severely limit macrophytes; time-varying breakage eventually will be modeled when wave action is simulated.

4.3 Animals

Animals: Simplifying Assumptions

- Ingestion is represented by a maximum consumption rate adjusted for conditions of food, temperature, sublethal toxicant effects, and habitat preferences
- Reproduction is implicit in the increase in biomass
- Macrophytes can provide refuge from predation
- AQUATOX is a food-web model including prey switching based on prey availability
- Specific dynamic action (the metabolic "cost" of digesting and assimilating prey) is represented as proportional to food assimilated
- Unless spawning dates are entered by the user, spawning occurs as a function of water temperature
- Zooplankton and fish will migrate vertically from an anoxic hypolimnion to the epilimnion
- Promotion from one size class of fish to the next is estimated as a fraction of total biomass growth

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Zooplankton, benthic invertebrates, benthic insects, and fish are modeled, with only slight differences in formulations, with a generalized animal submodel that is parameterized to represent different groups:

$$\frac{dBiomass}{dt} = Load + Consumption \text{ - } Defecation \text{ - } Respiration - Fishing$$

$$\text{- } Excretion \text{ - } Mortality \text{ - } Predation \text{ - } GameteLoss \pm Diffusion_{Seg}$$

$$\text{- } Washout + Washin \pm Migration \text{ - } Promotion + Recruit - Entrainment \qquad \textbf{(91)}$$

$$GrowthRate = Consumption - Defecation - Respiration - Excretion$$

where:

dBiomass/dt	=	change in biomass of animal with respect to time (g/m^3·d);
Load	=	biomass loading, usually from upstream, or calculated from user-supplied fish stocking data (g/m^3·d);
Consumption	=	consumption of food (g/m^3·d), see **(98)**;
Defecation	=	defecation of unassimilated food (g/m^3·d), see **(97)**;
Respiration	=	respiration (g/m^3·d), see **(100)**;
Fishing	=	loss of organism due to fishing pressure (g/m^3·d), user input fraction fished multiplied by the biomass.
Excretion	=	excretion (g/m^3·d), see **(111)**;
Mortality	=	nonpredatory mortality (g/m^3·d), see **(112)**;
Predation	=	mortality from being preyed upon (g/m^3·d), see **(99)**;
GameteLoss	=	loss of gametes during spawning (g/m^3·d), see **(126)**;
Washout	=	loss due to being carried downstream by washout and drift (g/m^3·d), see **(129)** and **(130)**;
Washin	=	loadings from linked upstream segments (g/m^3·d), see **(30)**;
Diffusion$_{Seg}$	=	gain or loss due to diffusive transport over the feedback link between two segments, pelagic inverts. only (g/m^3·d), see **(32)**;
Migration	=	loss (or gain) due to vertical migration (g/m^3·d), see **(133)**;
Promotion	=	promotion to next size class or emergence (g/m^3·d), see **(136)**;
Recruit	=	recruitment from previous size class (g/m^3·d), see **(128)**;
Entrainment	=	entrainment and downstream transport by floodwaters (g/m^3·d) **(132).**
GrowthRate	=	estimated growth rate as a function of derivative terms, output in units of percentage per day when animal's "rates output" is turned on.

The change in biomass (Figure 70) is a function of a number of processes (Figure 71) that are subject to environmental factors, including biotic interactions. Similar to the way algae are treated, parameters for different species of invertebrates and fish are loaded and available for editing by means of the entry screens. Biomass of zoobenthos and fish is expressed as g/m^2 instead of g/m^3.

Growth rates have been part of AQUATOX output since Release 3.0. However, this output has always been reported in units of "percent (of current biomass) per day." To better understand total predicted secondary and tertiary productivity, and to effectively compare model results against literature estimates, as of Release 3.2 growth rates are also output in "g AFDW/ m^2·day."

Figure 70. Predicted changes in biomass in a stream
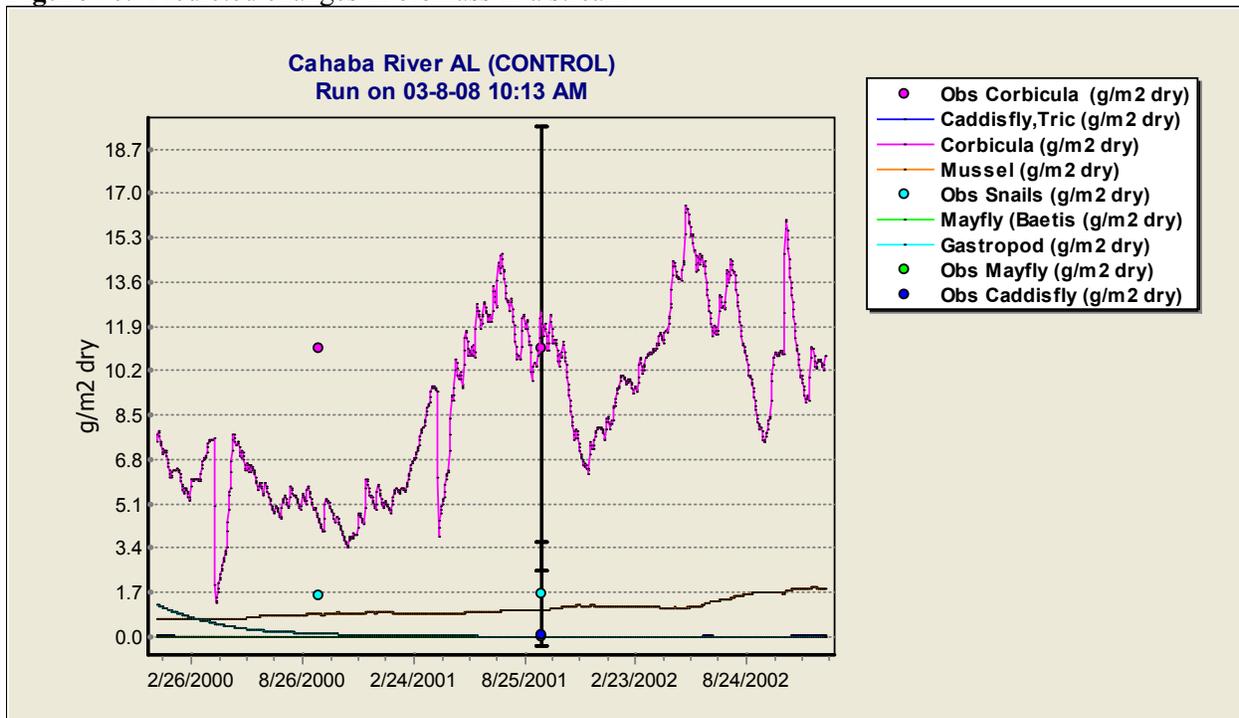
Figure 71. Predicted Process Rates for the Invasive Clam *Corbicula*, Expressed as Percent of Biomass; Yellow Spikes are Entrainment During Storm Events; Consumption Depends on Sloughing Periphyton..
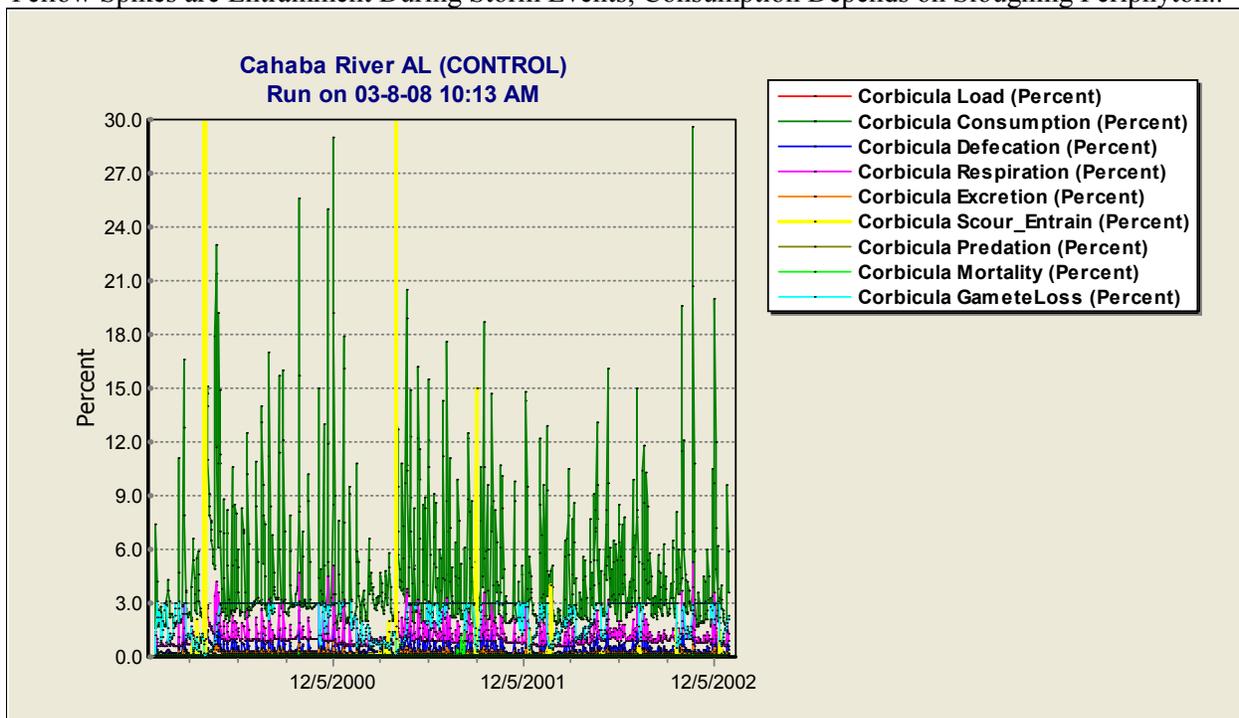
Consumption, Defecation, Predation, and Fishing

Several formulations have been used in various models to represent consumption of prey, reflecting the fact that there are different modes of feeding and that experimental evidence can be fit by any one of several equations (Mullin et al., 1975; Scavia, 1979; Straškraba and Gnauck, 1985).

Ingestion is represented in AQUATOX by a maximum consumption rate, adjusted for ambient food, temperature, oxygen, sediment, and salinity conditions, and reduced for sublethal toxicant effects and limitations due to habitat preferences of a given predator:

$$Ingestion_{prey,\,pred} = CMax_{pred} \cdot SatFeeding \cdot TCorr_{pred} \cdot FoodDilution$$
$$\cdot\, HabitatLimit \cdot ToxReduction \cdot HarmSS \cdot SaltEffect \cdot O2EffectFrac \cdot Biomass_{pred}$$

(92)

where:

$Ingestion_{prey,\,pred}$	=	ingestion of given prey by given predator (g/m^3·d);
$Biomass$	=	concentration of organism (g/m^3·d);
$CMax$	=	maximum feeding rate for predator (g/g·d);
$SatFeeding$	=	saturation-feeding kinetic factor, see **(93)**;
$TCorr$	=	reduction factor for suboptimal temperature (unitless), see Figure 59;
$FoodDilution$	=	factor to account for dilution of available food by suspended sediment (unitless), see **(120)**;
$ToxReduction$	=	reduction due to effects of toxicant (see **(424)**, unitless); and
$HarmSS$	=	reduction due to suspended sediment effects (see **(116)**, unitless);
$SaltEffect$	=	effect of salinity on ingestion rate (unitless), see **(440)**;
$O2EffectFrac$	=	effect of reduced oxygen on ingestion (unitless), see **(205)**; and
$HabitatLimit$	=	in streams, habitat limitation based on predator habitat preferences (unitless), see **(13)**.

The maximum consumption rate is sensitive to body size, so an alternative to specifying *CMax* for fish is to compute it using an allometric equation and parameters from the Wisconsin Bioenergetics Model (Hewett and Johnson, 1992; Hanson et al., 1997):

$$CMax = CA \cdot MeanWeight^{CB}$$

(93)

where:

CA	=	maximum consumption for a 1-g fish at optimal temperature (g/g·d);
$MeanWeight$	=	mean weight for a given fish species (g);
CB	=	slope of the allometric function for a given fish species.

Many animals adjust their search or filtration in accordance with the concentration of prey; therefore, a saturation-kinetic term is used (Park et al., 1974, 1980; Scavia and Park, 1976):

$$SatFeeding = \frac{Preference_{prey,\,pred} \cdot Food}{\Sigma_{prey}(\,Preference_{prey,\,pred} \cdot Food) + FHalfSat_{pred}}$$

(94)

where:

  Preference   =   preference of predator for prey (unitless);
  Food   =   available biomass of given prey (g/m^3);
  FHalfSat   =   half-saturation constant for feeding by a predator (g/m^3).

The food actually available to a predator may be reduced in two ways:

$$Food = (Biomass_{prey} - BMin_{pred}) \cdot Refuge_{Macro} \cdot Refuge_{Oyster} \cdot Refuge_{Marsh} \cdot Refuge_{Burrow} \quad \textbf{(95)}$$

where:

  $BMin$ =   minimum prey biomass needed to begin feeding (g/m^3); and
  $Refuge_{Macro}$ =   reduction factor for prey hiding in macrophytes or seagrass (unitless), see **(95)**;
  $Refuge_{Oyster}$ = reduction factor for prey hiding among oysters (unitless), see **(95)**;
  $Refuge_{Marsh}$ =   reduction factor for prey hiding in marsh edge; may also enhance predation if marsh is disintegrating (unitless), see **(95b)**;
  $Refuge_{Burrow}$ = reduction factor for prey's capability to burrow into sediment, characterized by "*BurrowIndex*" parameter (unitless), see **(95c)**.

Search or filtration may virtually cease below a minimum prey biomass (*BMin*) to conserve energy (Figure 72), so that a minimum food level is incorporated (Parsons et al., 1969; Steele, 1974; Park et al., 1974; Scavia and Park, 1976; Scavia et al., 1976; Steele and Mullin, 1977). However, some filter feeders such as cladocerans (for example, *Daphnia*) must constantly filter because the filtratory appendages also serve for respiration; therefore, in these animals there is no minimum feeding level and *BMin* is set to 0.

Figure 72. Saturation-kinetic consumption
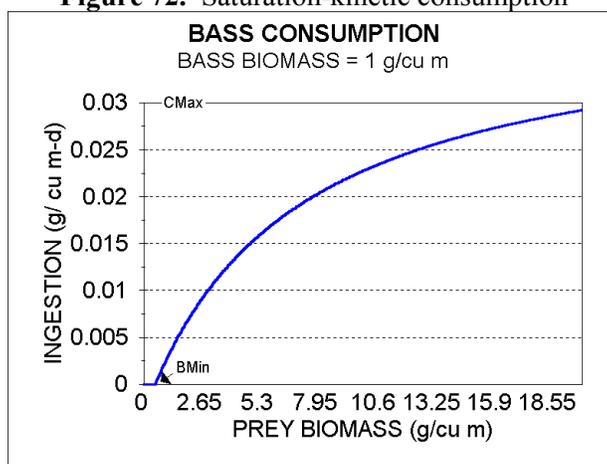
Refuge from Predation

Although AQUATOX is an ecosystem biomass model, it has some capability to represent habitat characteristics. In particular, the model can account for the function of macrophytes or seagrass

as a habitat structure that provides refuge from predation. This refuge is represented by a factor related to the macrophyte biomass that is original with AQUATOX (Figure 73):

$$Refuge_{Macro/Oyster} = 1 - \frac{Biomass_{Macro/Oyster}}{Biomass_{Macro/Oyster} + HalfSat}$$ **(96)**

where:

$HalfSat$	=	half-saturation constant (20 g/m^3),
$Biomass_{Macro}$	=	biomass of macrophyte (g/m^3), or
$Biomass_{Oyster}$	=	biomass of oyster (g/m^3).

Figure 73. Refuge from predation
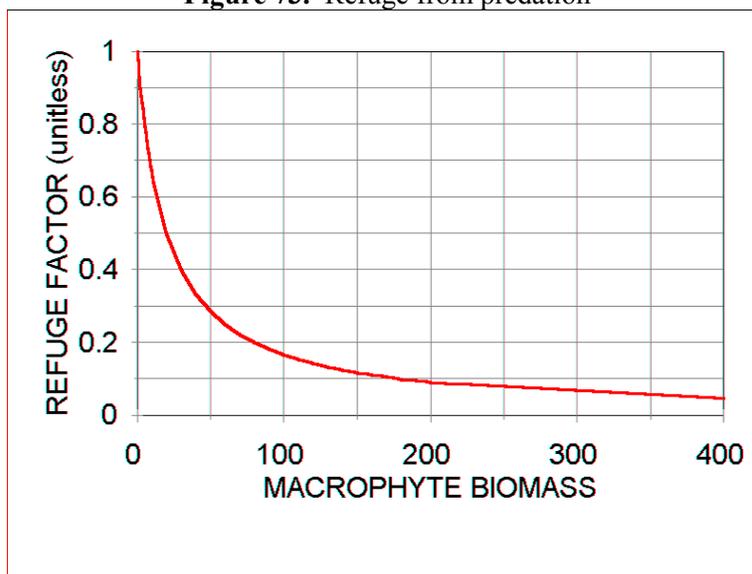
Similarly, oyster beds provide structural refuge whereby smaller animals may hide in crevices and dead shells. Using the same equation **(95)**, but based on biomass of oysters with a nominal *HalfSat* value of 80 g/m^3, we get a slightly different form of reduction in the predator-prey relationship (Figure 74). The parameter may be fine-tuned based on published studies (Lenihan 1999, Grabowski and Powers 2004).

A boolean parameter "*Can Seek Refuge*" in the animal underlying data specifies whether an animal can seek refuge within macrophytes or oyster beds. Many fish and invertebrates can, but not infauna. Similarly, a boolean parameter "*Is a Visual Feeder*" in the animal underlying data specifies whether an animal's prey can effectively seek refuge.

Figure 74. Refuge from predation
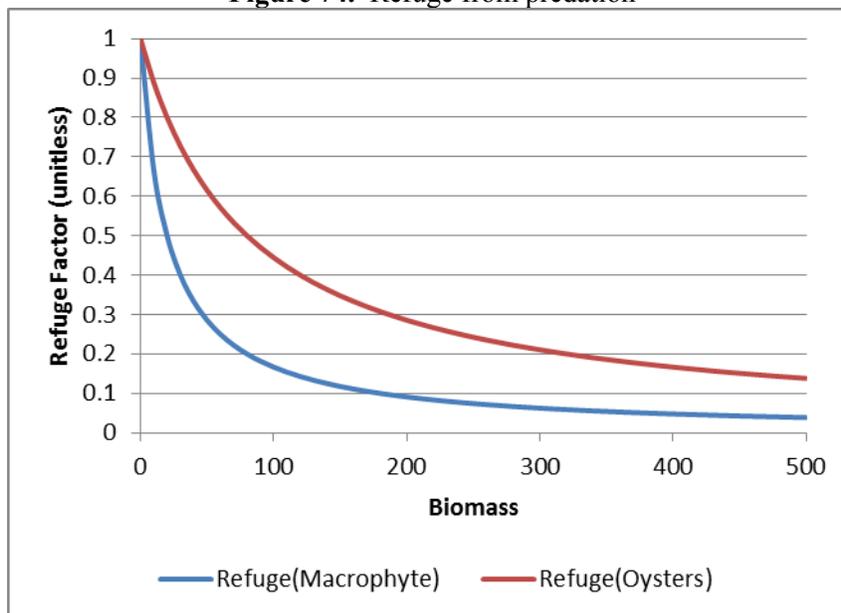
Fractal Dimension of Marsh Edge

Another type of refuge is provided by tidal creeks and the diffuse interface between marsh and water. The irregularity of the saltmarsh-water interface as a refuge capacity can be represented as a fractal dimension. This construct was originally developed for the Sea Level Affecting Marshes Model (SLAMM) (Park et al. 1989) and was approved by a peer review panel in 1990 (http://www2.epa.gov/exposure-assessment-models/peer-review-aquatox). Parameter values for brown and white shrimp were based on catch statistics provided by the National Marine Fisheries Service Galveston Lab (see also Zimmerman et al. 1991) and results were reported in Congressional testimony by Park (1991).

If the shoreline-marsh interface were a straight line it would have a fractal dimension of 1.0, corresponding to the Euclidean integer dimension; this is characteristic of coastlines subjected to erosional retreat. Healthy marshes have a fractal dimension in excess of 1.0 (intermediate between the Euclidean dimensions of a line and a surface). Examples of marsh areas with calculated fractal dimensions are taken from Grand Bay on the border between Mississippi and Alabama (Figure 75). With inundation due to a relative rise in sea level, as the interface becomes more irregular due to disintegration of the marsh, the fractal dimension becomes larger. Eventually, the marsh may break up into scattered remnants with a fractal dimension < 1.0 (intermediate between the Euclidean dimensions for a line and a point). These relationships, with the concomitant increase in refuge and even the loss of refuge, can be represented by a slightly different equation.

$$Refuge_{Marsh} = \left[\frac{1 + Coeff}{FractalD_{Marsh} + Coeff} \right]$$

(95b)

where:

$FractalD_{Marsh}$ = fractal dimension of marsh-water interface;

$Coeff$ = fractal dimension Refuge coefficient (-0.5 to 100 with the lowest values providing the strongest Refuge effect).
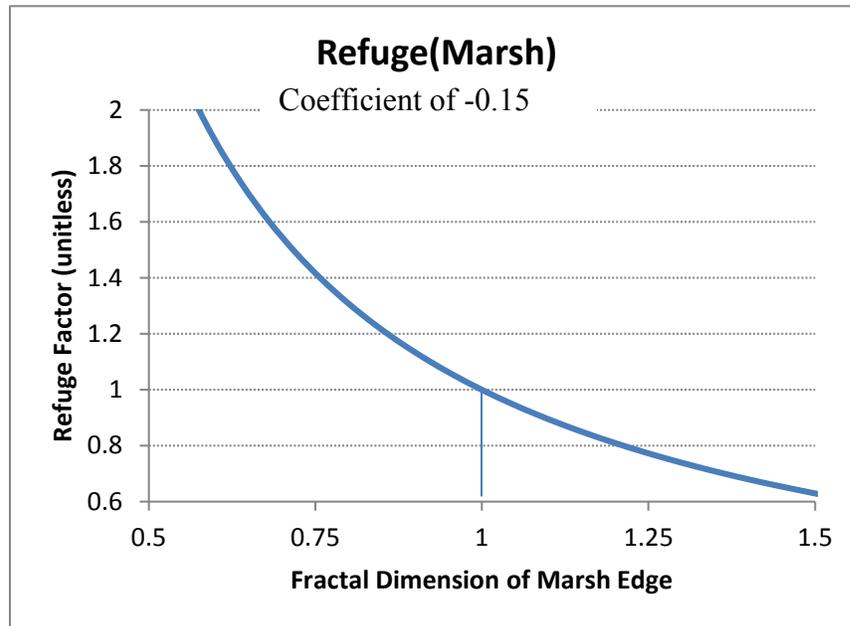
Figure 1. Refuge Factor as a Function of Marsh-Edge Fractal Dimension

The fractal dimension is computed based on the co-occurrence of marsh and water in the same GIS cells. Figure 75 shows three examples of computed fractal dimensions.

Figure 75. Examples of marsh areas with calculated fractal dimensions from Grand Bay, MS
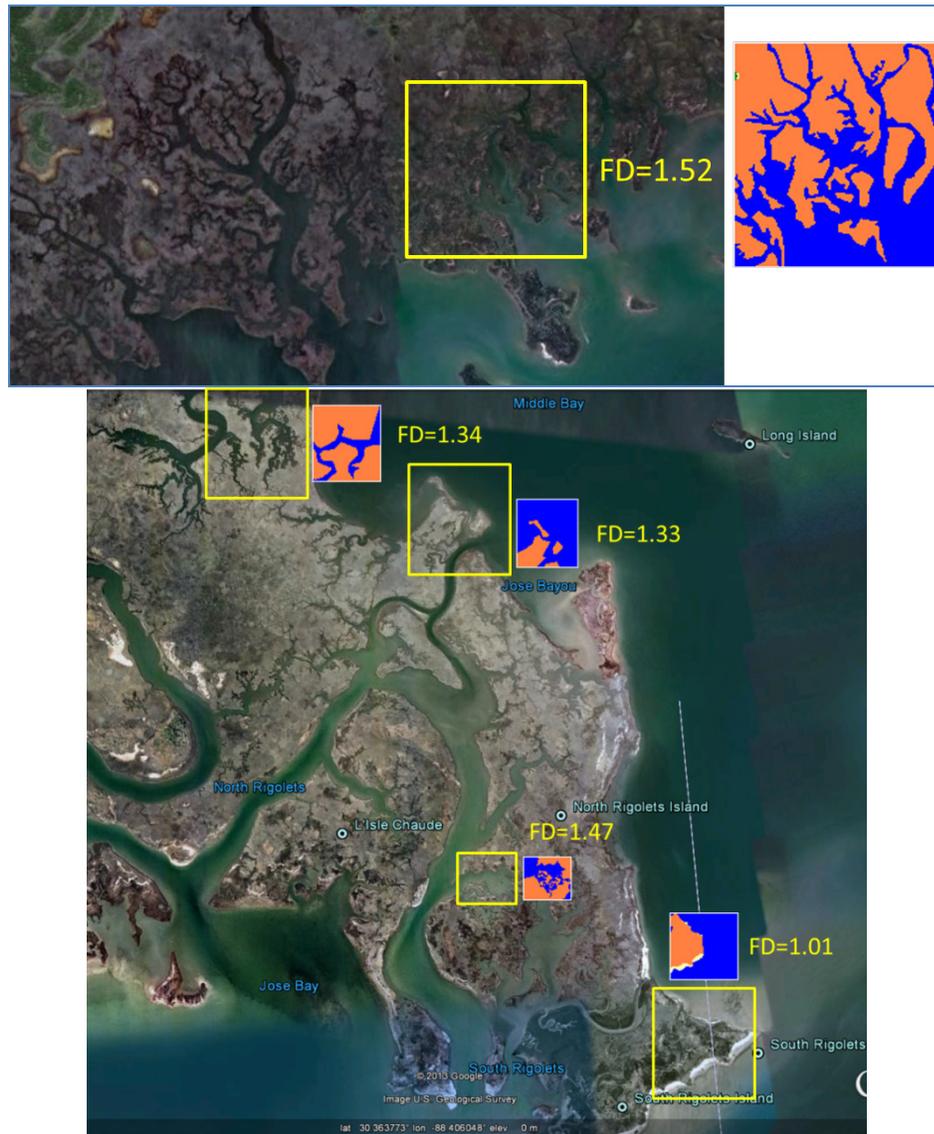
Burrowing Refuge for Invertebrates

Many marine benthic invertebrates have the capability to elude predators due to burrowing. To ensure that organisms with deep burrows are not subject to excess predation a burrowing refuge construct has been added to AQUATOX.

$$Refuge_{Burrow} = 1 - \left(\frac{BurrowIndex}{BurrowIndex + HalfSat_{Burrow}} \right)$$
(95c)

where:

$Refuge_{Burrow}$	=	unitless multiplier to represent burrowing refuge, see **(95);**
$BurrowIndex$	=	animal-specific parameter (unitless) with 0 representing no burrowing refuge;
$HalfSat_{Burrow}$	=	half saturation coefficient for burrowing (unitless), set to 3.2.

The *BurrowIndex* parameter may be calibrated on an animal-specific basis to best represent the extent of burrowing that reduces predation pressure on an organism (Figure 2). Some example starting points for calibration are listed below:

- Blue Crab (*Callinectes*) is a limited burrower so it would have a *BurrowIndex* of 0.5;
- Sand Crab (*Emerita*) creates shallow burrows so it would have a *BurrowIndex* of 1.0;
- *Donax* may be assumed to have more burrowing refuge than *Emerita* so it would have a *BurrowIndex* of 2.0;
- Ghost Shrimp (*Callichirus*) are deep burrowers so they would have the maximum *BurrowIndex* of 5.0.
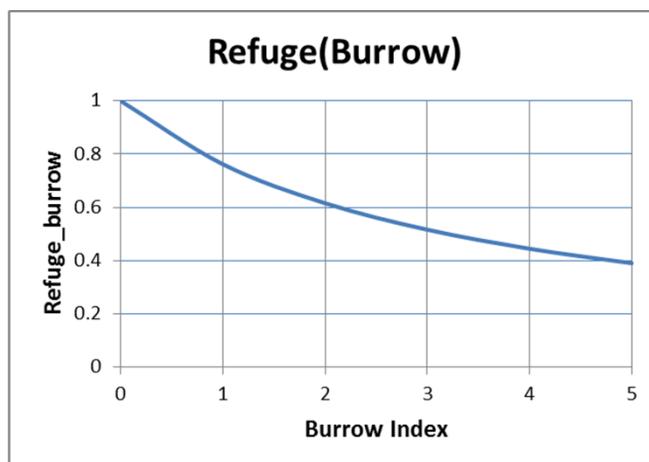
Figure 2. Relationship between "*Burrow Index*" Parameter and Calculated "*Refuge*"

Adaptive Food Preferences

AQUATOX is a food-web model with multiple potential food sources. Passive size-selective filtering (Mullin, 1963; Lam and Frost, 1976) and active raptorial selection (Burns, 1969; Berman and Richman, 1974; Bogdan and McNaught, 1975; Brandl and Fernando, 1975) occur among aquatic organisms. Relative preferences are represented in AQUATOX by a matrix of preference parameters first proposed by O'Neill (1969) and used in several aquatic models (Bloomfield et al., 1973; Park et al., 1974; Canale et al., 1976; Scavia et al., 1976). Higher values indicate increased preference by a given predator for a particular prey compared to the preferences for all possible prey. In other words, the availability of the prey is weighted by the preference factor.

The preference factors are normalized so that if a potential food source is not modeled or is below the *BMin* value, the other preference factors are modified accordingly, representing adaptive preferences:

$$Preference_{prey, pred} = \frac{Pref_{prey, pred}}{SumPref} \qquad \textbf{(97)}$$

where:

$Preference_{prey,pred}$	=	normalized preference of given predator for given prey (unitless);
$Pref_{prey, pred}$	=	initial preference value from the animal parameter screen (unitless); and
$SumPref$	=	sum of preference values for all food sources that are present above the minimum biomass level for feeding during a particular time step (unitless).

Similarly, different prey types have different potentials for assimilation by different predators. The fraction of ingested prey that is egested as feces or discarded (and which is treated as a source of detritus by the model, see **(153)** and **(154)**), is indicated by a matrix of egestion coefficients with the same structure as the preference matrix, so that defecation is computed as (Park et al., 1974):

$$Defecation_{pred} = \Sigma_{prey} \left(EgestCoeff_{prey, pred} \cdot Ingestion_{prey, pred} + IncrEgest \cdot Ingest_{NoTox} \right) \qquad \textbf{(98)}$$

where:

$Defecation_{pred}$	=	total defecation for given predator (g/m^3·d);
$Ingestion_{prey, pred}$	=	ingestion of given prey by given predator (g/m^3·d) **(91)**;
$EgestCoeff_{prey, pred}$	=	fraction of ingested prey that is egested (unitless); and
$IncrEgest$	=	increased egestion due to toxicant (see Eq. **(425)**, unitless);
$Ingest_{NoTox}$	=	ingestion excluding toxic effects, calculated as *Ingestion* divided by *ToxReduction* (see Eq. **(424)**, g/m^3·d).

Consumption of prey for a predator is also considered predation or grazing for the prey. Therefore, AQUATOX represents consumption as a source term for the predator and as a loss term for the prey:

$$Consumption_{pred} = \Sigma_{prey} \left(Ingestion_{prey, pred} \right) \qquad \textbf{(99)}$$

$$Predation_{prey} = \Sigma_{pred} \left(Ingestion_{prey, pred} \right) \qquad \textbf{(100)}$$

where

$Consumption_{pred}$	=	total consumption rate by predator (g/m^3·d); and
$Predation_{prey}$	=	total predation on given prey (g/m^3·d).

Fishing pressure is represented simply as a fraction of biomass removed each day. A potential future model enhancement could allow for temporally variable fishing pressures to better reflect harvesting seasons. Fish may also be stocked within a modeled system by entering time series in grams per day or grams per meter squared per day.

Respiration

Respiration can be considered as having three components (Cui and Xie, 2000), subject to the effects of salinity:

$$Respiration_{pred} = \left(StdResp_{pred} + ActiveResp_{pred} + SpecDynAction_{pred}\right) \cdot SaltEffect \quad \textbf{(101)}$$

where:

$Respiration_{pred}$	=	respiratory loss of given predator (g/m³·d);
$StdResp_{pred}$	=	basal respiratory loss modified by temperature (g/m³·d); see **(101)**;
$ActiveResp_{pred}$	=	respiratory loss associated with swimming (g/m³·d), see **(104)**;
$SpecDynAction_{pred}$	=	metabolic cost of processing food (g/m³·d), see **(110)**; and
$SaltEffect$	=	effect of salinity on respiration (unitless), see **(440)**.

Standard respiration is a rate at resting in which the organism is expending energy without consumption. Active respiration is modeled only in fish and only when allometric (weight-dependent) equations are used, so standard respiration can be considered as a composite "routine" respiration for invertebrates and in the simpler implementation for fish. The so-called specific dynamic action is the metabolic cost of digesting and assimilating prey. AQUATOX simulates standard respiration as a basal rate modified by a temperature dependence and, in fish, a density dependence (see Kitchell et al., 1974):

$$StdResp_{pred} = BasalResp_{pred} \cdot TCorr_{pred} \cdot Biomass_{pred} \cdot DensityDep \quad \textbf{(102)}$$

where:

$BasalResp_{pred}$	=	basal respiration rate at optimal temperature for given predator (g/g·d); parameter input by user as "Respiration Rate" or computed as a function of the weight of the animal (see below);
$TCorr_{pred}$	=	Stroganov temperature function (unitless), see Figure 59;
$Biomass_{pred}$	=	concentration of predator (g/m³); and
$DensityDep$	=	density-dependent respiration factor used in computing standard respiration, applicable only to fish (unitless). See **(109)**

As an alternative formulation, respiration in fish or invertebrates can be modeled as a function of the weight of the fish using an allometric equation (Hewett and Johnson, 1992; Hanson et al., 1997):

$$StdResp_{pred} = BasalResp_{pred} \cdot MeanWeight_{pred}^{RB_{pred}} \cdot TFn_{pred} \cdot Biomass_{pred} \cdot DensityDep \quad \textbf{(103)}$$

where:

$MeanWeight_{pred}$	=	mean weight for a given fish (g);
RB_{pred}	=	slope of the allometric function for a given fish;

TFn_{pred} =   temperature function (unitless).

The allometric functions are based on the well known Wisconsin Bioenergetics Model and, for convenience, use the published parameter values for that model (Hewett and Johnson, 1992; Hanson et al., 1997). Weight-based bioenergetic functions have been extended to invertebrates by several authors (for example, Brylawski and Miller 2003, Adamack et al. 2012) and that capability is available as an enhancement in the present version of AQUATOX.

The basal respiration rate in that model is expressed as g of oxygen per g organic matter of fish per day, and this has to be converted to organic matter respired:

$$BasalResp_{pred} = RA_{pred} \cdot 1.5$$ **(104)**

where:
RA_{pred} =   basal respiration rate, characterized as the intercept of the allometric mass function in the Wisconsin Bioenergetics Model documentation (g O_2/g organic matter $\cdot$d);
1.5   =   conversion factor (g organic matter/g O_2).

Swimming activity may be large and variable (Hanson et al., 1997) and is subject to calibration for a particular site, considering currents and other factors:

$$ActiveResp_{pred} = Activity_{pred} \cdot Biomass_{pred}$$ **(105)**

where:
$Activity_{pred}$ =   activity factor (g/g$\cdot$d).

Activity can be a complex function of temperature. The Wisconsin Bioenergetics Model (Hewett and Johnson, 1992; Hanson et al., 1997) provides two alternatives. **Equation Set 1** uses an exponential temperature function:

$$TFn = e^{(RQ \cdot Temp)}$$ **(106)**

where:
RQ =   the Q_{10} or rate of change per 10deg. C for respiration (1/deg. C);
$Temp$ =   ambient temperature (deg. C).

This is coupled with a complex function for swimming speed as an allometric function of temperature (Hewett and Johnson, 1992; Hanson et al., 1997):

$$Activity_{pred} = e^{(RTO \bullet Vel)}$$

$$\text{If } Temp > RTL \text{ Then } Vel = RK1 \cdot MeanWeight^{RK4}$$ **(107)**

$$\text{Else } Vel = ACT \cdot MeanWeight^{RK4} \cdot e^{(BACT \bullet Temp)}$$

where:
RTO =   coefficient for swimming speed dependence on metabolism (s/cm);

RTL   =   temperature below which swimming activity is an exponential function of temperature (deg. C);

Vel   =   swimming velocity (cm/s);

RK1   =   intercept for swimming speed above the threshold temperature (cm/s);

RK4   =   weight-dependent coefficient for swimming speed;

ACT   =   intercept for swimming speed for a 1 g fish at deg. C (cm/s); and

BACT   =   coefficient for swimming at low temperatures (1/deg. C),

Equation Set 2 uses the Stroganov function used elsewhere in AQUATOX:

$$TFn = TCorr \tag{108}$$

and activity is a constant:

$$Activity = ACT \tag{109}$$

where:

TCorr   =   reduction factor for suboptimal temperature (unitless), see **(59)**;

ACT   =   activity factor, which is not the same as ACT in Equation Set 1 (g/g·d).

Respiration in fish increases with crowding due to competition for spawning sites, interference in feeding, and other factors. This adverse intraspecific interaction helps to constrain the population to the carrying capacity; as the biomass approaches the carrying capacity for a given species the respiration is increased proportionately (Kitchell et al., 1974):

$$DensityDep = 1 + \frac{IncrResp \cdot Biomass}{KCap / ZMean} \tag{110}$$

where:

IncrResp   =   increase in respiration at carrying capacity (0.5);

KCap   =   carrying capacity (g/m^2);

ZMean   =   mean depth from site underyling data (m).

With the *IncrResp* value of 0.5, respiration is increased by 50% at carrying capacity (Kitchell et al., 1974), as shown in Figure 76. This density-dependence is used only for fish, and not for invertebrates.

Prior to AQUATOX Release 3.2, the benthic invertebrate "carrying capacity" parameter has had little impact on simulations. With some marine-benthic invertebrate species, (oysters, for example) available substrate becomes a limiting factor. For this reason, the model now enforces a hard-cap at the benthic invertebrate carrying capacity by increasing mortality if the biomass exceeds that level:

$$Mort_{KCap} = \min(Biomass_{Benthos} - KCap_{Benthos}, 0) \tag{109b}$$

where:

$Mort_{KCap}$ =   mortality of zoobenthos due to exceeding available substrate (g/m^2);

$Biomass_{Benthos}$ = biomass of zoobenthos (g/m^2); and

$KCap_{Benthos}$ = user input carrying capacity for this site and zoobenthos species (g/m^2).

Figure 76. Density-dependent factor for increase in respiration as fish biomass approaches the carrying capacity (10.0 in this example).
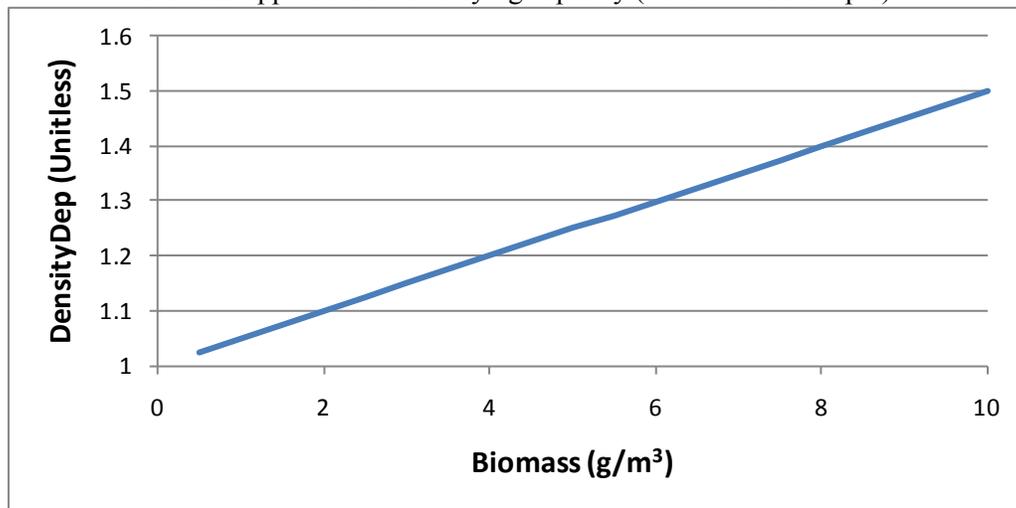
As a simplification, specific dynamic action is represented as proportional to food assimilated (Hewett and Johnson, 1992; see also Kitchell et al., 1974; Park et al., 1974):

$$SpecDynAction_{pred} = KResp_{pred} \cdot (Consumption_{pred} - Defecation_{pred}) \tag{111}$$

where:

$KResp_{pred}$ =   proportion of assimilated energy lost to specific dynamic action (unitless); parameter input by user as "Specific Dynamic Action;"

$Consumption_{pred}$ =   ingestion (g/m^3·d) see **(98)**; and

$Defecation_{pred}$ =   egestion of unassimilated food (g/m^3·d), see **(97)**.

Excretion

As respiration occurs, biomass is lost and nitrogen and phosphorus are excreted directly to the water (Horne and Goldman 1994); see **(169)** and **(183)**. Ganf and Blazka (1974) have reported that this process is important to the dynamics of the Lake George, Uganda, ecosystem. Their data were converted by Scavia and Park (1976) to obtain a proportionality constant relating excretion to respiration:

$$Excretion_{pred} = KExcr_{pred} \cdot Respiration_{pred} \tag{112}$$

where:

$Excretion_{pred}$ =   excretion rate (g/m^3·d);

$KExcr_{pred}$ =   proportionality constant for excretion:respiration (unitless);

$Respiration_{pred}$ =   respiration rate (g/m^3·d), see **(100)**.

Excretion is approximately 17 percent of respiration, which is not an important biomass loss term for animals, but it is important in nutrient recycling. All biomass lost due to animal excretion is assumed to convert to dissolved labile detritus, see **(151)**.

Nonpredatory Mortality

Nonpredatory mortality is a result of both environmental conditions and the toxicity of pollutants:

$$Mortality_{pred} = D_{pred} \cdot Biomass_{pred} + Poisoned_{pred} + Mort_{Ammonia} \\ + Mort_{LowO2} + Mort_{SedEffects} + Mort_{Salinity} + Mort_{KCap} \tag{113}$$

where:

$Mortality_{pred}$	=	nonpredatory mortality (g/m^3·d);
D_{pred}	=	environmental mortality rate; the maximum value of **(113)** and **(114)**, is used (1/d);
$Biomass_{pred}$	=	biomass of given animal (g/m^3);
$Poisoned$	=	mortality due to toxic effects (g/m^3·d), see **(417);**
$Mort_{Ammonia}$	=	ammonia mortality, (g/m^3·d), see **(179);**
$Mort_{LowO2}$	=	low oxygen mortality, (g/m^3·d), see **(203)**;
$Mort_{SedEffects}$	=	mortality from suspended sediments, (g/m^3·d), see **(115)**
$Mort_{Salinity}$	=	mortality from salinity, (g/m^3·d), see **(112)**; and
$Mort_{KCap}$	=	mortality from benthic invertebrate exceeding available substrate, (g/m^3·d), see **(109b)**.

Under normal conditions a baseline mortality rate is used:

$$D_{pred} = KMort_{pred} \tag{114}$$

where:
$KMort_{pred}$ =   normal nonpredatory mortality rate (1/d).

An exponential function is used for temperatures above the maximum (Figure 77):

$$D_{pred} = KMort_{pred} + \frac{e^{Temperature - TMax_{pred}}}{2} \tag{115}$$

where:

$Temperature$	=	ambient water temperature (°C); and
$TMax_{pred}$	=	maximum temperature tolerated (°C).

Figure 77. Mortality as a function of temperature
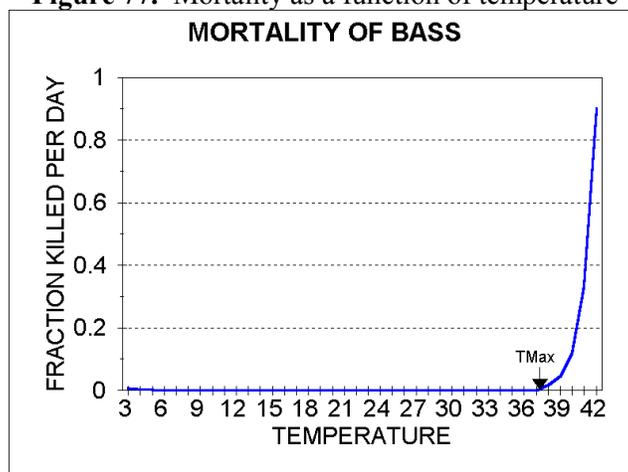
The lower lethal temperature is often 0°C (Leidy and Jenkins, 1976), so it is ignored at this time.

Stocking and Harvesting of Animals

Given the importance of anthropogenic impacts to both fish and invertebrate populations within the nearshore marine environment, an interface has been added to allow time-series stocking or removal for all animals. These data may be input in units of g/(m² day) (stocking or removal) or percent/day (removal).

The result of fish stocking is an increase in the "load" portion of equation **(90)**. The result of fish removal is a decrease in the "load" rate that can become a negative number. The input of "stocked" organisms is assumed to have no organic-chemical burden. Removal of toxicants or nutrients from the system due to fishing or invertebrate removal is tracked with the "fishing loss" mass-balance tracking variables. This procedure ensures the accounting for all mass balances of nutrients and chemicals.

Suspended Sediment Effects

The approach used to quantify lethal and sublethal effects of suspended sediments is based on logarithmic models described by Newcombe (for example, Newcombe 2003).

> **Summary of Sediment Effects:**
>
> - Mortality
> - Reduction in feeding
> - Dilution of food by sediment particles
> - Stimulation of invertebrate drift
> - Loss of spawning and protective habitat in interstices

They take the form of:

$$LethalSS = SlopeSS \cdot \ln(SS) + InterceptSS + SlopeTime \cdot \ln(TExp) \tag{116}$$

where:

LethalSS	=	cumulative fraction killed by given exposure to a given suspended sediment concentration (fraction/d)
SlopeSS	=	slope for sediment response (unitless)
SS	=	suspended inorganic sediment concentration (mg/L)
InterceptSS	=	intercept for suspended sediment response (unitless)
SlopeTime	=	slope for duration of exposure (unitless)
TExp	=	duration of exposure (d)

Unfortunately, there is a dearth of quantitative data on response to sediments. Therefore, the responses are grouped according to sensitivity, and parameters for surrogate species are used. The user can specify different parameter values; the values given below are provided as defaults.

For sublethal effects, avoidance behavior is noted at SS of about 100 mg/L (Doisy and Rabeni 2004); however, this could only be used as a cue for migration in the model and has been ignored at this time.

Reduction in feeding occurs in game fish due to visual impairment (Crowe and Hay 2004). SS of 25 mg/L seems to be threshold for response (Rowe et al. 2003). The general equation **(115)** is used to represent a decrease in food due to turbidity, but without the exposure factor because the response is instantaneous:

$$HarmSS = SlopeSS \cdot \ln(SS) + InterceptSS \qquad \qquad \textbf{(117)}$$

where:

HarmSS	=	reduction factor for impairment of visual predation (unitless)
SlopeSS	=	slope for suspended sediment response (-0.36, unitless)
SS	=	suspended inorganic sediment concentration (mg/L). If TSS is modeled see **(244)** otherwise, the sum of inorganic sediments in the water column (e.g. *Sand+Silt+Clay*);
InterceptSS	=	intercept for suspended sediment reponse (2.11, unitless)

The equation is parameterized using data for coho salmon with 1-hr exposure (Berry et al. 2003). It was verified with numerous other qualitative observations for salmon, Arctic grayling, and trout (Berry et al. 2003). This equation is used for all visual-feeding fish, especially game fish. The user has the option of turning on this factor

Figure 78. Reduction in feeding by coho salmon (*Oncorhynchus kisutch*)
due to suspended sediments. Data from (Berry et al. 2003).
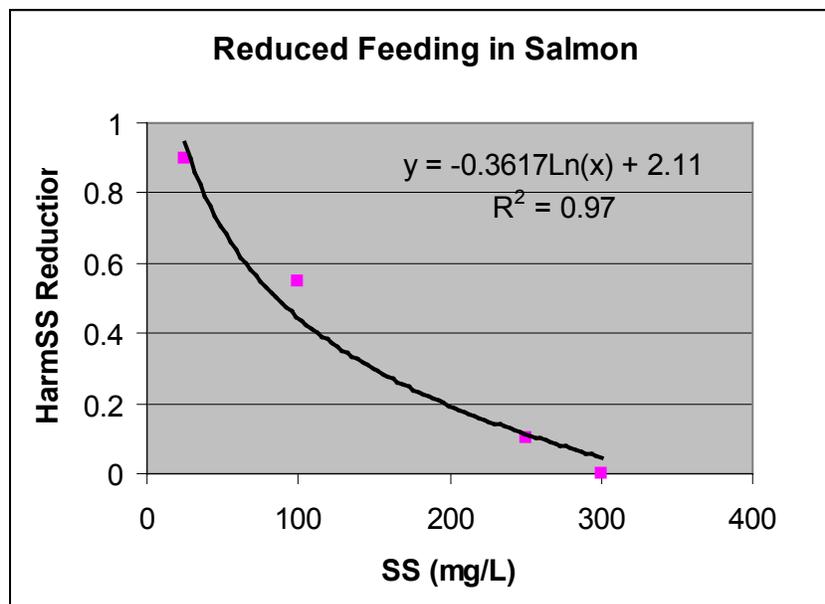
For modeling lethal effects, mortality can occur in fish over a range of suspended sediments. Because of the lack of suitable quantitative data, these responses are divided into sensitivity categories specific to this model and differing from Clarke and Wilber (2000) with parameters for surrogate species that can be considered representative for groups of organisms. The factor also can be turned off for those organisms that are completely insensitive.

Tolerant

This category represents those species having a 24-hr $LC_{10} > 5000$ mg/L SS. Generally, these are benthic species exposed to the flocculent zone and bottom sediments. The general equation **(115)** is parameterized to accommodate the 24-hr lethality observations and is extended to other times of exposure by fitting to observed 48-hr lethal responses:

$$LethalSS = 1.62 \cdot \ln(SS) - 14.2 + 3.5 \cdot \ln(TExp) \tag{118}$$

where:

LethalSS	=	cumulative fraction killed by given exposure to a given suspended sediment concentration (fraction/d)
TExp	=	time of exposure to given level of suspended sediment (d)
SS	=	minimum suspended inorganic sediment concentration over exposure time (mg/L). If TSS is modeled see **(244)** otherwise, the sum of inorganic sediments in the water column (e.g. *Sand+Silt+Clay*).

The parameters are based on the benthic estuarine fish spot (*Leiostomus xanthurus*), using data compiled in Berry et al. (2003).

Due to lack of data beyond 48 hours, this equation is applied using one- and two-day exposure times only. The maximum effect is chosen from these two equation results.

Figure 79. Lethality of suspended sediments to spot (*Leiostomus xanthurus*), a tolerant species, based on data compilation of Berry et al. (2003).
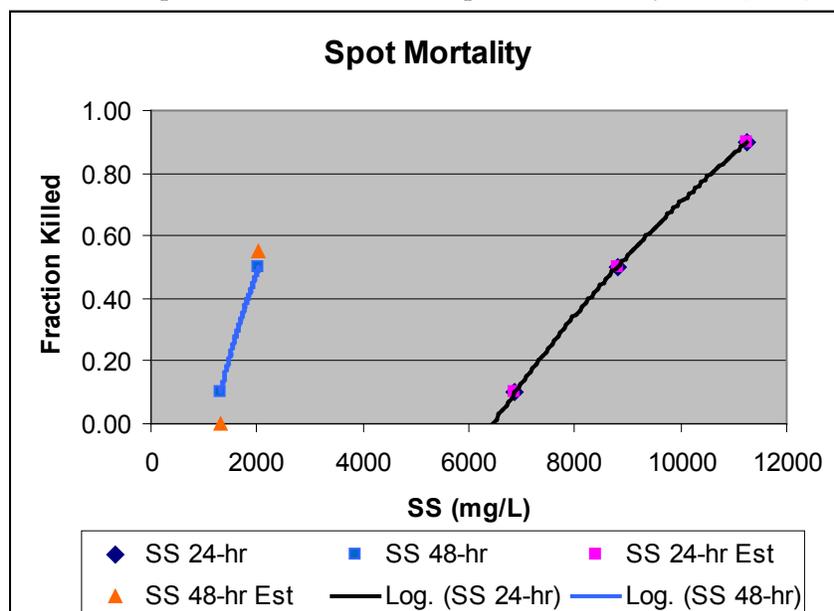
Sensitive

This category represents those species having 250 mg/L < 24-hr LC_{10} <5000 mg/L SS. Small estuarine species seem to be highly sensitive to suspended sediment (Figure 84). The general parameters are based on a composite fit to data for bay anchovy, menhaden, and Atlantic silversides taken from a compilation by Berry et al. (2003). The equation is:

$$LethalSS = 0.34 \cdot \ln(SS) - 1.85 + 0.1 \cdot \ln(TExp) \tag{119}$$

This equation is applied using one- and two-day exposure times along with effects from one, two, and three weeks exposure. The maximum effect is chosen from these multiple calculations.

Figure 80 illustrates the response curve for white perch. The equation exhibits good extension to juvenile rainbow trout with a 28-d exposure to SS (Figure 81) and Chinook salmon with a 1.5-d exposure (Figure 82). In both cases the equation is slightly over-protective, but that is considered appropriate.

Figure 80. Lethality of suspended sediments to white perch (Morone americana), a sensitive species, based on data compilation of (Berry et al. 2003).

White Perch Mortality, 24-hr

$y = 0.341\ln(x) - 1.851$
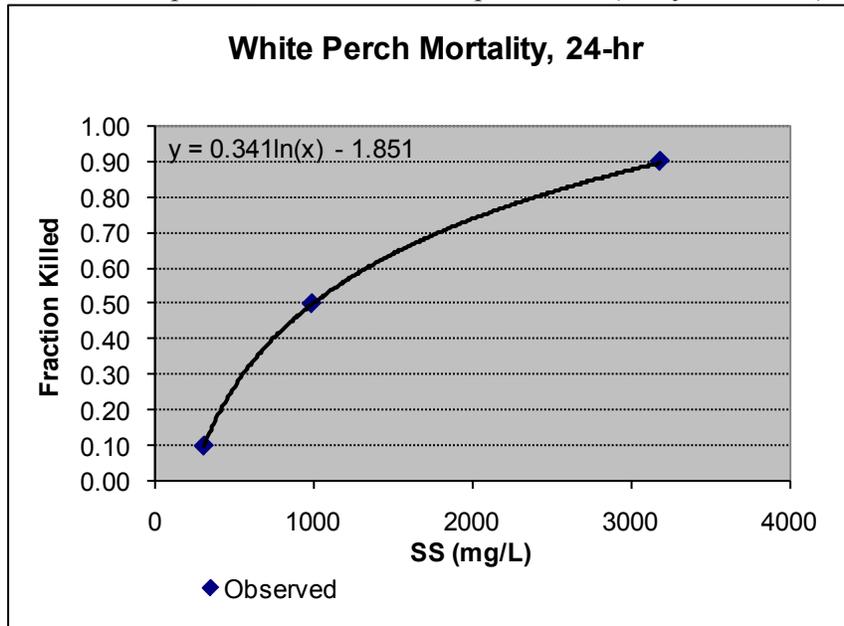
Figure 81. Lethality of suspended sediments to juvenile rainbow trout (*Oncorhynchus mykiss*) using parameters for sensitive species. Data from Berry et al. (2003).

Juvenile Rainbow Trout Mortality, 19-d,
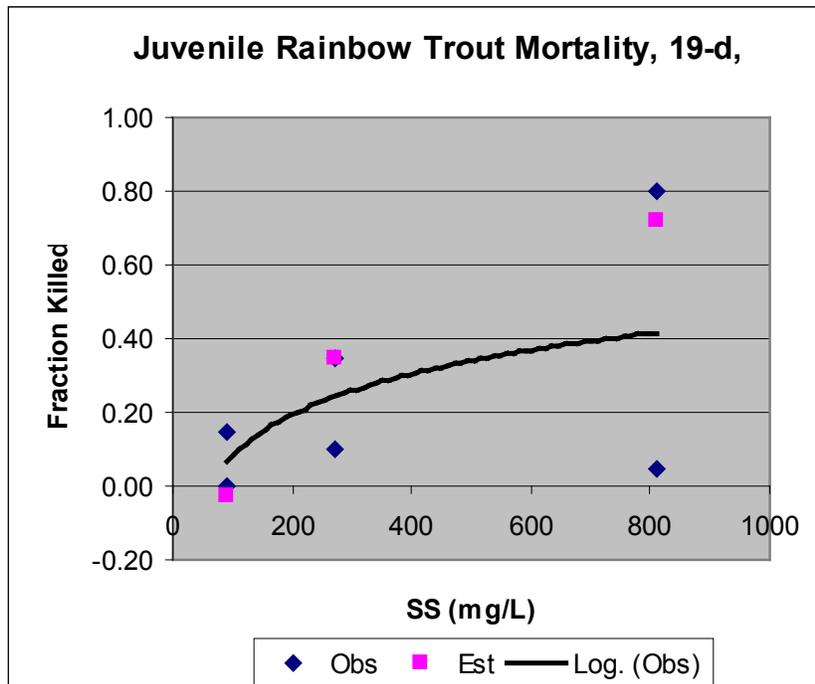
Figure 82. Lethality of suspended sediments to Chinook salmon (*Oncorhynchus tshawytscha*) using parameters for sensitive species. Data from Berry et al. (2003).
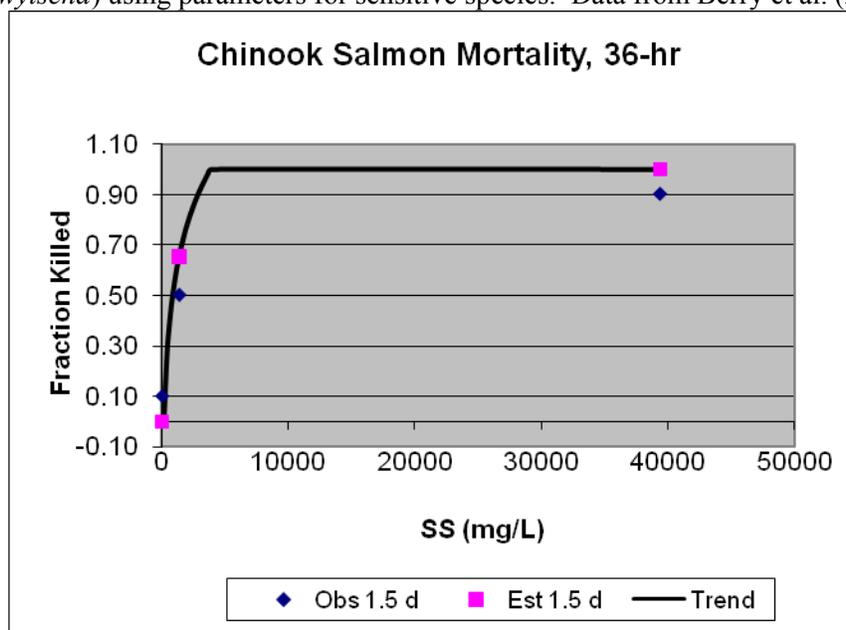
Highly Sensitive

This category represents those species having a 24-hr $LC_{10} \leq 250$ mg/L SS. Small estuarine species seem to be highly sensitive to suspended sediment (Figure 84). The general parameters are based on a composite fit to data for bay anchovy, menhaden, and Atlantic silversides taken from a compilation by (Berry et al. 2003). The equation is:

$$LethalSS = 0.328 \cdot \ln(SS) - 1.375 + 0.1 \cdot \ln(TExp) \qquad \textbf{(120)}$$

This equation is applied using one and two day exposure times along with effects from one two and three weeks exposure. The maximum effect is chosen from these multiple calculations.

Figure 83. Three-dimensional plot of equation for highly sensitive fish
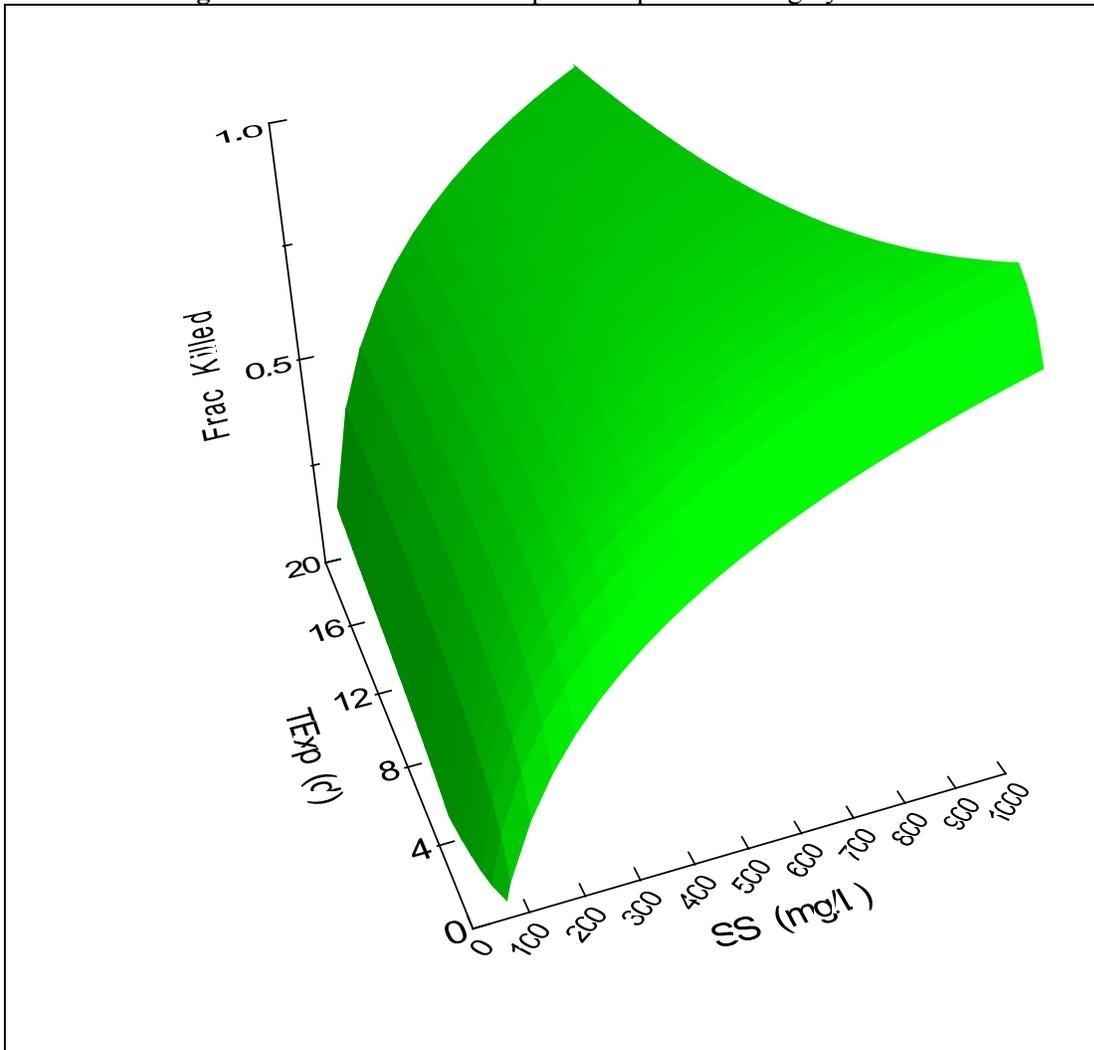
Although not verified with observed data from longer exposure periods, the equation appears to be robust; it yields reasonable predictions of mortality for a range of SS concentrations and exposure periods.

Figure 84. Response of bay anchovy to SS. Data from (Berry et al. 2003)

Composite of Highly Sensitive Spp., 24-hr

$y = 0.3278Ln(x) - 1.3751$
$R^2 = 0.7125$
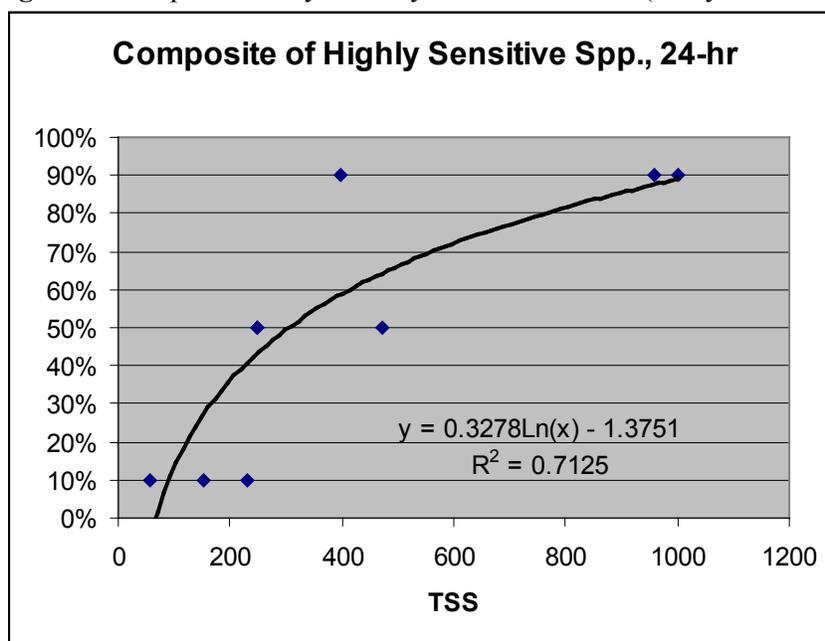
Sediment Effects on Filter Feeders

Sediments can clog filter-feeding apparatuses in invertebrates and some fish. A 25% reduction in feeding in *Daphnia* occurs with SS of 6 NTU (~22 mg/L) (Henley, 2000); rotifers are not affected (Rowe et al. 2003).   Equation **(116)** can be parameterized to reflect the *Daphnia* response (*SlopeSS* = -0.46 and *InterceptSS* = 2.2, **Figure 85**).

Figure 85. Reduction in feeding by Daphnia due to suspended sediments.
Points represent LC75 and supposed LC50, and LC5 values**.**

Reduced Feeding in Daphnia
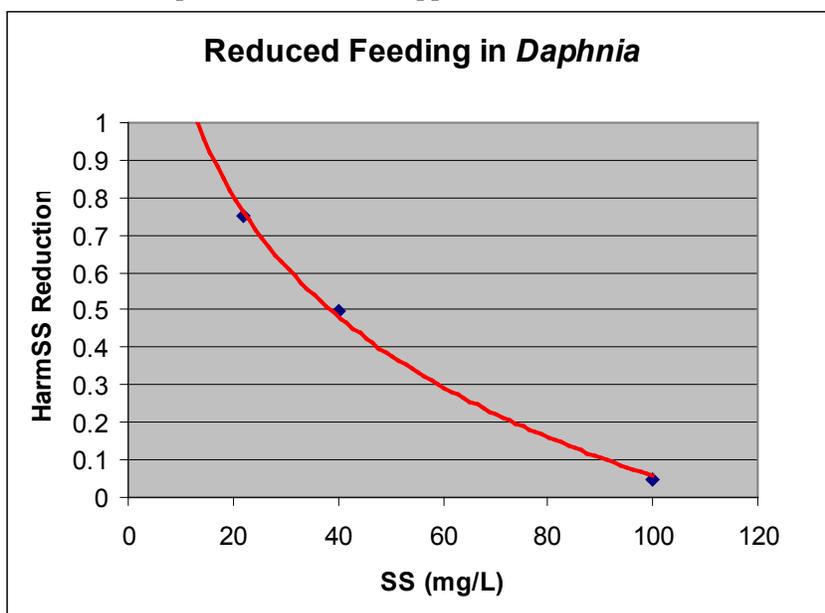
Increased turbidity can inhibit feeding by mussels; 600 to 750 mg SS/L reduced clearance rates in several mussel species (Henley et al. 2000). This can be used to parameterize Equation **(116)** (*SlopeSS* = -0.47 and *InterceptSS* = 3.1, **Figure 86**).

Figure 86. Reduction in clearance of sediment by freshwater mussels due to suspended sediments. Points represent supposed LC95, LC50, and LC10 values**.**
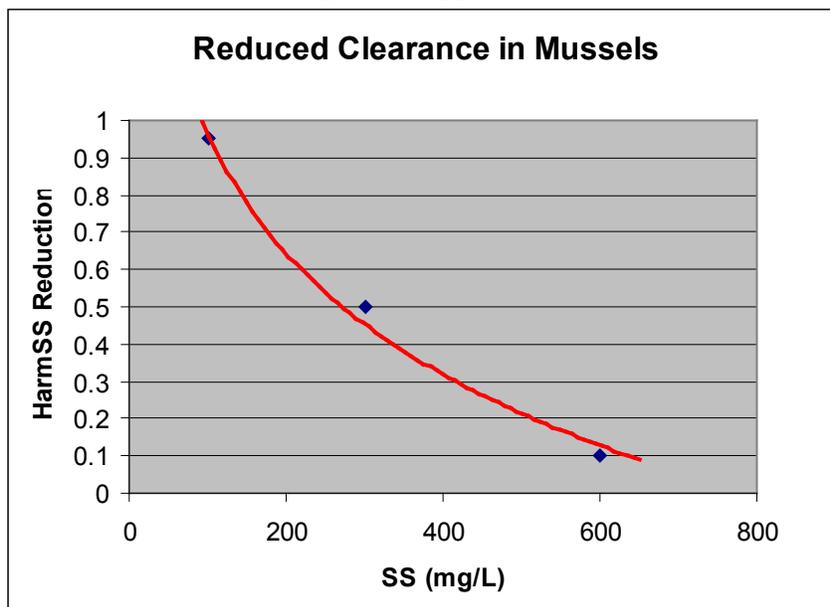
Reduced pumping was observed at SS > 1000 mg/L in the Eastern oyster (Berry et al. 2003). This too can be used to parameterize Equation **(116)**. (*SlopeSS* = -0.61 and *InterceptSS* = 4.72, **Figure 87**).

Figure 87. Reduced pumping in Eastern oysters (*Crassostrea virginica*).
Points represent supposed LC90, LC50, and LC5 values.
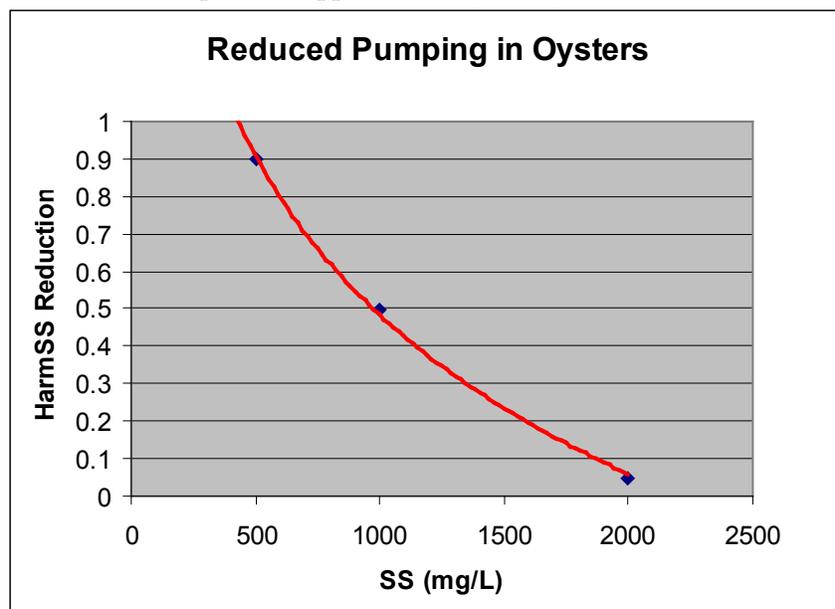
A related factor, which is treated separately in the model, is the degree to which there is dilution of food by inorganic particles, offset by selective sorting of particles and feeding (Henley, 2000). *Mytilus edulis*, the blue mussel, and *Crassostrea virginica*, the Eastern oyster, actively sort particles; their food intake should not be affected by SS until very high levels that clog the filter feeding mechanism are reached. In contrast, there is limited selective feeding among many clear-water clams, including the surf clam *Spisula solidissima,* the Iceland scallop *Chlamys islandica*, and probably many of the endangered freshwater mussels (Henley, 2000). The dilution of available food for both filter feeders and grazers decreases as a proportionate function of sediment corrected for the degree to which there is selective feeding (**Figure 88**):

$$FoodDilution \quad = \quad \frac{Food}{Food + Sed \cdot Proportion \cdot (1 - Sorting)} \qquad \textbf{(121)}$$

where:

FoodDilution =		factor to account for dilution of available food by suspended sediment (unitless)
Food	=	preferred food for filter feeders (mg/L) and for grazers (g/m^2) (see **(94)**)
Sed	=	suspended sediment for filter feeders (mg/L) and deposited sediment for benthic grazers (g/m^2)
Sorting	=	degree to which there is selective feeding (unitless)
Proportion	=	proportionality constant, set to 0.01 for snails and grazers and set to 1.0 for all other organisms. (unitless)

To account for the fact that snails and grazers feed on periphyton above the depositional surface, a proportionality constant is utilized for those organisms.

The intermediate variable *Sed* depends on the computation of suspended sediment for filter feeders and the computation of deposited sediment for benthic grazers. If the optional sediment transport submodel (Section 6.1) is used then:

$$Sed = (Conc(Silt) + Conc(Clay)) \qquad or$$
$$Sed = (Deposit(Silt) + Deposit(Clay)) \cdot Vol / SurfArea \cdot 1000 \cdot 1.0 \tag{122}$$

where:

Sed	=	suspended sediment for filter feeders (taxa = 'Susp. Feeder' or 'Clam' in units of mg/L or g/m^3) and deposited sediment for benthic grazers (taxa = 'Sed Feeder' or 'Snail' or 'Grazer' in units of g/m^2);
$Conc_{Sed}$	=	concentration of suspended silt or clay (mg/L) **(224)**;
1000	=	conversion factor for kg to g;
$Deposit_{Sed}$	=	amount of sediment deposited (kg/m^3 day) **(230)**;
Volume	=	water volume, (m^3);
SurfArea	=	surface area, (m^2); and
1.0	=	days' accumulation of sediment (day)

If the sediment transport submodel is not used and TSS is used as a driving variable then suspended sediment is computed for filter feeders. Additionally, when TSS is used as a driving variable, deposited sediment (*Sed*) is calculated using the relationship shown in **Figure 91**.

$$Sed_{Suspended} = InorgSed$$

$$\tag{123}$$

$$Sed_{Deposited} = 0.270 \ln(InorgSed_{60day}) - 0.072$$

where:

Sed	=	food dilution equation input **(120)**, (mg/L or g/m^2);
InorgSed	=	suspended inorganic sediment computed from TSS (mg/L) (see **(244)**);
$InorgSed_{60day}$	=	60 day average of suspended inorganic sediment computed from TSS (mg/L) (see **(244)**)

Figure 88. The *FoodDilution* factor as a function of TSS with Food kept constant at 10 mg/L and with Sorting set to 0 and 0.5.
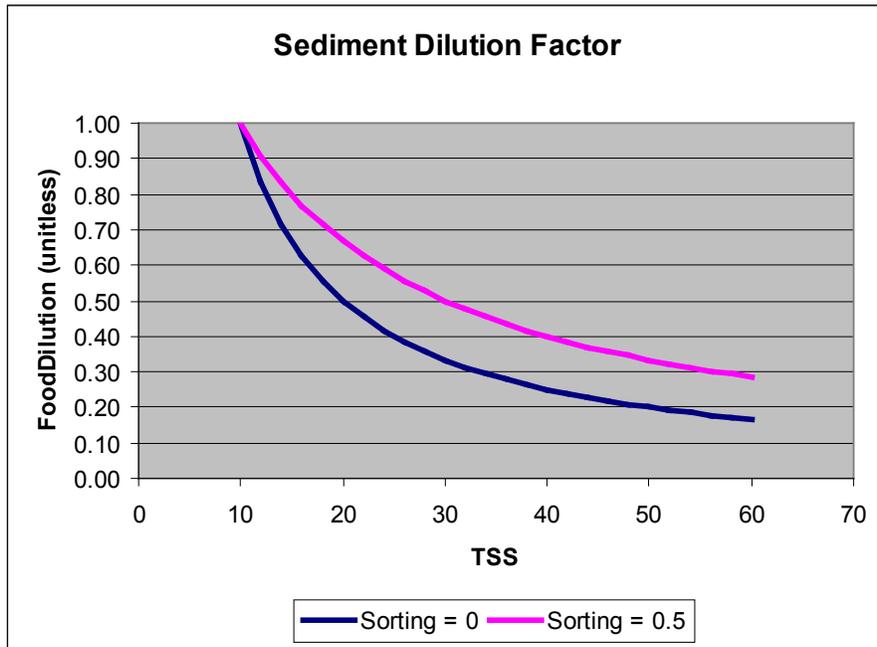
Continued high levels of SS can cause mortality in oysters as shown in **Figure 89**. However, this can be interpreted as the natural consequence of reduced filtration as predicted by parameterization of **(115)**. Therefore, oyster mortality due to SS is not simulated separately.

Figure 89. Response of oysters to SS. Data from (Berry et al. 2003).
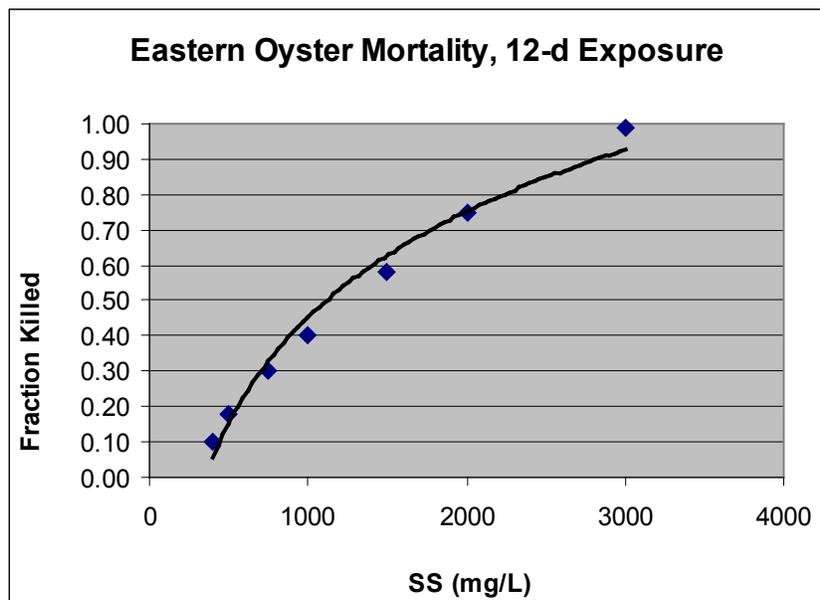
Sediment Effects on Grazers

Sediment reduces preference of New Zealand mud snails and mayflies for periphyton (Suren 2005), which is ignored by the model. More important, the food quality of periphyton declines linearly with increasing fine sediment content (Broekhuizen et al. 2001). This is represented as food dilution by **(120)**.

Riffle areas are degraded or lost by deposition of fine sediment, including sand (Crowe and Hay 2004). A 12-17% increase in fines in riffles areas resulted in 27-55% decrease in mayfly abundance; this did not affect chironomids and simulids, and riffle beetles actually increased (Crowe and Hay 2004). Drift rates doubled from 2.3%/d to 5.2%/d with a 16% increase in fine interstitial sediments; chironomids and caddisflies were affected (Suren and Jowett 2001). This is represented by a function in which the deposition rate is compared to a trigger value beyond which there is accelerated drift:

$$Drift = Dislodge \cdot Biomass \qquad \textbf{(124)}$$

where:

$Drift$ = loss of zoobenthos due to downstream drift ($g/m^3 \cdot d$); and

$Dislodge$ = fraction of biomass subject to drift per day (unitless).

Nocturnal drift is a natural phenomenon:

$$Dislodge = AvgDrift \cdot AccelDrift \qquad \textbf{(125)}$$

where:

$AvgDrift$ = fraction of biomass subject to normal drift per day (unitless).

$$AccelDrift \;\; = \;\; e^{(Deposit - Trigger)} \qquad \textbf{(126)}$$

where:

$AccelDrift$ = factor for increasing invertebrate drift due to sediment deposition (unitless);

$Deposit$ = total rate of inorganic sediment deposition (kg/m^2 day), **(125b)**;

$Trigger$ = deposition rate at which drift is accelerated (kg/m^2 day).

Figure 90. AccelDrift as a function of depth-corrected
sediment deposition with Trigger = 0.2**.**
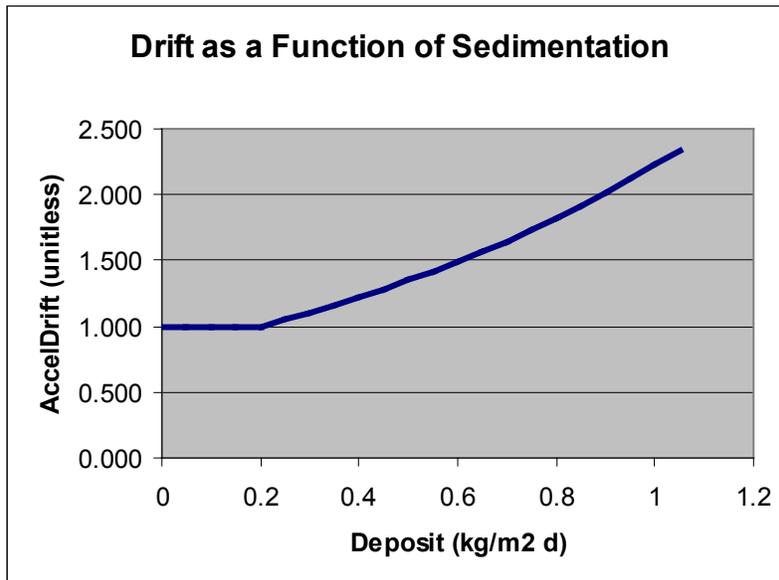
The model computes daily sediment deposition rate based on suspended sediment using the
following relationship:

$$Deposit = 2.70 \cdot \ln(SS) \qquad \textbf{(125b)}$$

where:

Deposit	=	total rate of inorganic sediment deposition (kg/m^2 day), **(125b)**;
SS	=	suspended inorganic sediment concentration (mg/L). If TSS is modeled see **(244)** otherwise, the sum of inorganic sediments in the water column (i.e. *Sand+Silt+Clay*);

Figure 91. Relationship of one-day sedimentation
to average TSS; data from Larkin and Slaney (1996)..
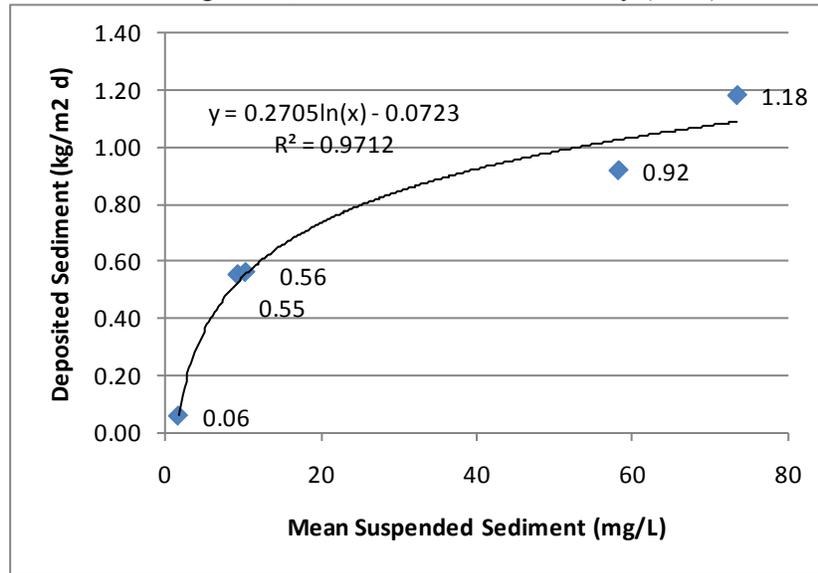
Ephemeroptera, Pteroptera, and Trichoptera (mayfly, stonefly, and caddisfly or EPT) diversity declines when the fines (<0.25 mm) exceed 0.8% (Kaller and Hartman 2004). This change in composition should result from proper parameterization of Equation **(125)**.

Interstitial Sediments

Salmonid reproduction is adversely affected by deposition of fines, with 27% fines being a threshold (Nelson and Platts, unpublished report, cited by Rowe et al. 2003). "Multiple age classes of both salmonids and sculpins were uncommon where average instream surface fines were greater than 30%, and nearly absent above 40%" (Rowe et al. 2003). Both the eggs and the yolk-fry or alevins are sensitive to sedimentation of fines, including sand. Sedimentation in spawning gravels can be related to average suspended sediment (TSS) concentrations (Larkin and Slaney 1996). The relationship is logarithmic for average TSS over a 60-day period (Figure 92).

Figure 92. Relationship of 60-day sedimentation to average TSS; data from (Larkin and Slaney 1996).
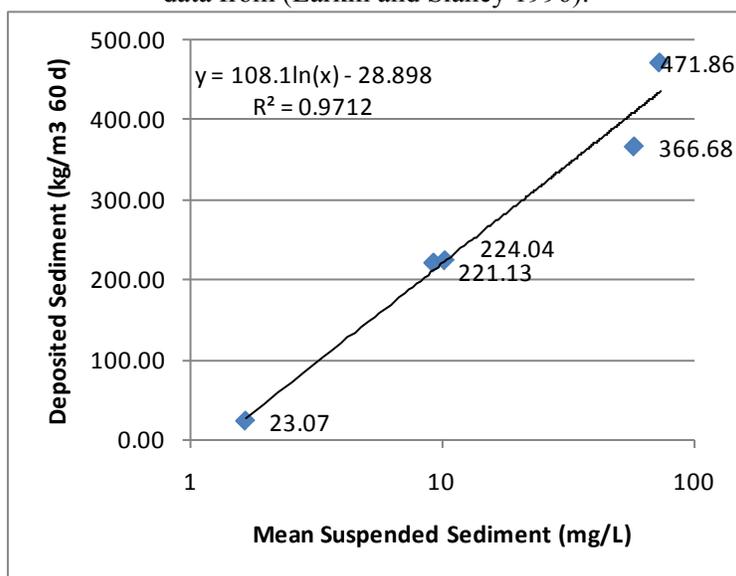
A similar measure of fines is embeddedness, which is the extent to which sand, silt, and clay fill the interstitial spaces among gravel and cobbles (Osmond et al. 1995). Good spawning substrate is characterized as less than 25% embedded (Flosi et al. 1998). The data that allow us to predict percent fines also yield an estimate of percent embeddedness (Figure 93), and that relationship is used in the model. Although the training data only go to 34% embeddedness, the log relationship using averaged data allows the regression to extend to any reasonable level of suspended sediment. The user can enter an observed "baseline embeddedness" in the site record, and that can be used as an initial condition. A corresponding embeddedness threshold value can be entered in the animal record. If that value is exceeded then exclusion can be assumed (mortality = 100%). Although this functionality is intended for salmonids, it can also apply to other fish such as sculpins and to invertebrates that hide in the interstices. In practice, the maximum 60-day moving average of suspended sediments is used to compute the percent embeddedness; if the initial percent embeddedness is exceeded then the new simulated percent embeddedness is used. The possibility of scour from a high-discharge event resetting the percent embeddedness is ignored.

Figure 93. Relationship of 60-day percent embeddedness to average TSS;
data from (Larkin and Slaney 1996).
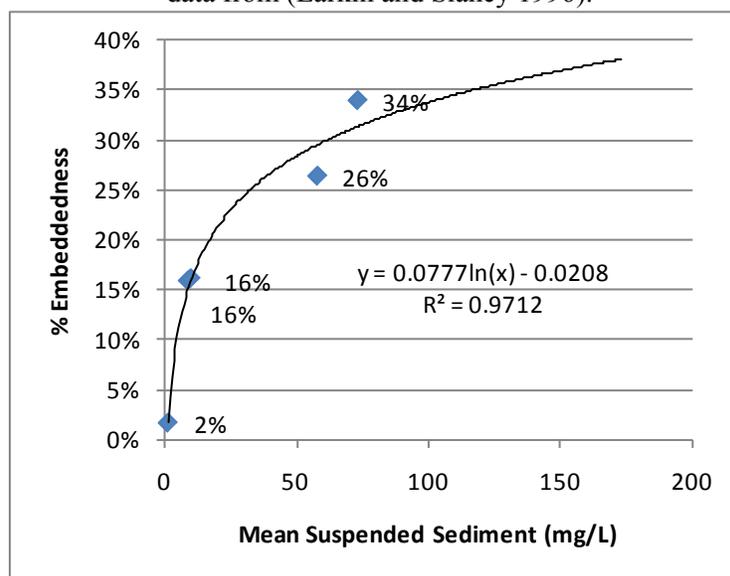
Gamete Loss and Recruitment

Eggs and sperm can be a significant fraction of adult biomass; in bluegills these can be 13 percent and 5 percent, respectively (Toetz, 1967), giving an average of 9 percent if the proportion of sexes is equal. Because only a small fraction of these gametes results in viable young when shed at the time of spawning, the remaining fraction is lost to detritus in the model.

There are two options for determining the date or dates on which spawning will take place. A user can specify up to three dates on which spawning will take place. Alternatively, one may use a construct that was modified from a formulation by Kitchell et al. (1974). As a simplification, rather than requiring species-specific spawning temperatures, it assumes that spawning occurs when the temperature first enters the range from six tenths of the optimum temperature to 1° less than the optimal temperature. This is based on a comparison of the optimal temperatures with the species-specific spawning temperatures reported by Kitchell et al. (1974). Depending on the range of temperatures, this simplifying assumption usually will result in one or two spawnings per year in a temperate ecosystem when a simple sinusoidal temperature function is used. However, the user also can specify a maximum number of spawnings.

The loss rate for gametes is estimated for both fish and invertebrates as a function of user-specified intrinsic gamete mortality and increased mortality due to effects of organic toxicants, low oxygen, and salinity on adults (*FracAdults* being a function of carrying capacity).

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$$\text{If } (0.6 \cdot TOpt) < Temperature\ < (TOpt - 1.0) \text{ then}$$

$$GameteLoss = (GMort + IncrMort + O2EffectFrac\ ) \cdot FracAdults \cdot PctGamete \\ \cdot SaltMort \cdot Biomass \tag{127}$$

$$\text{else } GameteLoss = 0$$

where:

Temperature	=	ambient water temperature (°C);
TOpt	=	optimum temperature (°C);
GameteLoss	=	loss rate for gametes (g/m^3·d);
GMort	=	gamete mortality (1/d);
IncrMort	=	increased gamete and embryo mortality due to toxicant (see **(426)**, 1/d);
O2EffectFrac	=	calculated fraction of gametes lost at a given oxygen concentration and exposure time (1/d), see **(205);**
PctGamete	=	fraction of adult predator biomass that is in gametes (unitless); and
FracAdults	=	fraction of biomass that is adult (unitless);
SaltMort	=	effect of salinity on gamete loss rate (unitless), see **(440)**; and
Biomass	=	biomass of predator (g/m^3).

As the biomass of a population reaches its carrying capacity, reproduction is usually reduced due to stress; this results in a population that is primarily adults. Therefore, the proportion of adults and the fraction of biomass in gametes are assumed to be at a maximum when the biomass is at the carrying capacity (Figure 94):

Figure 94. Correction for population-age structure

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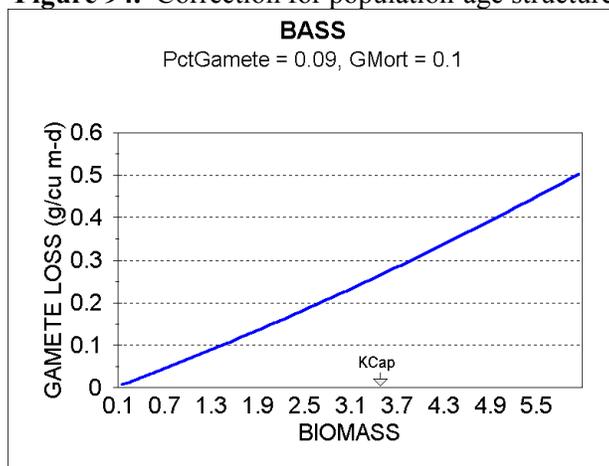
$$FracAdults = 1.0 - \left(\frac{Capacity}{KCap / ZMean} \right)$$

(128)

if Biomass $> KCap / ZMean$ then Capacity $= 0$ else Capacity $= KCap / ZMean$ - Biomass

where:

KCap	=	carrying capacity, the maximum sustainable biomass (g/m²);
ZMean	=	mean depth from site underyling data (m).

Spawning in large fish results in an increase in the biomass of small fish if both small and large size classes are of the same species. Gametes are lost from the large fish, and the small fish gain the viable gametes through recruitment:

$$Recruit = (1 - (GMort + IncrMort)) \cdot FracAdults \cdot PctGamete \cdot Biomass$$

(129)

where:

Recruit	=	biomass gained from successful spawning (g/m³·d).

Washout and Drift

Downstream transport is an important loss term for invertebrates. Zooplankton are subject to transport downstream similar to phytoplankton:

$$Washout = \frac{Discharge}{Volume} \cdot Biomass$$

(130)

where:

Washout	=	loss of zooplankton due to downstream transport (g/m³·d);
Discharge	=	discharge (m³/d), see Table 3;
Volume	=	volume of site (m³), see **(2)**; and
Biomass	=	biomass of invertebrate (g/m³).

Likewise, zoobenthos exhibit drift, which is detachment followed by washout, and it is represented by a construct that is original with AQUATOX:

$$Washout_{Zoobenthos} = Drift = Dislodge \cdot Biomass$$

(131)

where:

Drift	=	loss of zoobenthos due to downstream drift (g/m³·d); and
Dislodge	=	fraction of biomass subject to drift per day (unitless), see **(131)** and **(132)**.

Nocturnal drift is a natural phenomenon:

$$Dislodge = AvgDrift$$

(132)

where:

$AvgDrift$ = fraction of biomass subject to normal drift per day (unitless).

Animals also are subject to entrainment and downstream transport in flood waters. In fact, annual variations in fish populations in streams are due largely to variations in flow, with almost 100% loss during large floods in Shenandoah National Park (NPS, 1997). A simple exponential loss function was developed for AQUATOX:

$$Entrainment = Biomass \cdot MaxRate \cdot e^{\frac{Vel - VelMax}{Gradual}} \qquad \textbf{(133)}$$

where:

$Entrainment$	=	entrainment and downstream transport (g/m^3·d);
$Biomass$	=	biomass of given animal (g/m^3);
$MaxRate$	=	maximum loss per day (1/d);
Vel	=	velocity of water (cm/s), **(14)**;
$VelMax$	=	velocity at which there is total loss of biomass (cm/s); and
$Gradual$	=	slope of exponential, set to 25 (cm/s).

Figure 95. Entrainment of animals as a function of stream velocity with *VelMax* of 400 cm/s
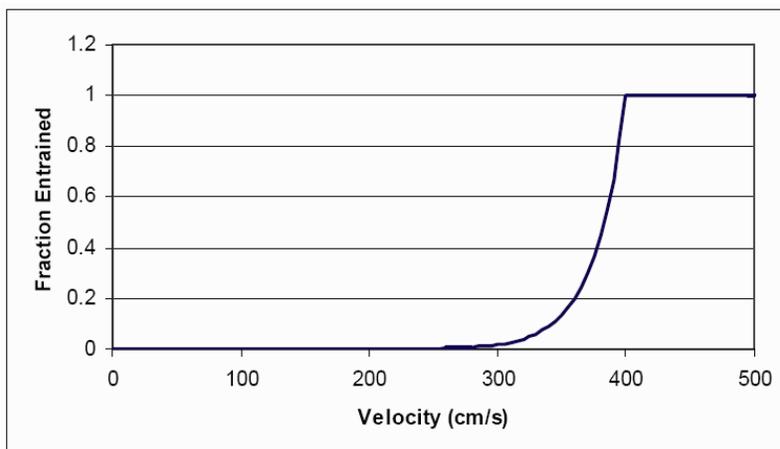
Entrainment is not applied to pelagic invertebrates as these organisms already passively wash out of a system during a flood event **(129)**.

Vertical Migration

When presented with unfavorable conditions, most animals will attempt to migrate to an adjacent area with more favorable conditions. The current version of AQUATOX, following the example of CLEANER (Park et al., 1980), assumes that zooplankton and fish will exhibit avoidance behavior by migrating vertically from an anoxic hypolimnion to the epilimnion. AQUATOX assumes that $EC50_{growth}$ is the best indicator of when the species has become so intolerant of the oxygen climate that it is going to migrate. This also allows more tolerant species to spend more time in the hypolimnion and less tolerant species to migrate earlier. The assumption is that anoxic conditions will persist until overturn.

The construct calculates the absolute mass of the given group of organisms in the hypolimnion, then divides by the volume of the epilimnion to obtain the biomass being added to the epilimnion:

$$\text{If } VSeg = Hypo \text{ and } Anoxic$$

(134)

$$Migration = \frac{HypVolume \cdot Biomass_{pred,\ hypo}}{EpiVolume}$$

where:

$VSeg$	=	vertical segment;
$Hypo$	=	hypolimnion;
$Anoxic$	=	boolean variable for anoxic conditions when $O_2 < EC50_{growth}$;
$Migration$	=	rate of migration (g/m^3·d);
$HypVolume$	=	volume of hypolimnion (m^3), see Figure 36;
$EpiVolume$	=	volume of epilimnion (m^3), see Figure 36; and
$Biomass_{pred,hypo}$	=	biomass of given predator in hypolimnion (g/m^3).

In the estuarine model, fish will also migrate vertically based on salinity cues (see Section 10.5). In the multi-segment version of AQUATOX, fish will vertically migrate to achieve equality on a biomass basis if the system becomes well mixed (see Section 3.).

Migration Across Segments

To simulate seasonal migration patterns animals may be set up to move from one segment to another during a multi-segment model run. Animals may migrate to or from a segment on any date of the year to represent an appropriate seasonal pattern; however, reaches must be linked together with "feedback links" for migration to be enabled. The user must specify the date on which migration occurs, the fraction of the state variable's concentration expected to migrate, and the segment(s) involved. The calculation of state variable movement to and from each segment must be normalized to the volume of water in the destination segment:

$$Migration_{FromSeg} = Conc_{SourceSeg} \cdot FracMoving \qquad \text{(135)}$$

$$Migration_{ToSeg} = \frac{Conc_{SourceSeg} \cdot Volume_{SourceSeg} \cdot FracMoving}{Volume_{Destination}} \qquad \text{(136)}$$

where:

$Migration_{FromSeg}$	=	loss of state variable in source segment (mg/L$_{SourceSeg}$·d);
$Migration_{ToSeg}$	=	gain of state variable in destination segment (mg/L$_{DestinationSeg}$·d);
$Conc_{Segment}$	=	concentration of state variable in given segment (mg/L);
$Volume_{Segment}$	=	volume of given segment (m^3);
$FracMoving$	=	user input fraction of animals migrating on given date (unitless);

Anadromous Migration Model

A new option in AQUATOX is to model the migration of fish into and out of the main study area in order to approximate anadromous migration behavior. Anadromous fish live most of their adult life in saltwater, but they return to freshwater to spawn, and juveniles grow for a few months to a few years before going to saltwater; during their time in freshwater they may be exposed to and bioaccumulate organic toxicants. Chinook salmon and Pacific lamprey are two species in the animal database that can be used with this model. The anadromous migration component is a fairly simple model that holds off-site fish in what is assumed to be a clean "holding tank." No additional exposure of the fish to the toxicant is predicted to occur while off-site, but growth dilution and depuration of toxicant is assumed to occur.

To get to this model, a size-class fish must be modeled and then an "Anadromous" button will appear in the fish loading options screen. Inputs for this model are shown below

- *Day-of-year of migration* (integer)
- *Fraction of biomass migrating* (fraction)
- *Day-of-year of adult return* (integer)
- *Years spent off site* (integer)
- *Mortality fraction* (fraction)

Based on these parameters and the weight of the juvenile and adult organisms, the biomass returning to the freshwater study area may be calculated as follows.

$$Biomass_{Loading,Adult} = Biomass_{Departing,Juvenile}(1 - MortalityFrac)\frac{MeanWeight_{Adult}}{MeanWeight_{Juvenile}} \quad \textbf{(135b)}$$

The chemical concentration in these returning fish can also be estimated, given the depuration rate for the chemical in the fish:

$$Conc_{Loading,Adult} = Conc_{Departing,Juvenile}(1 - Depuration)^{t,days}\frac{MeanWeight_{Juvenile}}{MeanWeight_{Adult}} \quad \textbf{(135c)}$$

where:
Biomass	=	predicted loading or migrating biomass (g/m^3);
MortalityFrac	=	user-input assumed fraction of juveniles that do not survive to return (frac);
MeanWeight	=	user-input mean weight of the juvenile or adult size-class organism;
Conc$_{organism}$	=	concentration of chemical in departing or returning fish (µg/kg ww);
Depuration	=	user-input depuration rate for the given chemical in the given organism (1/day);

A spreadsheet version of this sub-model is available in "Anadromous_Model.xlsx" and is installed in the STUDIES directory when AQUATOX is installed.

Promotion and Emergence

Although AQUATOX is an ecosystem model, promotion to the next size class is important in representing the emergence of aquatic insects, and therefore loss of biomass from the system, and in predicting bioaccumulation of hydrophobic organic compounds in larger fish. The model assumes that promotion is determined by the rate of growth. Growth is considered to be the sum of consumption and the loss terms other than mortality and migration; a fraction of the growth goes into promotion to the next size class (cf. Park et al., 1980):

$$Promotion = KPro_{pred} \cdot (Consumption - Defecation - Respiration - Excretion - GameteLoss) \quad \textbf{(137)}$$

where:

Promotion	=	rate of promotion to the next size class or insect emergence **(137)** $(g/m^3 \cdot d)$;
KPro	=	fraction of growth that goes to promotion or emergence (0.5, unitless);
Consumption	=	rate of consumption $(g/m^3 \cdot d)$, see **(98)**;
Defecation	=	rate of defecation $(g/m^3 \cdot d)$, see **(97)**;
Respiration	=	rate of respiration $(g/m^3 \cdot d)$, see **(100)**;
Excretion	=	rate of excretion $(g/m^3 \cdot d)$, see **(111)**; and
GameteLoss	=	loss rate for gametes $(g/m^3 \cdot d)$, see **(126)**.

This is a simplification of a complex response that depends on the mean weight of the individuals. However, simulation of mean weight would require modeling both biomass and numbers of individuals (Park et al., 1979, 1980), and that is beyond the scope of this model at present. Promotion of multi-age fish is straightforward; each age class is promoted to the next age class on the first spawning date each year. The oldest age class merely increments biomass from the previous age class to any remaining biomass in the class. Of course, any associated toxicant is transferred to the next class as well. Recruitment to the youngest age class is the fraction of gametes that are not subject to mortality at spawning. Note that the user specifies the age at which spawning begins on the "multi-age fish" screen.

Insect emergence can be an important factor in the dynamics of an aquatic ecosystem. Often there is synchrony in the emergence; in AQUATOX this is assumed to be cued to temperature with additional forcing as twice the promotion that would ordinarily be computed, and is represented by:

$$\text{If } Temperature > (0.8 \cdot TOpt) \text{ and } Temperature < (TOpt - 1.0) \text{ then}$$

$$\textbf{(138)}$$

$$EmergeInsect = 2 \cdot Promotion$$

where:

EmergeInsect	=	insect emergence $(mg/L \cdot d)$;
Temperature	=	ambient water temperature (°C); and
TOpt	=	optimum temperature (°C);

Because emergence is a function of the organism's growth rate, if the temperature passes through the optimal temperature interval while the growth rate of the organism is zero or below zero, emergence of insects does not occur.

Size Classes for Crabs

The capability to model fish with size classes (juvenile and adult) has been part of AQUATOX nearly since the model's creation. However, this capability had not been extended to invertebrates. Size classes have now been added to the AQUATOX model to better reflect the differences in life history for some predatory invertebrates (crabs in particular). This change allows the model to represent differential bioenergetics within life stages, and the different vulnerability of these organisms to predation pressures and organic toxicants.
No modifications were made to the fish size-class model described here. However, the model's interface now includes two small predatory invertebrate compartments that may be linked to the larger predatory invertebrate categories.

4.4 Oysters

New to AQUATOX Release 3.2 is a size-class model for oysters, containing four specified life stages for oysters (Figure 96).

Figure 96. Schematic of AQUATOX Oyster Size-Class Model
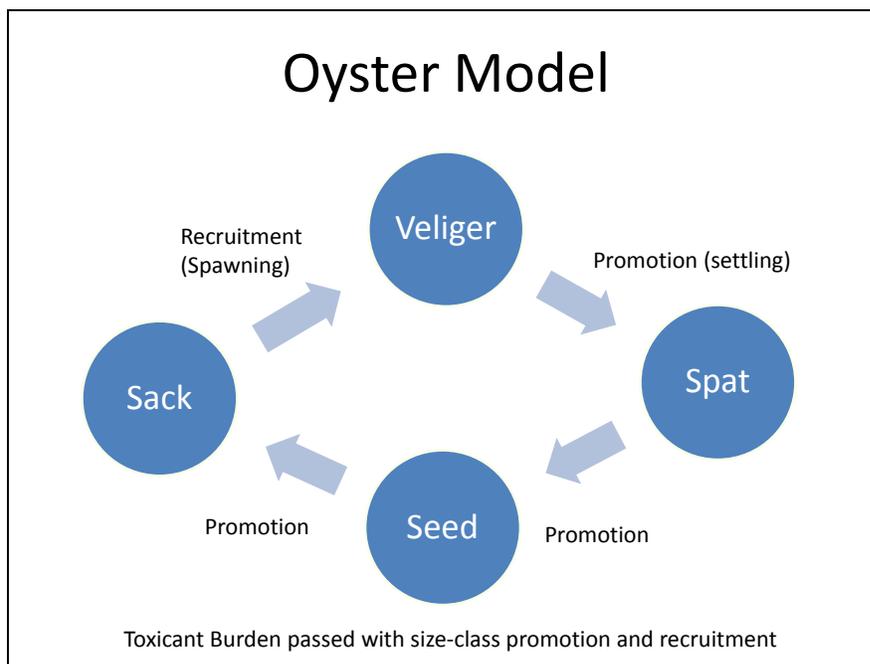
Oysters are modeled using the same differential equations that govern all animals within AQUATOX; clams and other bivalves have always been included in the model. Oysters are unique in AQUATOX, however, due to their life-history classifications and the promotion and recruitment of biomass from one biotic compartment to the next.

Oyster veligers are assumed to be suspended in the water column and are modeled with mg/L units. Oyster veligers can be modeled alone in non-oyster-reef habitats. If seed oysters or sack oysters are included then it is assumed that an oyster reef is specifically being modeled. Rules for promotion and recruitment between size classes follow.

- Veliger promotion to Spat
    - If salinity is sufficient (between 5 and 30 ppt) then it is assumed that veliger successfully settles over its 3-week life span. Cake (1983) cites multiple sources (Carriker 1951, Davis 1958, Calabrese & Davis 1970) who indicate veligers will settle at salinities 5-30 ppt.)
    - 5% of biomass is assumed to settle each day and is assumed "competent" spat. This rate is estimated using a 20-day settlement period consistent with the veliger life span cited in Galtsoff (1964) cited in Cake (1983) and Bahr and Lanier (1981) cited in VanderKooy (2012).
- Spat promotion to Seed
    - Spat are generally parameterized with high mortality rates, including predation. VanderKooy (2012) cites several papers which collectively estimate spat to seed mortality to range from 15-100%.
    - 50% of biomass growth is assigned to the seed category. This is the same promotion algorithm that has historically been used for fish size-class promotion in AQUATOX **(136).**
    - This promotion assumption is a simplification of a complex response that depends on the mean weight of the individuals. However, simulation of mean weight would require modeling both biomass and numbers of individuals (Park et al., 1979, 1980) which is presently beyond the scope of this model.
- Seed promotion to Sack oyster
    - Like spat promotion, 50% of biomass growth is assigned to the sack category.
- Sack spawning to Veliger (recruitment)
    - As a simplifying assumption, Sack are the exclusive contributors to overall spawned biomass. Menzel (1951) is cited in VanderKooy (2012), indicating that oysters in the Gulf can become sexually mature within 4 weeks of settlement (i.e. Seed can also contribute to recruitment). However, VanderKooy (2012) states that "the number of gametes released during each spawn is directly correlated with oyster size and gonadal development (Davis and Chanley 1955, Galtsoff 1964, Thompson et al. 1996) For this reason, it is assumed that Sack are the dominant contributors.
    - Spawning is triggered when salinity is greater than 10 ppt and temperature is greater than 20 degrees C. VanderKooy (2012) claim that "salinity fluctuations do not appear to play a significant role in controlling spawning in oysters, however, salinities below 5-6 ppt can inhibit gametogenesis (Butler 1949, Loosanoff

1953)." However, there is support for the 10 ppt threshold in Cake (1983), who claims "optimal spawning salinity ranges from 10 to 30 parts per thousand (ppt)."

o With regards to temperature, Cake (1983) cites multiple sources (Ingle 1951, Menzel 1955, Hayes and Menzel 1981) who indicate mass spawnings typically occur when temperatures reach and/or exceed 25 degrees C. However, there is ample support for the 20 degree C threshold, as VanderKooy (2012) cites multiple authors (Butler 1949, Loosanoff 1953, Schlesselman 1955, Hofstetter 1977, 1983) who indicate the threshold is indeed 20 degrees C.

o The "percent gamete" parameter determines the extent of biomass expelled. This is spread over 275 days of spawning, based on Gulf-of-Mexico data. Cake (1983) cites (Butler 1954), who claims that spawning generally occurs year-round in the Gulf of Mexico, but does not occur during the three-month span from December to February. A site-specific number of spawning days may be specified for other locations.

o The *Gamete loss* equation **(126)** splits spawning between viable veliger biomass and non-viable organic matter (detritus).

4.5 Aquatic-Dependent Vertebrates

Herring gulls and other shorebirds were added to AQUATOX Release 3 as a bioaccumulative endpoint—not as a dynamic variable but as a post-processed variable reflecting dietary exposure to a contaminant. In fact, the endpoint can be used to simulate bioaccumulation for any aquatic feeding organism, such as bald eagles, mink, and dolphins, provided that the organism feeds exclusively on biotic compartments modeled within AQUATOX. The user can specify a biomagnification factor (BMF) and the preferences for various food sources so that alternate exposures can be computed. Dietary preferences are input as fraction of total food consumed by the modeled species and are normalized to 100% when the model is run.

The concentration of each chemical is based on the chemical concentration in prey at a given time-step.

$$PPBBird_{Toxicant} = \sum_{i=1}^{n} \left(Pref_{Prey} \cdot BMF_{Tox} \cdot PPB_{Prey,Tox} \right) \tag{139}$$

where:

$PPBBird_{Toxicant}$ = estimated concentration of this toxicant in bird or other organism (µg/kg);

BMF_{Tox} = biomagnification factor for this chemical in bird or other organism (unitless);

$PPB_{Prey,Tox}$ = concentration of this chemical in prey (µg/kg), see **(310)**.

Uptake of toxicant is assumed to be instantaneous, but depuration of the chemical is governed by the user-input clearance rate. If the concentration of chemical is declining in shorebirds (due to

the concentrations of the chemical declining in prey), the lowest the chemical concentration in birds can fall to at any time is calculated as follows:

$$PPBBird_{Lowest,Tox} = PPBBird_{Tox,t-1}(1 - Clear_{Tox})\Delta T \tag{140}$$

where:

$PPBBird_{Lowest,Tox}$ =   lowest conc. of this toxicant in gulls or other organism at this time-step (µg/kg);
$PPBBird_{Tox,t-1}$ =   concentration of this toxicant in in the previous time-step (µg/kg);
$Clear_{Tox}$ =   clearance rate for the given toxicant, (1/day)

4.6 Steinhaus Similarity Index

Within the differences graph portion of the output interface, a user may 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. Typically it is computed from monitoring data from perturbed and unperturbed, or reference, sites.   When calculated by AQUATOX it is a measure of the difference between the control and perturbed simulations. 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:

$$S = \frac{2 \cdot \sum_{i=1}^{n} \min(Biomass_{i\_control}, Biomass_{i\_perturbed})}{\sum_{i=1}^{n}(Biomass_{i\_control} + Biomass_{i\_perturbed})} \tag{141}$$

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.

4.7 Biological Metrics

Ecological indicators are defined as primarily biological and are measurable characteristics of the structure, composition, and function of ecological systems (Niemi and McDonald 2004). The term "indicator" as used by Niemi and McDonald is a rather broad one, and includes two terms

often used within the biocriteria program, "metric" and "index". A biological metric is a numerical value that represents a quantitative community parameter, such as species diversity, or percent EPT (see below). A multimetric index is a number that integrates several metrics to express a site's condition or health, such as an IBI (Index of Biological Integrity). AQUATOX has the ability to calculate numerous metrics, some of which can be compared to similar metrics derived from monitoring data. However, there are limitations in the application of many such metrics that reflect the differing capabilities of simulation models as opposed to field studies. Models can predict continuing complex responses to changing conditions, while field measurements usually represent snapshots of existing conditions with limited empirical predictive power. Aquatic models have limited taxonomic resolution and usually represent biomass; most metrics and indices applied in the field are based on detailed taxonomic identifications and involve counting the numbers of individual organisms per sample. Therefore, only a subset of possible indicators can be implemented with AQUATOX; however, given the biologic realism of the model, the list is much more extensive than for other models.

Biotic metrics and indices have been widely used for several decades, stimulated in part by inclusion in rapid bioassessment protocols (RBP) by the US EPA (Plafkin et al. 1989). Most are applicable to streams and wadeable rivers (Barbour et al. 1999), though there is a suite of indices (the trophic state indices) that were developed as a measure of eutrophication in lakes. Metrics can be calculated for algae, which indicate short-term impacts; macroinvertebrates, which integrate short-term impacts on localized areas; and fish, which are indicators of long-term impacts over broad reaches (Barbour et al. 1999).

Ecological indicator measures fall into several well defined categories. Those metrics that are presently calculated in AQUATOX are shown below in boldface; the others enumerated here can be calculated offline using exported Excel output files:

- Composition—many metrics related to community composition are suitable for simulation with AQUATOX by selecting the appropriate "Benthic metric designation" category on the underlying data screen; they include:
  - **% EPT** (the following three combined) (Barbour et al. 1999)
    - **% Ephemeroptera** (mayfly larvae) (Maloney and Feminella 2006)
    - **% Plecoptera** (stonefly larvae) (Barbour et al. 1999)
    - **%Trichoptera** (caddisfly larvae) (Barbour et al. 1999)
  - **% chironomids** (midge larvae) (Barbour et al. 1999)
  - **% oligochaetes** (aquatic worms) (Barbour et al. 1999)
  - % *Corbicula* (invasive Asian clam) (Barbour et al. 1999)
  - **% *Eunotia*** (interstitial diatom characteristic of low-nutrient conditions) (Lowe et al. 2006)
  - **% cyanobacteria** (cyanobacteria characteristic of high-nutrient, turbid conditions) (Trimbee and Prepas 1987).

- Trophic—these include metrics that can be calculated from AQUATOX output:
  - **Trophic Level** (Odum, 1971)
  - **Periphytic chlorophyll *a*** (Barbour et al. 1999)
  - **Sestonic chlorophyll *a*** (Barbour et al. 1999)

- o % predators (can apply to both macroinvertebrates and fish) (Barbour et al. 1999)
- o % omnivores (best applied to fish in AQUATOX) (Barbour et al. 1999)
- o % forage or insectivorous fish (Barbour et al. 1999)
- o **Pelagic Invt. Biomass** (mg/L), **Benthic Invt. Biomass** (g/m^2), **Fish Biomass** (g/m^2) sum of biomass within these three animal categories.

- Trophic state—surrogates for lake and reservoir algal biomass adjusted to a common scale (Gibson et al. 2000):
   - o **TSI(TN)** (total nitrogen)
   - o **TSI(SD)** (Secchi depth)
   - o **TSI(CHL)** (chlorophyll *a*)
   - o **TSI(TP)** (total phosphorus)

- Ecosystem bioenergetic—whole ecosystem metrics:
   - o **Gross primary productivity, GPP** (g O_2/m^2 d) (Odum 1971), more meaningful if expressed as an annual measure (g O_2/m^2 yr) (Wetzel 2001)
   - o **Net primary productivity, NPP (g** O_2/m^2 d) GPP minus dark respiration
   - o **Community respiration, R** (g O_2/m^2 d) (Odum 1971), more meaningful if expressed as an annual measure (g O_2/m^2 yr) (Wetzel 2001)
   - o **P/R** (ratio of GPP to community respiration) (Odum 1971)
   - o **Turnover time** (P/B, ratio of GPP to biomass in days) (Odum 1971)

In addition to those listed above, there are several ecological indicators that are not suitable for simulation modeling in general or for AQUATOX in particular:

- Richness—these are based on numbers of observed taxonomic groups and are not suitable for simulation modeling;
- Tolerance/intolerance—based on number of tolerant or intolerant species and therefore unsuitable for modeling;
- Life cycle—percent of organisms with short or long life cycles, not easily modeled with AQUATOX.

The trophic state indices are applicable to lakes and reservoirs. They are lognormal-transformed values that attempt to convert environmental variables to a common value representing algal biomass (Gibson et al. 2000):

Secchi Depth (m):	TSI (SD)	= 60 - 14.41 ln(SD)
Chlorophyll *a* (µg/L):	TSI (CHL)	= 9.81 ln(CHL) + 30.6
Total Phosphorus (mg/L):	TSI (TP)	= 14.42 ln(TP) + 4.15
Total Nitrogen (mg/L):	TSI(TN)	= 54.45 + 14.43 ln(TN)

The user can specify over what time period the indices are averaged. This enables better comparison with field-derived TSIs, which are generally calculated from samples taken during the growing season. Obviously, chlorophyll *a* is the best representation of algal biomass, and that metric should generally be used in determining the trophic state of a lake or reservoir (Table 8). However, comparing the TSIs is also informative (Table 9).

The bioenergetic metrics are widely used by ecologists and have practical value as indicators of accumulating organic matter (Odum 1971) and response to watershed disturbance (Dale and Maloney 2004).

Table 8. Changes in Temperate Lake Attributes According to Trophic State (Gibson et al. 2000, adapted from Carlson and Simpson 1996).

TSI Value	SD (m)	TP (µg/L)	Attributes	Water Supply	Recreation	Fisheries
<30	>8	<6	Oligotrophy: Clear water, oxygen throughout the year in the hypolimnion			Salmonid fisheries dominate
30-40	8-4	6-12	Hypolimnia of shallower lakes may become anoxic			Salmonid fisheries in deep lakes
40-50	4-2	12-24	Mesotrophy: Water moderately clear but increasing probability of hypolimnetic anoxia during summer	Iron and manganese evident during the summer. THM precursors exceed 0.1 mg/L and turbidity >1 NTU		Hypolimnetic anoxia results in loss of salmonids. Walleye may predominate
50-60	2-1	24-48	Eutrophy: Anoxic hypolimnia, macrophyte problems possible	Iron, manganese, taste, and odor problems worsen		Warm-water fisheries only. Bass may be dominant
60-70	0.5-1	48-96	Blue-green algae dominate, algal scums and macrophyte problems		Weeds, algal scums, and low transparency discourage swimming and boating	
70-80	0.25-0.5	96-192	Hypereutrophy (light limited). Dense algae and macrophytes			
>80	<0.25	192-384	Algal scums, few macrophytes			Rough fish dominate, summer fish kills possible

Table 9. Conditions Associated with Various Trophic State Index Variable Relationships (Gibson et al. 2000).

Relationship Between TSI Variables	Conditions
TSI (CHL) = TSI(CHL) = TSI(SD)	Algae dominate light attenuation
TSI(CHL) > TSI(SD)	Large particulates, such as Aphanizomenon flakes, dominate
TSI(TP) = TSI(SD) > TSI(CHL)	Nonalgal particulates or color dominate light attenuation
TSI(SD) = TSI(CHL) > TSI(TP)	Phosphorus limits algal biomass (TN/TP ratio greater than 33:1)
TSI(TP) > TSI(CHL) = TSI(SD)	Zooplankton grazing, nitrogen, or some factor other than phosphorus limits algal biomass

Trophic Level

Trophic Level output has been added for each animal to clarify how its feeding preferences have been translated into feeding practices within the dynamic simulation (Odum, 1971). The unitless trophic level is calculated within AQUATOX as follows. First, algae and organic matter are assigned trophic levels of 1.0. For animals, the idealized trophic level is assigned based on the position of their prey in the food chain; organisms that are exclusively herbivores or detritivores are assigned to a trophic level of 2.0; organisms that are exclusively predators will be assigned to a trophic level of 3.0 or higher. The trophic level can then be calculated for each time step as a function of the trophic level of its prey being consumed at that time step (based on actual prey availability):

$$TL_{Predator} = \sum \left(TL_{Prey} + 1.0\right) Frac_{Prey} \qquad \textbf{(140b)}$$

where:

$TL_{Predator}$	=	calculated trophic level of the predator (unitless);
TL_{Prey}	=	calculated trophic level of one prey item (unitless);
$Frac_{Prey}$	=	fraction of the prey item consumed compared to all food being consumed in that time step by the predator (unitless).

Fractional trophic-level outputs are likely based on the complexity of the foodweb. If a heterotroph is not feeding in a given time step it is assigned to a trophic level of 2.0.

It can be useful to calculate an average trophic level over a year, weighting by the organism's growth rate at each time step. This method provides the best estimate of the trophic level that represents the organism's biomass; it ensures that dormant periods of non-feeding or low-feeding behavior do not bias the trophic level derived.

Invertebrate Biotic Indices

As noted above, some invertebrate biotic indices can be readily computed by AQUATOX with one caveat: they are based on relative biomass rather than numerical density (number of individuals representing a taxonomic group). The simplifying assumption is that weights of individuals are roughly comparable. Of course, this is not actually the case, but individual weights vary greatly depending on the growth stage, so use of biomass has less error.

Computation of benthic invertebrate indices by AQUATOX requires that the taxonomic affiliations be designated as:

- oligochaete (worm)
- chironomid (midge) and other fly larvae
- mayfly
- stonefly
- caddisfly
- beetle
- mussel
- other bivalve
- amphipod
- gastropod
- other.

With these designations AQUATOX can compute % EPT (Ephemeroptera or mayflies, Plecoptera or stoneflies, and Trichoptera or caddisflies) as a percentage of the total biomass of benthic invertebrates. Mussels are excluded from the computation in AQUATOX because the potential biomass of a single individual may exceed that of all other invertebrates. The EPT are usually the most sensitive aquatic insect orders, so this index is often useful. A detailed study of Fort Benning, Georgia streams showed that %Ephemeroptera, %Plecoptera, and %Trichoptera were significantly inversely correlated with the degree of disturbance in the watershed (Maloney and Feminella 2006, Mulholland et al. 2007). The index has been used in evaluating remediation (Purcell et al. 2002). The user is cautioned to ensure that the benthic metric chosen is appropriate for the region; e.g. one wouldn't expect Plecoptera to be prevalent in Florida, due to their temperature preferences.

Chironomids (midge larvae) are generally tolerant (Maloney and Feminella 2006), so the % Chironomids index is useful as an indicator of disturbance (Figure 97). Another index that might indicate disturbance is the computed value of % Oligochaetes; however, that metric has exhibited mixed results in Georgia (Maloney and Feminella 2006).

Figure 97. Example of % Chironomid index computed for Upatoi Creek, Fort Benning, Georgia; observed values are courtesy of George Williams
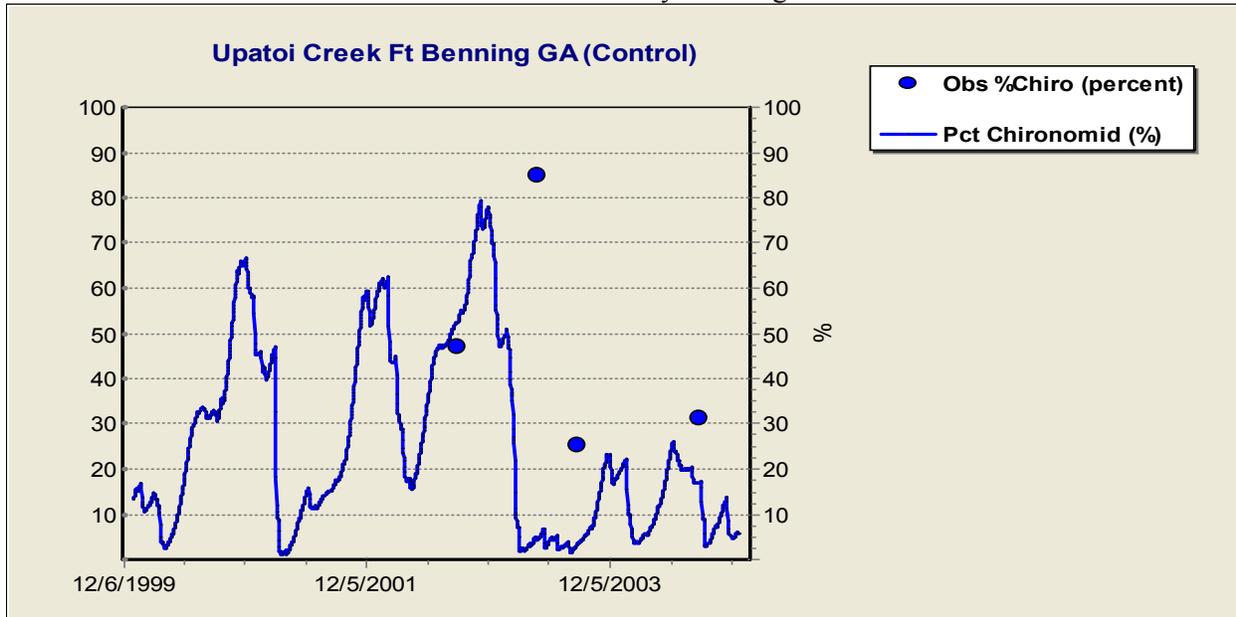
5.   REMINERALIZATION

5.1 Detritus

For the purposes of AQUATOX, the term "detritus" is used to include all non-living organic material and associated decomposers (bacteria and fungi). As such, it includes both particulate and dissolved material in the sense of Wetzel (1975), but it also includes the microflora and is analogous to "biodetritus" of Odum and de la Cruz (1963) . Detritus is modeled as eight compartments: refractory (resistant) dissolved, suspended, sedimented, and buried detritus; and labile (readily decomposed) dissolved, suspended, sedimented, and buried detritus (Figure 98). This degree of disaggregation is considered necessary to provide more realistic simulations of the detrital food web; the bioavailability of toxicants, with orders-of-

Detritus: Simplifying Assumptions
• Refractory detritus does not decompose directly but is converted to labile detritus through colonization
• Detrital sedimentation is modeled with simplifying assumptions (unless the sediment submodel for streams is included)
• Biomass of bacteria is not explicitly modeled

magnitude differences in partitioning; and biochemical oxygen demand, which depends largely on the decomposition rates. Buried detritus is considered to be taken out of active participation in the functioning of the ecosystem. In general, dissolved organic material is about ten times that of suspended particulate matter in lakes and streams (Saunders, 1980), and refractory compounds usually predominate; however, the proportions are modeled dynamically.

Figure 98. Detritus compartments in AQUATOX

* connection to detritivores   + connection to nutrients
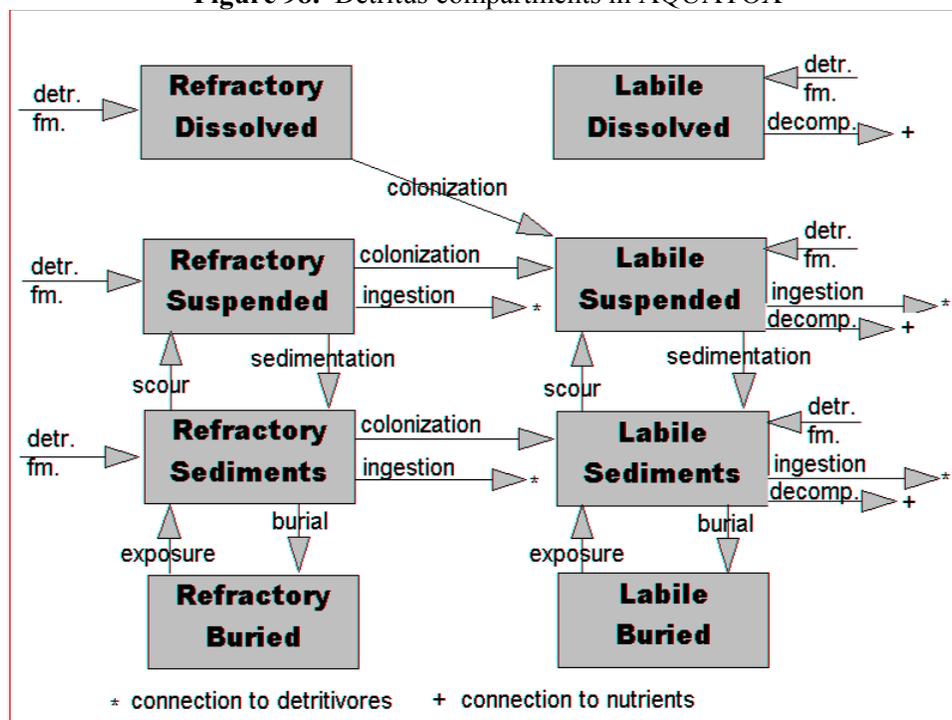
The concentrations of detritus in these eight compartments are the result of several competing processes:

$$\frac{dSuspRefrDetr}{dt} = Loading + DetrFm - Colonization - Washout + Washin$$
$$- Sedimentation - Ingestion + Scour \pm Sinking \pm TurbDiff \pm Diffusion_{Seg} \tag{142}$$

$$\frac{dSuspLabDetr}{dt} = Loading + DetrFm + Colonization - Decomposition$$
$$- Washout + Washin- Sedimentation - Ingestion + Scour \tag{143}$$
$$\pm Sinking \pm TurbDiff \pm Diffusion_{Seg}$$

$$\frac{dDissRefrDetr}{dt} = Loading + DetrFm - Colonization - Washout + Washin$$
$$\pm TurbDiff \pm Diffusion_{Seg} \tag{144}$$

$$\frac{dDissLabDetr}{dt} = Loading + DetrFm - Decomposition - Washout + Washin$$
$$\pm TurbDiff \pm Diffusion_{Seg} \tag{145}$$

$$\frac{dSedRefrDetr}{dt} = Loading + DetrFm + Sedimentation + Exposure$$
$$- Colonization - Ingestion - Scour - Burial \tag{146}$$

$$\frac{dSedLabileDetr}{dt} = Loading + DetrFm + Sedimentation + Colonization$$
$$- Ingestion - Decomposition - Scour + Exposure - Burial \tag{147}$$

$$\frac{dBuriedRefrDetr}{dt} = Sedimentation + Burial - Scour - Exposure \tag{148}$$

$$\frac{dBuriedLabileDetr}{dt} = Sedimentation + Burial - Scour - Exposure \tag{149}$$

where:

$dSuspRefrDetr/dt$	=	change in concentration of suspended refractory detritus with respect to time (g/m^3·d);
$dSuspLabileDetr/dt$	=	change in concentration of suspended labile detritus with respect to time (g/m^3·d);
$dDissRefrDetr/dt$	=	change in concentration of dissolved refractory detritus with respect to time (g/m^3·d);

dDissLabDetr/dt	=	change in concentration of dissolved labile detritus with respect to time (g/m^3·d);
dSedRefrDetr/dt	=	change in concentration of sedimented refractory detritus with respect to time (g/m^3·d);
dSedLabileDetr/dt	=	change in concentration of sedimented labile detritus with respect to time (g/m^3·d);
dBuriedRefrDetr/dt	=	change in concentration of buried refractory detritus with respect to time (g/m^3·d);
dBuriedLabileDetr/dt	=	change in concentration of buried labile detritus with respect to time (g/m^3·d);
Loading	=	loading of given detritus from nonpoint and point sources, or from upstream (g/m^3·d);
DetrFm	=	detrital formation (g/m^3·d);
Colonization	=	colonization of refractory detritus by decomposers (g/m^3·d), see **(155)**;
Decomposition	=	loss due to microbial decomposition (g/m^3·d), see **(159)**;
Sedimentation	=	transfer from suspended detritus to sedimented detritus by sinking (g/m^3·d); in streams with the inorganic sediment model attached see **(235)**, for all other systems see **(165)**;
Scour	=	resuspension from sedimented detritus (g/m^3·d); in streams with the inorganic sediment model attached see **(233)**, for all other systems see **(165)** (resuspension);
Exposure	=	transfer from buried to sedimented by scour of overlying sediments (g/m^3·d);
Burial	=	transfer from sedimented to deeply buried (g/m^3·d), see **(167b)**;
Washout	=	loss due to being carried downstream (g/m^3·d), see **(16)**;
Washin	=	loadings from upstream segments (g/m^3·d), see **(30)**;
Diffusion$_{Seg}$	=	gain or loss due to diffusive transport over the feedback link between two segments, (g/m^3·d), see **(32)**;
Ingestion	=	loss due to ingestion by detritivores and filter feeders (g/m^3·d), see **(91)**;
Sinking	=	detrital sinking from epilimnion and to hypolimnion under stratified conditions, see **(165)**; and
TurbDiff	=	transfer between epilimnion and hypolimnion due to turbulent diffusion (g/m^3·d), see **(22)** and **(23)**.

As a simplification, refractory detritus is considered not to decompose directly, but rather to be converted to labile detritus through microbial colonization. Labile detritus is then available for both decomposition and ingestion by detritivores (organisms that feed on detritus). Because detritivores digest microbes and defecate the remaining organic material, detritus has to be conditioned through microbial colonization before it is suitable food. Therefore, the assimilation efficiency of detritivores for refractory material is usually set to 0.0, and the assimilation efficiency for labile material is increased accordingly.

Sedimentation and scour (resuspension) are opposite processes. In shallow systems there may be no long-term sedimentation (Wetzel et al., 1972), while in deep systems there may be little resuspension. In the classic AQUATOX model, sedimentation is a function of flow, ice cover and, in very shallow water, wind based on simplifying assumptions. Scour and exposure of organic matter are applicable only in streams where they are keyed to the behavior of clay and silt. Scour as an explicit function of wave and current action is not implemented, however, the capability to link to hydrodynamic models is provided. See chapter 6 for a discussion of the various inorganic sediment models and their implications to organic sediments.

Within AQUATOX, the user must specify the percentage particulate and percentage refractory for each source of organic matter. Table 10 presents some guidance on populating these variables based on Allan (1995), Hessen and Tranvik (1998), and Wetzel (2001). These percentages can be specified as constant variables or by using a time-series.

Table 10. Suggested detrital boundary conditions based on literature and in the absence of data

Ecosystem	Particulate %	Refractory %	OM conc. (mg/L)
Oligotrophic lakes	10%	90%	4
Eutrophic lakes	15%	86%	24
Forested streams	20%	60%	5
Rivers	30%	60%	14
Blackwater stream	5%	95%	26

AQUATOX simulates detritus as organic matter (dry weight); however, the user can input data as organic carbon or carbonaceous biochemical oxygen demand (CBOD) and the model will make the necessary conversions. Organic matter is assumed to be $1.90 \cdot$ organic carbon as derived from stoichiometry (Winberg 1971). The conversion from BOD includes the simplifying assumption that any BOD data input into the model are primarily based on carbonaceous oxygen demand:

$$OM = CBOD \cdot \left(\frac{CBOD5\_CBOD_U}{O2Biomass} \right) \qquad \textbf{(148b)}$$

where:

$$CBOD5\_CBOD_U = \left(\frac{1}{100\% - PercentRefr_{Time}} \right) \qquad \textbf{(148c)}$$

and:

OM = organic matter input as required by AQUATOX (g OM/m^3);

CBOD = carbonaceous biochemical demand 5-day from user input (g O_2 /m^3);

$CBOD5\_CBOD_u$ = $CBOD_5$ to ultimate carbonaceous BOD conversion factor, also defined as $CBOD_U$:$CBOD_5$ ratio;

$PercentRefr_{Time}$ = user-defined percent refractory matter for given source of organic matter, may be a time series; and

$O2Biomass$ = ratio O_2 to organic matter (*OM*). (remineralization parameter, the default is 0.575 based on Winberg (1971));

AQUATOX has always assumed that user-input BOD_5 loadings are primarily composed of carbonaceous oxygen demand but this assumption has been made more explicit in Release 3.1. The equations above are used by AQUATOX when converting initial conditions and loadings in $CBOD_5$ to organic matter, when estimating $CBOD_5$ from organic matter for simulation output, and when linking HSPF BOD data. Equations **(148b)** and **(148c)** are new to AQUATOX Release 3.1 and beyond; a warning message is displayed if an older study that utilizes BOD loadings is imported into the current version.

Detrital Formation

Detritus is formed in several ways: through mortality, gamete loss, sinking of phytoplankton, excretion and defecation:

$$DetrFm_{SuspRefrDetr} = \Sigma_{biota}(Mort2_{detr,\ biota} \cdot Mortality_{biota}) \tag{150}$$

$$DetrFm_{DissRefrDetr} = \Sigma_{biota}(Mort2_{detr,biota} \cdot Mortality_{biota}) + \Sigma_{biota}(Excr2_{detr,biota} \cdot Excretion) \tag{151}$$

$$DetrFm_{DissLabileDetr} = \Sigma_{biota}(Mort2_{detr,biota} \cdot Mortality_{biota}) + \Sigma_{biota}(Excr2_{detr,biota} \cdot Excretion) \tag{152}$$

$$DetrFm_{SuspLabileDetr} = \Sigma_{biota}(Mort2_{detr,biota} \cdot Mortality_{biota}) + \Sigma_{animals} GameteLoss \tag{153}$$

$$DetrFm_{SedLabileDetr} = \Sigma_{pred}(Def2_{detr,\ pred} \cdot Defecation_{pred}) + \Sigma_{compartment}(Sinking_{compartment}) \tag{154}$$

$$DetrFm_{SedRefrDetr} = \Sigma_{pred}(Def2_{detr,\ pred} \cdot Defecation_{pred})$$
$$+ \Sigma_{compartment}(Sedimentation_{compartment} \cdot PlantSinkToDetr) \tag{155}$$

where:

$DetrFm$ = formation of detritus (g/m³·d);

$Mort2_{detr,\ biota}$ = fraction of given dead organism that goes to given detritus (unitless);

$Excr2_{detr,\ biota}$ = fraction of excretion that goes to given detritus (unitless), see Table 11;

$Mortality_{biota}$ = death rate for organism (g/m³·d), see **(66)**, **(87)** and **(112)**;

$Excretion$ = excretion rate for organism (g/m³·d), see **(64)** and **(111)** for plants and animals, respectively;

$GameteLoss$ = loss rate for gametes (g/m³·d), see **(126)**;

Def2$_{detr, biota}$	=	fraction of defecation that goes to given detritus (unitless);
Defecation$_{pred}$	=	defecation rate for organism (g/m^3·d), see **(97)**;
Sedimentation	=	loss of phytoplankton to bottom sediments (g/m^3·d), see **(69)**; and
PlantSinkToDetr	=	labile and refractory portions of phytoplankton (unitless, 0.92 and 0.08 respectively).

A fraction of mortality, including sloughing of leaves from macrophytes, is assumed to go to refractory detritus; a much larger fraction goes to labile detritus. Excreted material goes to both refractory and labile detritus, while gametes are considered to be labile. Half the defecated material is assumed to be labile because of the conditioning due to ingestion and subsequent inoculation with bacteria in the gut (LeCren and Lowe-McConnell, 1980); fecal pellets sink rapidly (Smayda, 1971), so defecation is treated as if it were directly to sediments. Phytoplankton that sink to the bottom (that are not linked to periphyton compartments) are considered to become detritus; most are consumed quickly by zoobenthos (LeCren and Lowe-McConnell, 1980) and are not available to be resuspended.

Table 11. Mortality and Excretion to Detritus

	Algal Mortality	Macrophyte Mortality	Bryophyte Mortality	Animal Mortality
Dissolved Labile Detritus	0.27	0.24	0.00	0.27
Dissolved Refractory Detritus	0.03	0.01	0.25	0.03
Suspended Labile Detritus	0.65	0.38	0.00	0.56
Suspended Refractory Detritus	0.05	0.37	0.75	0.14

	Algal Excretion	Macrophyte Excretion	Bryophyte Excretion	Animal Excretion
Dissolved Labile Detritus	0.9	0.8	0.8	1.0
Dissolved Refractory Detritus	0.1	0.2	0.2	0.0

Colonization

Refractory detritus is converted to labile detritus through microbial colonization. When bacteria and fungi colonize dissolved refractory organic matter, they are in effect turning it into particulate matter. Detritus is usually refractory because it has a deficiency of nitrogen compared to microbial biomass. In order for microbes to colonize refractory detritus, they have to take up additional nitrogen from the water (Saunders et al., 1980). Thus, colonization is nitrogen-limited, as well as being limited by suboptimal temperature, pH, and dissolved oxygen:

$$Colonization = ColonizeMax \cdot DecTCorr \cdot NLimit \cdot pHCorr$$
$$\cdot DOCorrection \cdot RefrDetr$$

(156)

where:

Colonization	=	rate of conversion of refractory to labile detritus (g/m^3·d);

ColonizeMax   =   maximum colonization rate under ideal conditions (g/g·d);
Nlimit   =   limitation due to suboptimal nitrogen levels (unitless), see **(157)**;
DecTCorr   =   the effect of temperature (unitless), see **(156)**;
pHCorr   =   limitation due to suboptimal pH level (unitless), see **(162)**;
DOCorrection   =   limitation due to   suboptimal oxygen level (unitless), see **(160)**; and
RefrDetr   =   concentration of refractory detritus in suspension, sedimented, or dissolved (g/m³).

Because microbial colonization and decomposition involves microflora with a wide range of temperature tolerances, the effect of temperature is modeled in the traditional way (Thomann and Mueller, 1987), taking the rate at an observed temperature and correcting it for the ambient temperature up to a user-defined, high maximum temperature, at which point it drops to 0:

$$DecTCorr = Theta^{Temp - TObs} \text{ where}$$
$$Theta = 1.047 \text{ if } Temp \geq 19° \text{ else}$$
$$Theta = 1.185 - 0.00729 \cdot Temp$$

(157)

$$\text{If } Temp > TMax \text{ Then } DecTCorr = 0$$

The resulting curve has a shoulder similar to the Stroganov curve, but the effect increases up to the maximum rate (Figure 99).

Figure 99. Colonization and decomposition as an effect of temperature
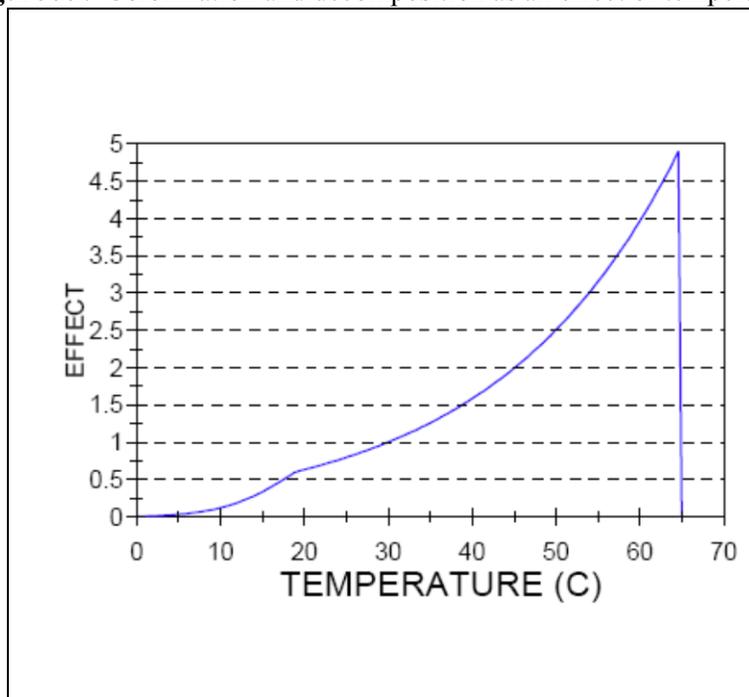
The nitrogen limitation construct, which is original with AQUATOX, is parameterized using an analysis of data presented by Egglishaw (1972) for Scottish streams. It is computed by:

$$NLimit = \frac{N - MinN}{N - MinN + HalfSatN}$$ **(158)**

$$N = Ammonia + Nitrate$$ **(159)**

where:

N	=	total available nitrogen (g/m^3);
$MinN$	=	minimum level of nitrogen for colonization (= 0.1 g/m^3);
$HalfSatN$	=	half-saturation constant for nitrogen stimulation (= 0.15 g/m^3);
$Ammonia$	=	concentration of ammonia (g/m^3); and
$Nitrate$	=	concentration of nitrite and nitrate (g/m^3).

Although it can be changed by the user, a default maximum colonization rate of 0.007 (g/g·d) is provided, based on McIntire and Colby (1978, after Sedell et al., 1975). The rates of decomposition (or colonization) of refractory dissolved organic matter are comparable to those for particulate matter. Saunders (1980) reported values of 0.007 (g/g·d) for a eutrophic lake and 0.008 (g/g·d) for a tundra pond. Anaerobic rates were reported by Gunnison et al. (1985).

Decomposition

Decomposition is the process by which detritus is broken down by bacteria and fungi, yielding constituent nutrients, including nitrogen, phosphorus, and inorganic carbon. Therefore, it is a critical process in modeling nutrient recycling. In AQUATOX, following a concept first advanced by Park et al. (1974), the process is modeled as a first-order equation with multiplicative limitations for suboptimal environmental conditions (see section 4.1 for a discussion of similar construct for photosynthesis):

$$Decomposition = DecayMax \cdot DOCorrection \cdot DecTCorr \cdot pHCorr \cdot Detritus$$ **(160)**

where:

$Decomposition$	=	loss due to microbial decomposition (g/m^3·d);
$DecayMax$	=	maximum decomposition rate under aerobic conditions (g/g·d);
$DOCorrection$	=	correction for anaerobic conditions (unitless), see **(160)**;
$DecTCorr$	=	the effect of temperature (unitless), see **(156)**;
$pHCorr$	=	correction for suboptimal pH (unitless), see **(162)**; and
$Detritus$	=	concentration of detritus, including dissolved but not buried (g/m^3).

Note that biomass of bacteria is not explicitly modeled in AQUATOX. In some models (for example, EXAMS, Burns et al., 1982) decomposition is represented by a second-order equation using an empirical estimate of bacteria biomass. However, using bacterial biomass as a site

constant would constrain the model, potentially forcing the rate. Decomposers were modeled explicitly as a part of the CLEAN model (Clesceri et al., 1977). However, if conditions are favorable, decomposers can double in 20 minutes; this can result in stiff equations, adding significantly to the computational time. Ordinarily, decomposers will grow rapidly as long as conditions are favorable. The only time the biomass of decomposers might need to be considered explicitly is when a new organic chemical is introduced and the microbial assemblage requires time to become adapted to using it as a substrate.

The effect of temperature on biodegradation is represented by Equation **(156)**, which also is used for colonization. The function for dissolved oxygen, formulated for AQUATOX, is:

$$DOCorrection = Factor + (1 - Factor) \cdot \frac{KAnaerobic}{DecayMax} \qquad \textbf{(161)}$$

where the predicted DO concentrations are entered into a Michaelis-Menten formulation to determine the extent to which degradation rates are affected by ambient DO concentrations (Clesceri, 1980; Park et al., 1982):

$$Factor = \frac{Oxygen}{HalfSatO + Oxygen} \qquad \textbf{(162)}$$

and:

Factor	=	Michaelis-Menten factor (unitless);
KAnaerobic	=	decomposition rate at 0 g/m^3 oxygen (g/m^3·d or µg/L·d); Set to 0.3 g/m^3·d for microbial degradation of sediments. For chemicals, **(160)** is also used and the "rate of anaerobic microbial degr." from the chemical underlying data is used (*KMDegrAnaerobic*).
Oxygen	=	dissolved oxygen concentration (g/m^3); and
HalfSatO	=	half-saturation constant for oxygen (g/m^3) (0.5 g/m^3 in the water column or 8.0 g/m^3 for sedimented detritus).

DOCorrection accounts for both decreased and increased (Figure 100) degradation rates under anaerobic conditions, with *KAnaerobic/DecayMax* having values less than one and greater than one, respectively. Detritus will always decompose more slowly under anaerobic conditions; but some organic chemicals, such as some halogenated compounds (Hill and McCarty, 1967), will degrade more rapidly. Half-saturation constants of 0.1 to 1.4 g/m^3 have been reported (Bowie et al., 1985); a value of 0.5 g/m^3 is used in the water column and a calibrated value of 8.0 g/m^3 is used for the sediments to force anoxic conditions.

Figure 100. Correction for dissolved oxygen
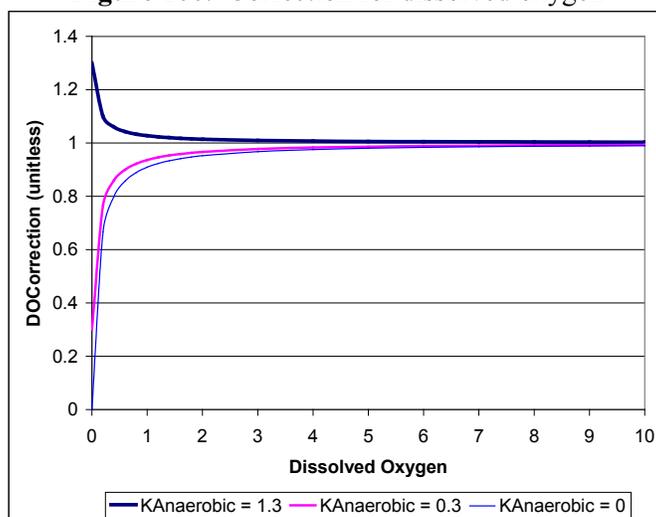
Another important environmental control on the rate of microbial degradation is pH. Most fungi grow optimally between pH 5 and 6 (Lyman et al., 1990), and most bacteria grow between pH 6 to about 9 (Alexander, 1977). Microbial oxidation is most rapid between pH 6 and 8 (Lyman et al., 1990). Within the pH range of 5 and 8.5, therefore, pH is assumed to not affect the rate of microbial degradation, and the suboptimal factor for pH is set to 1.0. In the absence of good data on the rates of biodegradation under extreme pH conditions, biodegradation is represented as decreasing exponentially beyond the optimal range (Park et al., 1980a; Park et al., 1982). If the pH is below the lower end of the optimal range, the following equation is used:

$$pHCorr = e^{(pH - pHMin)} \qquad \textbf{(163)}$$

where:

pH = ambient pH, and
$pHMin$ = minimum pH below which limitation on biodegradation rate occurs.

If the pH is above the upper end of the optimal range for microbial degradation, the following equation is used:

$$pHCorr = e^{(pHMmax - pH)} \qquad \textbf{(164)}$$

where:

$pHMax$ = maximum pH above which limitation on biodegradation rate occurs.

These responses are shown in Figure 101.

Figure 101. Limitation due to pH
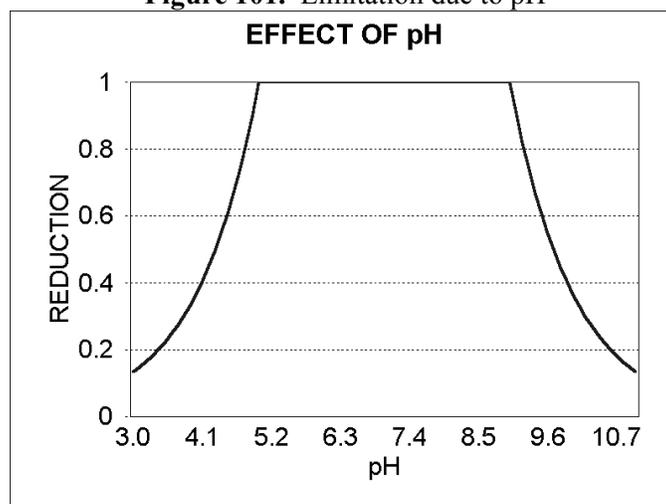
Sediment oxygen demand (SOD in g O_2/m^2 d) is also calculated by taking the sum of detrital decomposition and then multiplying by *O2Biomass* (the ratio of oxygen to organic matter). This can be compared with SOD values derived from the optional sediment diagenesis model (Chapter 7).

Sedimentation

Depending upon which options the user chooses, sedimentation (i.e., the sinking of suspended particles to the sediment bed) is calculated differently (Table 12). When the inorganic-sediment model (sand-silt-clay) is included, the sedimentation and deposition of detritus is assumed to mimic the sedimentation and resuspension of silt (see **(235)** and **(233)**).   If the multi-layer sediment model is included (using user-input erosion and deposition time-series) the sedimentation of detritus is calculated using the deposition velocity for cohesives (assumed to be a surrogate for organic matter) as follows:

$$Sedimentation = \frac{DepVel}{Thick} \cdot State \qquad (165)$$

When the inorganic-sediment model or the multiple-layer sediment model are not included in a simulation (i.e. "classic" AQUATOX formulations are used), the sedimentation of suspended particulate detritus to bottom sediments can be modeled using simplifying assumptions **(165)**. The constructs are intended to provide general responses to environmental factors, but they could be considerably improved upon by linkage to a hydrodynamic model (currently only available with the multi-layer sediment model).

$$Sedimentation = \frac{KSed}{Thick} \cdot Decel \cdot State \cdot DensityFactor \qquad (166)$$

where:

Sedimentation   =   transfer from suspended to sedimented by sinking (g/m³·d),   if negative is effectively *Resuspension* (see below);

KSed	=	sedimentation rate (m/d);
DepVel	=	user input time-series of deposition velocities for cohesives (multi-layer model only; m/d);
Thick	=	depth of water or thickness of layer if stratified (m);
Decel	=	deceleration factor (unitless), see **(166)**;
State	=	concentration of particulate detrital compartment (g/m^3); and
DensityFactor	=	if salinity is modeled, correction factor for water densities based on salinity and temperature, see **(442)**.

Table 12: Summary of Detrital Deposition and Resuspension in AQUATOX

Deposition of Suspended Detritus & Phytoplankton

	Assumption	Equation
"Classic" AQUATOX model	Sedimentation is a function of Mean Discharge	**(165)**
Sand-Silt-Clay submodel	Follows "silt" as calculated by the Sand-Silt-Clay submodel	**(235)**
Multi-layer Sediment Model	Follows "cohesives" class, (which may be user input or calculated using the sand-silt-clay model)	**(164)**; **(235)**
Sediment Diagenesis	Choice of "Classic" AQUATOX or Sand-Silt-Clay assumptions	

Resuspention of Sedimented Detritus

	Assumption	Equation
"Classic" AQUATOX model	Resuspension is a function of Mean Discharge	**(165)**
Sand-Silt-Clay submodel	Follows "silt" in inorganic sediments model	**(233)**
Multi-layer Sediment Model	Follows "cohesives" class, (which may be user input or calculated using the sand-silt-clay model)	**(167)**; **(233)**
Sediment Diagenesis	Resuspension is not enabled.	

If the discharge exceeds the mean discharge then sedimentation is slowed proportionately (

Figure 102):

$$\text{If } TotDischarge > MeanDischarge \text{ then}$$

$$Decel = \frac{MeanDischarge}{TotDischarge}$$

$$\text{else } Decel = 1.0$$

(167)

where:

TotDischarge	=	total epilimnetic and hypolimnetic discharge (m^3/d); and
MeanDischarge	=	mean discharge, recalculated on an annual basis at the beginning of each year of the simulation (m^3/d).

Figure 102. Relationship of *decel* to discharge with a mean discharge of 5 m^3/s.
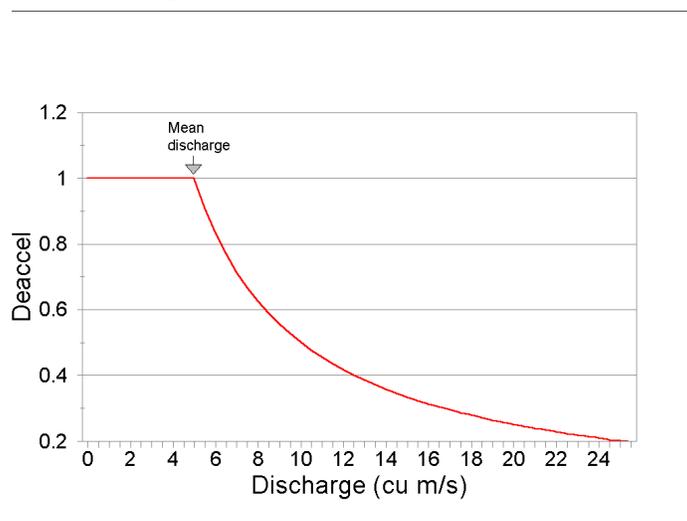
If the depth of water is less than or equal to 1.0 m and wind speed is greater than or equal to 5.5 m/s then the sedimentation rate is negative, effectively becoming the rate of resuspension. For plants, if the depth of water is is less than or equal to 1.0 m and wind speed is greater than or equal to 2.5 m/s then the sedimentation rate is assumed to be zero. If there is ice cover, then the sedimentation rate is doubled to represent the lack of turbulence.

If the multi-layer sediment model is included (using user-input erosion and deposition time-series) the resuspension of detritus is calculated using the erosion velocity for cohesives (assumed to be surrogate for organics) as follows

$$Resuspension = \frac{ErodeVel}{Thick} \cdot SedState \tag{168}$$

where:

Resuspension	=	transfer from sediment to suspended by erosion (g/m^3·d);
ErodeVel	=	user input time-series of cohesives erosion velocities (multi-layer model only m/d);
Thick	=	depth of water or thickness of layer if stratified (m);

Daily Burial

When the quantity of sedimented refractory detritus exceeds its initial condition, it is transferred to the deeply buried category (buried detritus).

$$Burial_{Detritus} = ABS\left(Conc_{Detritus} - InitialCondition_{Detritus}\right) \tag{167b}$$

where:

Burial$_{Detritus}$	=	daily burial of detritus (g/m^3·d);
Conc$_{Detritus}$	=	sedimented detritus concentration (g/m^3)

165

$InitialCondition =$ initial condition of detritus (g/m^3)

5.2 Nitrogen

In the water column, 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 **(177)**. In the sediment bed, if the optional sediment diagenesis model is included (see chapter 7), nitrogen is explicitly modeled; otherwise inorganic nitrogen in the sediment bed is ignored, but organic nitrogen is implicitly modeled as a component of sedimented detritus.

> **Nitrogen: Simplifying Assumptions**
>
> - Nitrite is not explicitly modeled
> - Both nitrogen fixation and denitrification are subject to environmental controls; therefore, the nitrogen cycle is represented with considerable uncertainty.
> - Lethal effects from un-ionized and ionized ammonia are assumed additive.
> - Ammonia makes up stoichiometric imbalances between trophic levels.

In the water column, ammonia is assimilated by algae and macrophytes and is converted to nitrate as a result of nitrification:

$$\frac{dAmmonia}{dt} = Loading + Remineralization - Nitrify - Assimilation_{Ammonia}$$
$$- Washout + Washin \pm TurbDiff \pm Diffusion_{Seg} + Flux_{Diagenesis} \tag{169}$$

where:

$dAmmonia/dt$	=	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 **(169)**;
$Nitrify$	=	nitrification (g/m^3·d), see **(174)**;
$Assimilation$	=	assimilation of nutrient by plants (g/m^3·d), see **(171)**;
$Washout$	=	loss of nutrient due to being carried downstream (g/m^3·d), see **(16)**
$Washin$	=	loadings from linked upstream segments (g/m^3·d), see **(30)**;
$Diffusion_{Seg}$	=	gain or loss due to diffusive transport over the feedback link between two segments, (g/m^3·d), see **(32)**;
$TurbDiff$	=	depth-averaged turbulent diffusion between epilimnion and hypolimnion if stratified (g/m^3·d), see **(22)** and **(23)**;
$Flux_{Diagenesis}$	=	potential flux from the sediment diagenesis model, (g/m^3·d), see **(273)**

Remineralization includes all processes by which ammonia is produced from animal, plants, and detritus, including decomposition and excretion required to maintain variable stoichiometry (see Table 14):

$$Remineralization = PhotoResp + DarkResp + AnimalResp + AnimalExcr$$
$$+ DetritalDecomp + AnimalPredation + NutrRelDefecation$$
$$+ NutrRelPlantSink + NutrRelMortality + NutrRelGameteLoss$$
$$+ NutrRelColonization + NutrRelPeriScour$$

(170)

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·d);
AnimalExcr	=	animal excretion of excess nutrients to ammonia to maintain constant org. to N ratio as required (g/m^3·d);
DetritalDecomp	=	nitrogen release due to detrital decomposition (g/m^3·d);
AnimalPredation	=	change in nitrogen content necessitated when an animal consumes prey with a different nutrient content (g/m^3·d), see discussion in "Mass Balance of Nutrients" in Section 5.4;
NutrRelDefecation	=	ammonia released from animal defecation (g/m^3·d);
NutrRelPlantSink	=	ammonia balance from sinking of plants and conversion to detritus (g/m^3·d);
NutrRelMortality	=	ammonia balance from biota mortality and conversion to detritus (g/m^3·d);
NutrRelGameteLoss	=	ammonia balance from gamete loss and conversion to detritus (g/m^3·d);
NutrRelColonization	=	ammonia balance from colonization of refractory detritus into labile detritus (g/m^3·d);
NutrRelPeriScour	=	ammonia balance when periphyton is scoured and converted to phytoplankton and suspended detritus. (g/m^3·d);

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

$$\frac{dNitrate}{dt} = Loading + Nitrify - Denitrify - Assim_{Nitrate} - Washout + Washin$$
$$\pm\ TurbDiff \pm Diffusion_{Seg} + Flux_{Diagenesis}$$

(171)

where:

dNitrate/d*t*	=	change in concentration of nitrate with time (g/m^3·d);
Washin	=	loadings from linked upstream segments (g/m^3·d), see **(30)**;
Diffusion$_{Seg}$	=	gain or loss due to diffusive transport over the feedback link between two segments, (g/m^3·d), see **(32)**;
Loading	=	user entered loading of nitrate, including atmospheric deposition;
Denitrify	=	denitrification (g/m^3·d), see **(175)**;
Flux$_{Diagenesis}$	=	potential flux from the sediment diagenesis model, (g/m^3·d), see **(273)**

Free nitrogen can be fixed by cyanobacteria. 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.

Figure 103. Components of nitrogen remineralization
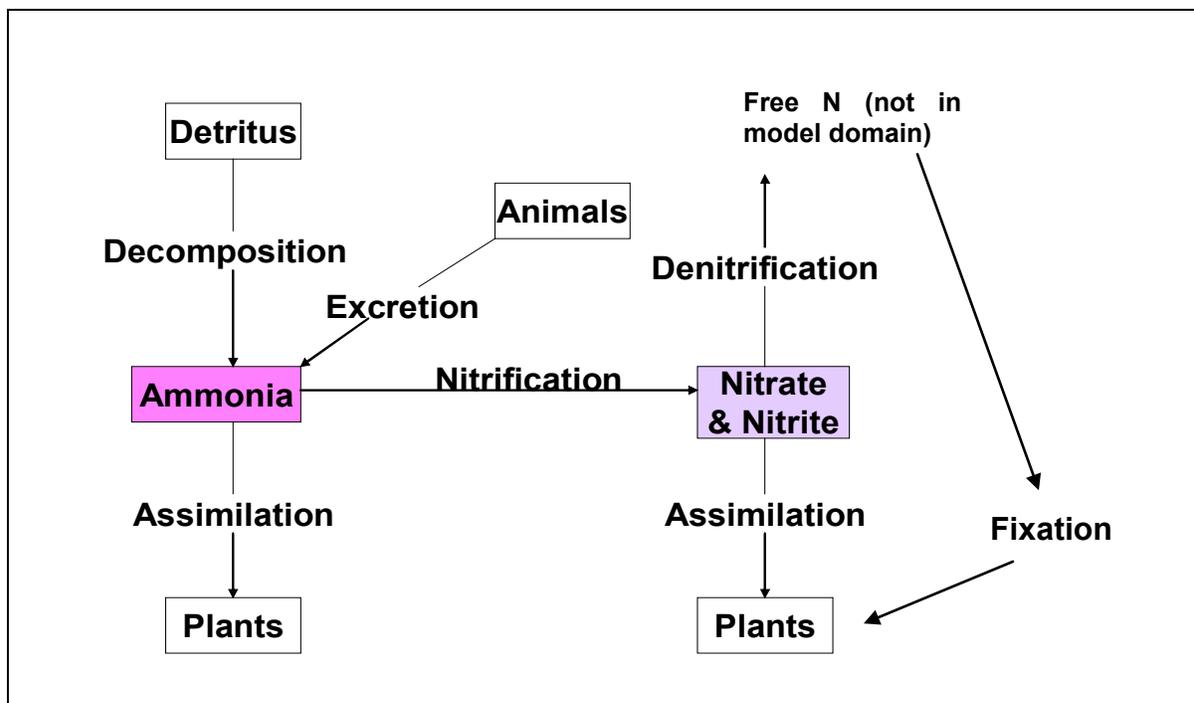
AQUATOX will estimate and output total nitrogen (TN) in the water column. Total nitrogen is the sum of ammonia and nitrate in the water column as well as nitrogen associated with dissolved and suspended particulate organic matter and phytoplankton (see section 5.4 for further details).

Assimilation

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

$$Assimilation_{Ammonia} = \sum\nolimits_{Plant} (\, Photosynthesis_{Plant} \cdot N2Org_{Plant} \cdot NH4Pref) \qquad \textbf{(172)}$$

$$Assimilation_{Nitrate} = \sum\nolimits_{Plant} (\, Photosynthesis_{Plant} \cdot N2Org_{Plant} \cdot (1 - NH4Pref)) \qquad \textbf{(173)}$$

When internal nutrients are modeled, the equations are slightly different

$$Assimilation_{Ammonia} = \sum\nolimits_{Plant} (PhytoUpN \cdot 1e3 \cdot NH4Pref) \qquad \textbf{(171b)}$$

$$Assimilation_{Ammonia} = \Sigma_{Plant}(PhytoUpN \cdot 1e3 \cdot (1 - NH4Pref)) \tag{172b}$$

where:

Assimilation	=	assimilation rate for given nutrient (g/m³·d);
Photosynthesis	=	rate of photosynthesis (g/m³·d), see **(35)**;
N2Org $_{Plant}$	=	fraction of photosynthate that is nitrogen (unitless, user input as part of plant underlying data);
PhytoUpN	=	uptake of internal nutrients (mg/m³·d), see **(55e)**;
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):

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

$$\tag{174}$$

$$\frac{N2NH4 \cdot Ammonia \cdot KN}{(N2NH4 \cdot Ammonia + N2NO3 \cdot Nitrate) \cdot (KN + N2NO3 \cdot Nitrate)}$$

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/m³);
Ammonia	=	concentration of ammonia (g/m³); and
Nitrate	=	concentration of nitrate (g/m³).

For algae other than cyanobacteria, *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 cyanobacteria is represented by using a smaller uptake ratio, thus "creating" nitrogen. Nitrogen fixation is not tracked explicitly as a separate rate in the plant's derivative.

Nitrification and Denitrification

Nitrification is the conversion of ammonia to nitrite and then to nitrate by nitrifying bacteria; it occurs at the sediment-water interface (Effler et al., 1996) and in the water column (Schnoor 1996). The maximum rate of nitrification 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:

$$Nitrify = KNitri \cdot DOCorrection \cdot TCorr \cdot pHCorr \cdot Ammonia \tag{175}$$

where:

Nitrify = nitrification rate ($g/m^3 \cdot d$);
KNitri = maximum rate of nitrification (m/d);
DOCorrection = correction for anaerobic conditions (unitless) see **(160)**;
TCorr = correction for suboptimal temperature (unitless); see **(59)**;
pHCorr = correction for suboptimal pH (unitless), see **(162)**; and
Ammonia = concentration of ammonia (g/m^3).

If the Sediment Diagenesis model is used, the *KNitri* value may need to be decreased to account for sediment nitrification being represented separately. 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 101, Figure 102).

Figure 104. Response to pH, nitrification
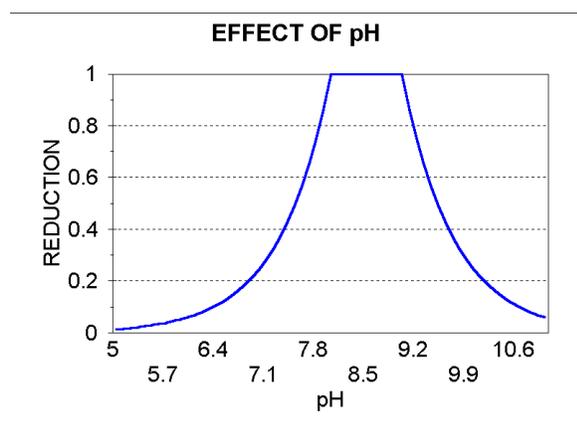
Figure 105. Response to temperature, nitrification
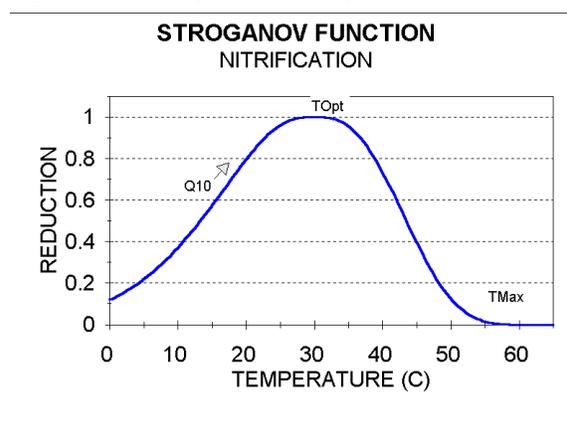
Denitrification is the conversion of nitrate and nitrite to free nitrogen and occurs as an anaerobic process. However, only a small part of the denitrification occurs at the sediment-water interface and it can also occur in the water column due to "anoxic microsites" such as the interior of detrital particles (Di Toro 2001). Therefore, AQUATOX follows the convention of other models in representing denitrification as a bulk process (by combining sediment and water-column denitrification). This approach is a change from earlier model versions, including AQUATOX Release 3.0, where denitrification processes at the sediment-water interface and in the water column were considered separately. Low oxygen levels enhance the denitfification process (Ambrose et al., 1991):

$$Denitrify = KDenitri \cdot (1 - DOCorrection) \cdot TCorr \cdot pHCorr \cdot Nitrate \qquad (176)$$

where:

Denitrify = denitrification rate ($g/m^3 \cdot d$);
KDenitri = user-input maximum rate of denitrification (1/d);
TCorr = effect of suboptimal temperature (unitless), see **(59)**;
pHCorr = effect of suboptimal pH (unitless), see **(162)**; and

$Nitrate$ =   concentration of nitrate (g/m^3).

KDenitri might need to be reduced when the sediment diagenesis model is included, because denitrification in the sediment bed is explicitly tracked within that model (see **(278)**)

Furthermore, denitrification is accomplished by a large number of reducing bacteria under anaerobic conditions and with broad environmental tolerances (Bowie et al., 1985; Figure 103**,** Figure 104).

Figure 106. Response to pH, denitrification
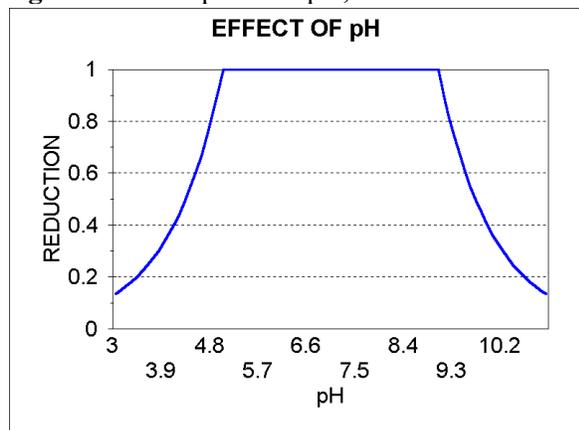
Figure 107. Response to temperature, denitrif.
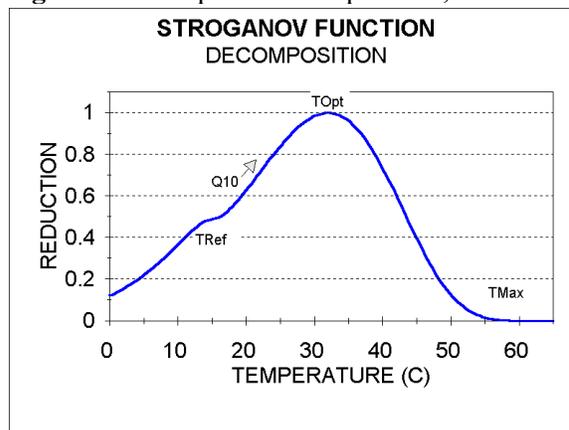
Ionization of Ammonia

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. 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):

$$FracNH3 \quad = \quad \frac{1}{1 + 10^{pkh - pH}}$$

(177)

$$NH3 \quad = \quad FracNH3 \cdot Ammonia$$

(178)

$$pkh \quad = \quad 0.09018 + \frac{2729.92}{TKelvin}$$

(179)

where:
FracNH3	=	fraction of un-ionized ammonia (unitless);
pkh	=	hydrolysis constant;
NH3	=	un-ionized ammonia (mg/L);
Ammonia	=	total ammonia (mg/L) see **(168)**;
TKelvin	=	temperature (ºK).

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 (Figure 108 and Figure 109). 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 108. Fraction of un-ionized ammonia roughly following temperature.
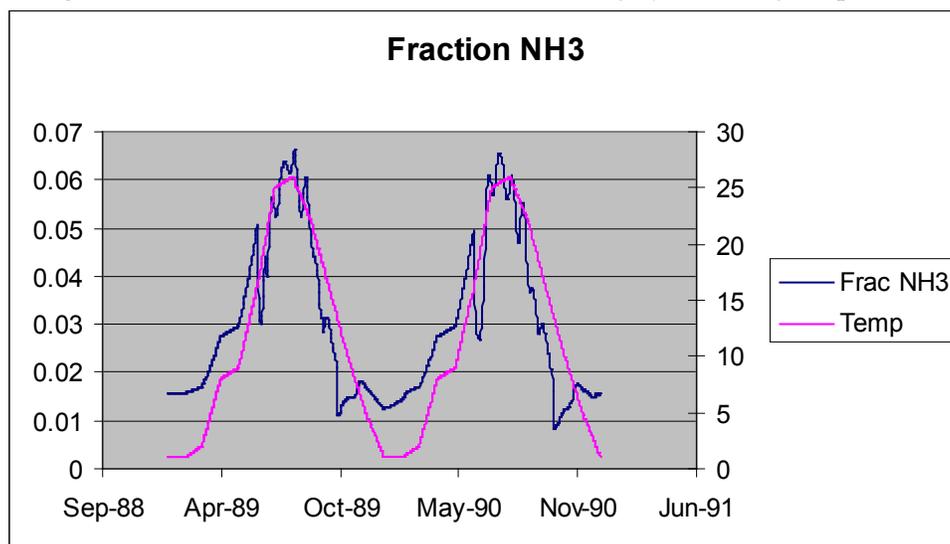
Figure 109. Fraction of un-ionized ammonia affected by extreme values of pH.
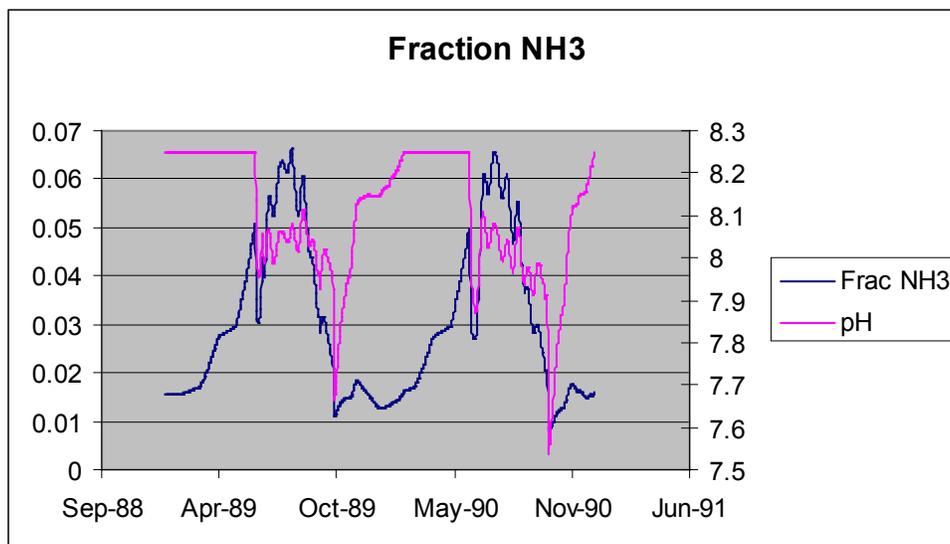
The construct was verified with the same set of data from Lake Onondaga as was used for the pH verification (Effler et al. 1996), see section 5.7. It fits the observed data well (Figure 110).

Fraction NH3
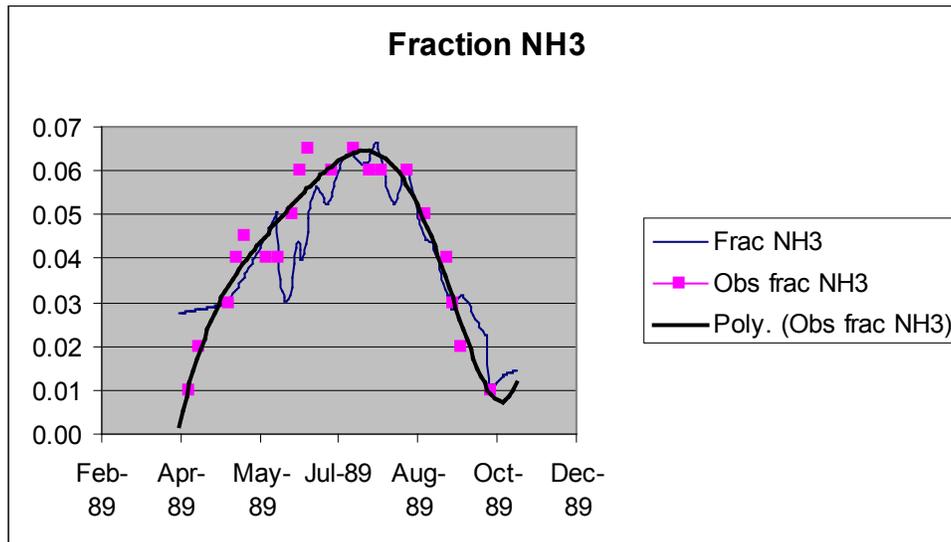
Ammonia Toxicity

Lethal effects of ammonia on animals have been implemented in AQUATOX based on *Update of Ambient Water Quality Criteria for Ammonia* (U.S. Environmental Protection Agency, 1999). Based on this document, it is preferable to base toxicity on total ammonia, taking into account the contributions from the un-ionized and ionized ammonia (*LC50u* and *LC50i*):

$$LC50_u = \left(\frac{LC50_{t,8}}{\frac{R}{1+10^{pH_T-8}} + \frac{1}{1+10^{8-pH_T}}} \right) \left(\frac{R}{1+10^{pH_T-pH}} \right) \tag{180}$$

$$LC50_i = \left(\frac{LC50_{t,8}}{\frac{R}{1+10^{pH_T-8}} + \frac{1}{1+10^{8-pH_T}}} \right) \left(\frac{1}{1+10^{pH-pH_T}} \right) \tag{181}$$

where:

LC50$_u$	=	LC50 for the unionized concentrations of ammonia
LC50$_i$	=	LC50 for the ionized concentrations of ammonia.
LC50$_{total\ ammonia}$	=	*LC50$_u$* + *LC50$_i$*

pH_T	=	transition pH at which LC50 is the average of the high- and low-pH intercepts (7.204);
R	=	shape parameter defined as the ratio of the high- and low-pH intercepts (0.00704), along with pH_T, defines the shape of the curve;
$LC50_{t,8}$	=	user-input $LC50_{total\ ammonia}$ at 20 degrees centigrade and pH of 8.

LC50 parameters derived with the equations above are then applied to the external toxicity formulation (see section 9.3, equations **(429)-(431)**). The slope of the Weibull curve is a constant 0.7 for both forms of ammonia. This value produces the best general match of data from Appendix 6 from the Ammonia Criteria update (U.S. Environmental Protection Agency, 1999). Lethal effects from un-ionized and ionized ammonia are assumed to be additive.

5.3 Phosphorus

The phosphorus cycle is simpler than the nitrogen cycle. Decomposition, excretion, and assimilation are important processes that are similar to those described above. As was the case with ammonia and nitrate, if the optional sediment diagenesis model is included (see Chapter 7), flux of phosphate from the sediment bed may be added to the water column, especially under anoxic conditions. Additionally,

> **Phosphorus: Simplifying Assumption**
>
> - Total bioavailable soluble phosphorus is modeled
> - A constant sorption rate for calcite is used
> - Soluble phosphorus makes up stoichiometric imbalances between trophic levels.

sorption to calcite may have a significant effect on phosphate predictions in high pH systems due to precipitation of calcium carbonate. This optional formulation is important to adequately simulate marl lakes.

$$\frac{dPhosphate}{dt} = Loading + Remineralization - Assimilation_{Phosphate} - Washout$$
$$+ Washin \pm TurbDiff \pm Diffusion_{Seg} - SorptionP + Flux_{Diagenesis}$$

(182)

$$Assimilation = \Sigma_{Plant}\ (\ Photosynthesis_{Plant} \cdot Uptake_{Phosphorus}\ )$$

(183)

where:

$dPhosphate/dt$	=	change in concentration of phosphate with time (g/m^3·d);
$Loading$	=	loading of nutrient from inflow and atmospheric deposition (g/m^3·d);
$Remineralization$	=	phosphate derived from detritus and biota (g/m^3·d), see **(183)**;
$Assimilation$	=	assimilation by plants (g/m^3·d);
$TurbDiff$	=	depth-averaged turbulent diffusion between epilimnion and hypolimnion if stratified (g/m^3·d), see **(22)** and **(23)**;

Washout	=	loss of nutrient due to being carried downstream (g/m^3·d), see **(16)**
Washin	=	loadings from linked upstream segments (g/m^3·d), see **(30)**;
Diffusion$_{Seg}$	=	gain or loss due to diffusive transport over the feedback link between two segments, (g/m^3·d), see **(32)**;
SorptionP	=	rate of sorption of phosphorus to calcite (mgP/L·d), see **(218)**;
Flux$_{Diagenesis}$	=	potential flux from the sediment diagenesis model, (g/m^3·d), see **(273)**
Photosynthesis	=	rate of photosynthesis (g/m^3·d), see **(35)**, and
Uptake	=	fraction of photosynthate that is phosphate (unitless, 0.018).

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 15):

$$
\begin{aligned}
Remineralization = {} & PhotoResp + DarkResp + AnimalResp + AnimalExcr \\
& + DetritalDecomp + AnimalPredation + NutrRelDefecation \\
& + NutrRelPlantSink + NutrRelMortality + NutrRelGameteLoss \\
& + NutrRelColonization + NutrRelPeriScour
\end{aligned}
$$

(184)

where:

PhotoResp	=	algal excretion of phosphate due to photo-respiration (g/m^3·d);
DarkResp	=	algal excretion of phosphate due to dark respiration (g/m^3·d);
AnimalResp	=	excretion of phosphate due to animal respiration (g/m^3·d);
AnimalExcr	=	animal excretion of excess nutrients to phosphate to maintain constant org. to P ratio as required (g/m^3·d);
DetritalDecomp	=	phosphate release due to detrital decomposition (g/m^3·d);
AnimalPredation	=	change in phosphate content necessitated when an animal consumes prey with a different nutrient content (g/m^3·d), see discussion in "Mass Balance of Nutrients" below;
NutrRelDefecation	=	phosphate released from animal defecation (g/m^3·d);
NutrRelPlantSink	=	phosphate balance from sinking of plants and conversion to detritus (g/m^3·d);
NutrRelMortality	=	phosphate balance from biota mortality and conversion to detritus (g/m^3·d);
NutrRelGameteLoss	=	phosphate balance from gamete loss and conversion to detritus (g/m^3·d);
NutrRelColonization	=	phosphate balance from colonization of refractory detritus into labile detritus (g/m^3·d);
NutrRelPeriScour	=	phosphate balance when periphyton is scoured and converted to phytoplankton and suspended detritus. (g/m^3·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 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 default uptake parameter is the Redfield (1958) ratio; it may be edited if a different ratio is desired (cf. Harris, 1986).

AQUATOX estimates and outputs total phosphate (TP) in the water column. TP is the sum of dissolved phosphate in the water column as well as phosphate associated with dissolved and suspended particulate organic matter and phytoplankton(see section 5.4 for further details).

5.4 Nutrient Mass Balance

Variable Stoichiometry

The ratios of elements in organic matter are allowed to vary among but not within compartments.   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 has a default value of 5.

In order to maintain the specified ratios for each compartment, the model explicitly accounts for processes that balance the ratios during transfers, such as excretion coupled with consumption and nutrient uptake coupled with detrital colonization.   Nutritional value is not automatically related to stoichiometry in the model, but it

> **Nutrient Mass Balance: Simplifying Assumptions**
>
> - Stoichiometry within each model compartment is constant over time
> - Free nitrogen is not tracked within AQUATOX
> - Nutrients taken up by macrophyte roots come from sources that are outside the modeled system
> - Mass balance may fail if total nutrients in the water column drop to zero (due to inter-organism interactions)
> - Ammonia loadings are assumed to be 12 to 15% when total nitrate loadings are input by the user.
> - Dissolved nutrients make up stoichiometric imbalances between trophic levels.

is implicit in default egestion values provided with various food sources. Table 13 shows the default stoichiometric values suggested for the model, although these can be edited.

Table 13: Default stochiometric values in AQUATOX

Compartment	Frac. N (dry)	Frac. P (dry)	Reference
Refrac. detritus	0.002	0.0002	Sterner & Elser 2002
Labile detritus	0.079	0.018	Redfield (1958) ratios
Phytoplankton	0.059	0.007	Sterner & Elser 2002
Cyanobacteria	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 & George 2000
Shiner	0.1	0.025	Sterner & George 2000
Perch	0.1	0.031	Sterner & George 2000
Smelt	0.1	0.016	Sterner & George 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 accept both loadings and initial conditions as "Total N" and "Total P." This approach 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:

$$N_{Dissolved} = N_{Total} - N_{SuspendedDetritus} - N_{SuspendedPlants} \tag{185}$$

where:

$N_{Dissolved}$ = bioavailable dissolved nitrogen (g/m^3 d); see **(170)**;
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).

When Total N inputs are used, ammonia is assumed to be a fixed percentage of bioavailable dissolved nitrogen, based on the type of input:

- Inflow waters: Ammonia content of dissolved inorganic nitrogen = 12%
- Point sources: Ammonia content of dissolved inorganic nitrogen = 15%
- Non-point sources: Ammonia content of dissolved inorganic nitrogen = 12%

These percentages are based on professional judgement, they are averages from several large data sets. However, if the user wishes to use a different percentage, separate ammonia and nitrate data sets can be derived from the Total N time-series and input individually.

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

$$TSP = FracAvail(P_{Total}) - P_{SuspendedDetritus} - P_{SuspendedPlants} \tag{186}$$

where:

TSP = bioavailable phosphorus (g/m^3 d); see **(181)**;
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 calculated as output variables. This approach 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.

Carbonaceous biochemical oxygen demand ($CBOD_5$) is estimated considering the sum of detrital decomposition.   The contributions from phytoplankton and labile dissolved and particulate organic matter are included using an oxygen to biomass conversion factor entered in the remineralization record.

Mass Balance of Nutrients

Variables for tracking mass balance and nutrient fate are included in the output as detailed below. Phosphorus and Nitrogen 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. (Macrophyte root uptake is currently assumed to occur from below the modeled sediment layer) , kg
> **Nitrogen Fixation:** Load of nitrate into system since start via nitrogen fixation, 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 nutrient movement to or from paired vertical layer, kg (This value is the sum of sinking, turbulent diffusion and migration. This quantity also accounts for nutrient transport caused by water movement when the thermocline depth changes.)
> **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

It is important to 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."

Simplified diagrams of the nitrogen and phosphorus cycles can be found in Figure 108 and

Figure 109. A full accounting of the 18 nutrient linkages and all external loads and losses for nitrogen and phosphorus is also provided in Table 14 and Table 15.

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. However, this implicit "nutrient pumping" is tracked in the mass balance output. Nitrogen fixation is another addition of nutrients from outside of the model domain that is tracked with the mass balance output varaible called "N fixation."

Additionally, some simplifications are required as a result of dietary imbalances. For example, herbivores generally have higher nutrient concentrations than the plants that they are consuming. When biomass is converted from a plant into an animal through consumption the imbalance has to be satisfied to maintain mass balance. Sterner and Elser (2002) state: "There is no single way that consumers maintain their stoichiometry in the face of imbalanced resources." As a simplification, AQUATOX takes nutrients from the dissolved water-column compartments to make up this difference (see *AnimalPredation* in **(169)**). However, these same herbivores ingest plants with higher nutrient concentrations than the fecal matter that they defecate. When biomass is converted from plants to detrital matter through defecation the model simulates a release of nutrients into the water column (see *NutrRelDefecation* in **(169)**). These two simplifying algorithms, therefore, balance each other for the most part, and such interactions will have only a minor effect on predicted water-column nutrient concentrations. Likewise, nutrient-poor refractory detritus is converted to labile detritus through microbial colonization and growth; this is stimulated by uptake of nutrients from the water column (Sterner and Elser 2002) and is represented in the model.

Figure 111

Nitrogen Cycle in AQUATOX

mortality, defecation, gameteloss

animals

ingestion

mortality

ingestion

detritus

plants

excretion,
respiration

assimilation

excretion, respiration

Loadings

Washout

decomp.

dissolved in water

macrophyte
root uptake

nitrification

NO_3

NH_4

free nitrogen
(not in model domain)

denitrification

N in pore waters
(outside model domain)
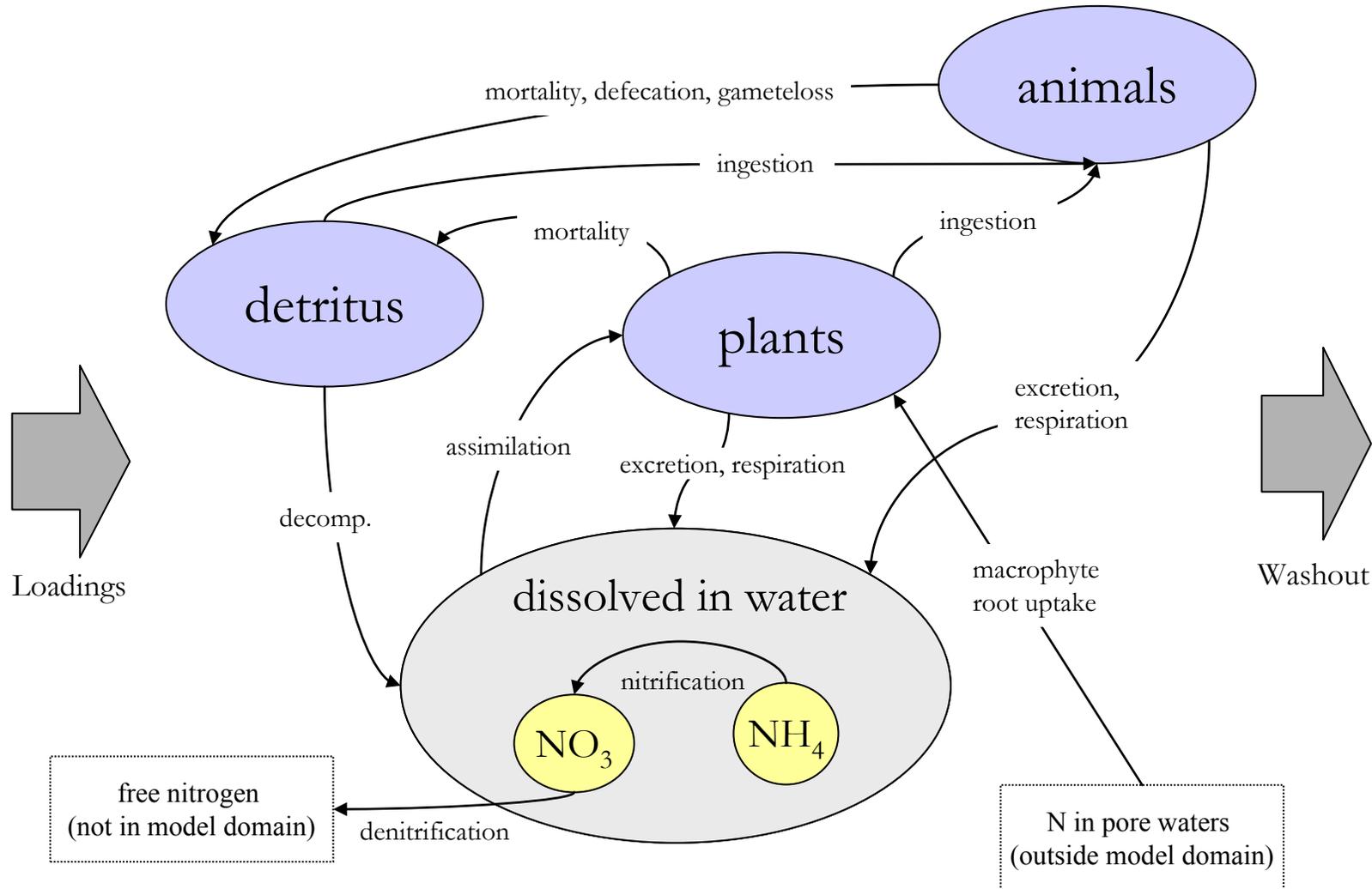
Table 14

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 50-50. 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 converts 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.

Figure 112

Phosphorus Cycle in AQUATOX

animals

mortality, defecation, gameteloss

ingestion

ingestion

mortality

detritus

plants

excretion,
respiration

assimilation

excretion, respiration

decomp.

macrophyte
root uptake

phosphate
dissolved in water

P in pore waters
(outside model domain)

Loadings

Washout
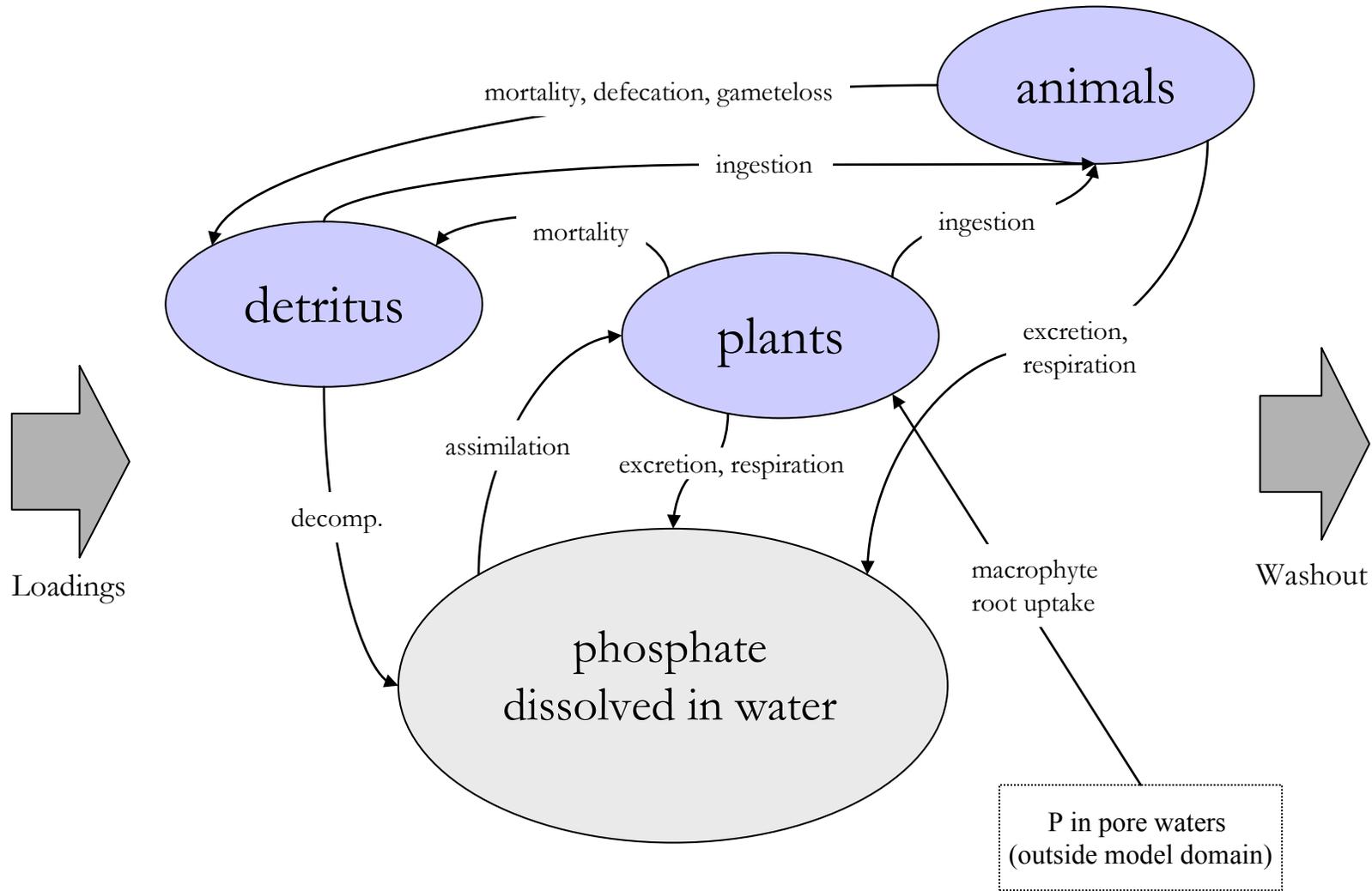
Table 15

Phosphorus Mass Balance: Accounting

Total Soluble P	link	
Load	external load	
Assimilation	to plant	b
Excretion	from anim/plt	c,o
Respiration	from anim/plt	m,n
DetritalDecomp	from LabileDetr	d
Washout	external loss	
TurbDiff	layer accountg	

Detritus, Sed. Refractory	link	
Load	external load	
Defecation	from animal	e
Plant Sedmtn	from plant	f
Colonz	to SedLabDetr	g
Predation	to Animal	h
Sedimentation	from PartRefrDetr	i
Scour	to PartRefrDetr	j
Burial	external loss	
Exposure	external load	

Detritus, Sed. Labile	link	
Load	external load	
Defecation	from animal	e
Plant Sedmtn	from plant	f
Colonz	from SedRefrDetr	g
Predation	to Animal	h
Decomp	to TSP	d
Sedimentation	from PartLabDetr	i
Scour	to PartLabDetr	j
Burial	external loss	
Exposure	external load	

Detritus, Dissolved	link	
Load	external load	
Decomp (labile)	to TSP	d
Mortality	from anim/plt	k
Colonz	DissRefr->PartLab	g
Excretion	from anim/plt	l
Washout	external loss	
TurbDiff	layer accountg	

Detritus, Particulate Refr.	link	
Load	external load	
mortality	from anim/plt	k
Colonz	to PartLabDetr	g
Washout	external loss	
Predation	to Animal	h
Sedimentation	to SedRefrDetr	i
Scour	from SedRefrDetr	j
SinkToHyp	layer accountg	
SinkFromEpi	layer accountg	
TurbDiff	layer accountg	

Detritus, Particulate	link	
Load	external load	
Decomp	to TSP	d
mortality	from anim/plt	k
GamLoss	from Animal	q
Colonz	from Diss,PartRefr	g
Washout	external loss	
Predation	to Animal	h
Sedimentation	to SedLabDetr	i
Scour	from SedLabDetr	j
SinkToHypo	layer accountg	
SinkFromEpi	layer accountg	
TurbDiff	layer accountg	

Algae	link	
Load	external load	
Photosyn	from TSP	b
Respiration	to TSP	b
Photo Resp	to diss detr, TSP	l,c
Mortality	to Diss / Part Detr	k
Predation	to Animal	h
Washout	external loss	
Sedimntn (Sink)	to Sed Detr	f
TurbDiff	layer accountg	
SinkToHypo	layer accountg	
SinkFromEpi	layer accountg	
Sloughing	to detr., phytoplk	r
ToxDislodge	to detr., as mort	k

Macrophytes	link	
Load	external load	
Photosyn	root uptake, external	
Respiration	to TSP	m
Photo Resp	to diss detr, TSP	l,c
Mortality	to Part Detr	k
Predation	to animal	h
Breakage	to detr., as mort	k

Animals	link	
Load	external load	
Consumption	from anim/plt	h
Defecation	to sed detr	e
Respiration	to TSP if req.	n
Excretion	to TSP if req.	l,o
TurbDiff	layer accountg	
Predation	to animal	h
Mortality	to Part Detr	k
GameteLoss	to PartLabDetr	q
Drift	external loss	
Entrain	external loss	
Promotion	to animal	p
Recruit	from animal	p
EmergeI	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 P 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 P ratio as required.

o Animal excretion of excess nutrients to P to maintain constant org. to P 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.

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 113.

Figure 113 Distribution of predicted mass of nitrogen in Lake Onondaga NY.
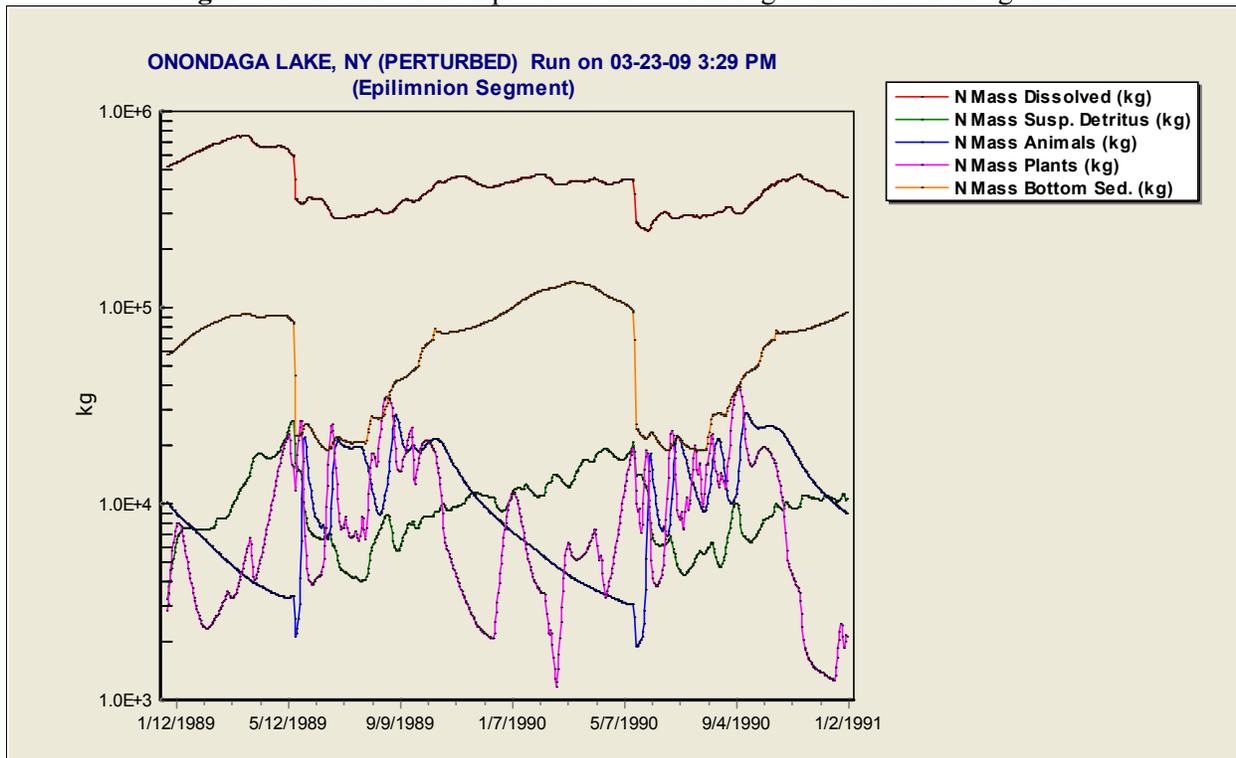
5.5 Dissolved Oxygen

Oxygen is an important regulatory endpoint; very low levels can result in mass mortality for fish and other organisms, mobilization of nutrients and metals, and decreased degradation of toxic organic materials. Dissolved oxygen is usually simulated as a daily average and does not account for diurnal fluctuations (however, see **Diel Oxygen** below). It is a function of reaeration, photosynthesis, respiration, decomposition, and nitrification:

> **Oxygen: Simplifying Assumptions**
>
> - Reaeration is set to zero if ice cover is predicted
> - Cyanobacteria blooms limit the depth of oxygen reaeration

$$\frac{dOxygen}{dt} = Loading + Reaeration + Photosynthesized - BOD - \sum Respiration$$

$$- NitroDemand - Washout + Washin \pm TurbDiff \pm Diffusion_{Seg} \tag{187}$$

$$Photosynthesized = O2Photo \cdot \Sigma_{Plant}(Photosynthesis_{Plant}) \tag{188}$$

$$BOD = O2Biomass \cdot \left(\Sigma_{Detritus}(Decomposition_{Detritus})\right) \tag{189}$$

$$NitroDemand = O2N \cdot Nitrify \tag{190}$$

where:

$dOxygen/dt$	=	change in concentration of dissolved oxygen (g/m^3·d);
$Loading$	=	loading from inflow (g/m^3·d);
$Reaeration$	=	atmospheric exchange of oxygen (g/m^3·d), see **(190)**;
$Photosynthesized$	=	oxygen produced by photosynthesis (g/m^3·d);
$O2Photo$	=	ratio of oxygen to photosynthesis (1.6, unitless);
BOD	=	instantaneous biochemical oxygen demand (g/m^3·d);
$NitroDemand$	=	oxygen taken up by nitrification (g/m^3·d);
$Washout$	=	loss due to being carried downstream (g/m^3·d), see **(16)**;
$Washin$	=	loadings from linked upstream segments (g/m^3·d), see **(30)**;
$Diffusion_{Seg}$	=	gain or loss due to diffusive transport over the feedback link between two segments, (g/m^3·d), see **(32)**;
$O2Biomass$	=	ratio of oxygen to organic matter (unitless);
$Photosynthesis$	=	rate of photosynthesis (g/m^3·d), see **(35)**, **(85)**;
$Decomposition$	=	rate of decomposition (g/m^3·d), see **(159)**;
$\sum Respiration$	=	sum of respiration for all organisms (g/m^3·d), **(63)** and **(100)**;
$O2N$	=	ratio of oxygen to nitrogen (unitless); and
$Nitrify$	=	rate of nitrification (g N/m^3·d) see **(174)**.

Reaeration is a function of the depth-averaged mass transfer coefficient *KReaer*, corrected for ambient temperature, multiplied by the difference between the dissolved oxygen level and the saturation level (cf. Bowie et al., 1985):

$$Reaeration = KReaer \cdot (O2Sat \text{ - } Oxygen) \tag{191}$$

where:

Reaeration	=	mass transfer of oxygen (g/m^3·d);
KReaer	=	depth-averaged reaeration coefficient (1/d);
O2Sat	=	saturation concentration of oxygen (g/m^3), see **(198)**; and
Oxygen	=	concentration of oxygen (g/m^3).

For reaeration in estuaries, see Chapter 10 and equation **(445)**.

In conditions where ice cover is assumed, as well as in the hypolimnetic segment of a stratified simulation, *Reaeration* is generally set to zero. However, to prevent excessive oxygen buildup under these conditions, oxygen is not allowed to exceed two times saturation (*O2Sat)*. Any oxygen buildup beyond two times saturation is added to *Reaeration* as a loss term.

KReaer may be entered as a constant value within the site's "underlying data." Alternatively, AQUATOX will calculate *KReaer* based on the site-type and other characteristics. In standing water *KReaer* is computed as a minimum transfer velocity plus the effect of wind on the transfer velocity (Schwarzenbach et al., 1993) divided by the thickness of the mixed layer to obtain a depth-averaged coefficient (Figure 111):

$$KReaer = \frac{(4E\text{-}4 + 4E\text{-}5 \cdot Wind^2) \cdot 864}{Thick} \tag{192}$$

where:

Wind	=	wind velocity 10 m above the water (m/sec);
864	=	conversion factor (cm/sec to m/d); and
Thick	=	thickness of mixed layer (m).

Algal blooms can generate dissolved oxygen levels that are as much as 400% of saturation (Wetzel, 2001). However, near-surface cyanobacteria blooms, which are modeled as being in the top 0.1 m, produce high levels of oxygen that do not extend significantly into deeper water. An adjustment is made in the code so that if the cyanobacteria biomass exceeds 1 mg/L and is greater than other phytoplankton biomass, the thickness subject to oxygen reaeration is set to 0.1 m. This does not affect the *KReaer* that is used in computing volatilization (see section 8.5).

In streams, reaeration is a function of current velocity and water depth (Figure 112) following the approach of Covar (1978, see Bowie et al., 1985) and used in WASP (Ambrose et al., 1991). The decision rules for which equation to use are taken from the WASP5 code (Ambrose et al., 1991).

If *Vel* < 0.518 m/sec:

$$TransitionDepth = 0 \tag{193}$$

else:

$$TransitionDepth = 4.411 \cdot Vel^{2.9135} \qquad \textbf{(194)}$$

where:

Vel	=	velocity of stream (converted to m/sec) see **(14)**; and
TransitionDepth	=	intermediate variable (m).

If *Depth* < 0.61 m (but > 0.06), the equation of Owens et al. (1964, cited in Ambrose et al., 1991) is used:

$$KReaer = 5.349 \cdot Vel^{0.67} \cdot Depth^{-1.85} \qquad \textbf{(195)}$$

where:

Depth	=	mean depth of stream (m).

Otherwise, if *Depth* is > *TransitionDepth*, the equation of O'Connor and Dobbins (1958, cited in Ambrose et al., 1991) is used:

$$KReaer = 3.93 \cdot Vel^{0.50} \cdot Depth^{-1.50}$$

Else, if *Depth* ≤ *TransitionDepth* but not <0.60 m, the equation of Churchill et al. (1962, cited in Ambrose et al., 1991) is used:

$$KReaer = 5.049 \cdot Vel^{0.97} \cdot Depth^{-1.67} \qquad \textbf{(196)}$$

In extremely shallow streams, especially experimental streams where depth is < 0.06 m, an equation developed by Krenkel and Orlob (1962, cited in Bowie et al. 1985) from flume data is used:

$$KReaer = \frac{234 \cdot (U \cdot Slope)^{0.408}}{H^{0.66}} \qquad \textbf{(197)}$$

where:

U	=	velocity (converted to fps);
Slope	=	longitudinal channel slope (m/m); and
H	=	water depth (converted to ft).

If reaeration due to wind exceeds that due to current velocity, the equation for standing water is used. Reaeration is set to 0 if ice cover is expected (i.e., when the depth-averaged temperature < 3deg. C).

Figure 114. Reaeration as a Function of Wind
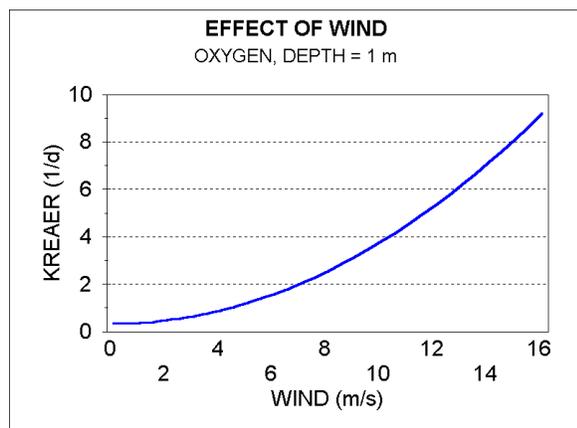
Figure 115. Reaeration in Streams
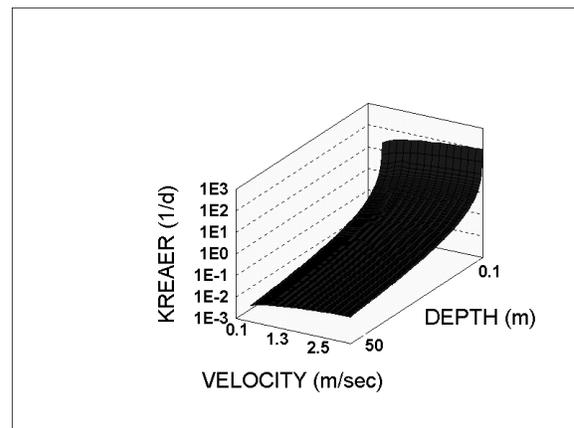
Reaeration is assumed to be representative of 20 deg. C, so it is adjusted for ambient water temperature using (Thomann and Mueller 1987):

$$KReaer_T = KReaer_{20} \cdot Theta^{(Temperature - 20)} \tag{198}$$

where:

$KReaer_T$ = Reaeration coefficient at ambient temperature (1/d);
$Kreaer_{20}$ = Reaeration coefficient for 20deg. C (1/d);
$Theta$ = temperature coefficient (1.024); and
$Temperature$ = ambient water temperature (deg. C).

In Release 3, oxygen saturation is calculated using the formulation of Thomann and Mueller (1987, p 277), see also APHA et al (1995). Oxygen saturation is calculated as a function of temperature (Figure 113), salinity (Figure 114), and altitude (Figure 118):

$$O2Sat = AltEffect \cdot \exp\left[\begin{array}{c} -139.3441 + \dfrac{1.57570E + 5}{TKelvin} - \dfrac{6.64231E + 7}{TKelvin^2} + \dfrac{1.2438E + 10}{TKelvin^3} \\ -\dfrac{8.62195E + 11}{TKelvin^4} - S\left(0.017674 - \dfrac{10.754}{TKelvin} + \dfrac{2140.7}{TKelvin^2}\right) \end{array}\right]$$

$$\tag{199}$$

where
$$AltEffect = \frac{100 - (0.0035 \cdot 3.28083 \cdot Altitude)}{100}$$

and where:

$AltEffect$ = Fractional reduction in oxygen saturation due to the effects of altitude (Thomann and Mueller 1987, from Zison et al. 1978);
$TKelvin$ = Kelvin temperature;
S = salinity driving variable, set to zero if not included in model (ppt); and
$Altitude$ = site specific altitude (m).

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Figure 116. Saturation as a Function of Temp.   **Figure 117.** Saturation as a Function of Salinity
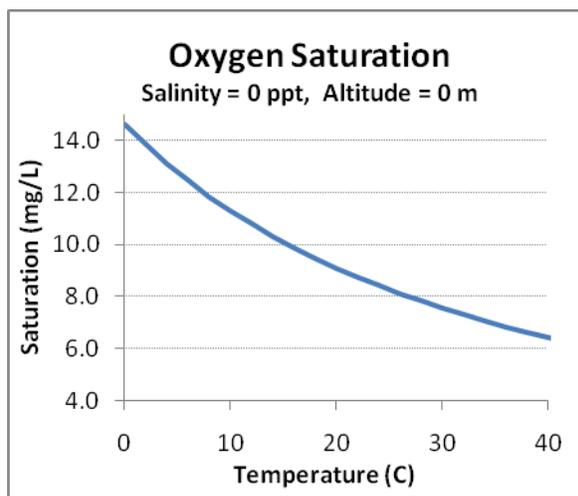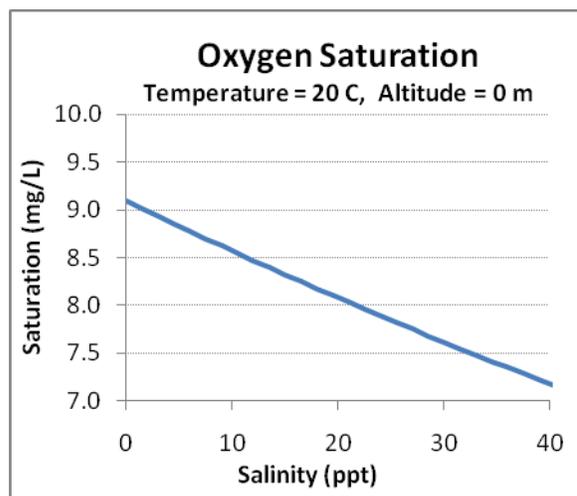
Figure 118. Saturation as a function of altitude
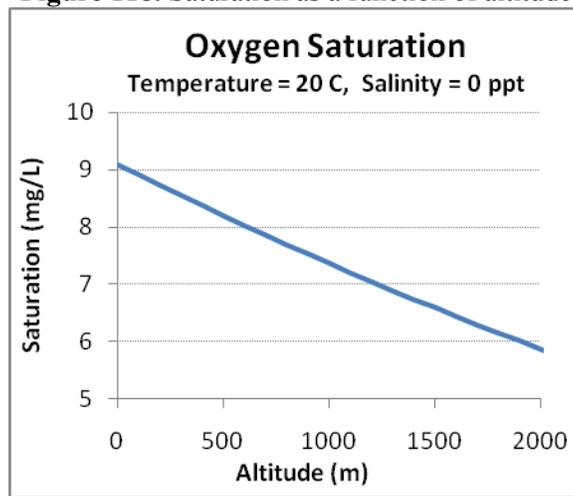
Diel Oxygen

Significant fluctuations in oxygen are possible over the course of each day, particularly under eutrophic conditions. This type of fluctuation may now be captured within AQUATOX when the model is run with an hourly time-step. If the model is run with a larger reporting time step (but an hourly integration time-step) the minimum and maximum oxygen concentrations will be output on the basis of the hourly results.

The instantaneous light climate **(28)** affects the photosynthesis within the system and this, in turn, affects the amount of oxygen released into the water column **(187)**. To assist in this simulation, hourly oxygen loadings may be input into AQUATOX if such data are available. Alternatively, the effects of oxygen loadings and washout may be turned off, assuming that upstream processes governing oxygen are producing water concentrations identical to the current stream segment being modeled; in this way, in-stream processes can be analyzed without being dominated by upstream loadings.

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AQUATOX can also output minimum and maximum predicted oxygen levels if the "data storage stepsize" is greater than the "simulation step size." In other words if a simulation is set up with an hourly step size but results are integrated daily, AQUATOX will plot the mininum and maximum hourly prediction during that day.

Lethal Effects due to Low Oxygen

AQUATOX represents both lethal and non-lethal effects from low concentrations of dissolved oxygen. The US EPA saltwater criteria document suggests the following general model for estimating time to mortality based on data from two species of saltwater juvenile fish, one species of juvenile freshwater fish, and three species of saltwater larval crustaceans (U.S. Environmental Protection Agency, 2000, Equation 9):

$$LC_{Time} = Slope_{\frac{conc.}{exptime}} \cdot \ln(LC_{24hours}) + Intercept_{\frac{conc.}{exptime}} \tag{200}$$

where:

$$LC_{Time} = \text{Lethal Concentration for a given percentage of a population over the given duration (mg/L);}$$

$$Slope_{\frac{conc.}{exptime}} = 0.191 \cdot LC_{24hours} + 0.064 \tag{201}$$

and

$$Intercept_{\frac{conc.}{exptime}} = 0.392 \cdot LC_{24hours} + 0.204 \tag{202}$$

To produce a general model of low oxygen effects, concentrations at which different percentages are killed (holding duration constant) also need to be related to one another. That is to say, a model that relates LC5 to LC50 to LC95 must be produced. Examining available data (Figure 119 to Figure 121), a linear model seems appropriate

$$LCFrac_{duration} = Slope_{\frac{conc.}{pctkilled}} \cdot LCKnown_{duration} + Intercept_{\frac{conc.}{pctkilled}} \tag{203}$$

where:

$$LCFrac_{duration} \quad = \quad \text{concentration at which given percentage of organisms are killed estimated from a known lethal concentration (holding duration}$$

constant).

$LCKnown_{duration}$ =   known lethal concentration for a given percentage of organisms at the given duration.

Further examination of available data indicates different slopes for different species (Figure 122). Most important, however, is that for all species, the range of slopes is quite narrow, ranging from -0.001 to -0.01. This indicates that for all species and all durations, the range at which mortality occurs due to insufficient oxygen is quite narrow. For this reason, the intermediate value of -0.007 was chosen as it is likely to reproduce available data reasonably well. This is preferable to having a user input this slope as these data are unlikely to be available to most users. Given a known lethal concentration at a known duration and using this slope, the Intercept can be calculated see (204).

Figure 119. Menhaden percent killed vs. O_2 exposure concentration
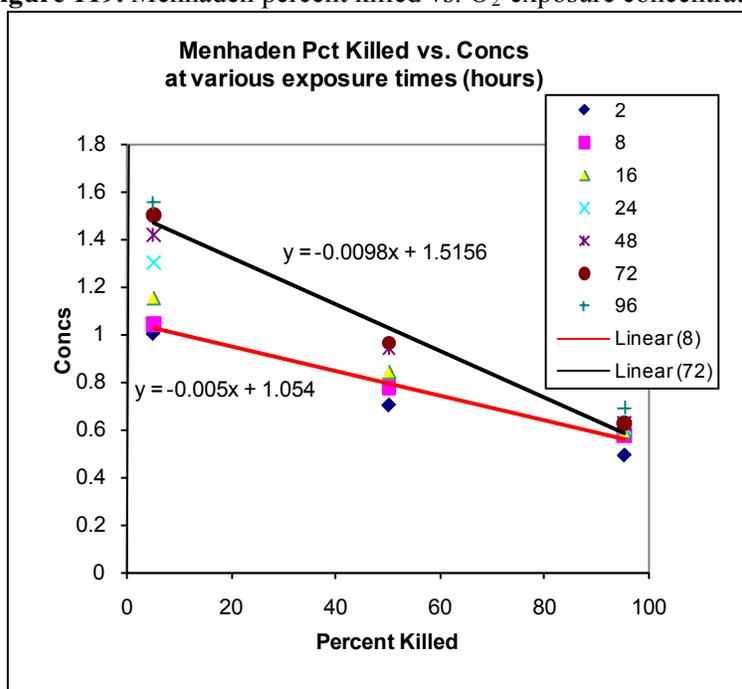
Figure 120. Blue Crab percent killed vs. O$_2$ exposure concentration
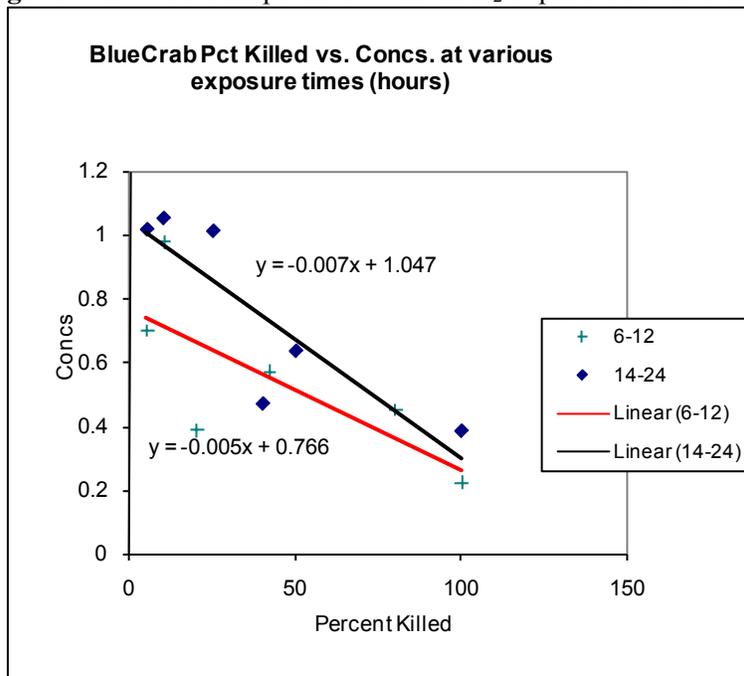
Figure 121. Spot percent killed vs. O$_2$ exposure concentration
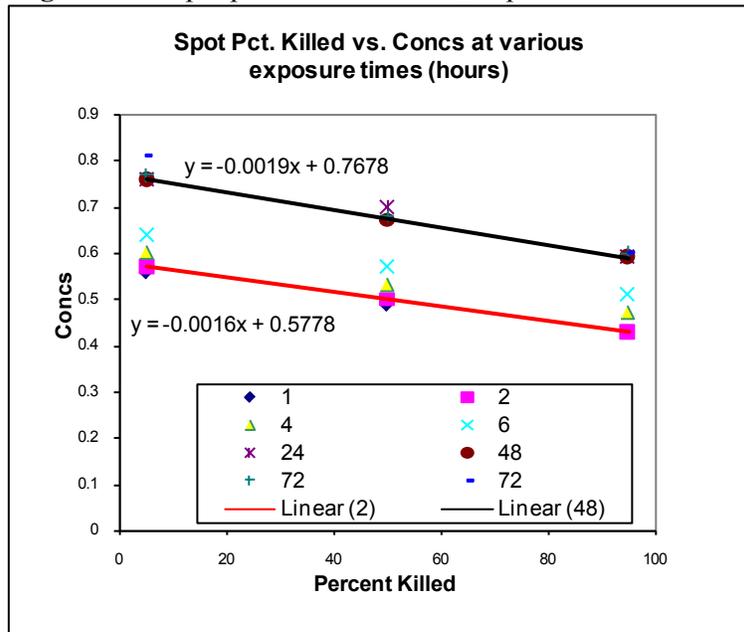
Figure 122. Slope vs. species type
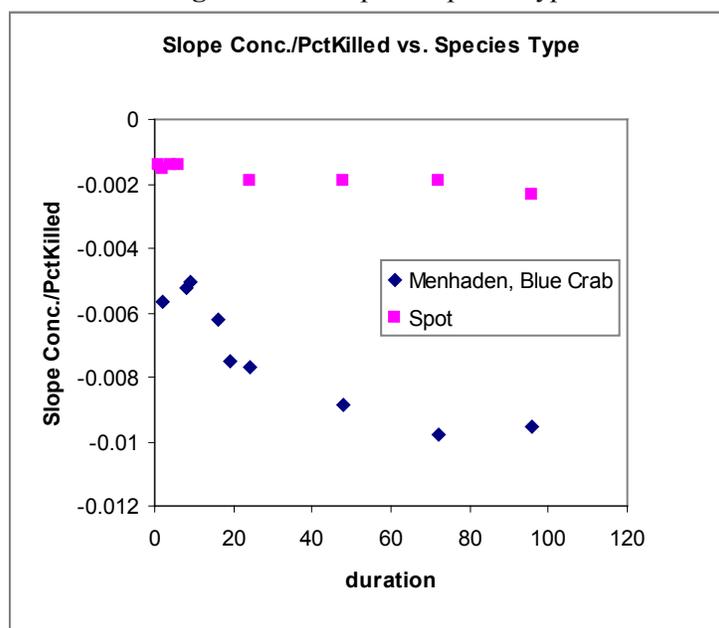
Combining equations **(199)** to **(202)**, given a user input 24-hour lethal concentration (in the "Animal underlying data" screen), the model can calculate the fraction killed at a given duration and at a given concentration.

$$PctKilled = \frac{\left(\dfrac{O_2Conc - 0.204 + 0.064 \cdot \ln(ExpTime)}{0.191 \cdot \ln(ExpTime) + 0.392}\right) - Intercept_{\frac{conc.}{pctkilled}}}{-0.007} \qquad \textbf{(204)}$$

where:

$$Intercept_{\frac{conc.}{pctkilled}} = LCKnown_{duration} + 0.007 \cdot PctKilled_{Known} \qquad \textbf{(205)}$$

and:

$PctKilled$	=	estimated percent killed at a given oxygen concentration and exposure time;
O_2Conc	=	concentration of oxygen (mg/L);
$ExpTime$	=	exposure time (hours);
$LCKnown_{duration}$	=	user input lethal concentration (24-hour) (mg/L);
$PctKilled_{Known}$	=	user input percentage for lethal concentration (percentage);

The model presented in equation **(203)** requires a user to input 24-hour lethal concentration as

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this is the basis for the general model presented in the saltwater criteria document. If a user has a lethal concentration at a different duration, the user must estimate the 24-hour lethal concentration, bearing in mind that the relationship between exposure time and lethal concentrations is usually logarithmic in nature (Figure 123). There are insufficient data to develop a general model that will estimate 24-hour lethal concentrations given different user input durations.

AQUATOX tracks oxygen concentrations over the previous 96 hours from the current time-step. The oxygen effects model is then applied with the durations shown below:

- 1 hour, 4 hours, 12 hours *(when model is run with hourly time-step only)*
- 1 day, 2 days, 4 days *(relevant to both hourly and daily time-steps)*

AQUATOX finds the minimum oxygen concentration over each of these time-periods and applies it to equation **(203)**. The maximum percent killed over all of the durations tested is then applied to the animal biomass by increasing mortality (equations **(90)** and **(112)**) .

Figure 124 shows an example of a three-dimensional response surface produced by this model. This is a model of low oxygen lethality for Atlantic menhaden produced by entering a 24-hour LC95 of 0.61 mg/L. Figure 125 shows model predictions using a 24 hour LC50 of 3 mg/L overlaid on a figure from the U.S. Environmental Protection Agency's 1986 *Quality Criteria for Water.* This plot shows that the default value of 3 mg/L works well for many species, but for white bass, for example, the LC50 should be set to a lower concentration.

Figure 123. LC50 to exposure time based on data from U.S. EPA 2000
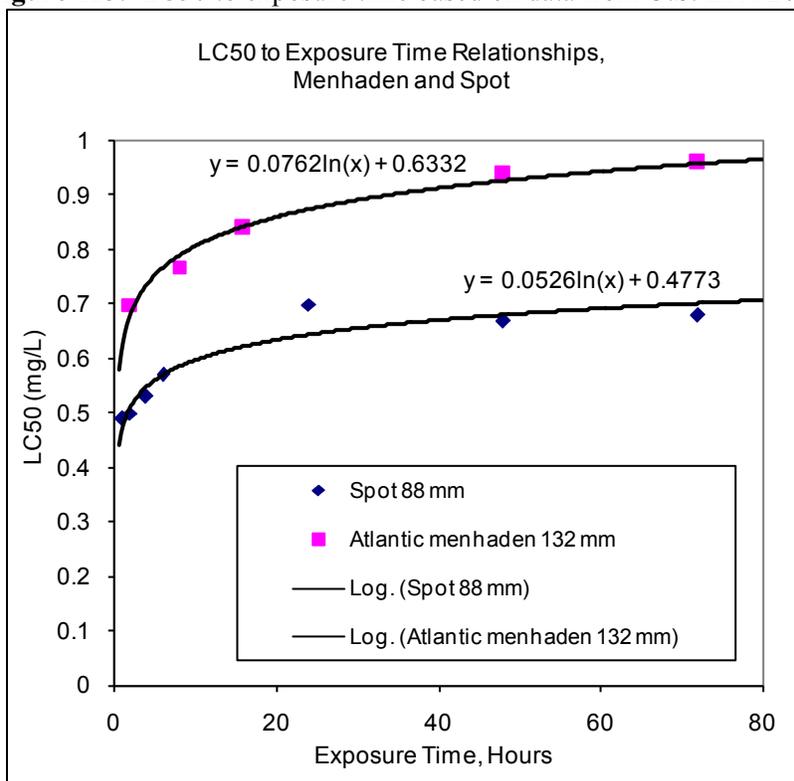
Figure 124. Example of low O_2 lethality model- menhaden response surface
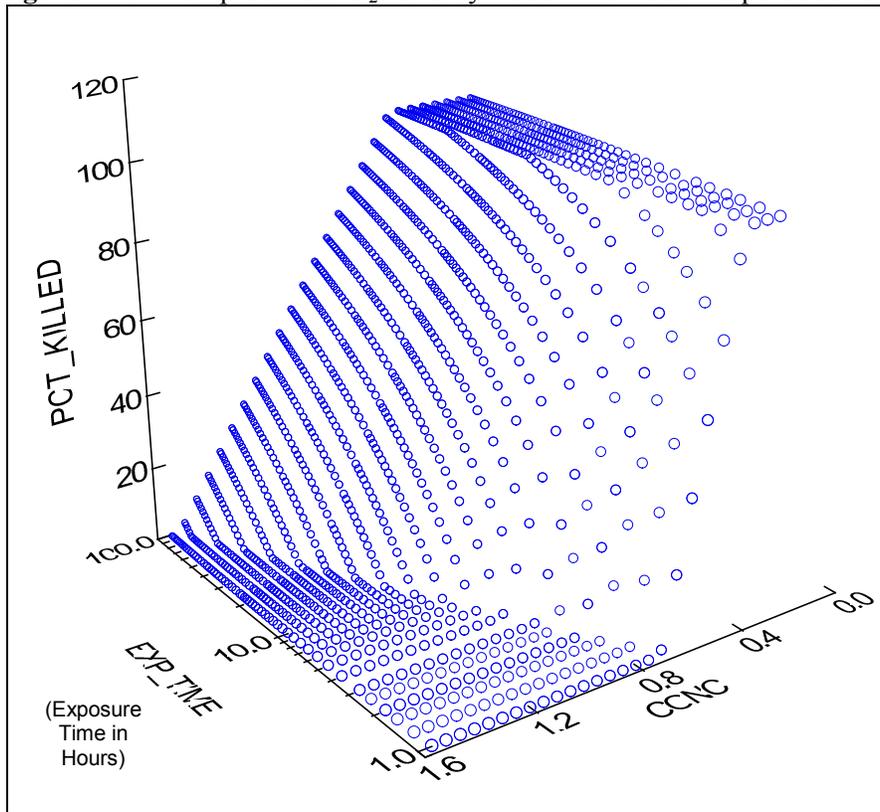
Figure 125. 96-hour model predictions (in red) compared against continuous exposure data (Data from U.S. EPA 1986, model set up using a 24-hour LC50 of 3.0mg/L)
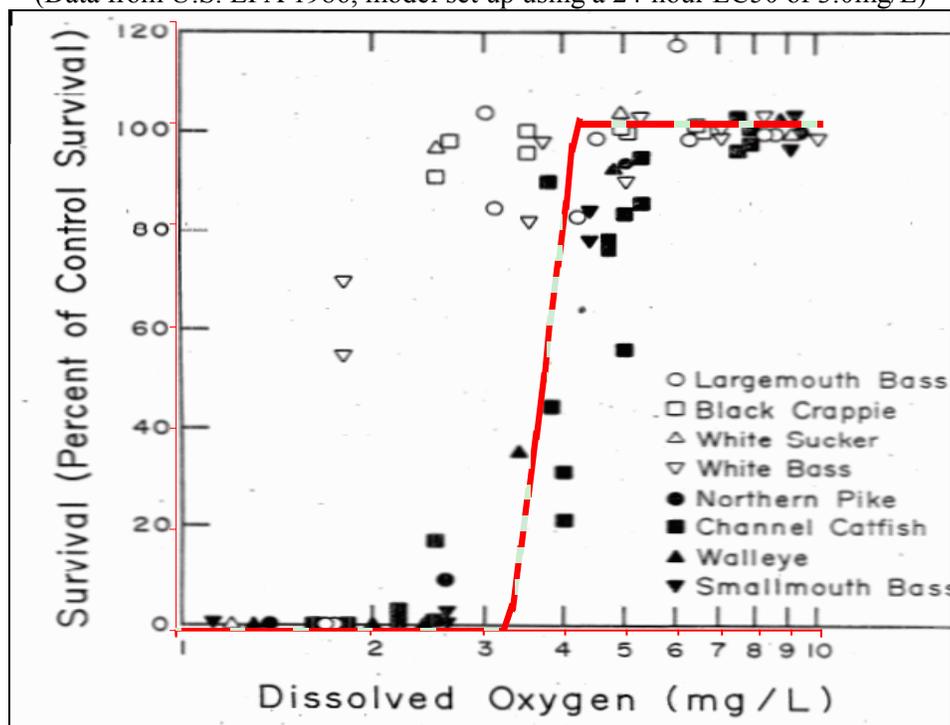
Non-Lethal Effects due to Low Oxygen

The same three dimensional model used for lethal effects is utilized to calculate non-lethal low oxygen effects (functions of exposure level and time.)   In this case, *EC50 reproduction* affects the fraction of gametes that are lost and *EC50 growth* affects consumption rates.

$$O2EffectFrac = \frac{\left(\dfrac{O_2Conc - 0.204 + 0.064 \cdot \ln(ExpTime)}{0.191 \cdot \ln(ExpTime) + 0.392}\right) - Intercept_{\frac{conc.}{pctkilled}}}{-0.007} \qquad \textbf{(206)}$$

and:

$$Intercept_{\frac{conc.}{pctkilled}} = EC50_{duration} + 0.007 \cdot 50 \qquad \textbf{(207)}$$

where:

O2EffectFrac	=	calculated fraction of gametes lost or reduction in growth rate at a given oxygen concentration and exposure time;
O₂Conc	=	concentration of oxygen (mg/L);

ExpTime   =   exposure time (hours);
EC50$_{duration}$ =   user input 50% effect concentration (24-hour) (mg/L);

O2EffectFrac is then applied to ingestion (91) and gamete loss (126).

5.6 Inorganic Carbon

Many models ignore carbon dioxide as an ecosystem component (Bowie et al., 1985). However, it can be an important limiting nutrient. Similar to other nutrients, it is produced by decomposition and is assimilated by plants; it also is respired by organisms:

> **Carbon Dioxide: Simplifying Assumptions**
>
> - Atmospheric exchange is treated similar to that for oxygen.
> - For saltwater systems, an alternative option is to import a time-series of equilibrium CO_2 levels.

$$\frac{dCO2}{dt} = Loading + Respired + Decompose - Assimilation - Washout$$
$$+ Washin \pm CO2AtmosExch \pm TurbDiff \pm Diffusion_{Seg} \tag{208}$$

where:

$$Respired = CO2Biomass \cdot \Sigma_{Organism}(Respiration_{Organism}) \tag{209}$$

$$Assimilation = \Sigma_{Plant}(Photosynthesis_{Plant} \cdot UptakeCO2) \tag{210}$$

$$Decompose = CO2Biomass \cdot \Sigma_{Detritus}(Decomp_{Detritus}) \tag{211}$$

and where:

dCO2/dt	=	change in concentration of carbon dioxide (g/m^3·d);
Loading	=	loading of carbon dioxide from inflow (g/m^3·d);
Respired	=	carbon dioxide produced by respiration (g/m^3·d);
Decompose	=	carbon dioxide derived from decomposition (g/m^3·d);
Assimilation	=	assimilation of carbon dioxide by plants (g/m^3·d);
Washout	=	loss due to being carried downstream (g/m^3·d), see **(16)**;
Washin	=	loadings from linked upstream segments (g/m^3·d), see **(30)**;
Diffusion$_{Se}$	=	gain or loss due to diffusive transport over the feedback link between two segments, (g/m^3·d), see **(32)**;
CO2AtmosExch	=	interchange of carbon dioxide with atmosphere (g/m3·d);
CO2Biomass	=	ratio of carbon dioxide to organic matter (unitless);
Respiration	=	rate of respiration (g/m^3·d), see **(63)** and **(100)**;
Decomposition	=	rate of decomposition (g/m^3·d), see **(159)**;
Photosynthesis	=	rate of photosynthesis (g/m^3·d), see **(35)**; and
UptakeCO2	=	ratio of carbon dioxide to photosynthate (= 0.53).

Carbon dioxide also is exchanged with the atmosphere; this process is important, but is not instantaneous: significant undersaturation and oversaturation are possible (Stumm and Morgan, 1996). The treatment of atmospheric exchange is similar to that for oxygen:

$$CO2AtmosExch = KLiqCO2 \cdot (CO2Sat - CO2) \qquad \textbf{(212)}$$

In fact, the mass transfer coefficient is based on the well-established reaeration coefficient for oxygen, corrected for the difference in diffusivity of carbon dioxide as recommended by Schwarzenbach et al. (1993):

$$KLiqCO2 = KReaer \cdot \left(\frac{MolWtO_2}{MolWtCO_2} \right)^{0.25} \qquad \textbf{(213)}$$

where:

$CO2AtmosExch$	=	interchange of carbon dioxide with atmosphere (g/m³·d);
$KLiqCO2$	=	depth-averaged liquid-phase mass transfer coefficient (1/d);
CO_2	=	concentration of carbon dioxide (g/m³);
$CO2Equil$	=	equilibrium concentration of carbon dioxide (g/m³), see **(213)**;
$KReaer$	=	depth-averaged reaeration coefficient for oxygen (1/d), see **(191)**-**(195)**;
$MolWtO2$	=	molecular weight of oxygen (=32); and
$MolWtCO2$	=	molecular weight of carbon dioxide (= 44).

Keying the mass-transfer coefficient for carbon dioxide to the reaeration coefficient for oxygen is very powerful in that the effects of wind (Figure 123) and the velocity and depth of streams can be represented, using the oxygen equations (Equations **(191)-(195)**).

Figure 126. Carbon dioxide mass transfer
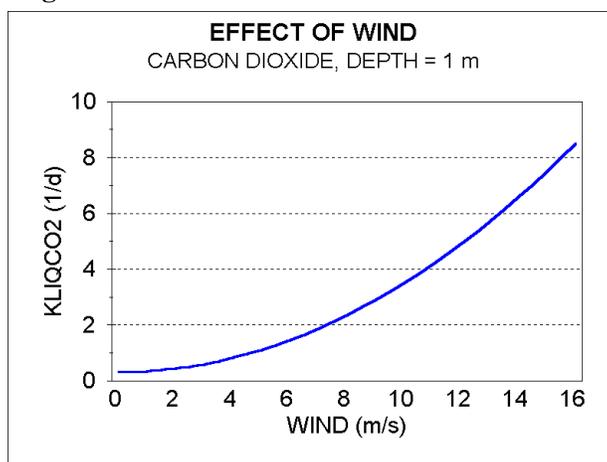
Based on this approach, the predicted mass transfer under still conditions is 0.92, compared to the observed value of 0.89 ± 0.03 (Lyman et al., 1982). This same approach is used, with minor modifications, to predict the volatilization of other chemicals (see Section 8.5). Computation of equilibrium of carbon dioxide is based on the method in Bowie et al. (1985; see also Chapra and

Reckhow, 1983) using Henry's law constant, with its temperature dependency (Figure 124), and the partial pressure of carbon dioxide:

$$CO2Equil = CO2Henry \cdot pCO2 \qquad\qquad (214)$$

where:

$$CO2Henry = MCO2 \cdot 10^{\frac{2385.73}{TKelvin} - 14.0184 + 0.0152642 \bullet TKelvin} \qquad (215)$$

$$TKelvin = 273.15 + Temperature \qquad\qquad (216)$$

and where:

CO2Equil	=	equilibrium concentration of carbon dioxide (g/m^3);
CO2Henry	=	Henry's law constant for carbon dioxide (g/m^3-atm):
pCO2	=	atmospheric partial pressure of carbon dioxide (= 0.00035);
MCO2	=	mg carbon dioxide per mole (= 44000);
TKelvin	=	temperature in deg.K, and
Temperature	=	ambient water temperature (deg. C).

Figure 127. Saturation of carbon dioxide
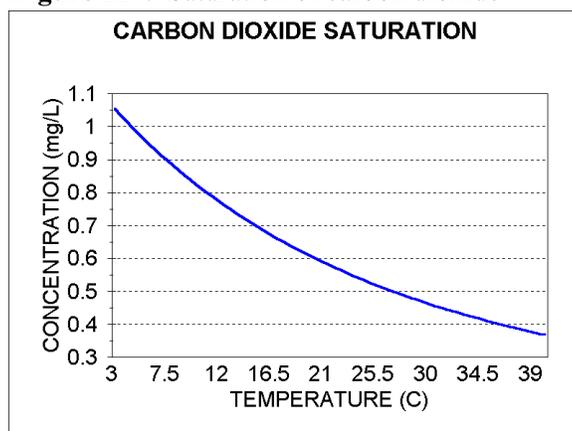
The equilibrium CO_2 equations described above cannot be applied to a seawater system as the chemistry in seawater is significantly different from freshwater. Over the years, several models and constants used to describe the dissociation of carbon dioxide in seawater have been proposed by investigators.

For saline conditions, the equilibrium parameters of the CO_2 system can be derived by using CO2SYS (Yuan, 2006) or CO2calc (USGS, 2010) and the results used as inputs for *CO2Equil* in the AQUATOX simulation. Within these models, the user needs to provide two of the five measurable CO_2 system parameters: Total alkalinity (TA), Total carbon dioxide (TCO2), pH and Partial pressure of carbon dioxide (pCO2) or fugacity of carbon dioxide (fCO2); along with temperature (T), pressure (P) and salinity (S). The user can then select appropriate constants

from proposed literature values and the program will calculate the remaining carbonate system parameters including a time-series of CO_2 concentrations in water.

For maximum flexibility, AQUATOX has an interface that will accept these time-series of *CO2Equil*. In this manner, the user can select the most appropriate model for their site and import these values into the AQUATOX interface. A time-series of pH can also be estimated by these ocean-water chemistry models.

5.7 Modeling Dynamic pH

Dynamic pH is important in simulations for several reasons:

<div style="float:right; border:1px solid #000; padding:8px;">

Dynamic pH: Simplifying Assumptions

- Simple semi-empirical formulation
- Computation is good for the pH range of 3.75 to 8.25

</div>

- o pH affects the ionization of ammonia and potential resulting toxicity;
- o pH affects the hydrolysis and ionization of organic chemicals which potentially has effects on chemical fate and the degree of toxicity;
- o pH also affects the decay of organic matter and denitrification of nitrate which could eventually feed back to the animals;
- o if pH exceeds 7.5, calcite precipitation can take place which has a significant effect on the food-web.

A user-input time-series of pH levels may be used to drive the model or AQUATOX can calculate pH levels.

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 3.75 to 8.25, where the carbonate ion is negligible and can thus be ignored. (Any predictions above 8.25 are truncated to 8.25 and any predictions below 3.75 are set to 3.75.) 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:

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

(217)

where:

pHCalc	=	pH;
ArcSinH	=	inverse hyperbolic sine function;
Alkalinity	=	mean Gran alkalinity (μeq CaCO$_3$/L);
DOC	=	refractory dissolved organic carbon (mg/L); sum of **(143)**, **(144)**;
5.1	=	average μeq of organic ions per mg of *DOC;*

$$A = -Log\sqrt{Alpha}$$

$$B = 1/\ln(10)$$

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

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

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

where:

H2CO3*	=	first acidity constant;
CCO2	=	CO$_2$ expressed as μeq/L; see **(207)** multiplied by conversion factor of 22.73 (ueq/mg);
pkw	=	ionization constant for water (1e-14);
T	=	temperature (ºC); see **(24)**;
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 128). 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 128. Comparison of predicted and observed pHs from selected lakes.
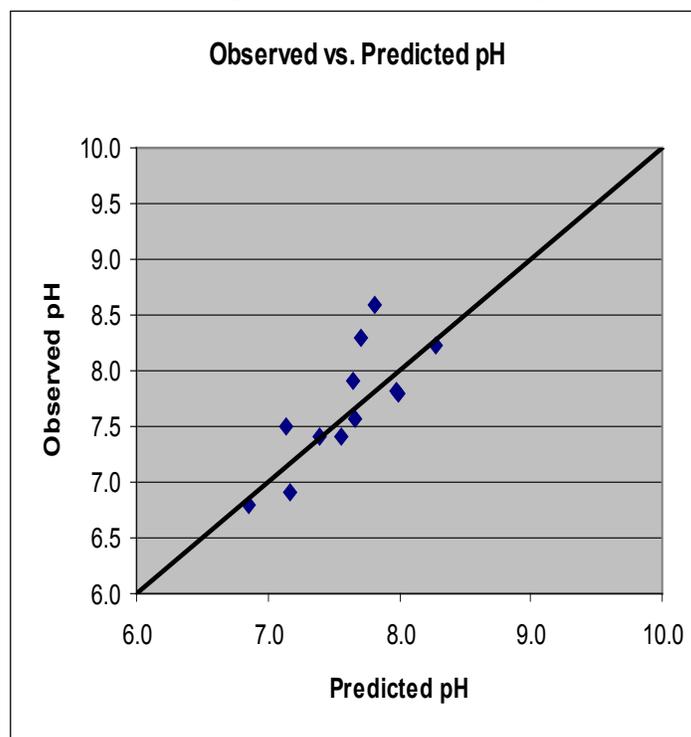
The construct also was verified using time-series data from Lake Onondaga, NY (Figure 129). The observed data were interpolated from the 2-m depth pH isopleths on a graph (Effler et al. 1996), introducing some uncertainty into the comparison.

Figure 129. Comparison of predicted and observed pH values for Lake Onondaga, NY. Data from (Effler et al. 1996).
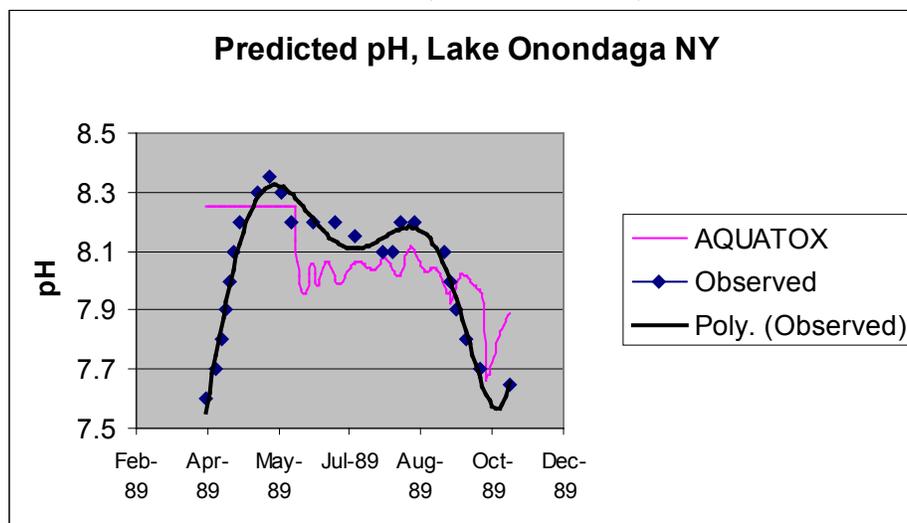
5.8 Modeling Calcium Carbonate Precipitation and Effects

Precipitation of calcium carbonate (mostly calcite in freshwater), with the potential for sorption and removal of phosphorus, is modeled as an extension of the pH approach. The prediction of pH in AQUATOX does not extend past 8.25 because the carbonate-bicarbonate system becomes dominant. We use a predicted pH of 7.5 as a threshold for precipitation of calcium carbonate in freshwater ecosystems.   Almost all calcite is formed

> **Calcite Precipitation: Simplifying Assumptions**
> - Biogenic origin
> - pH of 7.5 is considered as a threshold for precipitation
> - Dissolved phosphate sorbs to calcium carbonate but desorption is not modeled

biogenically, primarily by plants using bicarbonate as a source of carbon (McConnaughey et al. 1994). Even "whitings" (sudden precipitation of fine-grained calcite) have been shown to be a consequence of cyanobacteria photosynthesis (Thompson et al. 1997). Calcareous plants are characterized by pH polarization with acidic and alkaline poles; calcification occurs at the alkaline pole (McConnaughey et al. 1994). Proton generation leads to formation of twice as much CO_2 than is used in the process, providing CO_2 that is immediately taken up for photosynthesis. As a result, calcification and photosynthesis use equivalent moles of C, as shown by both theory and experiments (McConnaughey et al. 1994). Three chemical reactions represent this process:

$$Ca^{2+} + CO_2 + H_2O \rightarrow CaCO_3 + 2H^+$$
$$2H^+ + 2HCO_3^- \rightarrow 2CO_2 + 2H_2O$$
$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

Not all plants can use bicarbonate. However, it is difficult to generalize; mosses do not and many chrysophytes (golden algae) do not.   Evidence suggests that other groups, including greens, cyanobacteria, diatoms, and macrophytes, have species that do use bicarbonate and that these will dominate in alkaline systems.

The algorithm simulates precipitation of calcite as being the molar equivalent to photosynthesis of most plants and as occurring when the threshold pH of 7.5 is reached:

$$If \ pH \ >= \ 7.5 \ then \quad CalcitePcpt = C2Calcite \cdot \frac{Photosynthesis_{PlantSubset}}{C2OM} \qquad \textbf{(218)}$$

where:

pH	=	pH calculated by Eq. 204 or observed time series;
CalcitePcpt	=	calcite precipitated (mg calcite/L · d);
C2Calcite	=	stoichiometric constant for C and calcite (8.33, g calcite /g C);
Photosynthesis	=	rate of photosynthesis for a subset of plants (g/m^3 · d);
PlantSubset	=	all plants except Bryophytes and Other Algae;
C2OM	=	stoichiometric constant for C and organic matter (1.9, g C/g OM).

Precipitated calcite is protected, in part, by sorbed organic material. Therefore, it is assumed to be insoluble—an assumption also made in the sediment diagenesis model (Di Toro 2001). Because the settling rate is fast, it is also assumed that the calcite goes directly to the sediment.

Phosphorus is adsorbed to the surface and coprecipitates with calcium carbonate (Wetzel 2001). The rate of coprecipitation seems to be dependent on the rate of calcite precipitation (Otsuki and Wetzel 1972).   However, the sorption is weak and can be reversed easily (Murphy et al. 1983). Therefore, the default partition coefficient (300 L/kg) is based on equilibration experiments with sediments from a marl lake (Van Rees et al. 1991).

$$SorptionP \quad = \quad KDPCalcite \cdot Phosphate \cdot CalcitePcpt \cdot 1e - 6 \qquad \textbf{(219)}$$

where:

SorptionP	=	rate of sorption of phosphorus to calcite (mgP/L · d);
KDPCalcite	=	partition coefficient for phosphorus to calcite (L/kg);
Phosphate	=	concentration of phosphorus in water (mg P/L) (see **(181))**;
1 e-6	=	conversion factor (kg/mg).

Ironically, precipitation is impeded by phosphorus levels that are too high. The threshold for inhibition is about 30 mg-P/L (Neal 2001). Furthermore, dissolved organic matter also can inhibit precipitation, with 120 mg C/L being the threshold (Neal 2001). However, these concentrations are so high that they are ignored in the model.

6. INORGANIC SEDIMENTS

Inorganic sediments can have significant effects on light climate and inorganic sediment effects on biota can also be explicitly modeled (see the section on suspended sediment effects starting on page 119). Release 3 of AQUATOX contains four levels of inorganic sediment submodels:

- a very simple model based on a regression relationship between sediment deposition and total suspended sediments, see **(122)**. This approach should be used when the only inorganic sediment data available are TSS. Add the "TSS" state variable to use this option.

- a simple inorganic sediments submodel described in Section 6.1. This model can be used to estimate the scour and deposition of inorganic sediments at a site as a function of water flows; therefore it is only applicable to streams and rivers. This model requires additional data about the types of inorganic sediments (i.e., sand, silt, or clay) and their average rate of scour and deposition under different water-flow regimes. This model may be selected under the sediment menu by choosing "Add Sand Silt Clay Model."

- a complex multiple-layer sediment submodel described in Section 6.2. This model can be used to estimate the sequestration of organic toxicants within the deeper layers of the sediments and the potential for scour of such toxicants from these deep layers. This submodel should be linked to a hydrodynamic model to calculate the scour and deposition of sediments in the modeled segment. This model may be selected under the sediment menu by choosing "Add Multi-Layer Sediment." Additional layers may also be added or removed using the options listed under the sediment menu.

- a sediment diagenesis model described in Section 7. This model provides a more sophisticated accounting of the decay of organic matter and remineralization in an anaerobic sediment bed and the effects on sediment oxygen demand. The diagenesis model assumes a depositional environment; scour of sediments is not incorporated. This model may be selected under the sediment menu by choosing "Add Sediment Diagenesis."

Within an AQUATOX simulation it is also possible to ignore the effects of inorganic sediments on ecosystem characteristics altogether, by including none of the models listed above. However, the model will always track the remineralization of organic material within the sediment bed and the water column.

6.1 Sand Silt Clay Model

The original version was contributed by Rodolfo Camacho of Abt Associates Inc. AQUATOX simulates scour, deposition and transport of sediments and calculates the concentration of sediments in the water column and sediment bed within a river reach. For running waters, the sediment is divided into three categories according to the particle size:

- sand, with particle sizes between 0.062 to 2.0 millimeters (mm),

> **Sand, Silt, Clay: Simplifying Assumptions**
>
> - River reach is short and well-mixed
> - Channel is rectangular
> - Daily average flow regime determines scour, and deposition
> - Model for streams / rivers only

- silt (0.004 to 0.062 mm), and
- clay (0.00024 to 0.004 mm).

Wash load (primarily clay and silt) is deposited or eroded within the channel reach depending on the daily flow regime. Sand transport is also computed within the channel reach. The river reach is assumed to be short and well mixed so that concentration does not vary longitudinally. Flow routing is not performed within the river reach. The daily average flow regime determines the amount of scour, deposition and transport of sediment. Scour, deposition and transport quantities are also limited by the amount of solids available in the bed sediments and the water column.

Within the bed, the mass of sediment in each of the three sediment size classes is a function of the mass in the previous time step, and the mass of sediment in the overlying water column lost through deposition, and gained through scour:

$$MassBed_{Sed} = MassBed_{Sed,t=-1} + (Deposit_{Sed} - Scour_{Sed}) \cdot Volume_{Water} \cdot TimeStep \qquad \textbf{(220)}$$

where:

$MassBed_{Sed}$	=	mass of sediment in channel bed (kg);
$MassBed_{Sed, t = -1}$	=	mass of sediment in channel bed on previous day (kg);
$Deposit_{Sed}$	=	amount of suspended sediment deposited (kg/m^3 d); see **(230)**;
$Scour_{Sed}$	=	amount of silt or clay resuspended (kg/m^3 d); see **(227)**;
$Volume_{Water}$	=	volume of stream reach (m^3); see **(2)**; and
$TimeStep$	=	derivative time-step (d).

The volumes of the respective sediment size classes are calculated as:

$$Volume_{Sed} = \frac{MassBed_{Sed}}{Rho_{Sed}} \qquad \textbf{(221)}$$

where:

$Volume_{Sed}$	=	volume of given sediment size class (m^3);
$MassBed_{Sed}$	=	mass of the given sediment size class (kg);
Rho_{Sed}	=	density of given sediment size class (kg/m^3);
Rho_{Sand}	=	2600 (kg/m^3); and
$Rho_{Silt, Clay}$	=	2400 (kg/m^3).

The porosity of the bed is calculated as the volume weighted average of the porosity of its components:

$$BedPorosity = \sum Frac_{Sed} \cdot Porosity_{Sed} \qquad \textbf{(222)}$$

where:

$BedPorosity$	=	porosity of the bed (fraction);
$Frac_{Sed}$	=	fraction of the bed that is composed of given sediment class; and
$Porosity_{Sed}$	=	porosity of given sediment class (fraction).

The total volume of the bed is calculated as:

$$BedVolume = \frac{Volume_{Sand} + Volume_{Silt} + Volume_{Clay}}{1 - BedPorosity}$$ **(223)**

where:

$BedVolume$ =   Volume of the bed   (m^3).

The depth of the bed is calculated as

$$BedDepth = \frac{BedVolume}{ChannelLength \cdot ChannelWidth}$$ **(224)**

where:

$BedDepth$	=	depth of the sediment bed (m);
$ChannelLength$	=	length of the channel (m); and
$ChannelWidth$	=	width of the channel (m).

The concentrations of silt and clay suspended in the water column are computed similarly to the mass of those sediments in the bed, with the addition of loadings from upstream and losses downstream:

$$Conc_{Sed} = \frac{KgLoad_{Sed}}{Q \cdot 86400} + Conc_{Sed, t = -1} + Scour_{Sed} - Deposit_{Sed} - Wash_{Sed}$$ **(225)**

where:

$Conc_{Sed}$	=	concentration of silt or clay in water column (kg/m^3);
$Conc_{Sed, t = -1}$	=	concentration of silt or clay on previous day (kg/m^3);
$KgLoad_{Sed}$	=	loading of clay or silt (kg/d);
Q	=	flow rate (m^3/s);
86400	=	conversion from m^3/s to m^3/d;
$Scour_{Sed}$	=	amount of silt or clay resuspended (kg/m^3); see **(227)**;
$Deposit_{Sed}$	=	amount of suspended sediment deposited (kg/m^3); see **(230)**; and
$Wash_{Sed}$	=	amount of sediment lost through downstream transport (kg/m^3); see **(231)**.

The concentration of sand is computed using a totally different approach, which is described in the section on Sand below.

Deposition and Scour of Silt and Clay

Relationships for scour and deposition of cohesive sediments (silts and clays) used in AQUATOX are the same as the ones used by the Hydrologic Simulation Program in Fortran (HSPF, U.S. Environmental Protection Agency, 1991). Deposition and scour of silts and clay are modeled using the relationships for deposition (Krone, 1962) and scour (Partheniades, 1965) as summarized by Partheniades (1971).

Shear stress is computed as (Bicknell et al., 1992):

$$Tau = H2ODensity \cdot Slope \cdot HRadius \tag{226}$$

where:

Tau	=	shear stress (kg/m^2);
H2ODensity	=	density of water (1000 kg/m^3);
Slope	=	slope of channel (m/m);

and hydraulic radius (*HRadius*) is (Colby and McIntire, 1978):

$$HRadius = \frac{Y \cdot Width}{2 \cdot Y + Width} \tag{227}$$

where:

HRadius	=	hydraulic radius (m);
Y	=	average depth over reach (m); and
Width	=	channel width (m).

Resuspension or scour of bed sediments is predicted to occur when the computed shear stress is greater than the critical shear stress for scour:

$$\text{if } Tau > TauScour_{Sed} \text{ then}$$
$$Scour_{Sed} = \frac{Erodibility_{Sed}}{Y} \cdot \left(\frac{Tau}{TauScour_{Sed}} - 1 \right) \tag{228}$$

where:

Scour$_{Sed}$	=	resuspension of silt or clay (kg/m^3 d);
Erodibility$_{Sed}$	=	erodibility coefficient (0.244 kg/m^2 d); and
TauScour$_{Sed}$	=	critical shear stress for scour of silt or clay (kg/m^2).

The amount of sediment that is resuspended is constrained by the mass of sediments stored in the bed. An intermediate variable representing the maximum potential mass that can be scoured is calculated; if the mass available is less than the potential, then scour is set to the lower amount:

$$Check_{Sed} = Scour_{Sed} \cdot Volume_{Water} \tag{229}$$

$$\text{if } Mass_{Sed} \leq Check_{Sed} \text{ then}$$
$$Scour_{Sed} = \frac{Mass_{Sed}}{Volume_{Water}} \tag{230}$$

where:

Check$_{Sed}$	=	maximum potential mass (kg); and

$Mass_{Sed}$ =   mass of silt or clay in bed (kg).

Deposition occurs when the computed shear stress is less than the critical depositional shear stress:

$$if\ Tau < TauDep_{Sed}\ then$$

$$Deposit_{Sed} = Conc_{Sed} \cdot \left(1 - e^{\frac{-VT_{Sed} \cdot SecPerDay}{Y} \cdot \left(1 - \frac{Tau}{TauDep_{Sed}} \right)} \right) \tag{231}$$

where:

$Deposit_{Sed}$ =   amount of sediment deposited (kg/m^3 day);
$TauDep_{Sed}$ =   critical depositional shear stress (kg/m^2);
$Conc_{Sed}$ =   concentration of suspended silt or clay (kg/m^3);
VT_{Sed} =   terminal fall velocity of given sediment type (m/s); and
$SecPerDay$ =   86400 (seconds / day).

The terminal fall velocity is specified in the site's underlying data.

Downstream transport is an important mechanism for loss of suspended sediment from a given stream reach:

$$Wash_{Sed} = \frac{Disch \cdot Conc_{Sed}}{SegVolume} \tag{232}$$

where:

$Wash_{Sed}$ =   amount of given sediment lost to downstream transport (kg/m^3 day);
$Disch$ =   discharge of water from the segment (m^3/day);
$Conc_{Sed}$ =   concentration of suspended sediment (kg/m^3);
$SegVolume$ =   volume of segment (m^3).

When the inorganic sediment model is included in an AQUATOX stream simulation, the deposition and erosion of detritus mimics the deposition and erosion of silt. The fraction of detritus that is being scoured or deposited is assumed to equal the fraction of silt that is being scoured or deposited. The following equations are used to calculate the scour and deposition of detritus:

$$Frac\ Scour_{Detritus} = Frac\ Scour_{Silt} = Scour_{Silt} \cdot \frac{Volume_{Silt}}{Mass_{Silt}} \tag{233}$$

$$Scour_{Detritus} = Frac\ Scour_{Detritus} \cdot Conc_{AllSedDetritus} \cdot 1000 \tag{234}$$

where:

$FracScour$ =   fraction of scour per day (fraction/day);
$Scour_{Silt}$ =   amount of silt scoured (kg/m^3 day) see **(227)**;
$Volume_{Silt}$ =   volume of silt initially in the bed (m^3);

$Mass_{Silt}$ = mass of silt initially in the bed (kg);

$Conc_{AllSedDetritus}$ = all sedimented detritus (labile and refractory) in the stream bed (kg/m^3);

$Scour_{Detritus}$ = amount of detritus scoured (g/m^3 day); and

1000 = conversion of kg to g.

The equations for deposition of detritus are similar:

$$Frac\ Deposition_{Detritus} = Frac\ Deposition_{Silt} = \frac{Deposition_{Silt} \cdot 1000}{Conc_{Silt}} \tag{235}$$

$$Deposition_{Detritus} = Frac\ Deposition_{Detritus} \cdot Conc_{SuspDetritus} \tag{236}$$

where:

$Deposition_{Silt}$ = amount of silt deposited (kg/m^3 day) see **(230)**;

$Conc_{Silt}$ = amount of silt initially in the water (g/m^3);

$FracDeposition$ = fraction of deposition per day (frac / day); and

$Conc_{SuspDetritus}$ = amount of suspended detritus initially in the water (g/m^3); and

$Deposition_{Detritus}$ = amount of detritus deposited (g/m^3 day).

Scour, Deposition and Transport of Sand

Scour, deposition and transport of sand are simulated using the Engelund and Hansen (1967) sediment transport relationships as presented by Brownlie (1981). This relationship was selected because of its simplicity and accuracy. Brownlie (1981) shows that this relationship gives good results when compared to 13 others using a field and laboratory data set of about 7,000 records.

$$PotConc_{Sand} = 0.05 \cdot \frac{Rho}{Rho_{Sand} - Rho} \cdot \frac{Velocity \cdot Slope}{\sqrt{\frac{Rho_{Sand} - Rho}{Rho} \cdot g \cdot D_{Sand}/1000}} \cdot \sqrt{TauStar} \tag{237}$$

where:

$PotConc_{Sand}$ = potential concentration of suspended sand (kg/m^3);

Rho = density of water (1000 kg/m3)

Rho_{Sand} = density of sand (2650 kg/m^3);

$Velocity$ = flow velocity (converted to m/s);

$Slope$ = slope of stream (m/m);

D_{Sand} = mean diameter of sand particle (0.30 mm converted to m); and

$TauStar$ = dimensionless shear stress.

The dimensionless shear stress is calculated by:

$$TauStar = \frac{Rho}{Rho_{Sand} - Rho} \cdot HRadius \cdot \frac{Slope}{D_{Sand}/1000} \tag{238}$$

where:

$HRadius$　　=　　hydraulic radius (m).

Once the potential concentration has been determined for the given flow rate and channel characteristics, it is compared with the present concentration. If the potential concentration is greater, the difference is considered to be made available through scour, up to the limit of the bed. If the potential concentration is less than what is in suspension, the difference is considered to be deposited:

$$Check_{Sand} = PotConc_{Sand} \cdot Volume_{Water} \qquad \textbf{(239)}$$

$$MassSusp_{Sand} = Conc_{Sand} \cdot Volume_{Water} \qquad \textbf{(240)}$$

$$TotalMass_{Sand} = MassSusp_{Sand} + MassBed_{Sand} \qquad \textbf{(241)}$$

$$\text{if } Check_{Sand} \leq MassSusp_{Sand} \text{ then}$$

$$Deposit_{Sand} = MassSusp_{Sand} - Check_{Sand} \qquad \textbf{(242)}$$

$$Conc_{Sand} = PotConc_{Sand}$$

$$\text{if } Check_{Sand} \geq TotalMass_{Sand} \text{ then}$$

$$MassBed_{Sand} = 0 \qquad \textbf{(243)}$$

$$Conc_{Sand} = \frac{TotalMass_{Sand}}{Volume_{Water}}$$

$$\text{if } Check_{Sand} > MassSusp_{Sand} \text{ and } < TotalMass_{Sand} \text{ then}$$

$$Scour_{Sand} = Check_{Sand} - MassSusp_{Sand} \qquad \textbf{(244)}$$

$$Conc_{Sand} = \frac{MassSusp_{Sand} + Scour_{Sand}}{Volume_{Water}}$$

Suspended Inorganic Sediments in Standing Water

At present, AQUATOX does not compute settling of inorganic sediments in standing water or scour as a function of wave action. However, suspended sediments are important in creating turbidity and limiting light, especially in reservoirs and shallow lakes. Therefore, the user can provide loadings of total suspended solids (TSS), and the model will back-calculate suspended inorganic sediment concentrations by subtracting the simulated phytoplankton and suspended detritus concentrations:

$$InorgSed = TSS - \sum Phyto - \sum PartDetr \qquad \textbf{(245)}$$

where:

InorgSed	=	concentration of suspended inorganic sediments (g/m^3);
TSS	=	observed concentration of total suspended solids (g/m^3);
Phyto	=	predicted phytoplankton concentrations (g/m^3); and
PartDetr	=	predicted suspended detritus concentrations (g/m^3).

A radio button on the TSS loadings screen is used to specify whether user-input TSS loadings are "total suspended (inorganic) sediments" or "total suspended solids." If "inorganic sediments" are specified then equation **(244)** is not required as the TSS loading is not assumed to include phytoplankton or organic matter.

6.2 Multi-Layer Sediment Model

As an alternative to the simple sand-silt-clay model described above (section 6.1), AQUATOX also includes a complex multiple layer sediment transport model. This model can simulate up to ten bottom layers of sediment. Within each sediment layer, the state variables consist of inorganic solids, pore waters, labile and refractory dissolved organic matter in pore waters, and sedimented detritus. Nutrient concentrations are not modeled in the pore waters of the sediment layers, although dissolved organic matter is. Each of these state variables can also have up to twenty organic toxicant concentrations associated with it. The AQUATOX sediment transport component is summarized in Figure 130.

> **Multi-Layer Sediment Model: Simplifying Assumptions**
>
> - Top layer is "active layer" that interacts with the water column
> - Individual sediment layers are well-mixed
> - Density of each sediment layer remains constant
> - Hardpan barrier assumed at the bottom of the system

Figure 130: Components of the AQUATOX sediment transport model and units.
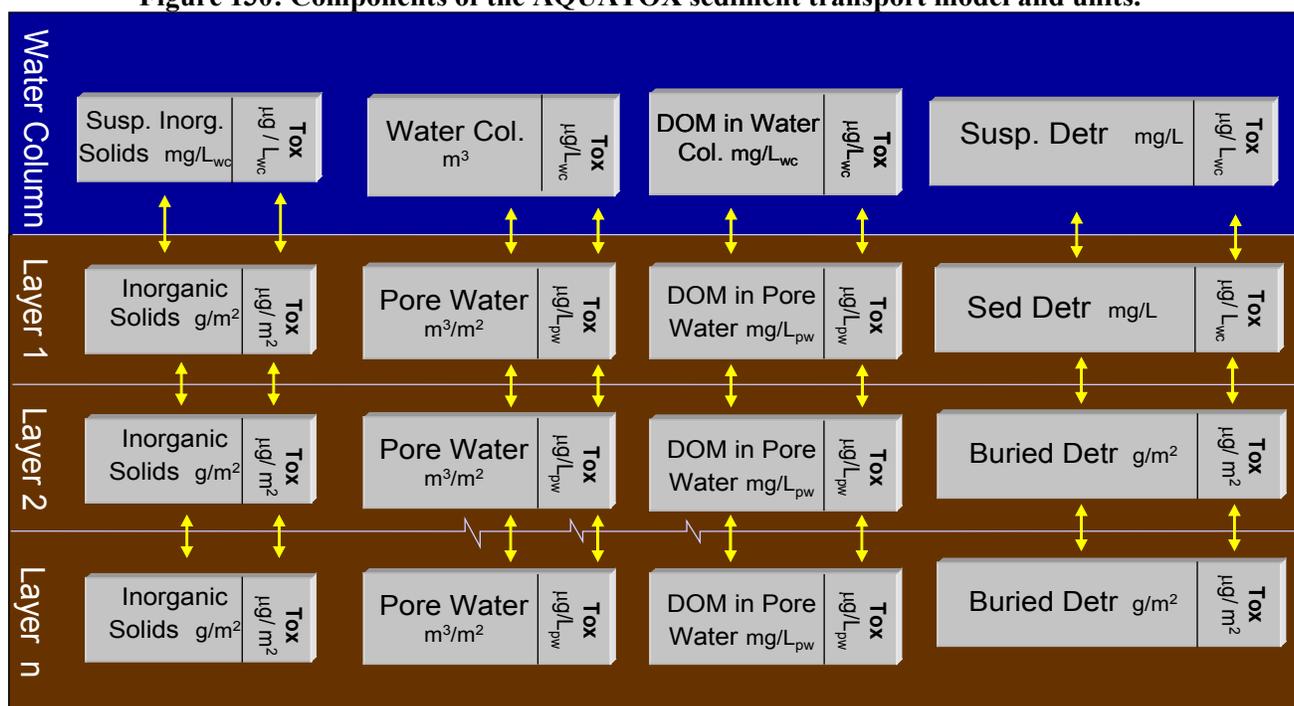
The AQUATOX sediment submodel was designed to be nearly identical in concept to IPX (In-Place Pollutant eXport) version 2.7.4 (Velleux et. al 2000). Erosion and deposition cause changes in the mass of sediments in the top or "active" layer. When the active layer becomes too large or too small, a conveyor-belt action takes place moving all of the layers up or down intact ("pez dispenser" action). Because all layers are assumed well-mixed, moving partial layers up and down and then recalculating concentrations within sediment layers would result in too much mixing throughout the sediment layers (and advection of pollutants from the bottom layer to the top). During development, the AQUATOX sediment submodel was closely tested against the IPX model and precisely reproduced results from that model.

Within AQUATOX, inorganic sediments in layered sediments are represented as three distinct state variables: cohesives (clay), non-cohesives (silt), and non-cohesives2 (sand). These correspond to the variables described in Section 6.1.

For each inorganic compartment, the sediment transport model accepts daily input parameters for interactions between the top sediment layer and the water column. These interactions are input as daily scour and daily deposition for each inorganic sediment type in units of grams per day. The model also requires deposition and erosion velocities for cohesive inorganic sediments. These inputs are then used to calculate the deposition and erosion of organic matter within the system.

AQUATOX assumes that the density of each sediment layer will remain constant throughout a simulation. Because of this, the volume and thickness of the top bed layer will vary in response to deposition and erosion. Additionally, the surface area of the multi-layer sediment bed is set to remain constant. Even if the sediment surface at a site grows or shrinks due to water volume changes, this model tracks sediments under the initial-condition surface area.

When the top layer has reached a maximum thickness, it is broken into two layers. Other layers in the system are moved down one layer without disturbing their concentrations or thicknesses. This allows the model to maintain a toxicant concentration gradient within the sediment layers during depositional regimes. Similarly, when the top layer has eroded to a minimum size, the layer beneath it is joined with the active layer to form a new top layer. In this case, lower layers are moved up one level, without changing their concentrations, densities, or thicknesses. More details about these processes can be found in section on sediment layer interactions below.

At the bottom of the system, a hardpan barrier is assumed. The model, therefore, has no interaction beneath its lowest layer. If enough erosion takes place so that this hardpan barrier is exposed, no further erosion will be possible. Deposition can, however, rebuild the sediment layer system. This hardpan bottom prevents the artificial inclusion of "clean" sediment and organic matter into the model's simulation during erosional events.   Because it is a barrier and not a boundary, it prevents loss of toxicant to the system under depositional regimes.

AQUATOX writes output data for a fixed number of sediment layers. When, due to deposition, a layer is buried below the fixed number of sediment layers, AQUATOX keeps track of that layer, but does not write daily output. That deep layer is stored in memory and state variables in that layer have the potential to move back into the system later due to erosion. When, due to erosion, there are fewer than the fixed number of sediment layers, AQUATOX writes zeros for all layers below the hardpan barrier.

Pore water moves up and down through the sediment system when layers move upward and downward in the system. Substances dissolved in pore water also move through the system as a result of diffusion.

Suspended Inorganic Sediments

As mentioned above, inorganic sediments are broken into three sets of state variables based on particle size. Each of these three inorganic sediment types are found in the water column as well as in each modeled sediment layer.

For inorganic sediments suspended in the water column, the derivative looks as follows:

$$\frac{dSuspSediment}{dt} = Loading + Scour - Deposition - Washout + Washin \qquad \textbf{(246)}$$

where:

dSuspSediment/dt	=	change in concentration of suspended sediment (g/m^3·d);
Loading	=	inflow loadings (excluding upstream segments) (g/m^3·d);
Scour	=	scour from the active sediment layer (g/m^3·d);
Deposition	=	deposition to the active sediment layer (g/m^3·d);
Washout	=	loss due to being carried downstream (g/m^3·d), see **(16)**;
Washin	=	loadings from upstream segments (g/m^3·d), see **(30)**;

There are two options for specifying deposition to and scour from the active layer when using the multi-layer sediment option. Deposition and scour can be simulated by a hydrodynamic model and imported into AQUATOX. In this case, for each of the three categories of suspended sediment, deposition to and scour from the active layer are input to AQUATOX as a daily time series in units of g/d. These inputs are converted into units of g/m3·d by dividing by the volume of the segment.

Alternatively, based on user specification, the model can calculate deposition and scour using the sand-silt-clay model specifications, see **(230)**, **(227)**. In the "Edit Sediment Layer Data" dialog, where cohesives or non-cohesives are being input there is a checkbox that states "use sand-silt-clay model" to toggle between these two options.

Unlike the simple sediment model, suspended sediments can sorb organic toxicants when the multi-layer sediment model is run. More specifications about sorption of organic chemicals to inorganic sediments can be found in Section 8.10 of this document.

Inorganics in the Sediment Bed

Inorganic sediments are found in each sediment layer that is modeled. The derivative, however is relevant only for the active (top) layer.

$$\frac{dBottomSediment}{dt} = Deposition - Scour + Bedload - Bedloss \qquad \textbf{(247)}$$

where:

dBottomSediment/dt	=	change in concentration of sediment in this bed layer (g/m^2·d);
Scour	=	movement to the water column (g/m^2·d);
Deposition	=	deposition from the water column (g/m^2·d);
Bedload	=	bedload from all upstream segments (g/m^2·d). Only relevant for the active layer of sediment, see **(247)**;
Bedloss	=	loss due to bedload to all downstream segments (g/m^2·d). Only relevant for the active layer of sediment, see **(248)**.

Deposition and scour are input into the model in units of g/d. These inputs are divided by the area of the system to get units of g/m2·d.

Bed load is input as a loading in g/d for each link between two segments, if multiple segments are being modeled. This process is only relevant for the top layer of sediment modeled. The total bed load for a particular segment can be calculated by summing the loadings over all incoming links.

$$BedLoad = \sum \frac{BedLoad_{Upstreamlink}}{AvgArea} \qquad \textbf{(248)}$$

where:

BedLoad	=	total bedload from all upstream segments (g/m^2·d);
BedLoad$_{Upstreamlink}$	=	bedload over one of the upstream links (g/d);
AvgArea	=	average area of the segment (m^2);

Similarly, total bed loss is the sum of the loadings over all outgoing links:

$$BedLoss = \sum \frac{BedLoss_{Upstreamlink}}{AvgArea} \qquad \textbf{(249)}$$

BedLoss	=	total bedloss to all downstream segments (g/m^2·d);
BedLoss$_{Downstreamlink}$	=	bedload over one of the downstream links (g/d);
AvgArea	=	average area of the segment (m^2);

As mentioned above, the derivative presented is relevant only for the active layer. Inorganic sediments below the active layer do move up and down through the system as a result of exposure or deposition. However, these sediments move as a part of their entire intact layer when the active layer has reached its maximum or minimum level.

When the top layer reaches a minimum thickness, the layer below the active layer is added to the active layer to form one new layer. The inorganic sediments within these two layers do undergo mixing during this process.

Detritus in the Sediment Bed

State variables tracking sedimented labile and refractory detritus are also included in each layer of sediment that is simulated. The equations for sedimented detritus in the active layer are the same as those for "classic" AQUATOX.

Like inorganic sediments, buried detritus below the active layer only moves up and down in the system when its layer moves up and down intact. Therefore, detritus found below the active layer has a very simple derivative:

$$\frac{dBuriedDetritus}{dt} = -Decomp \tag{250}$$

where:

$dBuriedDetritus/dt$	=	change in concentration of sediment on bottom (g/m^2·d);
$Decomp$	=	microbial decomposition in (g/m^2·d) see **(159)**.

Pore Waters in the Sediment Bed

Pore water quantities are also tracked in the sediment bed. The derivative for pore waters is quite straightforward:

$$\frac{dPoreWater}{dt} = Gain_{Up} - Loss_{Up} \tag{251}$$

where:

$dPoreWater/dt$	=	change in volume of pore water in the sediment bed normalized per unit area (m^3/m^2 ·d);
$GainUp$	=	gain of pore water from the water column above (m^3/m^2 ·d);
$LossUp$	=	loss of pore water to the water column above (m^3/m^2 ·d);

In the active layer, pore waters are assumed to move into the water column when scour occurs. To keep the bed density constant, the loss of pore waters can be solved as follows:

$$Loss_{Up} = \sum_{Sediments} \frac{(Erode_{Sed} Density_{Sed}) - (Erode_{Sed} / BedDensity)}{(1/BedDensity) - \ 1e-6} \tag{252}$$

where:

$Loss_{Up}$	=	loss of pore water to the water column above (cm^3/·d);
$Erode_{sed}$	=	scour of this sediment to the water column above, (g/d);
$Density_{sed}$	=	density of this sediment (g/m^3);
$BedDensity$	=	density of the active layer (g/m^3);

1e-6   =   one over the density of water (m^3/g);

Pore waters are taken from the water column when deposition occurs. Keeping the density constant, the gain of pore waters can be solved as follows:

$$Gain_{Up} = \sum_{Sediments} \frac{(Deposit_{Sed} Density_{Sed}) - (Deposit_{Sed} / BedDensity)}{(1/BedDensity) - 1e-6} \qquad (253)$$

where:

$Gain_{Up}$	=	gain of pore water from the water column above ($cm^3/\cdot d$);
$Deposit_{sed}$	=	deposit of this sediment from the water column, (g/d);
$Density_{sed}$	=	density of this sediment (g/m^3);
$BedDensity$	=	density of the active layer (g/m^3);
1e-6	=	one over the density of water (m^3/g);

When the active layer becomes too large it becomes split into two layers. During this split, the new second layer is assumed compressed to the density of the old second layer. This compression results in squeezing of pore water out into the water column. Details of this process can be found in the section on sediment layer interactions, below.

Dissolved Organic Matter within Pore Waters

Another state variable tracked within the sediment bed is dissolved organic matter within pore waters. Dissolved labile and refractory detritus within pore waters are tracked as separate state variables. Like other dissolved detritus, these variables use units of mg/L. However, it is important to note that these are liters of pore water and not liters in the water column.

$$\frac{dDOM_{PoreWater}}{dt} = GainDOM_{Up} - LossDOM_{Up} \pm Diff_{Down} \pm Diff_{Up} - Decomp \qquad (254)$$

where:

$dDOM_{PoreWater}/dt =$		change in concentration of DOM in pore water in the sediment bed normalized per unit area (mg/L$_{pw}$·d);
$GainDOM_{Up}$	=	active layer only: gain of DOM due to pore water gain from the water column (mg/L$_{pw}$·d);
$LossDOM_{Up}$	=	active layer only: loss of DOM due to pore water loss to the water column (mg/L$_{pw}$·d);
$Diff_{Up}, Diff_{Down}$	=	diffusion over upper or lower boundary (mg/L$_{pw}$·d), see **(256)**;
$Decomp$	=	microbial decomposition in (mg/L$_{pw}$·d), see **(159)**.

The increase of DOM due to pore water gain from the water column is simply the volume of

water that is moving from the water column above multiplied by the DOM concentration in the above sediment layer. However, the concentration then needs to be normalized for the volume of pore water in the current segment:

$$GainDOM_{Up} = ConcDOM_{n-1} \cdot GainPW_{Up} \left(\frac{AvgArea \cdot 1e3}{PoreWaterVol} \right)$$ **(255)**

where:

$GainDOM_{Up}$ = gain of DOM due to pore water gain from the layer above $(mg/L_{pw} \cdot d)$;

$ConcDOM_{n-1}$ = concentration of DOM in above layer $(mg/L_{upper\ water})$;

$GainPW_{up}$ = gain of pore water from above $(m^3_{upper\ water}/m^2 \cdot d)$;

$AvgArea$ = average area of the segment (m^2);

$1\ e\ 3$ = units conversion (L/m^3);

$PoreWaterVol$ = pore water volume (L);

The loss of DOM in pore water to the water column is a simpler equation due to the fact that there are no units conversions necessary:

$$LossDOM_{Up} = ConcDOM_n \left(\frac{LossPW_{Up}}{PoreWaterConc} \right)$$ **(256)**

where:

$LossDOM_{Up}$ = loss of DOM in pore water to the layer above $(mg/L_{pw} \cdot d)$;

$ConcDOM_n$ = concentration of DOM in this layer (mg/L_{pw});

$LossPW_{up}$ = loss of pore water to above layer $(m^3_{pw}/m^2 \cdot d)$;

$PoreWaterConc$ = pore water concentration (m^3_{pw}/m^2);

Because diffusion and decomposition of DOM in pore water occur throughout the system, not just the active layer, the above derivative is relevant for the whole system. DOM in pore water also moves up and down through a system when its layer moves intact due to erosion or deposition.

Diffusion within Pore Waters

AQUATOX calculates the diffusion of dissolved organic matter within pore waters in the sediment layers. This calculation requires that porosity be included in the diffusion equation:

$$Diffusion_{Up} = \frac{DiffCoeff \cdot Area \cdot AvgPor}{CharLength \cdot AvgPor} \left(\frac{Conc_{up}}{Porosity_{up}} - \frac{Conc_{down}}{Porosity_{down}} \right) \qquad (257)$$

where:

$Diffusion_{Up}$	=	gain of DOM due to diffusive transport over the upper boundary of the sediment layer, (g/d);
$DiffCoeff$	=	dispersion coefficient, (m^2 /d);
$Area$	=	interfacial area of the upper boundary of the sediment layer (m^2);
$AvgPor$	=	average porosity of the two layers. If the boundary is a sediment/water boundary, AvgPor is the porosity of the sediment. (fraction);
$CharLength$	=	characteristic mixing length, see text below, (m);
$Conc_{Layer}$	=	concentration of the relevant segment, (g/m^3);
$Porosity_{Layer}$	=	porosity of the relevant layer (fraction).

For the characteristic mixing length, AQUATOX uses the distance between two benthic segment midpoints. For pore water exchange with a surface water segment, the characteristic mixing length is taken to be the depth of the surficial benthic segment

Equation **(256)** is also used to calculate the diffusion of toxicants within pore waters. In this case, the units of Diffusion$_{Up}$ are mg/d rather than g/d and the concentrations of toxicants within the layers are in units of μg/L rather than mg/L.

Sediment Interactions

The mass of the top sediment layer increases and decreases as a result of deposition and scour. Because the density of this layer remains constant, the volume and thickness of the top sediment layer also increases and decreases. When the thickness of the top sediment layer reaches its maximum, as defined by the user, the upper bed is split horizontally into two layers. The top of these two layers maintains the same density it had before the layer was split up. It is assigned the initial condition depth of the active layer.

The lower level is assumed to be compressed to the same density as the level below it. This compression results in pore water being squeezed into the water column. The volume that is lost as a result of this compression can be solved as follows:

$$VolumeLost = \frac{BedMass_{Pr eCompress} - (Density_{Lower} \cdot BedVol_{Pr eCompress})}{1e6 - Density_{Lower}} \qquad (258)$$

where:

$VolumeLost$	=	volume of active layer lost due to compaction (m^3);
$BedMass_{PreCompress}$	=	mass of the new second layer before compression (g);
$BedVol_{PreCompress}$	=	volume of the new second layer before compression (m^3);
$Density_{lower}$	=	density of the layer below the active layer (g/m^3);
$1e6$	=	density of water (g/m^3)

The above equation also provides the quantity of pore water squeezed into the water column because the compression of the active layer is entirely the result of pore water being squeezed out. Toxicants, dissolved organic matter, and toxicants associated with dissolved organic matter in the pore water also move into the water column as a result of this compression. If there is only one layer in the system when the splitting of the active layer takes place, Densitylower is assumed to be the initial condition density of the second layer in the system.

The volume of a sediment layer is defined as follows:

$$BedVol_n = \frac{\sum SedMass}{BedDensity} \qquad (259)$$

where:

$BedVol_n$	=	volume of bed at layer n (m^3);
$SedMass$	=	mass of sediment type (g);
$BedDensity$	=	density of bed (g/m^3);

The porosity of a sediment layer is defined as:

$$FracWater_n = 1 - \sum_{SedTypes} \left(\frac{Conc_{Sed}}{Density_{Sed}} \right) \qquad (260)$$

where:

$FracWater_n$	=	porosity of the sediment layer (fraction);
$Conc_{sed}$	=	concentration of the sediment (g/m^3);
$Sedtypes$	=	all organic and inorganic sediments
$Density_{sed}$	=	density of the sediment (g/m^3);

When the thickness of the top sediment layer reaches a minimum, as defined by the user, the two top layers combine into one new active layer. The density of this new active layer is the weighted average of the densities of the combined layers.

$$NewBedDensity = \frac{Volume_{Layer2} \cdot Density_{Layer2} + Volume_{Layer1} \cdot Density_{Layer1}}{Volume_{Layer2} + Volume_{Layer1}} \qquad (261)$$

where:

$NewBedDensity$	=	density of new joined bed (g/m^3);
$Volume_{LayerN}$	=	volume of layer that was initially layer 1 or 2 (m^3)
$Density_{LayerN}$	=	density of layer that was initially layer 1 or 2 (g/m^3);

The height of the new layer is the sum of the heights of the two layers being joined.

The bottom of the system is composed of a hardpan barrier. When this bottom is exposed, no further erosion can take place. When deposition occurs on this hardpan bottom, it is rebuilt with the density of the layer that existed previously. If enough deposition occurs so that two layers are created, the new second layer is compressed to the density of the original second layer.

If a system starts with exposed hardpan as an initial condition, the user must still specify the density of the top layer so that AQUATOX knows what density to create the top layer with. If the user specifies a density for the second layer, this will be used when enough deposition occurs so that two layers are created.

7. SEDIMENT DIAGENESIS

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

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

Because AQUATOX simulates organic matter with stoichiometric ratios for nutrients and Di Toro's model simulates separate organic nutrients, the organic-nutrient

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

relationships are redefined for the sediments. The additional 21 state variables added when the sediment diagenesis model is enabled (and one driving variable) are as follows:

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

- **Biogenic Silica**: Silica in sediment is modeled using three state variables. Silica deposited from the water column is bioavailable or "biogenic silica" and is modeled in Layer 2. Biogenic silica can then either undergo deep burial or dissolution to dissolved silica.
- **Dissolved Silica:** two state variables (in Layers 1 and 2). Produced when biogenic silica breaks down due to dissolution. Available Silica in Layer 2 and Silica in Layers 1 & 2. Dissolved silica may undergo burial or flux to the water column.
- **COD**: Driving variable for chemical oxygen demand in the water column that affects the flux of sulfide to the water column.

Figure 131: Simplified schematic of the AQUATOX sediment diagenesis model
(Diagram does not include Silica, Sulfide or COD)
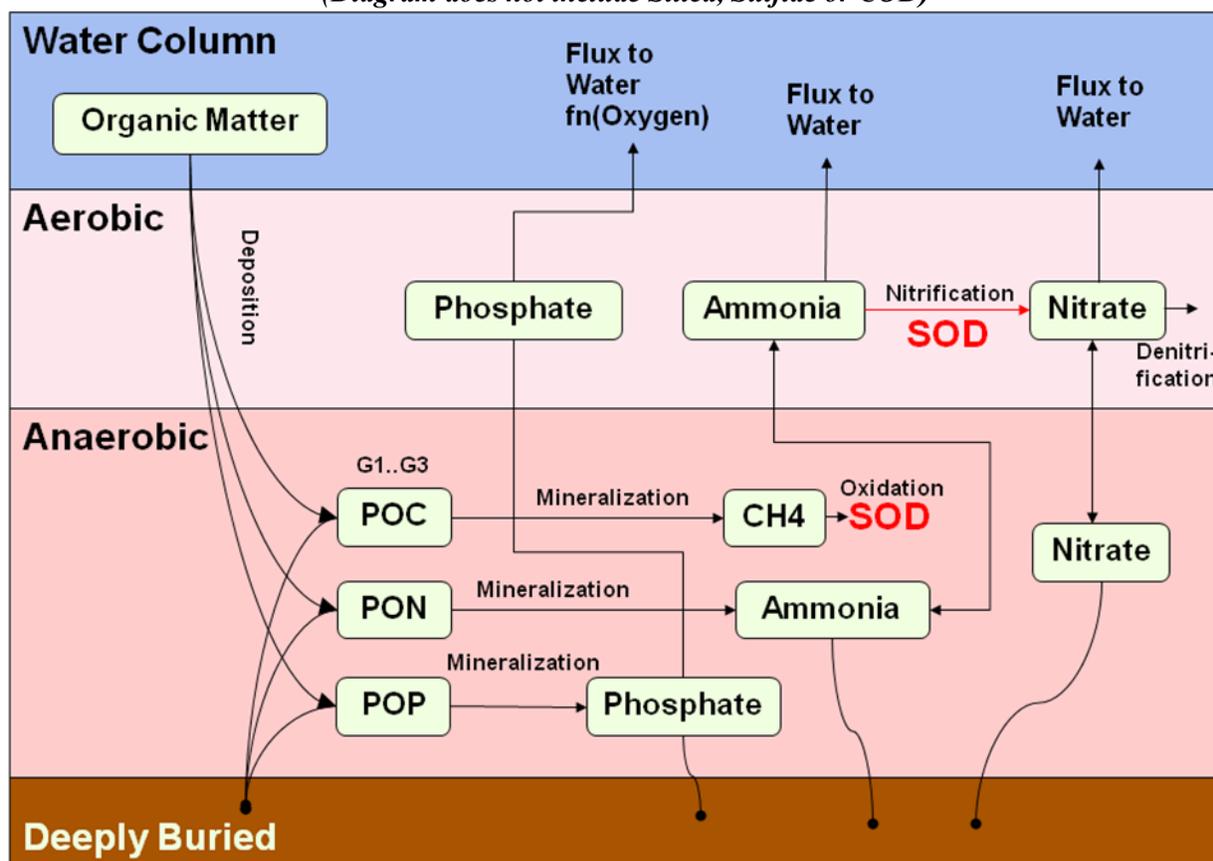
Particulate organic matter in the sediment bed (POC, PON, and POP) is divided into three reactivity classes as follows:

- G_1 – reactivity class 1, equivalent to labile organic matter
- G_2 – reactivity class 2, equivalent to refractory organic matter
- G_3 – reactivity class 3, nonreactive

Within the system of equations governing these state variables, sediment oxygen demand (SOD) is a function of specific chemical reactions following the decomposition of organic matter.

Specifically the oxidation of methane or sulfide and the nitrification of ammonia increases the predicted SOD . This in turn has effects on the amount of oxygen present in the water column. The amount of oxygen in the water column, however significantly affects the nitrification of ammonia **(275)**.

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

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

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

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

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

7.1 Sediment Fluxes

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

- Diffusion of the dissolved component of state variables to and from the water column;
- Diffusion of the dissolved component of the state variables between layers;
- Burial of the state variables below the lower layer and out of the modeled system; and

- Particulate mixing of the two layers and resultant exchange of state variable.

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

Diffusion Velocity Between Layers

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

$$KL = \frac{D_d \cdot \theta_{Dd}^{Temp \ -20}}{H_2}$$

(262)

KL	=	diffusion velocity between layers (m/d);
D_d	=	diffusion coefficient for pore water (m²/d);
θ_{Dd}	=	constant for temperature adjustment for D_d (unitless);
$Temp$	=	temperature of water (deg. C); and
H_2	=	depth of sediment layer 2 (m).

Particle Mixing Between Layers (Bioturbation)

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

$$\omega_{1,2} = \frac{10^{(Log(Benthic\_Biomass) \ - 2.778151 \ )} \cdot 1e\text{-}4}{H_2}$$

(263)

where:

$\omega_{1,2}$	=	particle mixing velocity between layers (m/d)
$Benthic\_Biomass$	=	sum of benthic invertebrate biomass (g/m² dry);
H_2	=	depth of sediment layer 2 (m); and
1e-4	=	pore water concentration (m²/cm²);

Figure 132: Relationship derived from Di Toro, 2001, Figure 13.1A
"Diffusion coefficient for particle mixing versus benthic biomass"
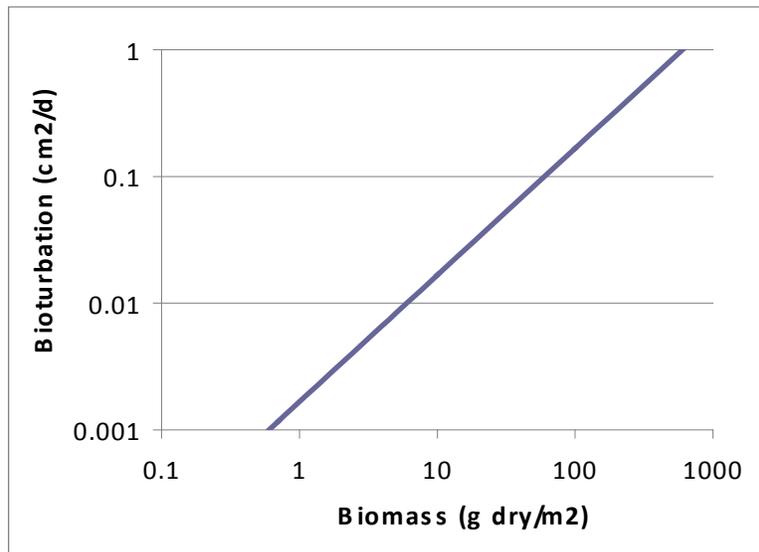
Additionally, the calculation of benthic biomass by AQUATOX includes benthic invertebrate mortality due to low oxygen conditions and recovery when oxygen concentrations rise. Because of this, Di Toro's benthic stress model incorporating accumulated stress and dissipation of stress is not required nor included within AQUATOX.

Surface Mass Transfer Coefficient

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

$$s = \frac{SOD}{Oxygen_{Water}}$$

(264)

$$SOD = CSOD + NSOD$$

where:

s	=	surface diffusive transfer (m/d)
SOD	=	sediment oxygen demand (g O_2 / m^2 d);
CSOD	=	carbon based sediment oxygen demand (g O_2 / m^2 d) see **(287)** or **(291)**;
NSOD	=	sediment oxygen demand due to nitrification (g O_2 / m^2 d) see **(275)**, converted into oxygen equivalent units (1.714 gO$_2$/gN);
$Oxygen_{Water}$	=	overlying water oxygen conc. (g O_2 / m^3) **(186)**.

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

7.2 POC

Particulate Organic Carbon in sediment is assumed to be located exclusively in the second layer of sediment. Three state variables are utilized to represent three reactivity classes (G_1 through G_3). POC is a component of the particulate organic matter that settles from the water column into the anaerobic layer and decomposes; it is also subject to consumption by detritivores. In this case, the POC uptake from that predation must be calculated separately from the POP and PON.

$$\frac{dPOC_{Sediment}}{dt} = Deposition - Mineralization - Burial - (Predation / Detr2OC) \qquad \textbf{(265)}$$

where:

$Deposition$ = deposition from water column (g C/ m^3 d) see **(266)**;
$Mineralization$ = decomposition (g C/ m^3 d) see **(267)** ;
$Burial$ = deep burial below modeled layer (g C/ m^3 d) see **(265)**;
$Predation$ = predation by detritivores (g C/ m^3 d) see **(99)**; and
$Detr2OC$ = detrital organic matter is assumed to be 1.90 • organic carbon as derived from stoichiometry (Winberg 1971).

For all state variables burial is solved as a function of the user input burial rate w_2:

$$Burial = POM \cdot \frac{w_2}{H_n} \qquad \textbf{(266)}$$

where:

$Burial$ = burial below modeled layer (g C/ m^3 d); and
POM = POP, POC, or PON (g C/ m^3);
w_2 = user input burial rate (m/d); and
H_n = depth of sediment layer n (m).

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

Deposition is solved as

$$Deposition_{POM\_Gi} = \left(\sum_{Animals} Def \cdot Def2POM_{Gi} + \sum_{Algae \& Detritus} Sed \cdot Sed2POM_{Gi} \right) \frac{vol_{water}}{vol_{sediment}} \qquad \textbf{(267)}$$

where:

$Deposition_{POM\_Gi}$ = deposition of G_i reactivity class of POP, POC, or PON from water column (g OM/ m^3 d);
Def = defecation of animals, see **(97)** (g OM/m^3$_{water}$ d);
$Def2POM_{Gi}$ = fraction of POP, POC, or PON reaction class G_i in defecated matter;

Sed	=	sedimentation of plants or detritus, see **(165)**, (g OM/m^3$_{water}$ d);
Sed2POM$_{Gi}$	=	fraction of POP, POC, or PON reaction class G_i in sedimented algae or detritus (unitless);
Vol$_{water}$	=	water volume (m^3); and
Vol$_{sediment}$	=	sediment volume (m^3);

Assigning fractions of defecation to the relevant POM class (i.e., determining *Def2POM$_{Gi}$*) is a two-part process. First, the fraction of POM, POC, or PON in the defecated material must be determined. Second, each fraction must be again multiplied by a fraction to assign it to the three reactivity classes (G_1 to G_3). In this manner, particulate organic matter is separated into nine different state variables in the sediment.

The fractions of POP and PON within defecated matter are assumed to equal the ratios of phosphate or nitrate to organic matter for sedimented labile detritus; these are editable parameters ("remineralization" screen). The fraction of POC within defecated matter is set to 52.6% (Winberg 1971). Defecated matter is split evenly between reactivity classes G_1 and G_2, with no defecation assigned to the non-reactive G_3 class (*Def2SedLabile*=0.5).

Similarly, assigning fractions of sedimentation to reactivity classes is a two-part process. As before, the fraction of POP and PON within sedimented matter is assumed equal to the ratio of phosphate or nitrate to organic matter for the given species or detritus (editable parameters). The fraction of POC within sedimented matter is again set to 52.6% (Winberg 1971). The amount of *refractory* detritus that is converted to reactivity class G_3 is a user entered parameter. The rest of the refractory detritus is assigned to G_2 and labile detritus becomes G_1. 92% of sinking plants are assumed to be labile (G_1) with no sinking algae being converted to the non-reactive compartment (G_3).

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

$$Mineralization_{POM\_Gi} = POM_{Gi} \cdot K_{POM\_Gi} \cdot \theta_{POM\_Gi}^{Temp-20} \qquad \textbf{(268)}$$

where:

Mineralization$_{POM\_Gi}$	=	decomposition of G_i reactivity class of POP, POC, or PON in the sediment bed (g/m^3 d);
POM$_{Gi}$	=	concentration of POM in reactivity class G_i (g/m^3);
K$_{POM\_Gi}$	=	decay rate of POM class (1/d);
θ_{POM_Gi}	=	exponential temperature adjustment for decomposition of POM class G_i (unitless); and
Temp	=	temperature (deg.C).

Feeding on G_1 is calculated based on preferences for labile detritus and feeding on G_2 is based on preferences for refractory detritus; these are set in the animal data screens. As a simplifying assumption, there is no feeding on nonreactive G_3.

7.3 PON

Particulate Organic Nitrogen in sediment is also assumed to be in the second layer of sediment. Three state variables are utilized to represent three reaction classes (G_1 through G_3).

$$\frac{dPON_{Sediment}}{dt} = Deposition - Mineralization - Burial - Predation \cdot N2Org \qquad \textbf{(269)}$$

where:

Deposition	=	deposition from water column (g N/ m^3 d) see **(266)**;
Mineralization	=	decomposition to ammonia (g N/ m^3 d) see **(267)** ;
Burial	=	deep burial below modeled layer (g N/ m^3 d) see **(265)**;
Predation	=	predation by detritivores (g N/ m^3 d) see **(99)**; and
N2Org	=	user input conversion factor between N and refractory or labile detritus (g N / g OC).

7.4 POP

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

$$\frac{dPOP_{Sediment}}{dt} = Deposition - Mineralization - Burial - Predation \cdot P2Org \qquad \textbf{(270)}$$

where:

Deposition	=	deposition from water column (g P/ m^3 d) see **(266)**;
Mineralization	=	decomposition to orthophosphate (g P/ m^3 d) see **(267)** ;
Burial	=	deep burial below modeled layer (g P/ m^3 d) see **(265)**;
Predation	=	predation by detritivores (g P/ m^3 d) see **(99)**; and
P2Org	=	user input conversion factor between P and refractory or labile detritus (g P / g OC).

7.5 Ammonia

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

$$\frac{dAmmonia_{L2\,Sed}}{dt} = Diag\_Flux - Burial + Flux2Anaerobic \qquad \textbf{(271)}$$

$$\frac{dAmmonia_{L1\,Sed}}{dt} = -Nitrification - Burial - Flux2Water - Flux2Anaerobic \qquad \textbf{(272)}$$

where:

$Diag\_Flux$	=	decomposition of PON, see **(267)** ;
$Burial$	=	burial below relevant layer (g N/ m^3 d) see **(265)**;
$Flux2Anaerobic$	=	flux to layer 2 from layer 1 (g N/ m^3 d, may be negative) see **(272)** ;
$Flux2Water$	=	flux to water from layer 1 (g N/ m^3 d, may be negative); see **(273)**;
$Nitrification$	=	conversion to nitrate (g N/ m^3 d) see **(275)**;

$$Flux2Anaerobic = -\left[\omega_{1,2}\left(f_{p2}Conc_2 - f_{p1}Conc_1\right) + KL\left(f_{d2}Conc_2 - f_{d1}Conc_1\right)\right]/H_{Layer} \qquad \textbf{(273)}$$

where:

$\omega_{1,2}$	=	particle mixing velocity between layers (m/d), see **(262)**;
KL	=	diffusion velocity between layers (m/d), see **(261)**;
$f_{p,layer}$	=	particulate fraction in layer 1 or 2 (unitless); see **(274)**
$f_{d,layer}$	=	dissolved fraction in layer 1 or 2 (unitless); see **(274)**
$Conc_{layer}$	=	total concentration of state variable in layer (g/m^3); and
H_{layer}	=	depth of layer being evaluated (m);

$$Flux2Water = s\left(f_{d1} \cdot conc_1 - conc_{water\,col.}\right)/H_1 \qquad \textbf{(274)}$$

where:

s	=	surface diffusive transfer (m/d); **(263)**
f_{d1}	=	dissolved fraction in layer 1;
$Conc_{layer}$	=	total concentration of state variable in layer (g/m^3); and
H_1	=	depth of layer 1 (m);

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

$$f_{d\,ammonia,\,layer} = \frac{1}{1 + m_{layer} \cdot Kd_{NH4}}$$

$$\qquad \textbf{(275)}$$

$$f_{p\,ammonia,\,layer} = 1 - f_{d\,ammonia,\,layer}$$

where:

$f_{d\,ammonia,layer}$	=	dissolved fraction in layer;
m_{layer}	=	user-input solids concentration in layer (kg/L);
Kd_{NH4}	=	editable partition coefficient for ammonium (L/kg); and
$f_{p\,ammonia,layer}$	=	particulate fraction in layer.

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

$$Nitrification = \frac{\left(\dfrac{DO_{WC.}}{2 \cdot KM_{O2} + DO_{WC.}}\right)\left(\dfrac{KM_{NH4}}{KM_{NH4} + NH4_1}\right)\kappa^2 \cdot \theta^{Temp-20}}{s}\left(\frac{NH4_1}{H_1}\right) \qquad (276)$$

where:

Nitrification	=	conversion of ammonia to nitrate (g N/m^{3}d);
$DO_{WC.}$	=	dissolved oxygen in the water column (g/m^3);
KM_{NH4}	=	user-input nitrification half-saturation coefficient for ammonium (g N/m^3);
KM_{O2}	=	user-input nitrification half-saturation coefficient for oxygen (g O$_2$/m^3);
κ	=	reaction velocity for nitrification (m/d); (user-input, differentiating between fresh and salt water)
s	=	surface diffusive transfer (m/d); **(263)**
$NH4_1$	=	concentration of ammonia in layer 1 (g/m^3); **(168)**
H_1	=	user-input depth of layer 1 (m);
θ	=	user-input exponential temperature adjustment for nitrification (unitless); and
Temp	=	temperature (deg.C).

7.6 Nitrate

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

$$\frac{dNitrate_{L2\,Sed}}{dt} = -Burial - Denitr + Flux2Anaerobic \qquad (277)$$

$$\frac{dNitrate_{L1\,Sed}}{dt} = Nitrification - Denitr - Burial - Flux2Water - Flux2Anaerobic \qquad (278)$$

where:

Burial	=	burial to layer below modeled layer or out of the system(g N/ m^3 d) see **(265)**;

  Flux2Anaerobic   =   flux to layer 2 from layer 1 (g N/ m^3 d, may be negative) see **(272)** ;
  Flux2Water   =   flux to water from layer 1 (g N/ m^3 d, may be negative);   see **(273)**;
  Nitrification   =   conversion of ammonia to nitrate (g N/ m^3 d), see **(275)**;
  Denitr   =   denitrification of nitrate to free nitrogen (g N/ m^3 d), see **(278)**;

Nitrate is assumed to be dissolved in the sediment bed so f_d = 1.0 and f_p = 0.0.

Denitrification is solved as follows

$$Denitr = \frac{\kappa_{layer, NO3}^{\ 2} \cdot \theta_{NO3}^{\ Temp-20}}{s}\left(\frac{NO3_{layer}}{H_{layer}}\right) \tag{279}$$

where:

  $\kappa_{layer, No3}$ =   user-input reaction velocity for denitrification given the layer and salinity regime (m/d);
  θ =   user-input exponential temperature adjustment for denitrification (unitless); and
  s =   surface diffusive transfer (m/d);   **(263)**
  H_{layer} =   depth of layer (m);
  $NO3_{layer}$ =   concentration of nitrate in layer (g/m^3); and
  Temp   =   temperature (deg.C).

7.7 Orthophosphate

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

$$\frac{dPO4_{\ L2\ Sed}}{dt} = Diag\_Flux - Burial + Flux2Anaerobic \tag{280}$$

$$\frac{dPO4_{\ L1\ Sed}}{dt} = -Burial - Flux2Water - Flux2Anaerobic \tag{281}$$

where:

  Diag_Flux   =   decomposition of POP, see **(267)** ;
  Burial   =   burial to layer below modeled layer or out of the system(g P/ m^3 d) see **(265)**;
  Flux2Anaerobic   =   flux to layer 2 from layer 1 (g P/ m^3 d, may be negative) see **(272)** ;
  Flux2Water   =   flux to water from layer 1 (g P/ m^3 d, may be negative);   see **(273)**;

When oxygen is present in the water column, the diffusion of phosphorus from sediment pore

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

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

$$\text{if } DO_{WC} > DO_{Crit,PO4} \text{ then } Kd_{PO4,1} = Kd_{PO4,2}\Delta Kd_{PO4,1}$$

$$\textbf{(282)}$$

$$\text{else } Kd_{PO4,1} = Kd_{PO4,2}\Delta Kd_{PO4,1}^{\frac{DO_{WC}}{DO_{Crit,PO4}}}$$

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

$$f_{d\ phosphate,\ layer} = \frac{1}{1 + m_{layer} \cdot Kd_{PO4,\ layer}} \qquad \textbf{(283)}$$

where:

$f_{d\ phosphate,layer}$	=	dissolved fraction in layer (unitless);
m_{layer}	=	user-input solids concentration in layer (kg/L); and
$Kd_{PO4,2}$	=	partition coefficient for phosphate in layer 2 (L/kg);
$\Delta Kd_{PO4,1}$	=	fresh or saltwater factor to increase the aerobic (L_1) partition coefficient of PO_4 relative to the anaerobic (L_2) coeff. (unitless);
DO_{WC}	=	dissolved oxygen in the water column (g/m^3), see **(186)**; and
$DO_{Crit,PO4.}$	=	critical oxygen concentration for adjustment of partition coefficient for inorganic P (g/m^3);

7.8 Methane

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

$$\frac{dMethane_{L2\ Sed}}{dt} = Diag\_Flux_{Methane} - Flux2Water_{Methane} - Oxidation_{Methane} \qquad \textbf{(284)}$$

where:

$Methane_{L2Sed}$	=	methane in the anaerobic layer expressed in oxygen equivalence units (g $O2_{equiv}$ / m^3)
$Diag\_Flux$	=	decomposition of POC in freshwater, adjusted for the organic carbon

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lost due to denitrification (g O2$_{equiv}$ / m^3 d) see **(284)**;

$Flux2Water$ =   methane flux to water (g O2$_{equiv}$ / m^3 d), see **(288)**; and

$Oxidation$ =   oxidation of methane (CSOD) (g O2$_{equiv}$ / m^3 d) see **(287)**;

In the manner of Di Toro, methane and sulfide are tracked in units of oxygen equivalents (g O2$_{equiv}$ / m^3) to easily balance the model's computations.

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

$$Diag\_Flux_{Methane,\,Sulfide} = Mineralization_{POC}\left(\frac{32}{12}\right) - 2.86 \cdot Denitrification \qquad \textbf{(285)}$$

where:

$Diag\_Flux_{Methane,Sulfide}$

    =   decomposition of POC in water, adjusted for the organic carbon lost due to denitrification (g O2$_{equiv}$ / m^3 d);

$Mineralization_{POC}$ =   decomposition of POC in freshwater, (g POC / m^3 d) see **(267)** ;

$Denitrification$ =   denitrification of nitrate, (g N/ m^3 d) see **(278)**;

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

2.86   =   conversion between Nitrate and oxygen equivalents;

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

$$CH4_{sat} = 100\left(1 + \frac{z_{mean}}{10}\right)1.024^{20-Temp} \qquad \textbf{(286)}$$

$$CSOD_{Max} = \min\left(\sqrt{2KL \cdot CH4_{sat} \cdot Diag\_Flux_{Methane}}, Diag\_Flux_{Methane}\right) \qquad \textbf{(287)}$$

$$Oxidation_{Methane} = \frac{CSOD_{Max}\left(1 - \sec h\left(\frac{\kappa_{CH4} \cdot \theta_{CH4}^{Temp-20}}{s}\right)\right)}{H_2} \qquad \textbf{(288)}$$

where:

$CH4_{Sat}$ =   saturation concentration of methane in pore water (g O2$_{equiv}$ / m^3);

z_{mean} =   mean depth of water column above the sediment bed (m);

$Temp$ =   temperature (deg.C);

$CSOD_{Max}$ =   maximum oxidation flux (g O2$_{equiv}$ / m^2 d);

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

$Diag\_Flux_{Methane}$ =   diagenesis flux of methane to water column, adjusted to be in units

of (g O2$_{equiv}$ / m^2 d);

$Oxidation_{Methane}$ = oxidation of methane (g O2$_{equiv}$ / m^3 d);

sec h = hyperbolic secant function

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

κ_{CH4} = reaction velocity for methane oxidation(m/d);

θ_{CH4} = exp. temperature adjustment for methane oxidation (unitless); and

H_2 = depth of layer 2 (m); *(methane mass arbitrarily tracked on the second layer)*

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

$$Flux2Water_{Methane} = Diag\_Flux_{Methane} - Oxidation_{Methane} \qquad \textbf{(289)}$$

where:

$Diag\_Flux$ = decomposition of POC in freshwater, adjusted for the organic carbon lost due to denitrification (g O2$_{equiv}$ / m^3 d), see **(284)**;

$Oxidation$ = oxidation of methane (g O2$_{equiv}$ / m^3 d), see **(287)**;

7.9 Sulfide

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

$$\frac{dSulfide_{L2\,Sed}}{dt} = Diag\_Flux_{Sulfide} - Burial + Flux2Anaerobic \qquad \textbf{(290)}$$

$$\frac{dSulfide_{L1\,Sed}}{dt} = -Oxidation - Burial - Flux2Water - Flux2Anaerobic \qquad \textbf{(291)}$$

where:

$Sulfide_{Ln\,Sed}$ = sulfide concentration in layer n of sediment, (g O2$_{equiv}$ / m^3);

$Diag\_Flux_{Sulfide}$ = decomposition of POC in salt water, adjusted for the organic carbon lost due to denitrification (g O2$_{equiv}$ / m^3 d), see **(284)**;

$Burial$ = burial to layer below modeled layer or out of the system (g O2$_{equiv}$ / m^3 d); see **(265)**;

$Flux2Anaerobic$ = flux to layer 2 from layer 1 (g O2$_{equiv}$ / m^3 d, may be neg.) see **(272)** ;

$Flux2Water$ = flux to water from L$_1$ (g O2$_{equiv}$ / m^3 d, may be neg.) *(Note the driving var. "COD" represents the water col. conc. of sulfide.)* see **(273)**;

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

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$$Oxidation_{Sulfide} = Conc_{H2S,L1} \frac{\left(\kappa_{H2S,d}{}^2 \cdot f_{d1} + \kappa_{H2S,p}{}^2 \cdot f_{p1}\right)\theta_{H2S}{}^{Temp-20}\left(\frac{DO_{WC}}{2KM_{H2S,DO}}\right)}{s \cdot H_1} \qquad \textbf{(292)}$$

where:

$Oxidation_{Sulfide}$	=	oxidation of sulfide (g O2$_{equiv}$ / m^3 d);
$Conc_{H2S,L1}$	=	concentration of sulfide in layer 1 (g O2$_{equiv}$ / m^3);
$\kappa_{H2S,d}$	=	reaction velocity for dissolved sulfide oxidation (m/d);
$\kappa_{H2S,p}$	=	reaction velocity for particulate sulfide oxidation (m/d);
$DO_{WC.}$	=	dissolved oxygen in the water column (g/m^3);
$KM_{H2S,DP}$	=	sulfide oxidation normalization constant for oxygen (g O$_2$/m^3);
θ_{H2S}	=	exp. temperature adjustment for sulfide oxidation (unitless);
s	=	surface diffusive transfer (m/d); and
H_1	=	depth of layer 1 (m);

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

$$f_{d\ sulfide,\ layer} = \frac{1}{1 + m_{layer} \cdot Kd_{H2S,Layer}} \qquad \textbf{(293)}$$

where:

$f_{d\ sulfide,layer}$	=	dissolved fraction in layer;
m_{layer}	=	solids concentration in layer (kg/L); and
Kd_{NH4}	=	partition coefficient for sulfide for layer (L/kg);

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

7.10 Biogenic Silica

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

$$\frac{dBiogenic\_Silica_{L2\ Sed}}{dt} = Deposition - Dissolution - Burial \qquad \textbf{(294)}$$

where:

$Deposition$	=	deposition from water column (g Si/ m^3 d) see **(294)**;
$Dissolution$	=	dissolution of biogenic silica (g Si/ m^3 d)
$Burial$	=	deep burial below modeled layer (g Si/ m^3 d) see **(265)**; and

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

$$Deposition_{Si} = \left(\sum_{Diatoms} Sed \cdot FracSilica \right) \frac{vol_{water}}{vol_{sediment}} \qquad \textbf{(295)}$$

where:

$Deposition_{Si}$	=	deposition of silica from water column (g Si/ m^3 d);
$FracSilica$	=	user-input fraction of silica in diatoms, (unitless);
Sed	=	sedimentation of diatoms, see **(165)**, (g OM/m^3$_{water}$ d);
Vol_{water}	=	water volume (m^3); and
$Vol_{sediment}$	=	sediment volume (m^3);

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

$$Dissolution = \kappa_{Si} \theta_{Si}^{Temp-20} \left(\frac{Conc_{Avail\_Si}}{Conc_{Avail\_Si} + KM_{PSi}} \right) \left(Si_{Sat} - f_{d,silica, L2} \cdot Conc_{Silica, L2} \right) \qquad \textbf{(296)}$$

where:

$Dissolution$	=	dissolution of biogenic silica (g Si/ m^3 d);
κ_{Si}	=	user-input reaction velocity for dissolved silica dissolution (1/d);
θ_{Si}	=	user-input exponential temperature adjustment for silica dissolution (unitless);
$Conc_{var,layer}$	=	concentration of available silica or silica in layer 2 (g Si/ m^3);
KM_{PSi}	=	user input silica dissolution half-saturation constant for biogenic silica (g Si/m^3);
Si_{Sat}	=	user-input saturation concentration of silica in pore water (g Si/m^3);
$f_{d\ silica,layer}$	=	dissolved fraction of silica in layer.

7.11 Dissolved Silica

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

$$\frac{dSilica_{L2\,Sed}}{dt} = Dissolution - Burial + Flux2Anaerobic \qquad \textbf{(297)}$$

$$\frac{dSilica_{L1\,Sed}}{dt} = -Burial - Flux2Water - Flux2Anaerobic \qquad \textbf{(298)}$$

where:

Dissolution	=	dissolution of biogenic silica (g Si / m^3 d), see **(295)**;
Burial	=	burial to layer below modeled layer or out of the system (g Si / m^3 d); see **(265)**;
Flux2Anaerobic	=	flux to layer 2 from layer 1 (g Si/ m^3 d, may be negative) see **(272)** ;
Flux2Water	=	flux to water from layer 1 (g Si/ m^3 d, may be negative); see **(273)**;

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

$$\text{if } DO_{WC} > DO_{Crit,Si} \text{ then } Kd_{Si,1} = Kd_{Si,2} \Delta Kd_{Si,1}$$

(299)

$$\text{else } Kd_{Si,1} = Kd_{Si,2} \Delta Kd_{Si,1}^{\frac{DO_{WC}}{DO_{Crit,Si}}}$$

$$f_{d\,Si,layer} = \frac{1}{1 + m_{layer} \cdot Kd_{Si,layer}}$$

(300)

where:

$f_{d\,silica,layer}$	=	dissolved fraction in layer (unitless);
m_{layer}	=	solids concentration in layer (kg/L); and
$Kd_{Si,2}$	=	partition coefficient for silica in layer 2 (L/kg);
$\Delta Kd_{Si,1}$	=	fresh or saltwater factor to increase the aerobic (L_1) partition coefficient of silica relative to the anaerobic (L_2) coeff. (unitless);
DO_{WC}	=	dissolved oxygen in the water column (g/m^3); and
$DO_{Crit,Si.}$	=	critical oxygen concentration for adjustment of partition coefficient for silica (g/m^3);

8. TOXIC ORGANIC CHEMICALS

The chemical fate module of AQUATOX predicts the partitioning of a compound between water, sediment, and biota (Figure 133), and estimates the rate of degradation of the compound (Figure 134). Microbial degradation, biotransformation, photolysis, hydrolysis, and volatilization are modeled in AQUATOX. Each of these processes is described generally, and again in more detail below.

Nonequilibrium concentrations, as represented by kinetic equations, depend on sorption, desorption, and elimination as functions of the chemical, and exposure through water and food as a function of bioenergetics of the organism. Equilibrium partitioning is no longer represented in AQUATOX except as a constraint on sorption to detritus and plants and as a basis for computing internal toxicity. Partitioning to inorganic sediments is not modeled unless the multi-layer sediment model is included.

> **Toxic Organic Chemicals: Simplifying Assumptions**
>
> - Kinetic model of toxicant fate
> - Photolysis in sediments is not included
> - A generalized equation is used to calculate partitioning of polar compounds
> - Direct sorption onto the body of an animal is ignored
> - The exchange of toxicant through the gill membrane is assumed to be facilitated by the same mechanism as the uptake of oxygen
> - Estimation of the elimination rate constant k2 may be made based on logKow with two alternative formulations available
> - Biotransformation occurs at a constant rate throughout a simulation

Microbial degradation is modeled by entering a maximum biodegradation rate for a particular organic toxicant, which is subsequently reduced to account for suboptimal temperature, pH, and dissolved oxygen. Biotransformation is represented by user-supplied first-order rate constants with the option of also modeling multiple daughter products. Photolysis is modeled by using a light screening factor (Schwarzenbach et al., 1993) and the near-surface, direct photolysis first-order rate constant for each pollutant. The light screening factor is a function of both the diffuse attenuation coefficient near the surface and the average diffuse attenuation coefficient for the whole water column. For those organic chemicals that undergo hydrolysis, neutral, acid-, and base-catalyzed reaction rates are entered into AQUATOX as applicable. Volatilization is modeled using a stagnant two-film model, with the air and water transfer velocities approximated by empirical equations based on reaeration of oxygen (Schwarzenbach et al., 1993).

Figure 133. In-situ uptake and release of chlorpyrifos in a pond, dominated by plants
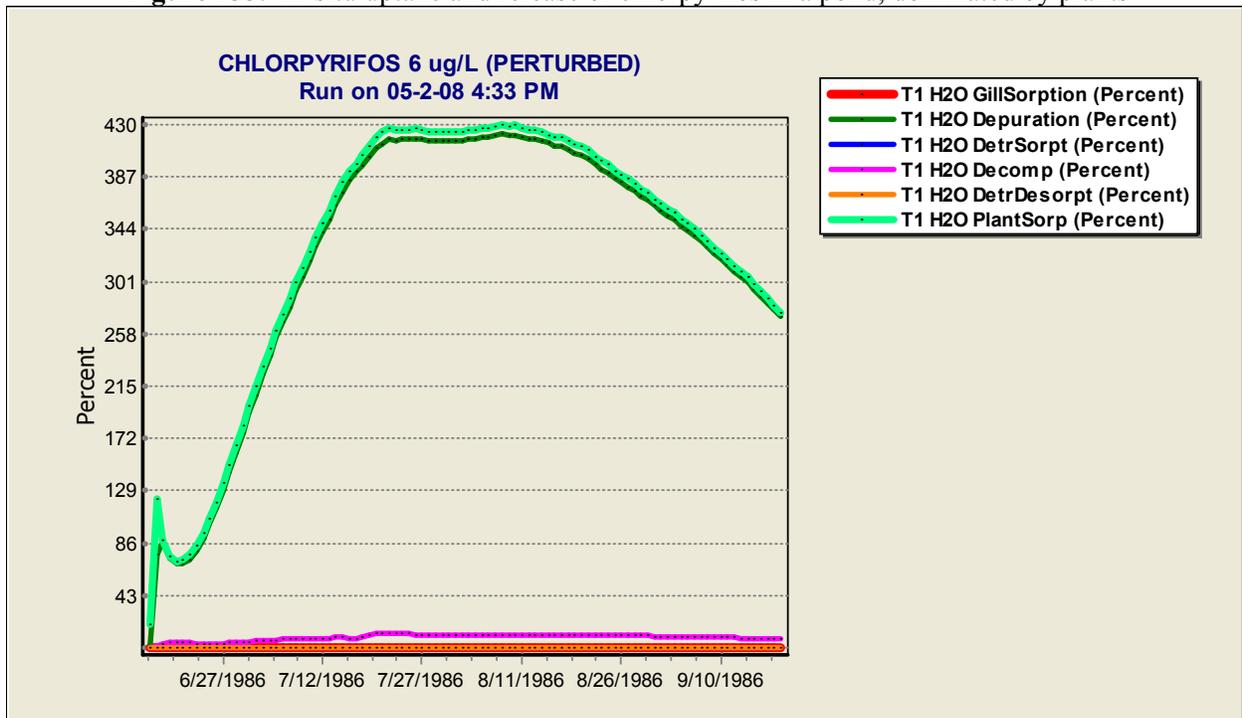
Figure 134. In-situ degradation rates for chlorpyrifos in pond
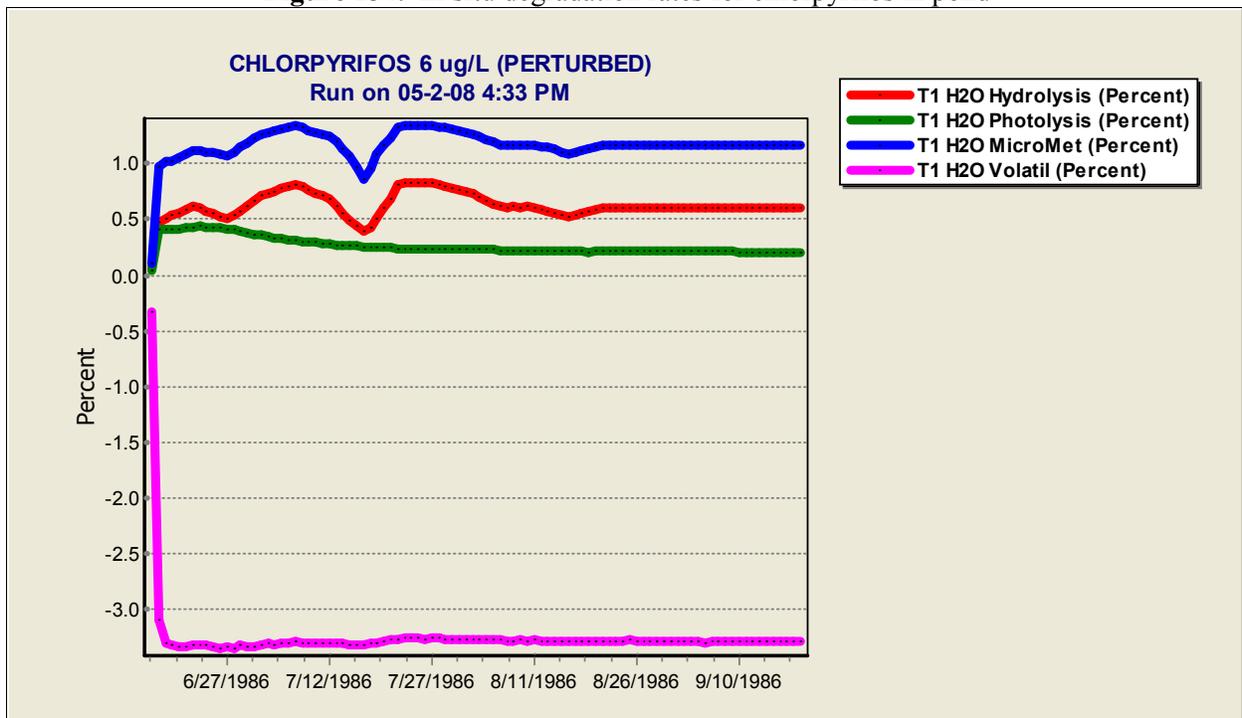
The mass balance equations follow. The change in mass of toxicant in the water includes explicit representations of mobilization of the toxicant from sediment to water as a result of decomposition of the labile sediment detritus compartment, sorption to and desorption from the detrital sediment compartments, uptake by algae and macrophytes, uptake across the gills of animals, depuration by organisms, and turbulent diffusion between epilimnion and hypolimnion:

$$
\begin{aligned}
\frac{d\, Toxicant_{Water}}{dt} = {}& Loading + \sum_{LabileDetr}(Decomposition_{LabileDetr} \cdot PPB_{LabileDetr} \cdot 1\mathrm{e}\text{-}6) \\
& + \sum Desorption_{DetrTox} + \sum Depuration_{Org} - \sum Sorption_{SedTox} \\
& - \sum GillUptake - MacroUptake - \sum AlgalUptake_{Alga} \\
& - Hydrolysis - Photolysis - MicrobialDegrdn + Volatilization \\
& - Discharge + Biotransform_{Microb\ In} \pm TurbDiff \pm Diffusion_{Seg} \\
& \pm Porewater_{Advection} \pm Diffusion_{Sediment} - Washout + Washin
\end{aligned}
$$

$$(301)$$

The equations for the toxicant associated with the two sediment detritus compartments are rather involved, involving direct processes such as sorption and indirect conversions such as defecation. However, photolysis is not included based on the assumption that it is not a significant process for detrital sediments:

$$
\begin{aligned}
\frac{d\, Toxicant_{SedLabileDetr}}{dt} = {}& Sorption - Desorption + \left(Colonization \cdot PPB_{SedRefrDetr} \cdot 1\mathrm{e}\text{-}6\right) \\
& + \sum_{Pred}\sum_{Prey}\left(Def2SedLabile \cdot DefecationTox_{Pred,\,Prey}\right) \\
& - (Resuspension + Scour + Decomposition) \cdot PPB_{SedLabileDetr} \cdot 1\mathrm{e}\text{-}6 \\
& - \sum_{Pred} Ingestion_{Pred,\,SedLabileDetr} \cdot PPB_{SedLabileDetr} \cdot 1\mathrm{e}\text{-}6 \\
& + Sedimentation \cdot PPB_{SuspLabileDetr} \cdot 1\mathrm{e}\text{-}6 \\
& + \sum\left(Sed2Detr \cdot Sink_{Phyto} \cdot PPB_{Phyto} \cdot 1\mathrm{e}\text{-}6\right) \\
& - Hydrolysis - MicrobialDegrdn - Burial + Expose \\
& \pm Biotransform_{Microbial}
\end{aligned}
$$

$$(302)$$

$$
\begin{aligned}
\frac{d\, Toxicant_{SedRefrDetr}}{dt} = {}& Sorption - Desorption \\
& + \sum_{Pred}\sum_{Prey}\left((1 - Def2SedLabile) \cdot DefecationTox_{Pred,\,Prey}\right) \\
& - \left(Resuspension + Scour + Colonization\right) \cdot PPB_{SedRefrDetr} \cdot 1\mathrm{e}\text{-}6 \\
& - \sum_{Pred} Ingestion_{Pred,\,SedRefrDetr} \cdot PPB_{SedRefrDetr} \cdot 1\mathrm{e}\text{-}6 \\
& + \left(Sedimentation + Scour\right) \cdot PPB_{SuspRefrDetr} \cdot 1\mathrm{e}\text{-}6 \\
& + \sum\left(Sed2Detr \cdot Sink_{Phyto} \cdot PPB_{Phyto} \cdot 1\mathrm{e}\text{-}6\right) \\
& - Hydrolysis - MicrobialDegrdn - Burial + Expose \\
& \pm Biotransform_{Microbial}
\end{aligned}
$$

$$(303)$$

Similarly for the toxicant associated with suspended and dissolved detritus, the equations are:

$$
\begin{aligned}
\frac{d\,Toxicant_{SuspLabileDetr}}{dt} &= Loading + Sorption - Desorption + Washin_{ToxCarrier} \\
&+ \sum_{Org}((Mort2Detr \cdot Mortality_{Org} + GameteLoss_{Org}) \cdot PPB_{Org} \cdot 1\,e\text{-}6) \\
&- (Sedimentation + Deposition + Washout + Decomposition \\
&+ \sum_{Pred} Ingestion_{Pred,\,SuspLabileDetr}) \cdot PPB_{SuspLabileDetr} \cdot 1\,e\text{-}6 \\
&+ Colonization \cdot PPB_{SuspRefrDetr} \cdot 1\,e\text{-}6 \pm Biotransform_{Microbial} \\
&+ (Resuspension + Scour) \cdot PPB_{SedLabileDetr} \cdot 1\,e\text{-}6 \pm SedToHyp \\
&- Hydrolysis - Photolysis - MicrobialDegrdn \pm TurbDiff \pm Diffusion_{Seg}
\end{aligned}
\tag{304}
$$

$$
\begin{aligned}
\frac{d\,Toxicant_{SuspRefrDetr}}{dt} &= Loading + Sorption - Desorption \\
&+ \sum_{Org}(Mort2Ref \cdot Mortality_{Org} \cdot PPB_{Org} \cdot 1\,e\text{-}6) \\
&- (Sedimentation + Deposition + Washout + Colonization \\
&\pm Biotransform_{Microbial} + \sum_{Pred} Ingestion_{SuspRefrDetr}) \cdot PPB_{SuspRefrDetr} \cdot 1\,e\text{-}6 \\
&+ (Resuspension + Scour) \cdot PPB_{SedRefrDetr} \cdot 1\,e\text{-}6 \\
&\pm SedToHyp - Hydrolysis - Photolysis - MicrobialDegrdn \\
&\pm TurbDiff \pm Diffusion_{Seg} + Washin_{ToxCarrier}
\end{aligned}
\tag{305}
$$

$$
\begin{aligned}
\frac{d\,Toxicant_{DissLabileDetr}}{dt} &= Loading + Sorption - Desorption + SumExcrToxToDiss_{Org} \\
&+ \sum_{Org}(Mort2Detr \cdot Mortality_{Org} \cdot PPB_{Org} \cdot 1\,e\text{-}6) \\
&- (Washout + Decomposition) \cdot PPB_{DissLabileDetr} \cdot 1\,e\text{-}6 \\
&\pm Biotransform_{Microbial} - Hydrolysis - Photolysis \\
&- MicrobialDegrdn \pm TurbDiff \pm Diffusion_{Seg} + Washin_{ToxCarrier} \\
&\pm Porewater_{Advection} \pm Diffusion_{Sediment}
\end{aligned}
\tag{306}
$$

$$
\begin{aligned}
\frac{d\,Toxicant_{DissRefrDetr}}{dt} &= Loading + Sorption - Desorption + SumExcToxToDiss_{Org} \\
&+ \sum_{Org}(Mort2Ref \cdot Mortality_{Org} \cdot PPB_{Org} \cdot 1\,e\text{-}6) \\
&- (Washout + Colonization) \cdot PPB_{DissRefrDetr} \cdot 1\,e\text{-}6 \\
&\pm Biotransform_{Microbial} - Hydrolysis - Photolysis \\
&- MicrobialDegrdn \pm TurbDiff \pm Diffusion_{Seg} + Washin_{ToxCarrier} \\
&\pm Porewater_{Advection} \pm Diffusion_{Sediment}
\end{aligned}
\tag{307}
$$

When the simple sediment model is run, there are no equations for buried detritus, as they are considered to be sequestered and outside of the influence of any processes which would change the concentrations of their associated toxicants.   When the multi-layer sediment model is included, equations for toxicants in pore waters and toxicants in buried sediments may be found in sections 8.10 and 8.11.

Toxicants associated with algae are represented as:

$$\frac{d\,Toxicant_{Alga}}{dt} = Loading + AlgalUptake - Depuration \pm TurbDiff \pm Diffusion_{Seg}$$

$$+ Washin_{ToxCarrier} - (Excretion + Washout + \sum_{Pred} Predation_{Pred,\,Alga} + Mortality \quad \textbf{(308)}$$

$$+ Sink \pm SinkToHypo \pm Floating) \cdot PPB_{Alga} \cdot 1\,e\text{-}6 \pm Biotransform_{Alga}$$

Macrophytes are represented similarly, but reflecting the fact that they are stationary unless specified as free-floating:

$$\frac{d\,Toxicant_{Macrophyte}}{dt} = Loading + MacroUptake - Depuration - (Excretion$$

$$+ \sum_{Pred} Predation_{Pred,\,Macro} + Mortality + Washout_{FreeFloating} + Breakage) \quad \textbf{(309)}$$

$$\cdot PPB_{Macro} \cdot 1\,e\text{-}6 \pm Biotransform_{Macrophyte} + Washin_{ToxCarrierFreeFloat}$$

The toxicant associated with animals is represented by an involved kinetic equation because of the various routes of exposure and transfer:

$$\frac{d\,Toxicant_{Animal}}{dt} = Loading + GillUptake + \sum_{PreyDietUptake} \pm TurbDiff$$

$$- (Depuration + \sum_{Pred} Predation_{Pred,\,Animal} + Mortality + Spawn \quad \textbf{(310)}$$

$$\pm Promotion + Drift + Migration + EmergeInsect) \cdot PPB_{Animal} \cdot 1\,e\text{-}6$$

$$\pm Biotransform_{Animal} + Washin_{ToxCarrier}$$

where:

$Toxicant_{Water}$	=	toxicant in dissolved phase in unit volume of water (µg/L);
$Toxicant_{SedDetr}$	=	mass of toxicant associated with each of the two sediment detritus compartments in unit volume of water (µg/L);
$Toxicant_{SuspDetr}$	=	mass of toxicant associated with each of the two suspended detritus compartments in unit volume of water (µg/L);
$Toxicant_{DissDetr}$	=	mass of toxicant associated with each of the two dissolved organic compartments in unit volume of water (µg/L);
$Toxicant_{Alga}$	=	mass of toxicant associated with given alga in unit volume of water (µg/L);
$Toxicant_{Macrophyte}$	=	mass of toxicant associated with macrophyte in unit volume of water(µg/L);
$Toxicant_{Animal}$	=	mass of toxicant associated with given animal in unit volume of water (µg/L);
$PPB_{SedDetr}$	=	concentration of toxicant in sediment detritus (µg/kg), see **(310)**;

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$PPB_{SuspDetr}$	=	concentration of toxicant in suspended detritus (μg/kg);
$PPB_{DissDetr}$	=	concentration of toxicant in dissolved organics (μg/kg);
PPB_{Alga}	=	concentration of toxicant in given alga (μg/kg);
$PPB_{Macrophyte}$	=	concentration of toxicant in macrophyte (μg/kg);
PPB_{Animal}	=	concentration of toxicant in given animal (μg/kg);
1 e -6	=	units conversion (kg/mg);
Loading	=	loading of toxicant from external sources (μg/L·d);
TurbDiff	=	depth-averaged turbulent diffusion between epilimnion and hypolimnion (μg/L·d), see **(22)** and **(23)**.
Washin	=	loadings from linked upstream segments (g/m^3·d), see **(30)**;
$Washin_{ToxCarrier}$	=	inflow load of toxicant sorbed to a carrier from an upstream segment (μg/L·d), see **(31)**;
$Diffusion_{Seg}$	=	gain or loss due to diffusive transport over the feedback link between two segments, (μg/L·d), see **(32)**;
$Diffusion_{Sediment}$	=	gain or loss due to diffusive transport to porewaters in the sediment (μg/L·d), see **(256)**;
$Porewater_{Advection}$	=	gain or loss of toxicant to porewater due to scour or deposition of sediment (μg/L$_{pw}$·d), see **(394)**, **(395)**;
Hydrolysis	=	rate of loss due to hydrolysis (μg/L·d), see **(313)**;
$Biotransform_{Microbial}$	=	biotransformation to or from given organic chemical in given detrital compartment due to microbial decomposition (μg/L·d), see **(375)**;
$Biotransform_{Org}$	=	biotransformation to or from given organic chemical within the given organism (μg/L·d); **(375)**
Photolysis	=	rate of loss due to direct photolysis (μg/L·d), see **(320)**; assumed not to be significant for bottom sediments;
MicrobialDegrdn	=	rate of loss due to microbial degradation (μg/L·d), see **(326)**;
Volatilization	=	rate of loss due to volatilization (μg/L·d), see **(331)**;
Discharge	=	rate of loss of toxicant due to discharge downstream (μg/L·d), see Table 3;
Burial	=	rate of loss due to deposition and resultant deep burial (μg/L·d) see **(167b)**;
Expose	=	rate of exposure due to resuspension of overlying sediments (μg/L·d), see **(227)**;
Decomposition	=	rate of decomposition of given detritus (mg/L·d), see **(159)**;
Depuration	=	elimination rate for toxicant due to clearance (μg/L·d), see **(362)**, **(363)**, and **(372)**;
Sorption	=	rate of sorption to given organic or inorganic compartment (μg/L·d), see **(350)**;
Desorption	=	rate of desorption from given organic or inorganic compartment (μg/L·d), see **(351)**;
Colonization	=	rate of conversion of refractory to labile detritus (g/m^3·d), see **(155)**;

$DefecationTox_{Pred, Pre}$ =		rate of transfer of toxicant due to defecation of given prey by given predator (μg/L·d), see **(379)**;
$Def2SedLabile$	=	fraction of defecation that goes to sediment labile detritus, = 0.5;
$Resuspension$	=	rate of resuspension of given sediment detritus (mg/L·d) without the inorganic sediment model attached, see **(165)**;
$Scour$	=	rate of resuspension of given sediment detritus (mg/L·d); in streams with the inorganic sediment model attached, see **(233)**;
$Sedimentation$	=	rate of sedimentation of given suspended detritus (mg/L·d); without the inorganic sediment model attached, see **(165)**;
$Deposition$	=	rate of sedimentation of given suspended detritus (mg/L·d) in streams with the inorganic sediment model attached, see **(235)**;
$Sed2Detr$	=	fraction of sinking phytoplankton that goes to given detrital compartment;
$Sink$	=	loss rate of phytoplankton to bottom sediments (mg/L·d), see **(69)**;
$Breakage$	=	loss of macrophytes due to breakage (g/m^2·d), see **(88)**;
$Mortality_{Org}$	=	nonpredatory mortality of given organism (mg/L·d), see **(66)**, **(87), and (112)**;
$Mort2Detr$	=	fraction of dead organism that is labile (unitless);
$GameteLoss$	=	loss rate for gametes (g/m^3·d), see **(126)**;
$Mort2Ref$	=	fraction of dead organism that is refractory (unitless);
$Washout$ or $Drift$	=	rate of loss of given toxicant, suspended detritus or organism due to being carried downstream (mg/L·d), see **(16)**, **(71)**, **(72)**, **(130)**, and **(131)**;
$SedToHyp$	=	rate of settling loss to hypolimnion from epilimnion (mg/L·d). May be positive or negative depending on segment being simulated, see **(69)**;
$Ingestion_{Pred, Prey}$	=	rate of ingestion of given food or prey by given predator (mg/L·d), see **(91)**;
$Predation_{Pred, Prey}$	=	predatory mortality by given predator on given prey (mg/L·d), see **(99)**;
$ExcToxToDiss_{Org}$	=	toxicant excretion from plants to dissolved organics (mg/L·d);
$Excretion$	=	excretion rate for given organism (g/m^3·d), see **(64), (111);**
$SinkToHypo$	=	rate of transfer of phytoplankton to hypolimnion (mg/L·d). May be positive or negative depending on segment being modeled, see **(69)**;
$AlgalUptake$	=	rate of sorption by algae (μg/L - d), see **(360)**;
$MacroUptake$	=	rate of sorption by macrophytes (μg/L - d), see **(356)**;
$GillUptake$	=	rate of absorption of toxicant by the gills (μg/L - d), see **(365)**;

DietUptake$_{Prey}$	=	rate of dietary absorption of toxicant associated with given prey (µg/L·d), see **(369)**;
Recruit	=	biomass gained from successful spawning (g/m³·d), see **(128)**;
Promotion	=	promotion from one age class to the next (mg/L·d), see **(136)**;
Migration	=	rate of migration (g/m³·d), see **(133)**; and
EmergeInsect	=	insect emergence (mg/L·d), see **(137)**.

The concentration in each carrier is given by:

$$PPB_i = \frac{ToxState_i}{CarrierState_i} \cdot 1e6 \tag{311}$$

where:

PPB_i	=	concentration of chemical in carrier *i* (µg/kg);
$ToxState_i$	=	mass of chemical in carrier *i* (µg/L);
CarrierState	=	biomass of carrier (mg/L); and
1e6	=	conversion factor (mg/kg).

8.1 Ionization

Dissociation of an organic acid or base in water can have a significant effect on its environmental properties. In particular, solubility, volatilization, photolysis, sorption, and bioconcentration of an ionized compound can be affected.   Rather than modeling ionization products, the approach taken in AQUATOX is to represent the modifications to the fate and transport of the neutral species, based on the fraction that is not dissociated. The acid dissociation constant is a measure of the strength of the acid or base, and is expressed as the negative log, *pKa*, and the fraction that is not ionized is:

$$Nondissoc = \frac{1}{1 + 10^{(pH - pKa)}} \tag{312}$$

where:

    Nondissoc   =   nondissociated fraction (unitless).

If the compound is a base then the fraction not ionized is:

$$Nondissoc = \frac{1}{1 + 10^{(pKa - pH)}} \tag{313}$$

Note: If *pKa* is set to zero then ionization is ignored (i.e. *NonDissoc* is set to 1.0).

When *pKa* = *pH* half the compound is ionized and half is not (Figure 132).   At ambient environmental *pH* values, compounds with a *pKa* in the range of 4 to 9 will exhibit significant dissociation (Figure 133).

Figure 135. Dissociation of pentachlorophenol (pKa = 4.75) at higher ph values
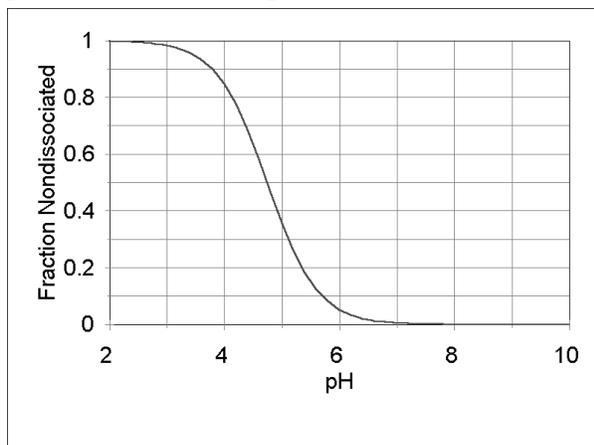
Figure 136. Dissociation as a function of pKa at an ambient pH of 7
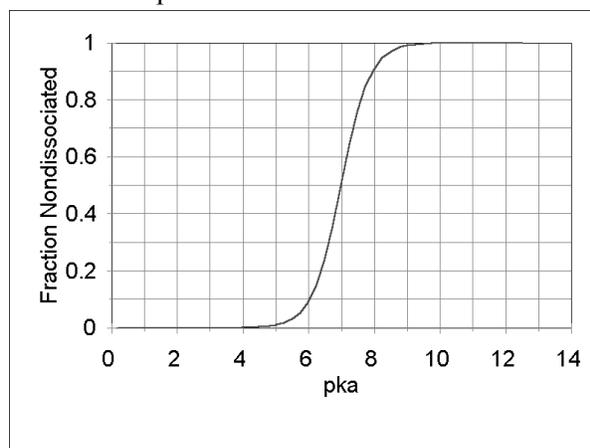
8.2 Hydrolysis

Hydrolysis is the degradation of a compound through reaction with water. During hydrolysis, both a pollutant molecule and a water molecule are split, and the two water molecule fragments (H^+ and OH^-) join to the two pollutant fragments to form new chemicals. Neutral and acid- and base-catalyzed hydrolysis are modeled using the approach of Mabey and Mill (1978) in which an overall pseudo-first-order rate constant is computed for a given pH, adjusted for the ambient temperature of the water:

$$Hydrolysis = KHyd \cdot Toxicant_{Phase} \tag{314}$$

where:

$$KHyd = (KAcidExp + KBaseExp + KUncat) \cdot Arrhen \tag{315}$$

and where:

KHyd	=	overall pseudo-first-order rate constant for a given pH and temperature (1/d);
KAcidExp	=	pseudo-first-order acid-catalyzed rate constant for a given pH (1/d);
KBaseExp	=	pseudo-first-order base-catalyzed rate constant for a given pH (1/d);
KUncat	=	the measured first-order reaction rate at pH 7 (1/d); and
Arrhen	=	temperature adjustment (unitless), see **(319)**.

In neutral hydrolysis reactions, the pollutant reacts with a water molecule (H_2O) and the concentration of water is usually included in *KUncat*. In acid-catalyzed hydrolysis, the hydrogen ion reacts with the pollutant, and a first-order decay rate for a given pH can be estimated as follows:

$$KAcidExp = KAcid \cdot HIon \tag{316}$$

where:

$$HIon = 10^{-pH} \tag{317}$$

and where:

KAcid	=	acid-catalyzed rate constant (L/mol·d);
HIon	=	concentration of hydrogen ions (mol/L); and
pH	=	pH of water column.

Likewise for base-catalyzed hydrolysis, the first-order rate constant for a reaction between the hydroxide ion and the pollutant at a given pH (Figure 137) can be described as:

$$KBaseExp = KBase \cdot OHIon \tag{318}$$

where:

$$OHIon = 10^{pH - 14} \tag{319}$$

and where:

KBase	=	base-catalyzed rate constant (L/mol · d); and
OHIon	=	concentration of hydroxide ions (mol/L).

Figure 137. Base-catalyzed hydrolysis of pentachlorophenol
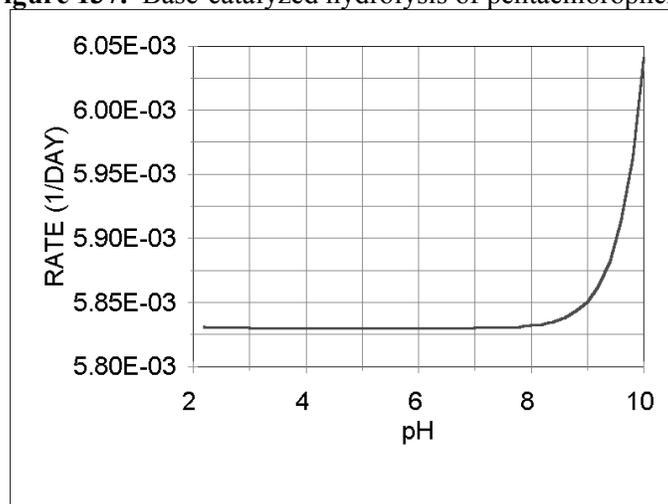
Hydrolysis reaction rates are adjusted for the temperature of the waterbody being modeled by using the Arrhenius rate law (Hemond and Fechner 1994). An activation energy value of 18,000 cal/mol (a mid-range value for organic chemicals) is used as a default:

$$Arrhen = e^{-\left(\frac{En}{R \bullet KelvinT} - \frac{En}{R \bullet TObs} \right)} \tag{320}$$

where:

En	=	Arrhenius activation energy (cal/mol);
R	=	universal gas constant (cal/mol · Kelvin);

KelvinT = temperature for which rate constant is to be predicted (Kelvin); and

TObs   = temperature at which known rate constant was measured (Kelvin).

8.3 Photolysis

Direct photolysis is the process by which a compound absorbs light and undergoes transformation:

$$Photolysis = KPhot \cdot Toxicant_{Phase}$$ **(321)**

where:

Photolysis = rate of loss due to photodegradation (μg/L·d); and

KPhot   = direct photolysis first-order rate constant (1/day).

For consistency, photolysis is computed for both the epilimnion and hypolimnion in stratified systems. However, photolysis is not a significant factor at hypolimnetic depths and is also ignored in sediments.

Ionization may result in a significant shift in the absorption of light (Lyman et al., 1982; Schwarzenbach et al., 1993). However, there is a general absence of information on the effects of light on ionized species. The user provides an observed half-life for photolysis, and this is usually determined either with distilled water or with water from a representative site, so that ionization may be included in the calculated lumped parameter *KPhot*.

Based on the approach of Thomann and Mueller (1987; see also Schwarzenbach et al. 1993), the observed first-order rate constant for the compound is modified by a light attenuation factor for ultraviolet light so that the process as represented is depth-sensitive (Figure 138); it also is adjusted by a factor for time-varying light:

$$KPhot = PhotRate \cdot ScreeningFactor \cdot LightFactor$$ **(322)**

where:

PhotRate = direct, observed photolysis first-order rate constant (1/day);

ScreeningFactor = a light screening factor (unitless), see **(322)**; and

LightFactor = a time-varying light factor (unitless), see **(323)**.

Figure 138. Photolysis of pentachlorophenol as a function of
light intensity and depth of water
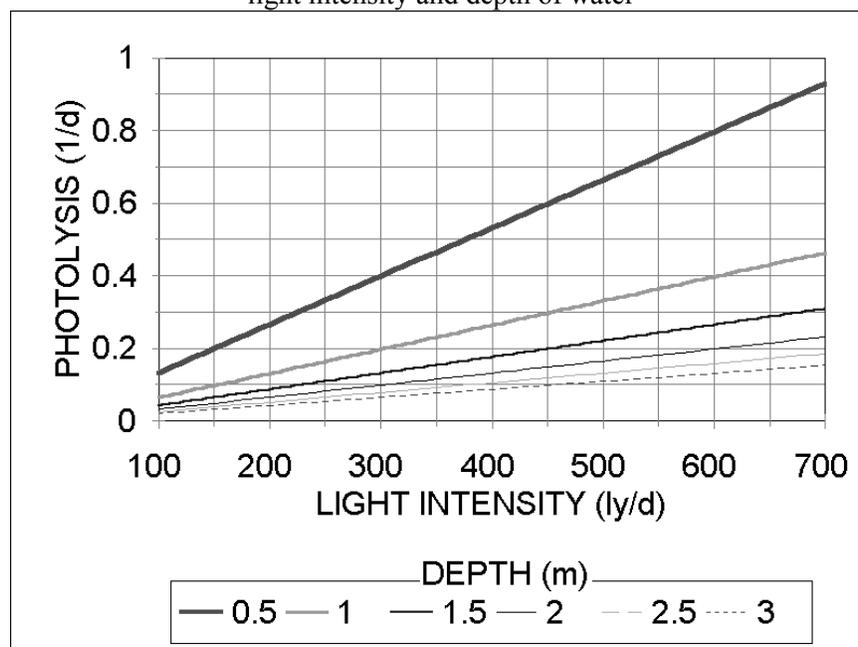
A light screening factor adjusts the observed laboratory photolytic transformation rate of a given pollutant for field conditions with variable light attenuation and depth (Thomann and Mueller, 1987):

$$ScreeningFactor = \frac{RadDistr}{RadDistr0} \cdot \frac{1 - \exp^{(-Extinct \bullet Thick)}}{Extinct \cdot Thick} \tag{323}$$

where:

RadDistr	=	radiance distribution function, which is the ratio of the average pathlength to the depth (see Schwarzenbach et al., 1993) (taken to be 1.6, unitless);
RadDistr0	=	radiance distribution function for the top of the segment (taken to be 1.2 for the top of the epilimnion and 1.6 for the top of the hypolimnion, unitless);
Extinct	=	light extinction coefficient (1/m) not including periphyton, see **(40)**;
Thick	=	thickness of the water body segment if stratified or maximum depth if unstratified (m).

The equation presented above implicitly makes the following assumptions:

- quantum yield is independent of wavelength; and,
- the value used for *PhotRate* is a representative near-surface, first-order rate constant for direct photolysis.

The rate is modified further to represent seasonally varying light conditions and the effect of ice cover:

$$LightFactor = \frac{Solar0}{AveSolar} \qquad\qquad (324)$$

where:

    $Solar0$ =   time-varying average light intensity at the top of the segment (ly/day); and

    $AveSolar$ =   average light intensity for late spring or early summer, corresponding to time when photolytic half-life is often measured (default = 500 Ly/day).

If the system is unstratified or if the epilimnion is being modeled, the light intensity is the light loading:

$$Solar0 = Solar \qquad\qquad (325)$$

otherwise we are interested in the intensity at the top of the hypolimnion and the attenuation of light is given as a logarithmic decrease over the thickness of the epilimnion:

$$Solar0 = Solar \cdot \exp^{(-Alpha \bullet MaxZMix)} \qquad\qquad (326)$$

where:

    $Solar$ =   incident solar radiation loading (ly/d), see **(25)**; and

    $MaxZMix$ =   depth of the mixing zone (m), see **(17)**.

Because the ultraviolet light intensity exhibits greater seasonal variation than the visible spectrum (Lyman et al., 1982), decreasing markedly when the angle of the sun is low, this construct could predict higher rates of photolysis in the winter than might actually occur. However, the model also accounts for significant attenuation of light due to ice cover (see section 3.6) so that photolysis, as modeled, is not an important process in northern waters in the winter.

8.4 Microbial Degradation

Not only can microorganisms decompose the detrital organic material in ecosystems, they also can degrade xenobiotic organic compounds such as fuels, solvents, and pesticides to obtain energy. In AQUATOX this process of biodegradation of pollutants, whether they are dissolved in the water column or adsorbed to organic detritus in the water column or sediments, is modeled using the same equations as for decomposition of detritus, substituting the pollutant and its degradation parameters for detritus in Equation **(159)** and supporting equations:

$$MicrobialDegrdn = KMDegrdn_{Phase} \cdot DOCorrection \cdot TCorr \cdot pHCorr$$
$$\cdot Toxicant_{Phase} \qquad\qquad (327)$$

where:

    $MicrobialDegrdn$ =   loss due to microbial degradation (g/m^3·d);

    $KMDegrdn$ =   maximum aerobic microbial degradation rate, either in water column or sediments (1/d), in sediments this is assumed to be four times the user-entered value for water;

DOCorrection	=	effect of anaerobic conditions (unitless), see **(160)**;
TCorr	=	effect of suboptimal temperature (unitless), see **(59)**;
pHCorr	=	effect of suboptimal pH (unitless), see **(162)**; and
Toxicant	=	concentration of organic toxicant (g/m^3).

Microbial degradation of toxicants proceeds more quickly if the material is associated with surficial or particulate sediments rather than dissolved in the water column (Godshalk and Barko, 1985); thus, in calculating the loss due to microbial degradation in the sorbed phase, the maximum degradation rate is converted by the model to four times the user entered maximum chemical degradation rate in the water (*Max. Rate of Aerobic Microbial Degradation*).   The model assumes that reported maximum microbial degradation rates are for the dissolved phase; if the reported degradation value is from a study with additional organic matter, such as suspended slurry or wet soil samples, then the parameter value that is entered should be one-fourth that reported.

8.5 Volatilization

Volatilization is modeled using the "stagnant boundary theory", or two-film model, in which a pollutant molecule must diffuse across both a stagnant water layer and a stagnant air layer to volatilize out of a waterbody (Whitman, 1923; Liss and Slater, 1974).   Diffusion rates of pollutants in these stagnant boundary layers can be related to the known diffusion rates of chemicals such as oxygen and water vapor.   The thickness of the stagnant boundary layers must also be taken into account to estimate the volatile flux of a chemical out of (or into) the waterbody.

The time required for a pollutant to diffuse through the stagnant water layer in a waterbody is based on the well-established equations for the reaeration of oxygen, corrected for the difference in diffusivity as indicated by the respective molecular weights (Thomann and Mueller, 1987, p. 533). The diffusivity through the water film is greatly enhanced by the degree of ionization (Schwarzenbach et al., 1993, p. 243), and the depth-averaged reaeration coefficient is multiplied by the thickness of the well-mixed zone:

$$KLiq = KReaer \cdot Thick \cdot \left(MolWtO\frac{2}{MolWt} \right)^{0.25} \cdot \frac{1}{Nondissoc} \qquad \textbf{(328)}$$

where:

KLiq	=	water-side transfer velocity (m/d);
KReaer	=	depth-averaged reaeration coefficient for oxygen (1/d), see **(191)**-**(195)**;
Thick	=	thickness of the water body segment if stratified or maximum depth if unstratified (m);
MolWtO2	=	molecular weight of oxygen (g/mol, =32);
MolWt	=	molecular weight of pollutant (g/mol); and
Nondissoc	=	nondissociated fraction (unitless), see **(311)**.

Likewise, the thickness of the air-side stagnant boundary layer is also affected by wind. Wind usually is measured at 10 m, and laboratory experiments are based on wind measured at 10 cm, so a conversion is necessary (Banks, 1975). To estimate the air-side transfer velocity of a pollutant, we used the following empirical equation based on the evaporation of water, corrected for the difference in diffusivity of water vapor compared to the toxicant (Thomann and Mueller, 1987, p. 534):

$$KGas = 168 \cdot \left(MolWtH2\frac{O}{MolWt} \right)^{0.25} \cdot Wind \cdot 0.5 \qquad (329)$$

where:

$KGas$	=	air-side transfer velocity (m/d);
$Wind$	=	wind speed ten meters above the water surface (m/s);
0.5	=	conversion factor (wind at 10 cm/wind at 10 m); and
$MolWtH2O$	=	molecular weight of water (g/mol, =18).

The total resistance to the mass transfer of the pollutant through both the stagnant boundary layers can be expressed as the sum of the resistances- the reciprocals of the air- and water-phase mass transfer coefficients (Schwarzenbach et al., 1993), modified for the effects of ionization:

$$\frac{1}{KOVol} = \frac{1}{KLiq} + \frac{1}{KGas \cdot HenryLaw \cdot Nondissoc} \qquad (330)$$

where:
     $KOVol$ =   total mass transfer coefficient through both stagnant boundary layers (m/d);

$$HenryLaw = \frac{Henry \cdot HLCSaltFactor}{R \cdot TKelvin} \qquad (331)$$

and where:

$HenryLaw$	=	Henry's law constant (unitless);
$Henry$	=	Henry's law constant (atm m^3 mol^{-1});
$HLCSaltFactor$ =		Correction factor for effect of salinity (unitless), see **(444)**.
R	=	gas constant (=8.206E-5 atm m^3 (mol K)$^{-1}$); and
$TKelvin$	=	temperature in °K.

The Henry's law constant is applicable only to the fraction that is nondissociated because the ionized species will not be present in the gas phase (Schwarzenbach et al., 1993, p. 179).

The atmospheric exchange of the pollutant can be expressed as the depth-averaged total mass transfer coefficient times the difference between the concentration of the chemical and the saturation concentration:

$$Volatilization = -\frac{KOVol}{Thick} \cdot \left(ToxSat - Toxicant_{water} \right) \qquad (332)$$

where:

Volatilization	=	interchange with atmosphere (µg/L·d);
Thick	=	depth of water or thickness of surface layer (m);
ToxSat	=	saturation concentration of pollutant in equilibrium with the gas phase (µg/L), see **(332)**; and
Toxicant_water	=	concentration of pollutant in water (µg/L).

The saturation concentration depends on the concentration of the pollutant in the air, ignoring temperature effects (Thomann and Mueller, 1987, p. 532; see also Schnoor, 1996), but adjusting for ionization and units:

$$ToxSat = \frac{Toxicant_{air}}{HenryLaw \cdot Nondissoc} \cdot 1000 \tag{333}$$

where:

Toxicant_air	=	gas-phase concentration of the pollutant (g/m^3); and
Nondissoc	=	nondissociated fraction (unitless).

Theoretically, toxicants can be transferred in either direction across the water-air interface. Often the pollutant can be assumed to have a negligible concentration in the air and *ToxSat* is zero. However, this general construct can represent the transferral of volatile pollutants into water bodies. Volatilization might become negative if toxicant concentrations are high in the air, and concentrations in the water column may increase as a result of this interchange. Because ionized species do not volatilize, the saturation level increases if ionization is occurring.

The nondimensional Henry's law constant, which relates the concentration of a compound in the air phase to its concentration in the water phase, strongly affects the air-phase resistance. Depending on the value of the Henry's law constant, the water phase, the air phase or both may control volatilization. For example, with a depth of 1 m and a wind of 1 m/s, the gas phase is 100,000 times as important as the water phase for atrazine (Henry's law constant = 3.0E-9), but the water phase is 50 times as important as the air phase for benzene (Henry's law constant = 5.5E-3). Volatilization of atrazine exhibits a linear relationship with wind (Figure 136) in contrast to the exponential relationship exhibited by benzene (Figure 137).

Figure 139. Atrazine *KOVol* as a function of Wind

VOLATILIZATION OF ATRAZINE
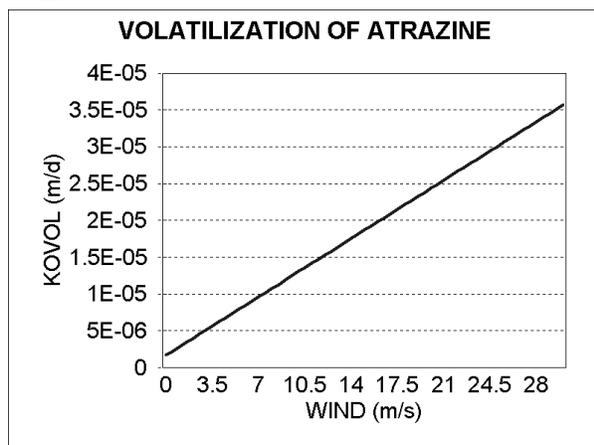
Figure 140. Benzene *KOVol* as a function of Wind

VOLATILIZATION OF BENZENE
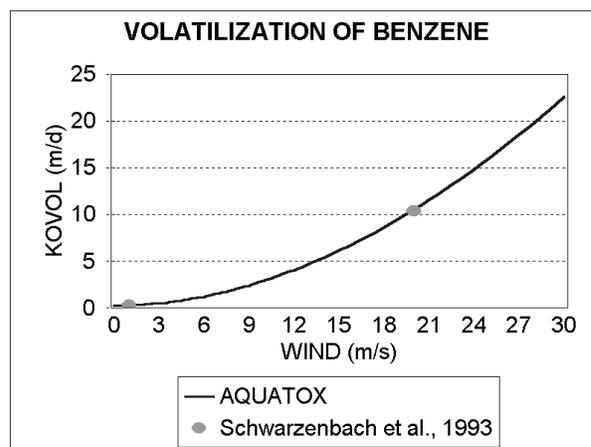
8.6 Partition Coefficients

Although AQUATOX is a kinetic model, steady-state partition coefficients for organic pollutants are computed in order to place constraints on competitive uptake and loss processes in detritus and plants, speeding up computations. Bioconcentration factors also are used in computing internal toxicity in plants and animals. They are estimated from empirical regression equations and the pollutant's octanol-water partition coefficient.

Detritus

Natural organic matter is the primary sorbent for neutral organic pollutants. Hydrophobic chemicals partition primarily in nonpolar organic matter (Abbott et al. 1995). Refractory detritus is relatively nonpolar; its partition coefficient (in the non-dissolved phase) is a function of the octanol-water partition coefficient (N = 34, r^2 = 0.93; Schwarzenbach et al. 1993):

$$KOM_{RefrDetr} = 1.38 \cdot KOW^{0.82} \tag{334}$$

where:

$KOM_{RefrDetr}$ = detritus-water partition coefficient (L/kg); and
KOW = octanol-water partition coefficient (unitless).

Detritus in sediments is simulated separately from inorganic sediments, rather than as a fraction of the sediments as in other models. When the multi-layer sediment model is not included, refractory detritus is used as a surrogate for sediments in general; and the sediment partition coefficient *KPSed*, which can be entered manually by the user, is the same as $KOM_{RefrDetr}$.

Equation **(334)** and the equations that follow are extended to polar compounds, following the approach of Smejtek and Wang (1993):

$$KOM_{RefrDetr} = 1.38 \cdot KOW^{0.82} \cdot Nondissoc$$
$$+ (1 - Nondissoc) \cdot IonCorr \cdot 1.38 \cdot KOW^{0.82}$$

(335)

where:

Nondissoc	=	un-ionized fraction (unitless); and
IonCorr	=	correction factor for decreased sorption, 0.01 for chemicals that are bases and 0.1 for acids. (unitless).

Using pentachorophenol as a test compound, and comparing it to octanol, the influence of pH-mediated dissociation is seen in Figure 141. This relationship is verified by comparison with the results of Smejtek and Wang (1993) using egg membrane. However, in the general model Eq. **(334)** is used for refractory detrital sediments as well.

Figure 141. Refractory detritus-water and octanol-water partition coefficients for pentachlorophenol as a function of pH
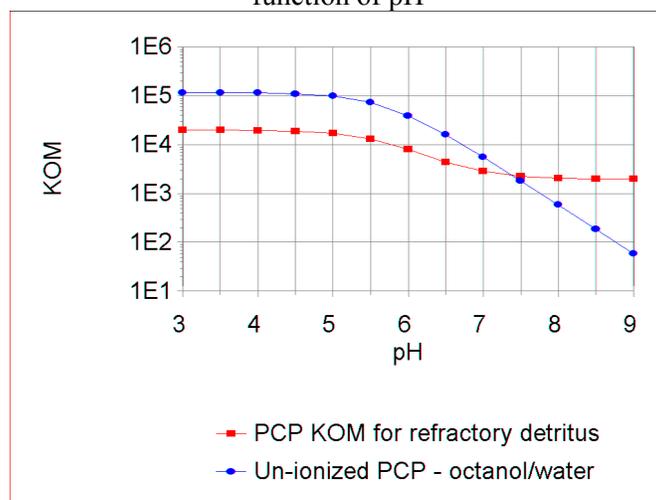
There appears to be a dichotomy in partitioning; data in the literature suggest that labile detritus does not take up hydrophobic compounds as rapidly as refractory detritus. Algal cell membranes contain polar lipids, and it is likely that this polarity is retained in the early stages of decomposition. KOC does not remain the same upon aging, death, and decomposition, probably because of polarity changes. In an experiment using fresh and aged algal detritus, there was a 100% increase in KOC with aging (Koelmans et al., 1995). KOC increased as the C/N ratio increased, indicating that the material was becoming more refractory. In another study, KOC doubled between day 2 and day 34, probably due to deeper penetration into the organic matrix and lower polarity (Cornelissen et al., 1997).

Polar substrates increase the pKa of the compound (Smejtek and Wang, 1993). This is represented in the model by lowering the pH of polar particulate material by one pH unit, which changes the dissociation accordingly.

The partition equation for labile detritus (non-dissolved) is based on a study by Koelmans et al. (1995) using fresh algal detritus (N = 3, r^2 = 1.0):

$$KOC_{LabPart} = 23.44 \cdot KOW^{0.61} \qquad \textbf{(336)}$$

In the model, the equation is generalized to polar compounds and transformed to an organic matter partition coefficient:

$$KOM_{LabDetr} = (23.44 \cdot KOW^{0.61} \cdot Nondissoc$$
$$+ (1 - Nondissoc) \cdot IonCorr \cdot 23.44 \cdot KOW^{0.61}) \cdot 0.526 \qquad \textbf{(337)}$$

where:

$KOC_{LabPart}$	=	partition coefficient for labile particulate organic carbon (L/kg);
$KOM_{LabDetr}$	=	partition coefficient for labile detritus (L/kg);
$IonCorr$	=	correction factor for decreased sorption, 0.01 for chemicals that are bases and 0.1 for acids. (unitless); and
0.526	=	conversion from KOC to KOM (g OC/g OM).

O'Connor and Connolly (1980; see also Ambrose et al., 1991) found that the sediment partition coefficient is the inverse of the mass of suspended sediment, and Di Toro (1985) developed a construct to represent the relationship. However, AQUATOX models partitioning directly to organic detritus and ignores inorganic sediments, which are seldom involved directly in sorption of neutral organic pollutants. Therefore, the partition coefficient is not corrected for mass of sediment.

Association of hydrophobic compounds with colloidal and dissolved organic matter (DOM) reduces bioavailability; such contaminants are unavailable for uptake by organisms (Stange and Swackhamer 1994, Gilek et al. 1996). Therefore, it is imperative that complexation of organic chemicals with DOM be modeled correctly. In particular, contradictory research results can be reconciled by considering that DOM is not homogeneous. For instance, refractory humic acids, derived from decomposition of terrestrial and wetland organic material, are quite different from labile exudates from algae and other indigenous organisms.

Humic acids exhibit high polarity and do not readily complex neutral compounds. Natural humic acids from a Finnish lake with extensive marshes were spiked with a PCB, but a PCB-humic acid complex could not be demonstrated (Maaret et al. 1992). In another study, Freidig et al. (1998) used artificially prepared Aldrich humic acid to determine a humic acid-DOC partition coefficient (n = 5, r^2, = 0.80), although they cautioned about extrapolation to the field. Landrum et al. (1984) found that KOC values for natural dissolved organic matter were approximately one order of magnitude less than for Aldrich humic acids (Gobas and Zhang 1994); incorporating that factor into the equation of Freidig et al. (1998) yields:

$$KOC_{RefrDOM} = 2.88 \cdot KOW^{0.67} \qquad \textbf{(338)}$$

where:

$KOC_{RefrDOM}$ = refractory dissolved organic carbon partition coefficient (L/kg).

Until a better relationship is found, we are using a generalization of this equation to include polar compounds, transformed from organic carbon to organic matter, in AQUATOX:

$$KOM_{RefrDOM} = (2.88 \cdot KOW^{0.67} \cdot Nondissoc$$
$$+ (1 - Nondissoc) \cdot IonCorr \cdot 2.88 \cdot KOW^{0.67}) \cdot 0.526$$

(339)

where:

  $KOM_{RefrDOM}$ = refractory dissolved organic matter partition coefficient (L/kg).

Algae

Nonpolar lipids in algae occur in the cell contents, and it is likely that they constitute part of the labile dissolved exudate, which may be both excreted and lysed material. Therefore, the stronger relationship reported by Koelmans and Heugens (1998) for partitioning to algal exudate ($n = 6$, r^2 = 0.926) is:

$$KOC_{LabDOC} = 0.88 \cdot KOW$$

(340)

which we also generalized for polar compounds and transformed:

$$KOM_{LabDOM} = (0.88 \cdot KOW \cdot Nondissoc$$
$$+ (1 - Nondissoc) \cdot IonCorr \cdot 0.88 \cdot KOW) \cdot 0.526$$

(341)

where:

  KOC_{LabDOC} = partition coefficient for labile dissolved organic carbon (L/kg); and
  KOM_{LabDOM} = partition coefficient for labile dissolved organic matter (L/kg).

Unfortunately, older data and modeling efforts failed to distinguish between hydrophobic compounds that were truly dissolved and those that were complexed with DOM. For example, the PCB water concentrations for Lake Ontario, reported by Oliver and Niimi (1988) and used by many subsequent researchers, included both dissolved and DOC-complexed PCBs (a fact which they recognized). In their steady-state model of PCBs in the Great Lakes, Thomann and Mueller (1983) defined "dissolved" as that which is not particulate (passing a 0.45 micron filter). In their Hudson River PCB model, Thomann et al. (1991) again used an operational definition of dissolved PCBs. AQUATOX distinguishes between truly dissolved and complexed compounds; therefore, the partition coefficients calculated by AQUATOX may be larger than those used in older studies.

Bioaccumulation of PCBs in algae depends on solubility, hydrophobicity and molecular configuration of the compound, and growth rate, surface area and type, and content and type of lipid in the alga (Stange and Swackhamer 1994). Phytoplankton may double or triple in one day and periphyton turnover may be so rapid that some PCBs will not reach equilibrium (cf. Hill and Napolitano 1997).

Hydrophobic compounds partition to lipids in algae, but the relationship is not a simple one. Phytoplankton lipids can range from 3 to 30% by weight (Swackhamer and Skoglund 1991), and not all lipids are the same. Polar phospholipids occur on the surface. Hydrophobic compounds preferentially partition to internal neutral lipids, but those are usually a minor fraction of the total lipids, and they vary depending on growth conditions and species (Stange and Swackhamer

1994). Algal lipids have a much stronger affinity for hydrophobic compounds than does octanol, so that the algal $BCF_{lipid} > K_{OW}$ (Stange and Swackhamer 1994, Koelmans et al. 1995, Sijm et al. 1998).

For algae, the approximation to estimate the dry-weight bioaccumulation factor ($r^2 = 0.87$), computed from Swackhamer and Skoglund's (1993) study of numerous PCB congeners, is:

$$\log(BCF_{Alga}) = 0.41 + 0.91 \cdot LogKOW \tag{342}$$

where:

BCF_{Alga} =   partition coefficient between algae and water (L/kg).

Rearranging and extending to hydrophilic and ionized compounds:

$$BCF_{Alga} = 2.57 \cdot KOW^{0.93} \cdot Nondissoc$$
$$+ (1 - Nondissoc) \cdot IonCorr \cdot 0.257 \cdot KOW^{0.93} \tag{343}$$

Comparing the results of using these coefficients, we see that they are consistent with the relative importance of the various substrates in binding organic chemicals (Figure 140).   Binding capacity of detritus is greater than dissolved organic matter in Great Lakes waters (Stange and Swackhamer 1994, Gilek et al. 1996).   In a study using Baltic Sea water, less than 7% PCBs were associated with dissolved organic matter and most were associated with algae (Björk and Gilek 1999).   In contrast, in a study using algal exudate and a PCB, 98% of the dissolved concentration was as a dissolved organic matter complex and only 2% was bioavailable (Koelmans and Heugens 1998).

The influence of substrate polarity is evident in Figure 139, which shows the effect of ionization on binding of pentachlorophenol to various types of organic matter. The polar substrates, such as algal detritus, have an inflection point which is one pH unit higher than that of nonpolar substrates, such as refractory detritus. The relative importance of the substrates for binding is also demonstrated quite clearly.

Macrophytes

For macrophytes, an empirical relationship reported by Gobas et al. (1991) for 9 chemicals with *LogKOW*s of 4 to 8.3 ($r^2 = 0.97$) is used:

$$\log(BCF_{Macro}) = 0.98 \cdot LogKOW - 2.24 \tag{344}$$

Again, rearranging and extending to hydrophilic and ionized compounds:

$$BCF_{Macro} = 0.00575 \cdot KOW^{0.98} \cdot (Nondissoc + 0.2) \tag{345}$$

Invertebrates

For the invertebrate bioconcentration factor, the following empirical equation is used for nondetritivores, based on 7 chemicals with *LogKOW*s ranging from 3.3 to 6.2 and bioconcentration factors for *Daphnia pulex* ($r^2 = 0.85$; Southworth et al., 1978; see also Lyman et al., 1982), converted to dry weight:

$$\log(\,BCF_{Invertebrate}\,) = (0.7520 \cdot LogKOW - 0.4362) \cdot WetToDry \qquad \textbf{(346)}$$

where:

$BCF_{Invertebrate}$ = partition coefficient between invertebrates and water (L/kg); and
$WetToDry$ = wet to dry conversion factor (unitless, default = 5).

Extending and generalizing to ionized compounds:

$$BCF_{Invertebrate} = 0.3663 \cdot KOW^{0.7520} \cdot (Nondissoc + 0.01) \qquad \textbf{(347)}$$

For invertebrates that are detritivores the following equation is used, based on Gobas 1993:

$$BCF_{Invertebrate} = \frac{FracLipid}{FracOC_{Detritus}} \cdot KOM_{RefrDetr} \cdot (Nondissoc + 0.01) \qquad \textbf{(348)}$$

where:

$BCF_{Invertebrate}$ = partition coefficient between invertebrates and water (L/kg);
$FracLipid$ = fraction of lipid within the organism;
$FracOC_{Detritus}$ = fraction of organic carbon in detritus (= 0.526);
$KOM_{RefrDetr}$ = partition coefficient for refractory sediment detritus (L/kg), see **(334)**.

Figure 142. Partitioning to Various Types of Organic Matter as Function of Kow
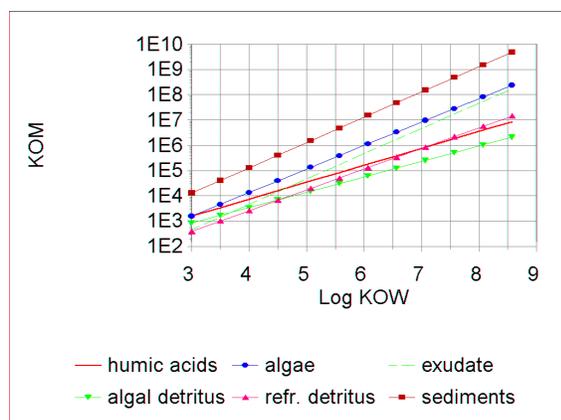
Figure 143. Partitioning to Various Types of Organic Matter as a Function of pH
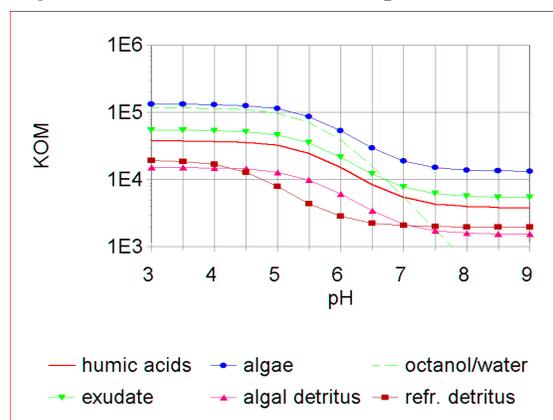
Fish

Fish take longer to reach equilibrium with the surrounding water; therefore, a nonequilibrium bioconcentration factor is used. For each pollutant, a whole-fish bioconcentration factor is based

on the lipid content of the fish extended to hydrophilic chemicals (McCarty et al., 1992), with provision for ionization:

$$KB_{Fish} = Lipid \cdot WetToDry \cdot KOW \cdot (Nondissoc + 0.01) \qquad (349)$$

where:

KB_{Fish}	=	partition coefficient between whole fish and water (L/kg);
$Lipid$	=	fraction of fish that is lipid (g lipid/g fish); and
$WetToDry$	=	wet to dry conversion factor (unitless, default = 5).

The bioconcentration factor is adjusted for the time to reach equilibrium as a function of the clearance or elimination rate and the time of exposure (Hawker and Connell, 1985; Connell and Hawker, 1988; Figure 144):

$$BCF_{Fish} = KB_{Fish} \cdot \left(1 - e^{(-Depuration \bullet TElapsed)}\right) \qquad (350)$$

where:

BCF_{Fish}	=	quasi-equilibrium bioconcentration factor for fish (L/kg);
$TElapsed$	=	time elapsed since fish was first exposed (d); and
$Depuration$	=	clearance, which may include biotransformation, see **(372)** (1/d).

Figure 144. Bioconcentration factor for fish as a function of time and log KOW
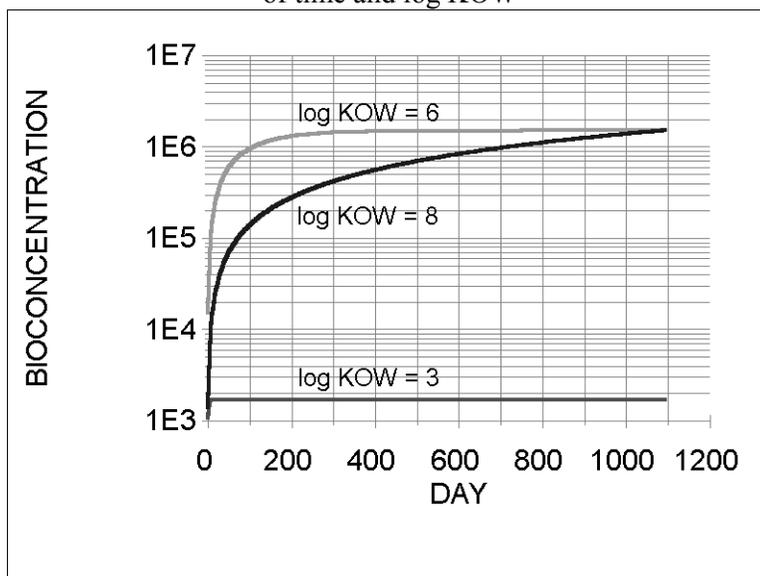
8.7 Nonequilibrium Kinetics

Often there is an absence of equilibrium due to growth or insufficient exposure time, metabolic biotransformation, dietary exposure, and nonlinear relationships for very large and/or superhydrophobic compounds (Bertelsen et al. 1998). Although it is important to have a knowledge of equilibrium partitioning because it is an indication of the condition toward which systems tend (Bertelsen et al. 1998), it is often impossible to determine steady-state potential due

to changes in bioavailability and physiology (Landrum 1998). For example, PCBs may not be at steady state even in large systems such as Lake Ontario that have been polluted over a long period of time. In fact, PCBs in Lake Ontario exhibit a 25-fold disequilibrium (Cook and Burkhard 1998). The challenge is to obtain sufficient data for a kinetic model (Gobas et al. 1995).

Sorption and Desorption to Detritus

Partitioning to detritus appears to involve rapid sorption to particle surfaces, followed by slow movement into, and out of, organic matter and porous aggregates (Karickhoff and Morris, 1985). Therefore attainment of equilibrium may be slow. Because of the need to represent sorption and desorption separately in detritus, kinetic formulations are used (Thomann and Mueller, 1987), with provision for ionization:

$$Sorption = k1_{Detr} \cdot Toxicant_{Water} \cdot (Nondissoc + 0.01)$$
$$\cdot Org2C \cdot Detr \cdot UptakeLimit \cdot 1e\text{-}6 \tag{351}$$

$$Desorption = k2_{Detr} \cdot Toxicant_{Detr} \tag{352}$$

where:

Sorption	=	rate of sorption to given detritus compartment (µg/L·d);
$k1_{Detr}$	=	sorption rate constant (user-editable, default value of 1.39 L/kg·d), see **(355)**;
Nondissoc	=	fraction not ionized (unitless), see **(311)**;
$Toxicant_{Water}$	=	concentration of toxicant in water (µg/L);
Org2C	=	conversion factor for organic matter to carbon (= 0.526 g C/g organic matter);
Detr	=	mass of each of the detritus compartments per unit volume (mg/L);
1e -6	=	units conversion (kg/mg);
Desorption	=	rate of desorption from given sediment detritus compartment (µg/L·d);
$k2_{Detr}$	=	desorption rate constant (1/d), see **(354)**;
UptakeLimit	=	factor to limit uptake as equilibrium is reached (unitless) see **(352)**; and
$Toxicant_{Detr}$	=	mass of toxicant in each of the detritus compartments (µg/L).

In order to limit sorption to detritus and algae as equilibrium is reached, *UptakeLimit* is computed as:

$$UptakeLimit_{Carrier} = \frac{Toxicant_{Water} \cdot kp_{Carrier} - PPB_{Carrier}}{Toxicant_{Water} \cdot kp_{Carrier}} \tag{353}$$

where:

$UptakeLimit_{Carrier}$ =   factor to limit uptake as equilibrium is reached (unitless);

$kp_{Carrier}$ =   partition coefficient (KOM) or bioconcentration factor (BCF) for each carrier (L/kg), see **(333)** to **(342)**;

$PPB_{Carrier}$ =   concentration of toxicant in each carrier (µg/kg), see **(310)**.

Desorption of the detrital compartments is the reciprocal of the reaction time, which Karickhoff and Morris (1985) found to be a linear function of the partition coefficient over three orders of magnitude ($r^2 = 0.87$):

$$\frac{1}{k2} \approx 0.03 \cdot 24 \cdot KOM \tag{354}$$

So *k2* is taken to be:

$$k2 = \frac{1.39}{KOM} \tag{355}$$

where:

KOM	=	detritus-water partition coefficient (L/kg OM, see section 8.6); and
24	=	conversion from hours to days.

Because the kinetic definition of the detrital partition coefficient *KOM* is:

$$KOM = \frac{k1}{k2} \tag{356}$$

the sorption rate constant *k1* is set by the user (*K1 Detritus*). The default value is 1.39 L/kg·d.

Bioconcentration in Macrophytes and Algae

Macrophytes: As Gobas et al. (1991) have shown, submerged aquatic macrophytes take up and release organic chemicals over a measurable period of time at rates related to the octanol-water partition coefficient.   Uptake and elimination are modeled assuming that the chemical is transported through both aqueous and lipid phases in the plant, with rate constants using empirical equations fit to observed data (Gobas et al., 1991), modified to account for ionization effects (Figure 145, Figure 146):

$$MacroUptake = k1 \cdot Toxicant_{Water} \cdot StVar_{Plant} \cdot 1e\text{-}6 \tag{357}$$

$$Depuration_{Plant} = k2 \cdot Toxicant_{Plant} \tag{358}$$

$$k1 = \frac{1}{0.0020 + \dfrac{500}{KOW \cdot Nondissoc}} \tag{359}$$

If the user selects to estimate the elimination rate constant based on KOW (see section 8.8), the following equation is used:

$$k2 = \frac{1}{1.58 + 0.000015 \cdot KOW \cdot Nondissoc} \tag{360}$$

where:

$MacroUptake$	=	uptake of toxicant by plant (μg/L·d);
$Depuration_{Plant}$	=	clearance of toxicant from plant (μg/L·d);
$StVar_{Plant}$	=	biomass of given plant (mg/L);
1 e -6	=	units conversion (kg/mg);
$Toxicant_{Plant}$	=	mass of toxicant in plant (μg/L);
$k1$	=	sorption rate constant (L/kg·d);
$k2$	=	elimination rate constant (1/d).
KOW	=	octanol-water partition coefficient (unitless); and
$Nondissoc$	=	fraction of un-ionized toxicant (unitless).

Figure 145. Uptake rate constant for macrophytes
(after Gobas et al., 1991)
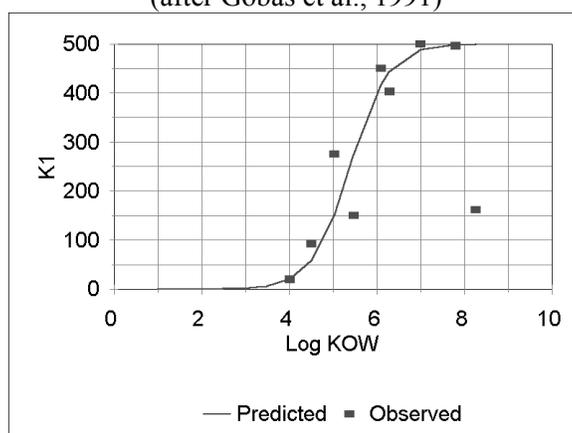
Figure 146. Elimination rate constant for macrophytes
(after Gobas et al., 1991)
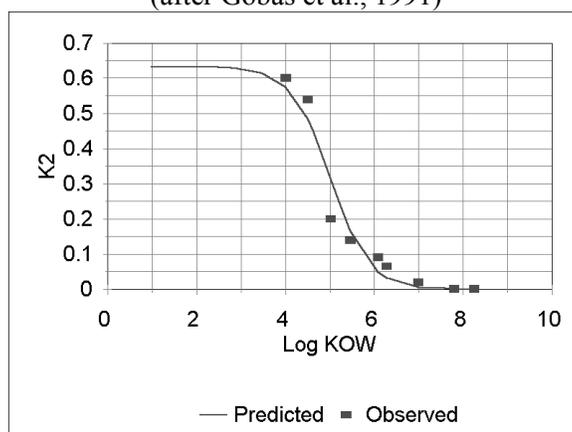
Algae: Aside from obvious structural differences, algae may have very high lipid content (20% for *Chlorella* sp. according to Jørgensen et al., 1979) and macrophytes have a very low lipid

content (0.2% in *Myriophyllum spicatum* as observed by Gobas et al. (1991), which affect both uptake and elimination of toxicants. However, the approach used by Gobas et al. (1991) in modeling bioaccumulation in macrophytes provides a useful guide to modeling kinetic uptake in algae.

There is probably a two-step algal bioaccumulation mechanism for hydrophobic compounds, with rapid surface sorption of 40-90% within 24 hours and then a small, steady increase with transfer to interior lipids for the duration of the exposure (Swackhamer and Skoglund 1991). Uptake increases with increase in the surface area of algae (Wang et al. 1997). Therefore, the smaller the organism the larger the uptake rate constant (Sijm et al. 1998). However, in small phytoplankton, such as the nannoplankton that dominate the Great lakes, a high surface to volume ratio can increase sorption, but high growth rates can limit internal contaminant concentrations (Swackhamer and Skoglund 1991). The combination of lipid content, surface area, and growth rate results in species differences in bioaccumulation factors among algae (Wood et al. 1997). Uptake of toxicants is a function of the uptake rate constant and the concentration of toxicant truly dissolved in the water, and is constrained by competitive uptake by other compartments; also, because it is fast, it is limited as it approaches equilibrium, similar to sorption to detritus :

$$AlgalUptake = k1 \cdot UptakeLimit_{Alga} \cdot ToxState \cdot Carrier \cdot 1e\text{-}6 \qquad (361)$$

where:

AlgalUptake	=	rate of sorption by algae (μg/L-d);
k1	=	uptake rate constant (L/kg-d), see **(361)**;
UptakeLimit$_{Alga}$	=	factor to limit uptake as equilibrium is reached (unitless), see **(352)**;
ToxState	=	concentration of dissolved toxicant (μg/L);
Carrier	=	biomass of algal compartment (mg/L); and
1e-6	=	conversion factor (kg/mg).

The kinetics of partitioning of toxicants to algae is based on studies on PCB congeners in The Netherlands by Koelmans, Sijm, and colleagues and at the University of Minnesota by Skoglund and Swackhamer. Both groups found uptake to be very rapid. Sijm et al. (1998) presented data on several congeners that were used in this study to develop the following relationship for phytoplankton (Figure 147):

$$k1 = \frac{1}{1.8\,E\text{-}6 + 1/(KOW \cdot (Nondissoc + 0.01))} \qquad (362)$$

Because size-dependent passive transport is indicated (Sijm et al., 1998), uptake by periphyton is set arbitrarily at ten percent of that for phytoplankton.

Depuration is modeled as a linear function; it does not include loss due to excretion of photosynthate with associated toxicant, which is modeled separately:

$$Depuration = k2 \cdot State \qquad (363)$$

where:

Depuration	=	elimination of toxicant (μg/L-d);
State	=	concentration of toxicant associated with alga (μg/L); and
k2	=	elimination rate constant (1/d).

As a simplifying assumption, the depuration rate for periphyton is assumed to be two orders of magnitude less:

$$Depuration = k2 \cdot State \cdot 0.01 \qquad \textbf{(364)}$$

The elimination rate in plants may be input in the toxicity record by the user or it may be estimated using the following equation based in part on Skoglund et al. (1996). Unlike Skoglund, this equation ignores surface sorption and recognizes that growth dilution is explicit in AQUATOX (see Figure 148):

$$k2_{Algae} = \frac{2.4\,E+5}{(KOW \cdot LFrac \cdot WetToDry)} \qquad \textbf{(365)}$$

where:

$k2_{Akgae}$	=	desorption rate constant (1/d);
LFrac	=	fraction lipid (wet weight), entered in the "chemical toxicity" screen; and
WetToDry	=	translation from wet to dry weight (user input).

Figure 147. Algal sorption rate constant as a function of octanol-water partition coefficient
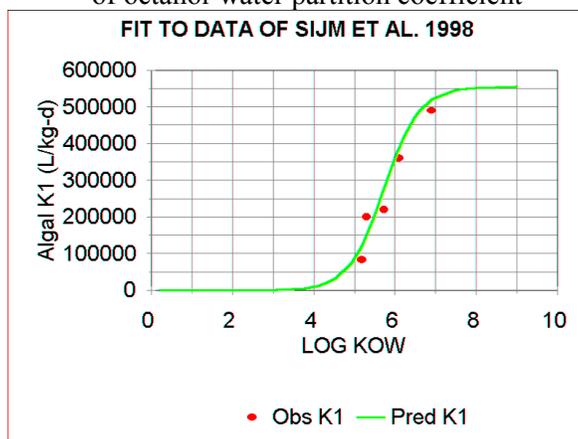
Figure 148. Rate of elimination by algae as a function of octanol-water partition coefficient
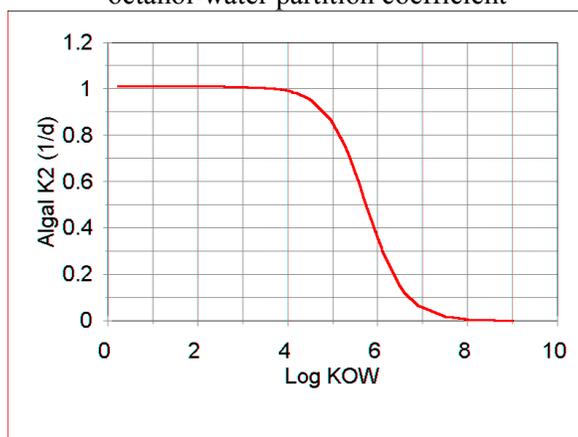
Bioaccumulation in Animals

Animals can absorb toxic organic chemicals directly from the water through their gills and from contaminated food through their guts. Direct sorption onto the body is ignored as a simplifying assumption in this version of the model. Reduction of body burdens of organic chemicals is accomplished through excretion and biotransformation, which are often considered together as empirically determined elimination rates. "Growth dilution" occurs when growth of the organism is faster than accumulation of the toxicant. Gobas (1993) includes fecal egestion, but in AQUATOX egestion is merely the amount ingested but not assimilated; it is accounted for indirectly in *DietUptake*. However, fecal loss is important as an input to the detrital toxicant pool, and it is considered later in that context. Inclusion of mortality and promotion terms is necessary for mass balance, but emphasizes the fact that average concentrations are being modeled for any particular compartment.

Gill Sorption:An important route of exposure is by active transport through the gills (Macek et al., 1977). This is the route that has been measured so often in bioconcentration experiments with fish. As the organism respires, water is passed over the outer surface of the gill and blood is moved past the inner surface. The exchange of toxicant through the gill membrane is assumed to be facilitated by the same mechanism as the uptake of oxygen, following the approach of Fagerström and Åsell (1973, 1975), Weininger (1978), and Thomann and Mueller (1987; see also Thomann, 1989). Therefore, the uptake rate for each animal can be calculated as a function of respiration (Leung, 1978; Park et al., 1980):

$$GillUptake = KUptake \cdot Toxicant_{Water} \cdot Frac_{WaterColumn} \qquad (366)$$

$$KUptake = \frac{WEffTox \cdot Respiration \cdot O2Biomass}{Oxygen \cdot WEffO2} \qquad (367)$$

where:

      GillUptake   =   uptake of toxicant by gills (µg/L - d);

KUptake	=	uptake rate (1/d);
Toxicant$_{Water}$	=	concentration of toxicant in water (μg/L);
Frac$_{WaterColumn}$	=	fraction of organism in water column (unitless), differentiates from pore-water uptake if the multi-layer sediment model is included;
WEffTox	=	withdrawal efficiency for toxicant by gills (unitless), see **(367)**;
Respiration	=	respiration rate (mg biomass/L·d), see **(100)**;
O2Biomass	=	ratio of oxygen to organic matter (mg oxygen/mg biomass; 0.575);
Oxygen	=	concentration of dissolved oxygen (mg oxygen/L), see **(186)**; and
WEffO2	=	withdrawal efficiency for oxygen (unitless, generally 0.62);

The oxygen uptake efficiency *WEffO2* is assigned a constant value of 0.62 based on observations of McKim et al. (1985). The toxicant uptake efficiency, *WEffTox*, can be expected to have a sigmoidal relationship to the log octanol-water partition coefficient based on aqueous and lipid transport (Spacie and Hamelink, 1982). This is represented by an inelegant but reasonable, piece-wise fit (Figure 149) to the data of McKim et al. (1985) using 750-g fish, corrected for ionization:

$$\text{If } LogKOW < 1.5 \text{ then}$$
$$WEffTox = 0.1$$

$$\text{If } 1.5 \le LogKOW > 3.0 \text{ then}$$
$$WEffTox = 0.1 + \text{Nondissoc} \cdot (0.3 \cdot LogKOW - 0.45)$$

$$\text{If } 3.0 \le LogKOW \le 6.0 \text{ then}$$
$$WEffTox = 0.1 + \text{Nondissoc} \cdot 0.45$$

(368)

$$\text{If } 6.0 < LogKOW < 8.0 \text{ then}$$
$$WEffTox = 0.1 + \text{Nondissoc} \cdot (0.45 - 0.23 \cdot (LogKOW - 6.0))$$

$$\text{If } LogKOW \ge 8.0 \text{ then}$$
$$WEffTox = 0.1$$

where:

LogKOW	=	log octanol-water partition coefficient (unitless); and
Nondissoc	=	fraction of toxicant that is un-ionized (unitless), see **(311)**.

Figure 149. Piece-wise fit to observed toxicant uptake data;
Modified from McKim et al., 1985
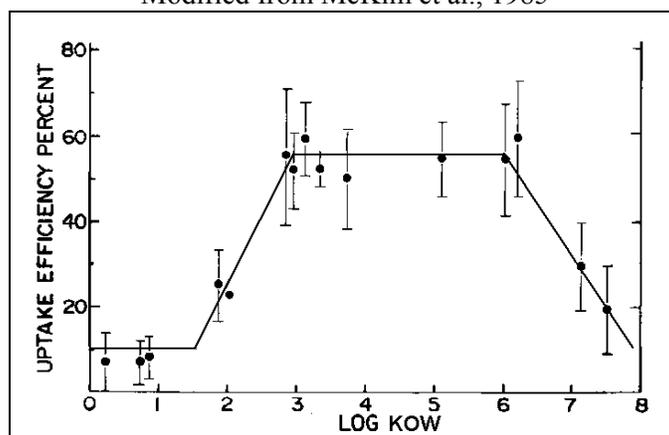
Ionization decreases the uptake efficiency (Figure 147). This same algorithm is used for invertebrates. Thomann (1989) has proposed a similar construct for these same data and a slightly different construct for small organisms, but the scatter in the data does not seem to justify using two different constructs.

Figure 150. The Effect of Differing Fractions of Un-ionized Chemical on Uptake Efficiency
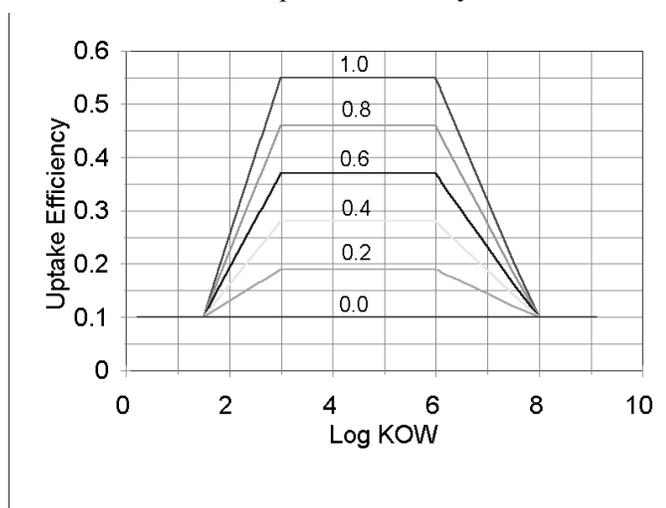
The user input $Frac_{WaterColumn}$ parameter is only relevant if the multi-layer sediment model is included. If so, this parameter determines how much gill uptake comes from the water column and how much from the pore waters of the active layer. Gill uptake from pore waters is calculated as follows and added to gill uptake from the water column:

$$GillUptake_{PoreWater} = KUptake \cdot Toxicant_{PoreWater} \cdot (1 - Frac_{WaterColumn}) \cdot \frac{Volume_{PoreWater}}{Volume_{WaterCol}} \quad \text{(369)}$$

where:

$GillUptake$ = uptake of toxicant by gills ($\mu g/L_{WaterCol}$ - d);
$Toxicant_{PoreWater}$ = concentration of toxicant in pore waters ($\mu g/L_{PoreWater}$);
$Volume_{PoreWater}$ = volume of pore water ($L_{PoreWater}$); and
$Volume_{WaterCol}$ = volume of water column ($L_{WaterCol}$).

Dietary Uptake: Hydrophobic chemicals usually bioaccumulate primarily through absorption from contaminated food.   Persistent, highly hydrophobic chemicals demonstrate biomagnification or increasing concentrations as they are passed up the food chain from one trophic level to another; therefore, dietary exposure can be quite important (Gobas et al., 1993). Uptake from contaminated prey can be computed as (Thomann and Mueller, 1987; Gobas, 1993):

$$DietUptake_{Prey} = KD_{Prey} \cdot PPB_{Prey} \cdot 1\text{e-}6 \qquad\qquad \textbf{(370)}$$

where:

$$KD_{Prey} = GutEffTox \cdot GutEffRed \cdot Ingestion_{Prey} \qquad\qquad \textbf{(371)}$$

and:

$DietUptake_{Prey}$ = uptake of toxicant from given prey (μg toxicant/L·d);
KD_{Prey} = dietary uptake rate for given prey (mg prey/L·d);
PPB_{Prey} = conc. of toxicant in given prey (μg toxicant/kg prey), see **(310)**;
1 e-6 = units conversion (kg/mg);
$GutEffTox$ = efficiency of sorption of toxicant from gut (unitless);
$GutEffRed$ = reduction in $GutEffTox$ due to non-lethal effects, see **(371)** ; and
$Ingestion_{Prey}$ = ingestion of given prey (mg prey/L·d), see **(91)**.

Gobas (1993) presents an empirical equation for estimating $GutEffTox$ as a function of the octanol-water partition coefficient. However, data published by Gobas et al. (1993) suggest that there is no trend in efficiency between $LogKOW$ 4.5 and 7.5 (Figure 151); this is to be expected because the digestive system has evolved to assimilate a wide variety of organic molecules. Therefore, the mean value of 0.62 is used in AQUATOX as a constant for small fish. Nichols et al. (1998) demonstrated that uptake is more efficient in larger fish; therefore, a value of 0.92 is used for large game fish because of their size. Invertebrates generally exhibit lower efficiencies; Landrum and Robbins (1990) showed that values ranged from 0.42 to 0.24 for chemicals with log KOWs from 4.4 to 6.7; the mean value of 0.35 is used for invertebrates in AQUATOX. These values cannot be edited at this time. (Note, the PFA model uses a relationship to chain length, see **(403)** and **(404)**.)

Figure 151. GutEffTox constant based on mean value for data
from Gobas et al., 1993
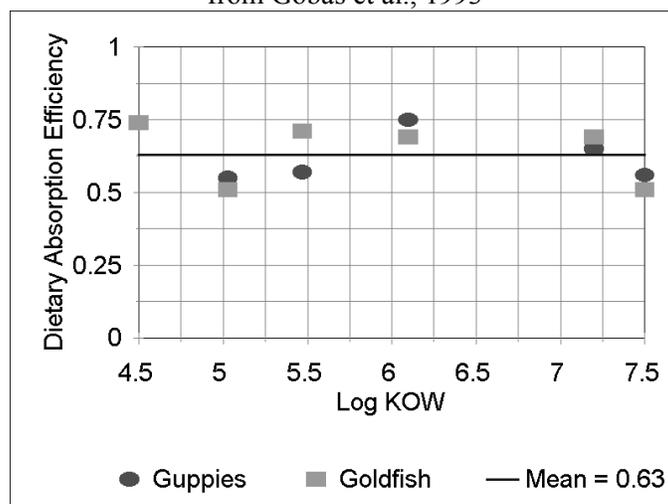
One potential non-lethal effect of toxicant exposure is an increase in the rate of egestion, see **(425)**. If *GutEffTox* is kept constant at the same time that the egestion rate is increased, toxicant concentrations will increase too much within organisms (biomass falls but toxicant uptake remains constant). To avoid this problem, and to reflect that the rate of toxicant uptake is more a function of assimilated rather than total ingested food, the *GutEffTox* must be reduced by the same quantity that assimilated food is decreased.

$$GutEffRed = 1 - RedGrow \tag{372}$$

where:

GutEffRed	=	reduction in *GutEffTox* due to toxicant induced increased egestion (unitless);
RedGrow	=	factor for reduced assimilation of food in animals (unitless); see **(422)**.

Despite this adjustment, if overall species growth rates become negative due to the reduced assimilation of food in animals, toxicant concentrations in animals will still increase (a process that is best conceived as the opposite of growth dilution.)

Elimination: Elimination or clearance includes both excretion (depuration) and biotransformation of a toxicant by organisms. Biotransformation may cause underestimation of elimination (McCarty et al., 1992). An overall elimination rate constant is estimated and reported in the toxicity record. The user may then modify the value based on observed data; that value is used in subsequent simulations. If, known, biotransformation also can be explicitly modeled.

For any given time the clearance rate is:

$$Depuration_{Animal} = k2 \cdot Toxicant_{Animal} \cdot TCorr \tag{373}$$

where:

$Depuration_{Animal}$	=	clearance rate (µg/L·d);
$k2$	=	elimination rate constant (1/d);
$Toxicant_{Animal}$	=	mass of toxicant in given animal (µg/L); and
$TCorr$	=	correction for suboptimal temperature (unitless), see **(59)**.

If the multi-layer sediment model is included, the amount of depuration that goes to the water column vs. the active layer of pore waters is determined by the user input "Frac. in Water Column" parameter.

Estimation of the elimination rate constant $k2$ is based on a slope related to log K_{OW} and an intercept that is a direct function of respiration, assuming an allometric relationship between respiration and the weight of the animal (Thomann, 1989), and an inverse function of the lipid content in a construct unique to AQUATOX:

If $WetWt < 5$ g then

$$\text{Log } k2 = -0.536 \cdot \text{Log } K_{OW} \cdot \text{Log } NonDissoc + 0.065 \cdot \frac{WetWt^{RB}}{LipidFrac} \quad \textbf{(374)}$$

else

$$\text{Log } k2 = -0.536 \cdot \text{Log } K_{OW} \cdot \text{Log } NonDissoc + 0.116 \cdot \frac{WetWt^{RB}}{LipidFrac} \quad \textbf{(375)}$$

where

K_{OW}	=	octanol-water partition coefficient (unitless);
$NonDissoc$	=	fraction of toxicant that is un-ionized (unitless), see **(311);**
$LipidFrac$	=	fraction of lipid in organism (g lipid/g organism wet);
$WetWt$	=	mean wet weight of organism (g);
RB	=	allometric exponent for respiration (unitless).

Figure 152. Depuration rate constants for invertebrates and fish
based on AQUATOX "classic" formulation (equations 373 and 374)
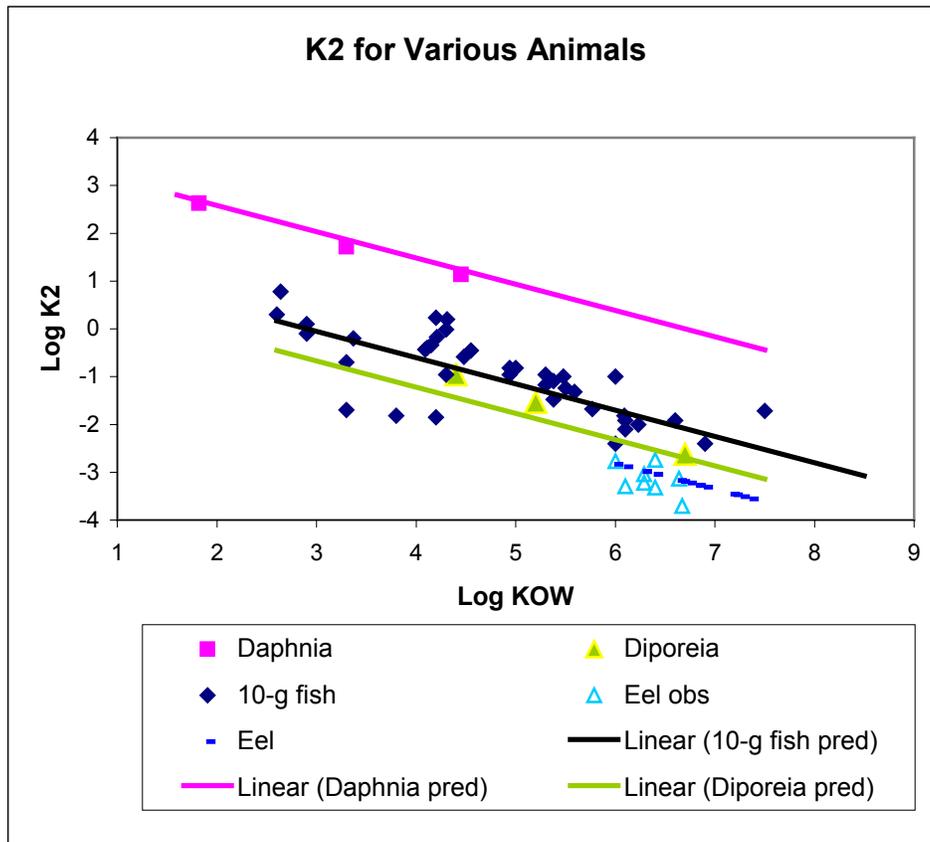
In AQUATOX Release 3.1 and after, an alternative $k2$ estimation procedure is available based on Barber (2003):

$$k2 = \frac{C \cdot WetWt^{-0.197}}{LipidFrac \cdot K_{OW}}$$ (374b)

where

C	=	constant of 445 for fish and 890 for invertebrates;
$WetWt$	=	mean wet weight of organism (g);
$LipidFrac$	=	fraction of lipid in organism (g lipid/g organism wet);
K_{OW}	=	octanol-water partition coefficient (unitless);

Barber's (2003) formulation is based on uptake rates divided by $LipidFrac \times K_{OW}$ (as a surrogate for BCF). The uptake rate equation utilized is based on an allometric analysis of 517 data points, though there is a high degree of uncertainty in this relationship. Figure 153 shows that the AQUATOX and Barber formulations have different relationships between predicted elimination rates and Kow. Our testing suggests that some studies benefit from one uptake formulation and some benefit from the other; however, at this point there is no general guidance as to which formulation to use in a given application.

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Figure 153. *k2* predictions by Log K$_{OW}$ for a 100g fish with 5% lipid
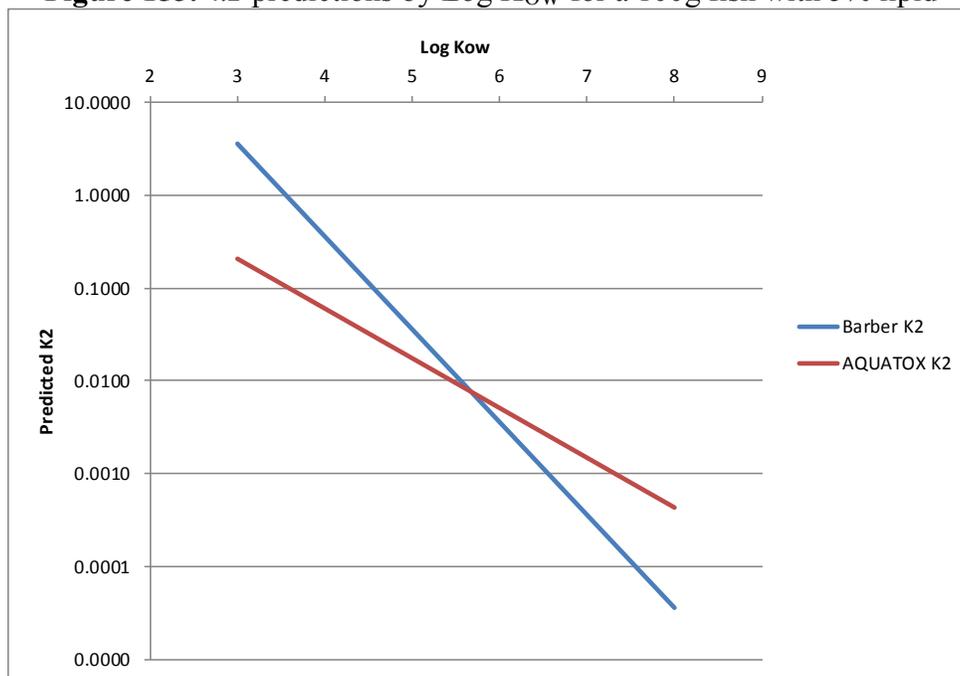
Biotransformation: Biotransformation can cause the conversion of a toxicant to another toxicant or to a harmless daughter product through a variety of pathways. Internal biotransformation to given daughter products by plants and animals is modeled by means of empirical rate constants provided by the user in the "Chemical Biotransformation" screen:

$$Biotransformation = Toxicant_{organism} \cdot BioRateConst_{organism, tox} \tag{376}$$

where

Biotransformation	=	rate of conversion of chemical by given organism (µg/L d),
BioRateConst	=	biotransformation rate constant to a given toxicant, provided by user (1/day)

with the model keeping track of both the loss and the gains to various daughter compartments. A simplifying assumption of the model is that biotransformation occurs at a constant rate throughout a simulation.

Biotransformation also can take place as a consequence of microbial decomposition. The percentage of microbial biotransformation from and into each of the organic chemicals in a simulation can be specified, with different values for aerobic and anaerobic decomposition. The amount of biotransformation into a given chemical can then be calculated as follows for aerobic conditions:

$$Biotransform_{Microb\ In} = \sum_{OrgTox} Microbial\ Degradn_{OrgTox} \cdot FracAerobic \cdot Frac_{OrgTox} \tag{377}$$

and for anaerobic conditions:

$$Biotransform_{Microb\,In} = \sum_{OrgTox} Microbial\,Degradn_{OrgTox} \cdot (1 - FracAerobic) \cdot Frac_{OrgTox} \quad \textbf{(378)}$$

where:

$Biotransform_{Microb\,In}$ = Biotransformation to a given organic chemical in a given detrital compartment due to microbial decomposition (µg/L d);

$MicrobialDegradn$ = total microbial degradation of a different toxicant in this detrital compartment (µg/L d) see **(326)**;

$FracAerobic$ = fraction of the microbial degradation that is aerobic (unitless), see **(378)**; and

$Frac_{OrgTox}$ = user input fraction of the organic toxicant that is transformed to the current organic toxicant (inputs can differ depending on whether the degradation is aerobic or anaerobic).

To calculate the fraction of microbial decomposition that is aerobic, the following equation is used:

$$FracAerobic = \frac{Factor}{DOCorrection} \quad \textbf{(379)}$$

where:

$Factor$ = Michaelis-Menten factor (unitless) see **(161)**;

$DOCorrection$ = effect of oxygen on microbial decomposition (unitless) see **(160)**.

Bioaccumulation Factor: Customarily, bioaccumulation is expressed as a bioaccumulation factor (BAF), which is the ratio of the concentration in the organism to that in the water. The BAF can be expressed as a wet-weight, dry-weight, or lipid-normalized basis (Gobas and Morrison 2000). In AQUATOX, the BAFs are output as both wet-weight and wet-weight lipid-normalized values. The concentration in an organism is wet-weight, and the lipid fraction is input by the user as a wet-weight value:

$$BAF_{Lipid} = Log10\left(\frac{PPB_{Organism} / Toxicant_{Water}}{FracLipid} \right)$$

$$\textbf{(378b)}$$

$$BAF_{Wet} = Log10\left(PPB_{Organism} / Toxicant_{Water} \right)$$

where:

$PPB_{Organism}$ = concentration of toxicant in given animal (µg/kg wet);

$FracLipid$ = fraction of organism that is lipid (g lipid/g organism wet); and

$Toxicant_{Water}$ = concentration of toxicant in water (µg/L);

Linkages to Detrital Compartments

Toxicants are transferred from organismal to detrital compartments through defecation and mortality. The amount transferred due to defecation is the unassimilated portion of the toxicant that is ingested:

$$DefecationTox = \sum(KEgest_{Pred, Prey} \cdot PPB_{Prey} \cdot 1\,e\text{-}6) \tag{380}$$

$$KEgest_{Pred, Prey} = (1 - GutEffTox \cdot GutEffRed) \cdot Ingestion_{Pred, Prey} \tag{381}$$

where::

$DefecationTox$	=	rate of transfer of toxicant due to defecation (µg/L·d);
$KEgest_{Pred, Prey}$	=	fecal egestion rate for given prey by given predator (mg prey/L·d);
PPB_{Prey}	=	concentration of toxicant in given prey (µg/kg), see **(310)**;
1 e-6	=	units conversion (kg/mg);
$GutEffTox$	=	efficiency of sorption of toxicant from gut (unitless); and
$GutEffRed$	=	reduction in $GutEffTox$ due to non-lethal effects, see **(371)** ;
$Ingestion_{Pred, Prey}$	=	rate of ingestion of given prey by given predator (mg/L·d), see **(91)**.

The amount of toxicant transferred due to mortality may be large; it is a function of the concentrations of toxicant in the dying organisms and the mortality rates:

$$MortTox = \sum(Mortality_{Org} \cdot PPB_{Org} \cdot 1e6) \tag{382}$$

where:

$MortTox$	=	rate of transfer of toxicant due to mortality (µg/L·d);
$Mortality_{Org}$	=	rate of mortality of given organism (mg/L·d), see **(66)**, **(87)** and **(112)**;
PPB_{Org}	=	concentration of toxicant in given organism (µg/kg), see **(310)**; and
1 e-6	=	units conversion (kg/mg).

8.8 Alternative Uptake Model: Entering BCFs, K1, and K2

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 Log K_{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 that are subject to very rapid uptake and depuration are not efficiently modeled using these relationships; the rapid rates create stiff equations that require shorter time-steps for solution. In addition, because of the rapid rates, the chemical does approach equilibrium quickly.

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+Km) and the third factor is calculated using the below relationship (Gobas and Morrison 2000, p204) *(note, if the option to estimate the K2 depuration rate based on BCF and K1 is selected, the elimination rate is estimated as the K2 parameter and the metabolism rate is considered to be zero.)*:

$$BCF = \frac{K1}{(K2 + K_m)} \qquad\qquad \textbf{(383)}$$

where: BCF = bioconcentration factor (L/kg dry);
           $K1$ = uptake rate constant (L/kg dry day);
           $K2$ = elimination rate constant (1/d);
           K_m = metabolism or biotransformation, see (375).

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

$$Uptake = K1 \cdot ToxState \cdot Biomass \cdot 1e\text{-}6 \qquad\qquad \textbf{(384)}$$

$$Depuration = K2 \cdot ToxState \qquad\qquad \textbf{(385)}$$

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)
           $1e\text{-}6$ = (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.

8.9 Half-Life Calculation, DT50 and DT95

AQUATOX 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.

$$Loss_{Water} = \frac{Hydrolysis_{Water} + Photolysis + Microbial_{Water} + Washout + Volatilization. + Sorption}{Mass_{Water}} \textbf{(386)}$$

$$Loss_{Sed} = \frac{Microbial_{Sed} + Hydrolysis_{Sed} + Desorption + Scour_{Sed}}{Mass_{Sed}}$$

(387)

where:

$Loss_{Media}$	=	loss rate within media (1/d);
$Hydrolysis_{Media}$	=	hydrolysis rate in given media (μg/L d), see **(313)**;
$Photolysis$	=	photolysis rate in the water column (μg/L d), see **(320)**;
$Microbial_{Media}$	=	rate of microbial metabolism in given media (μg/L d), see **(326)**;
$Washout$	=	rate of toxicant washout from the water column (μg/L d); see **(16)**;
$Volatilization$	=	rate of chemical volatilization in the water column (μg/L d), see **(331)**;
$Sorption$	=	sorption of toxicant to detritus, plants, and animals (μg/L d), see **(350)**;
$Mass_{Media}$	=	mass of chemical in the media (μg/L);
$Desorption$	=	desorption of toxicant from bottom sediment, (μg/L d) see **(351)**;
$Scour$	=	resuspension of toxicants in bottom sediments, (μg/L d) see **(233)**.

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

$$DT50_{Media} = 0.693 / Loss_{Media}$$

(388)

$$DT95_{Media} = 2.996 / Loss_{Media}$$

(389)

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);

8.10 Chemical Sorption to Sediments

When the complex multi-layer sediment model is included, chemicals can sorb to and desorb from suspended inorganic sediments based on user input rates that are applied to the model's equations for sorption **(249),** and desorption **(250)**. To activate this model, required rates are:

K1	*uptake rate constant*	L/kg dry day
K2	*depuration rate constant*	1/day
Kp	*partition coefficient*	L/kg dry

The derivative for toxicants sorbed to inorganic sediments is similar to that for suspended organics:

$$\frac{dToxicant_{SuspSed}}{dt} = Load - Microbial + Sorption - Desorption$$

$$- (Deposition + Washout) \cdot PPB_{SuspSed} \cdot 1\text{e-}6 \qquad \textbf{(390)}$$

$$+ (Washin \cdot PPB_{SuspSedUpstream} \cdot 1\text{e-}6)$$

$$+ (Scour \cdot PPB_{BottomSed} \cdot 1\text{e-}6)$$

where:

$Toxicant_{SuspSed}$	=	toxicant in relevant suspended sediment size-class (μg/L);
$Load$	=	loading of toxicant from external sources (μg/L·d);
$Microbial$	=	rate of loss due to microbial degradation (μg/L·d), see **(326)**;
$Sorption$	=	rate of sorption to given compartment (μg/L·d), see **(350)**;
$Desorption$	=	rate of desorption from given compartment (μg/L·d), see **(351)**;
$Deposition$	=	rate of sedimentation of given suspended detritus (mg/L·d) in streams with the inorganic sediment model attached, see **(230)**;
$Washout$	=	rate of loss of from sediment being carried downstream (mg/L·d), see **(16)**
$Washin$	=	rate of gain from sediment carried in from any upstream linked segments (mg/L·d), see **(30)**;
$Scour$	=	rate of resuspension of given sediment (mg/L·d), see **(227)**;

Chemicals also are tracked within inorganic sediments in the multi-layer sediment bed:

$$\frac{dToxicant_{BottomSed}}{dt} = Sorption - Desorption - Microbial$$

$$+ (Deposition \cdot PPB_{SuspSed} \cdot 1\text{e-}6) + BedLoad_{Tox}$$

$$- (Scour \cdot PPB_{BottomSed} \cdot 1\text{e-}6) - BedLoss_{Tox} \qquad \textbf{(391)}$$

where:

$Toxicant_{BottomSed}$	=	toxicant in bottom sediment (relevant sediment size-class μg/m^2);
$Microbial$	=	rate of loss due to microbial degradation (μg/m^2·d), see **(326)**;
$Sorption$	=	rate of sorption to given compartment (μg/m^2·d after units conversion), see **(350)**;
$Desorption$	=	rate of desorption from given compartment (μg/m^2·d after units conversion), see **(351)**;
$Deposition$	=	rate of sedimentation of given suspended detritus (μg/m^2·d after units conversion) in streams with the inorganic sediment model attached, see **(230)**;
$Scour$	=	rate of resuspension of given sediment (μg/m^2·d after units conversion), see **(227)**;
$BedLoad_{Tox}$	=	rate of bed load of given toxicant (μg/m^2·d), see **(391)**;

$BedLoss_{Tox}$ =   rate of bed loss of given toxicant (µg/m²·d), see **(392)**.

In several cases above, units need to be converted from µg/L·d to µg/m²·d when moving from sediment suspended in the water column to bed sediment. This is done by multiplying by water volume and then dividing by the sediment bed surface area. Toxicant mass balance has been verified to be conservative through this process.

Toxicant movement due to bedload and bedloss are straightforward calculations:

$$BedLoad_{Tox} = \sum \left(\frac{BedLoad_{Upstreamlink}}{AvgArea} \cdot PPB_{UpstreamBed} \cdot 1e\text{-}3 \right) \qquad \textbf{(392)}$$

where:

$BedLoad_{Tox}$	=	toxicant bedload from all upstream segments (µg/m²·d);
$BedLoad_{Upstreamlink}$	=	bedload over one of the upstream links (g/d);
$AvgArea$	=	average area of the segment (m²);
$PPB_{UpstreamBed}$	=	toxicant concentration in the relevant upstream link (µg/kg)
1e-3	=	units conversion (kg/g)

Similarly, total bed loss is the sum of the loadings over all outgoing links:

$$BedLoss_{Tox} = \sum \left(\frac{BedLoss_{Downstreamlink}}{AvgArea} \cdot PPB_{Bed} \cdot 1e\text{-}3 \right) \qquad \textbf{(393)}$$

$BedLoss_{Tox}$	=	toxicant bedloss from current segment (µg/m²·d);
$BedLoss_{Downstreamlink}$	=	bedloss over one of the downstream links (g/d);
$AvgArea$	=	average area of the segment (m²) ;
PPB_{Bed}	=	toxicant concentration in the current segment (µg/kg)
1e-3	=	units conversion (kg/g)

8.11 Chemicals in Pore Waters

When the complex multi-layer sediment model is included, pore waters may contain toxic organic chemicals. Chemicals in pore waters are separated into those that are freely dissolved and those that are complexed to dissolved organic carbon within the pore waters.

$$\frac{dToxicant_{FreelyDissolvedP.W.}}{dt} = GainTox_{Up} - LossTox_{Up} \pm Diff_{Down} \pm Diff_{Up} + Decomp$$
$$- GillUptake - Microbial - Sorption + Desorption + Depuration \qquad \textbf{(394)}$$

where:

$Toxicant_{FreelyDissolvedP.W.}$ = change in concentration of pore water in the sediment bed normalized per unit area ($\mu g/L_{pw} \cdot d$);

$GainTox_{Up}$ = active layer only: gain of toxicant due to pore water gain from the water column ($\mu g/L_{pw} \cdot d$), see **(394)**;

$LossTox_{Up}$ = active layer only: loss of toxicant due to pore water loss to the water column ($\mu g/L_{pw} \cdot d$), see **(395)**;

$Diff_{Up}, Diff_{Down}$ = diffusion over upper or lower boundary ($\mu g/L_{pw} \cdot d$), see **(256)**;

$Decomp$ = freely dissolved toxicant gain due to microbial decomposition of organic matter ($\mu g/L_{pw} \cdot d$), see **(159)**;

$GillUptake$ = active layer only: uptake of toxicant into organisms that reside at least partially in the sediment ($\mu g/L_{pw} \cdot d$) **(365)**;

$Depuration$ = active layer only: excretion of toxicant by organisms that reside at least partially in the sediment ($\mu g/L_{pw} \cdot d$), **(362)**;

$Microbial$ = loss of toxicant in pore waters due to microbial degradation ($\mu g/L_{pw} \cdot d$) see **(326)**;

$Sorption, Desorption$ = sorption to and desorption from organic matter and inorganic matter in the current layer ($\mu g/L_{pw} \cdot d$). **(350)**, **(351)**

$$GainTox_{Up} = \frac{Gain_{Up} \cdot Area_{SedLayer} \cdot ConcTox_{WaterCol} \cdot 1e3}{Volume_{PoreWater}} \tag{395}$$

$$LossTox_{Up} = \frac{Loss_{Up} \cdot Area_{SedLayer} \cdot ConcTox_{PoreWater} \cdot 1e3}{Volume_{PoreWater}} \tag{396}$$

where:

$GainTox_{Up}$ = gain of toxicant in pore water from the water col. ($\mu g/L_{pw} \cdot d$);

$LossTox_{Up}$ = loss of toxicant in pore water to the water column above ($\mu g/L_{pw} \cdot d$);

$Gain_{Up}, Loss_{Up}$ = gain or loss of pore water from the water column above ($m^3/m^2 \cdot d$); see **(252)**, **(251)**;

$Area_{SedLayer}$ = sediment layer area (m^2);

$ConcTox_{Media}$ = concentration of toxicant in relevant media ($\mu g/L$);

$Volume_{PoreWater}$ = pore water volume (L_{pw});

$1e3$ = units conversion (L/m^3).

Chemicals also sorb to dissolved organic matter within pore waters:

$$\frac{dToxicant_{DOMPoreWater}}{dt} = GainDOMTox_{Up} - LossDOMTox_{Up} \pm Diff_{Down} \pm Diff_{Up}$$

$$- (Decomp \cdot PPB \cdot 1e - 6) - Microbial - Sorption + Desorption \qquad \textbf{(397)}$$

where:

$GainDOMTox_{Up}$ = gain of toxicant sorbed to DOM from the water column ($\mu g/L_{pw} \cdot d$) see **(394)**;

$LossDOMTox_{Up}$ = loss of toxicant sorbed to DOM in pore water to the water column above ($\mu g/L_{pw} \cdot d$) see **(395)**;

$Diff_{Up}, Diff_{Down}$ = diffusion over upper or lower boundary ($\mu g/L_{pw} \cdot d$), see **(256)**;

$Decomp$ = Decomposition of DOM ($\mu g/L_{pw} \cdot d$), see **(159);**

$Microbial$ = loss of toxicant sorbed to DOM due to microbial degradation ($\mu g/L_{pw} \cdot d$) see **(326)**;

$Sorption$ = sorption to DOM ($\mu g/L_{pw} \cdot d$). **(350)**

$Desorption$ = desorption from DOM ($\mu g/L_{pw} \cdot d$). **(351)**

8.12 Mass Balance Capabilities and Testing

A chemical mass balance testing capability was added to the code during the development of the estuarine version of AQUATOX. This capability ensured that all linkages between stratified layers were properly developed with no loss of mass balance. New PFA (perfluorinated acid) formulations were also tested for mass balance with this capability. Current testing indicates that AQUATOX balances chemical mass to machine accuracy.

The chemical mass balance testing comprehensively tracks the mass of all chemical loadings and losses to the system. Chemical mass balance is explicitly tested with this capability; mass balance of state variables containing chemicals is implicitly tested. The Chemical *MBTest* output variable keeps track of all chemical by the following equation:

$$MBTest = Chemical\ Mass + Chemical\ Loss - Chemical\ Load - Net\ Layer\ Exchange \qquad \textbf{(398)}$$

In this manner, the *MBTest* will stay constant (within machine accuracy) throughout a simulation if mass balance is being maintained. However, the chemical mass balance function does not work if the "Keep Freely Dissolved Contaminant Constant" option is selected within the setup screen.

The chemical mass balance capability also provides a chemical tracking capability that allows the user to see exactly what is happening to the chemical within the system. Chemical fate may be tracked using the following output categories (all units are in kilograms):

Chem. MBTest: Mass balance test as described above, see **(397)**.

Chem. Mass: Total chemical mass in the system including chemicals within

biota.

Chem. Loss + Mass: Chemical loss plus chemical mass in the system.

Chem. Tot Wash: Washout of chemical from the system since the simulation start. The sum of the below four categories:
Chem. WashH2O: *Washout of chemical dissolved in water*
Chem. WashAnim: *Washout of chemical in drifting animals.*
Chem. WashDetr: *Washout of chemical in suspended & dissolved detritus.*
Chem. WashPlnt: *Washout of chemical in plants*

Chem. Tot Loss: Total loss of chemical from the system since the simulation start. The sum of the following eight categories plus washout:
Chem. Hydrol: *Chemical loss due to hydrolysis.*
Chem. Photol: *Chemical loss due to photolysis.*
Chem. Volatil: *Chemical loss due to volatilization.*
Chem. MicrobMet: *Chemical loss due to microbial metabolism.*
Chem. BioTrans: *Chemical loss due to biotransformation.*
Chem. EmergeI: *Chemical loss due to the emergence of insects.*
Chem. Fishing Loss: *Chemical loss due to fishing.*

Chem. Tot Load: Total loading of chemical into the system since the simulation start. The sum of the following three categories:
Chem. H2O Load: *Load of chemical directly into water.*
Chem. Detr Load: *Load of chemical within detritus loadings.*
Chem. Biota Load: *Load of chemical within plant and animal loadings.*

Net LayerExch: Net of layer exchange between the other layer in the system. The sum of the below five categories:
Chem. Net Sink: *Net sinking from upper to lower layer.*
Chem. Net Entrain: *Net entrainment of chemical.*
Chem. Net TurbDiff: *Net turbulent diffusion of chemical.*
Chem. Net Migrate: *Net migration of chemical in animals.*
Chem. Delta Thick: *Chemical movement due to changes in the thickness of the two layers.*

8.13 Perfluoroalkylated Surfactants Submodel

As mentioned in the introduction (section 1.5), the perfluorinated compounds of interest as bioaccumulators are the perfluorinated acids (PFAs). Perfluoroctane sulfonate (PFOS) belongs to the sulfonate group and perfluorooctanoic acid (PFOA) belongs to the carboxylate group. Due to their use in industrial manufacturing, these persistent chemicals are found in humans, fish, birds, and marine and terrestrial mammals throughout the world. PFOS has an especially high bioconcentration factor in fish.

Sorption

Perfluorinated surfactants are quite different from hydrocarbon surfactants. The nonpolar perfluorocarbon tail repels both water and oil, and the perfluorinated surfactants are much more active than their hydrocarbon counterparts (Moody and Field 2000). A field is provided for the user to input a value for the organic matter partition coefficient ("Kom for Sediments"); this empirical approach was taken in lieu of sufficient theory to support a mechanistic formulation. Sorption to algae and macrophytes are also modeled empirically ("BCF for Algae" and "BCF for Macrophytes" parameters).

Biotransformation and Other Fate Processes

PFOS and other related chemicals are anionic surfactants and, as such, they are not subject to volatilization. However, the worldwide detection of PFOS suggests that there are one or more precursors that are volatile. Therefore, a fate model for these compounds would not be complete if it were not able to represent the movement and transformation of significant precursors to PFOS and other bioaccumulative fluorinated organics. In particular, some fluorinated compounds are subject to biodegradation of the nonfluorinated portion (Key et al. 1998, Moody and Field 2000, Giesy and Kannan 2001); these can yield both volatile and nonvolatile biotransformation products (Key et al. 1998). For example, *N*-EtFOSE alcohol is subject to microbial degradation, yielding 92% PFOS and 8% PFOA (Lange 2000 cited in Cahill et al. 2003). AQUATOX has the capability of representing biotransformation from one congener or homolog to one or more others when there are sufficient data to parameterize that part of the model.

Bioaccumulation

PFOS and PFOA and similar compounds bioaccumulate differently than PCBs and chlorinated pesticides (Kannan et al. 2001). The perfluorinated compounds of interest as bioaccumulators are the acids. At least for PFOS the salts dissociate instantaneously at neutral pH (OECD 2002). Perfluorinated acids (PFAs) are oil repelling and are taken up by protein rather than lipids (Kannan quoted in *Scientific American*, March, 2001). Therefore, their kinetics cannot be modeled as functions of the octanol-water partition coefficient. Instead, relationships based on perfluoroalkyl chain length (Martin et al. 2003a) are used.

Gill Uptake

Data on PFAs were insufficient at the time this submodel was first developed (2005) to determine withdrawal efficiencies and explicitly include respiration such as is done for other organic compounds simulated by AQUATOX. Based on the data of (Martin et al. 2003a), the uptake rate for all but the longest chain-length carboxylates can be represented as:

$$k1 \quad = \quad SizeCorr \cdot 10^{-5.7213+0.7764 \cdot ChainLength} \tag{399}$$

where

$k1$ =   uptake transfer rate (L/kg d);
$ChainLength$ =   length of perfluoroalkyl chain (integer).

If chain length exceeds 11, the value for 11 is used. These data were based on 5-g trout, and uptake is implicitly a function of respiration, which is sensitive to size. A size correction is based on a standard allometric relationship and the reciprocal of that value for a 5-g fish:

$$SizeCorr \quad = \quad MeanWeight^{RB} \cdot \frac{1}{Sizeref} \tag{400}$$

where

$SizeCorr$ =   allometric correction for size (unitless);
$MeanWeight$ =   mean wet weight of organism (g);
RB =   allometric exponent for respiration (unitless);
$SizeRef$ =   reference value (0.7248).

The respiration rate decreases with larger sizes. The allometric exponent RB is assigned values based on the Wisconsin Bioenergetics Model (Hewett and Johnson 1992). If RB = -0.2 then the correction for a 10-g fish is 0.63, that is, uptake is 63% that of the fish for which the $k1$ values were determined; the correction for a 100-g fish is 55% of the reference; and the correction for a 1000-g fish is 35%. For invertebrates RB is assigned a value of -0.25 (Moloney and Field 1989).

Although there are only two data points for sulfonates (Martin et al. 2003a), the trend defined by those points provides an approximation:

$$k1 \quad = \quad SizeCorr \cdot 10^{-6.00+0.966 \cdot ChainLength} \tag{401}$$

However, the $k1$ values were determined from the first few observed uptake values and not the observations just before the depuration phase of the experiment. Adjusting the intercept actually provides a better fit to the overall experiment:

$$k1 \quad = \quad SizeCorr \cdot 10^{-5.85+0.966 \cdot ChainLength} \tag{402}$$

Uptake rates (*k1* values) must be estimated and entered in the "chemical toxicity" screen and estimates can be modified with user-supplied values if appropriate.

With the greater intercept, the sulfonates are taken up more rapidly than the carboxylates, as shown in Figure 154. Gill uptake is calculated as:

$$GillUptake \quad = Toxicant_{Water} \cdot k1 \cdot StVar_{Animal} \cdot 1e-6 \qquad \textbf{(403)}$$

where:

GillUptake	=	uptake of toxicant by gills (µg/L d);
WetToDry	=	conversion factor for wet to dry weights (5);
SizeCorr	=	allometric correction for size (unitless), see **(400)(400)**;
Toxicant_{Water}	=	concentration of toxicant in water (µg/L);
k1	=	uptake transfer rate (L/kg d);
StVar_{Animal}	=	biomass of given animal (mg/L);
1 e-6	=	units conversion (kg/mg).

Figure 154: Predicted and observed uptake transfer rates for carboxylates and sulfonates.
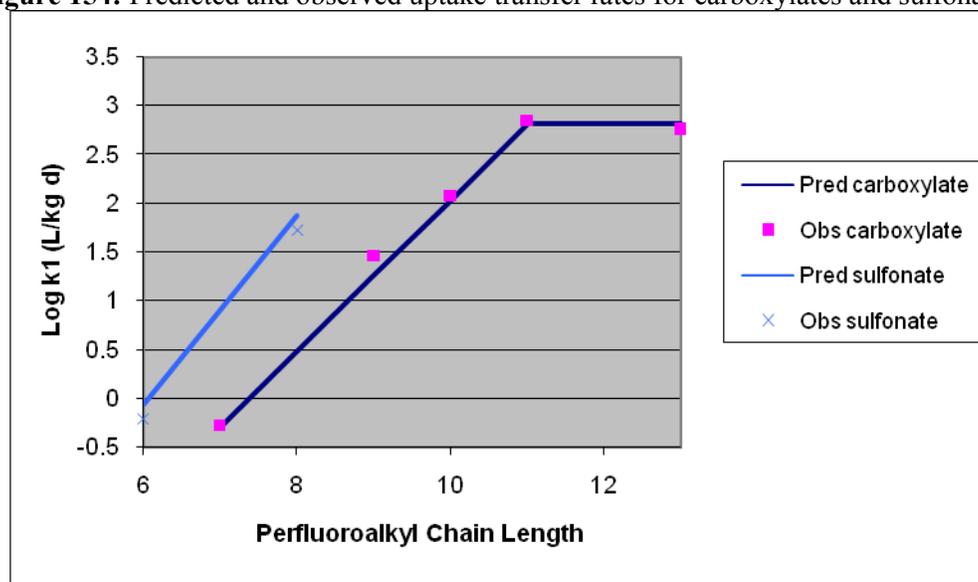
Dietary Assimilation

Martin et al. (2003b) found that assimilation of PFAs was quite efficient, exceeding that for the normal hydrophobic chemicals. However, many of the calculated values reported (Martin et al. 2003b) exceeded 1.0, so the observed assimilation efficiencies were normalized to a maximum of 1.0, and equations were derived for uptake from the gut (*GutEffTox*). If a carboxylate:

$$\log GutEff \quad = \quad -0.91+0.085 \cdot ChainLength \qquad r^2 = 0.897 \qquad \textbf{(404)}$$

If a sulfonate:

$$GutEff \quad = \quad -0.68 + 0.21 \cdot ChainLength \qquad r^2 = 1.0 \ \ (2 \ points) \qquad \textbf{(405)}$$

In the absence of information on other organisms, these equations are used for all animals.

Figure 155: Gut assimilation efficiency as a function of chain length**.**
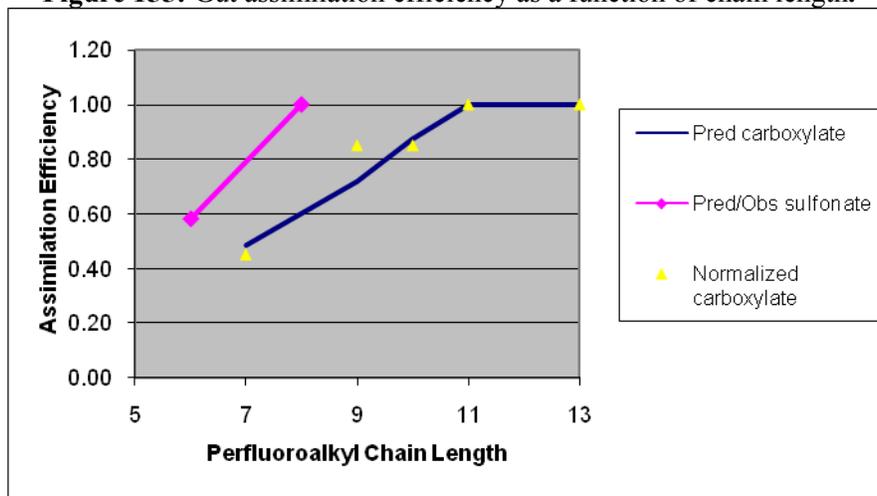
Depuration

Based on regression of published data from experiments with juvenile trout (Martin et al. 2003a, Martin et al. 2003b), carboxylate depuration can be estimated as:

$$k2 \quad = \quad SizeCorr \cdot 10^{-0.0873 \, - \, 0.1207 \cdot ChainLength} \qquad r^2 = 0.98 \qquad \textbf{(406)}$$

where:

$k2$ = depuration rate (1/d).
$SizeCorr$ = allometric correction for size (unitless), see **(400)**;

Only four data points are available for two sulfonate compounds (Martin et al. 2003a, Martin et al. 2003b); but they indicate that depuration is much slower than for carboxylates. The model extrapolates from those two pairs of points, but this estimation procedure should be used with caution (Figure 156):

$$k2 \quad = \quad SizeCorr \cdot 10^{-0.733 \, - \, 0.07 \cdot ChainLength} \qquad r^2 = 0.84 \qquad \textbf{(407)}$$

where:

$k2$ = depuration rate (1/d).
$SizeCorr$ = allometric correction for size (unitless), see **(400)**;

Because uptake is so efficient in the gut, depuration may be largely across the gills. If this is true

then depuration rate can be related to respiration rate, providing a correction for size.

In the absence of any data, this approach to modeling depuration is extended to invertebrates. When data become available on depuration of PFAs in invertebrates, this series of constructs may be modified. Depuration rates (*k2*s) must be estimated and entered in the "chemical toxicity" screen and estimates can be modified with user-supplied values if appropriate.

Figure 156. Depuration rate as a function of perfluoroalkyl chain length.
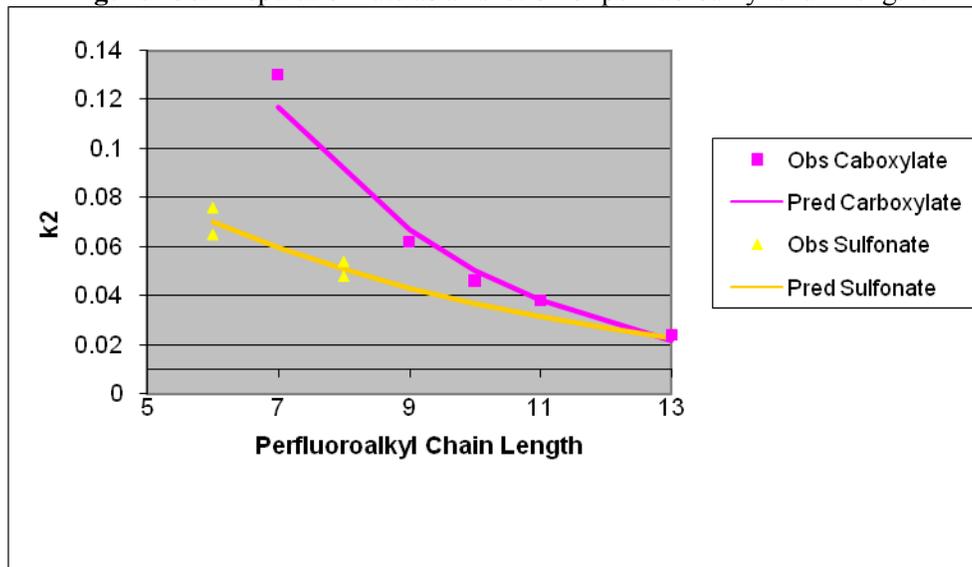
Available data indicate that concentrations of PFOS in wildlife are less than those known to cause toxic effects in laboratory animals (Giesy and Kannan 2001). AQUATOX provides a means of factoring in toxicity data as they become available for aquatic species.

Bioconcentration Factors

The steady-state bioconcentration factor (BCF) for carboxylates, used to compute time-dependent toxicity, can be estimated by (Martin et al. 2003a):

$$\log BCF \quad = \quad -5.724 + 0.9146 \cdot ChainLength \qquad r^2 = 0.995 \qquad \textbf{(408)}$$

where

BCF = bioconcentration factor (L/kg).

Similar to uptake, the slope for the BCFs of sulfonates closely parallels that of carboxylates but with a different intercept (Figure 157):

$$\log BCF_{sulfonate} \quad = \quad -5.195 + 1.03 \cdot ChainLength \qquad r^2 = 1.0 \ \ (2 \ points) \qquad \textbf{(409)}$$

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For compounds with perfluoroalkyl chain lengths in excess of 11, it is assumed that the BCF is the same as that for chain length 11, as suggested by the outlier (Figure 157).

Figure 157. Bioconcentration factors as functions of perfluoroalkyl chain length.
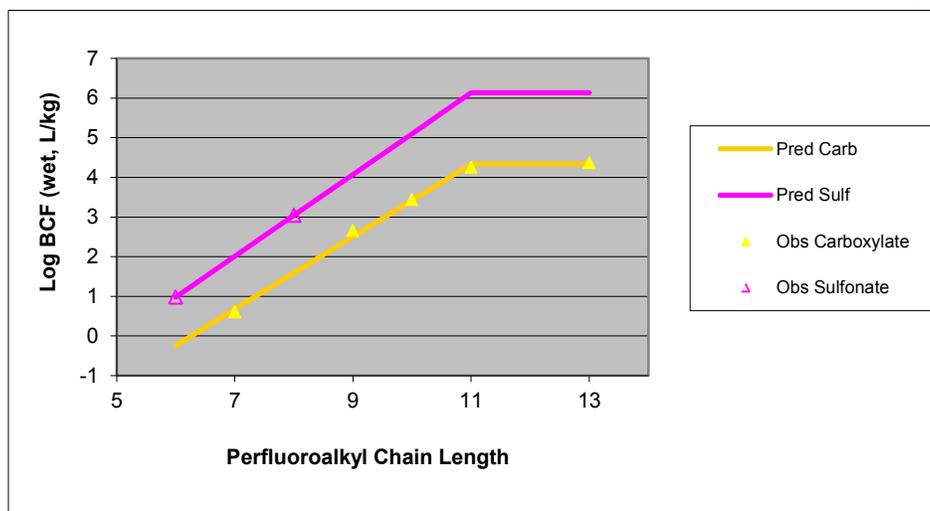
8.14 Aggregation of Organic Chemicals

When modeling entire classes of organic chemicals (e.g. Total PCBs), it is often advantageous to break up the classes into individual compounds or bins (binning individual analytes by octonol/water partition coefficient or K_{ow} for example). In this manner, the bioaccumulation and effects of each portion of the chemical class can be governed by its unique chemical properties. To enable this process, the modeling of up to 20 individual compounds (or K_{ow} bins) has always been a capability since AQUATOX 3.0.

However, this type of modeling can create a mismatch when comparing model results to data. If data are collected by chemical class (e.g. TPCB), individual bins must be summed together before performing comparisons. This was always possible to do within AQUATOX but it required a time-consuming export of data into Excel to perform these calculations and comparisons.

Additionally, chemical toxicity data can sometimes be expressed on a single aggregative class basis rather than an individual analyte basis (e.g. a site-specific LC50 for TPCB).   Unless the modeled bins are aggregated within the model, these types of toxicity data cannot be used.

To better support the modeling of complex groupings of organic chemicals, AQUATOX Release 3.2 has the capability to model one chemical compartment as an aggregated combination of the other compartments. To trigger this capacity, an organic toxicant must be added to the "T1" compartment and the checkbox in the **Setup** window under **Toxicant Modeling Options** that reads "T1 is an aggregate of all other toxicants in study" must be checked.

When this occurs, the following equations become relevant for the toxicant in water and biota

$$T1_{Water} = \sum_{i=2}^{20} Ti_{Water}$$

(408b)

$$T1_{Organism} = \sum_{i=2}^{20} Ti_{Organism}$$

(408c)

where:

$Ti_{Carrier}$ =   concentration of chemical i in carrier, ug/L or PPB;

Derivatives for the chemical in T1 become irrelevant as it is set as a function of the derivatives of all of its individual bins (T2 to T20).

Chemical toxicity data may be entered for this aggregated chemical compartment. When this occurs, though, chemical toxicity parameters must be left as blank for the individual analytes or double counting of toxic effects will occur. The choice of whether to use aggregated chemical toxicity data or analyte-specific toxicity data may be made on an organism-by-organism basis.

9. ECOTOXICOLOGY

Unlike most ecological models, AQUATOX contains an ecotoxicology submodel that computes both lethal and sublethal acute toxic effects from the concentration of a toxicant in a given organism. Furthermore, because AQUATOX is an ecosystem model, it can simulate indirect effects such as loss of forage base, reduction in predation, and anoxia due to decomposition following a fish kill.

User-supplied values for *LC50*, the concentration of a toxicant in water that causes 50% mortality, form the basis for a sequence of computations that lead to estimates of the biomass of a given organism lost through lethal toxicity each day. The sequence, which is documented in this chapter, is to compute:

> **Ecotoxicology: Simplifying Assumptions**
>
> - Toxic effects of multiple chemicals are additive
> - Sublethal effects levels of chemicals may be estimated as a fraction of lethal effects levels
> - Regressions from one species to another are available regardless of the mode of action
> - The external toxicity model assumes immediate toxic effect to a level of external exposure
> - Cumulative toxicity considers differing tolerances in a population, but ignores inherited tolerance
> - Resistance to lower doses is conferred for the lifetime of an animal and for one year for a plant.

- the internal concentration causing 50% mortality for a given period of exposure;
- the internal concentration causing 50% mortality after an infinite period of time based on an asymptotic concentration-response relationship;
- the time-varying lethal internal concentration of a chemical;
- the cumulative mortality for a given internal concentration;
- the biomass lost per day as an increment to the cumulative mortality.

The user-supplied *EC50*s, the concentrations in water eliciting sublethal toxicity responses in 50% of the population, are used to obtain factors relating the sublethal toxicities to the lethal toxicity. Because AQUATOX can simulate as many as twenty toxic organic chemicals simultaneously, the simplifying assumption is made that the toxic effects are additive.

9.1 Lethal Toxicity of Compounds

Interspecies Correlation Estimates (ICE)

Often *LC50* data will only be available for one or two of the many species that a user wishes to include in a simulation. To alleviate this problem, a substantial database of regressions (Interspecies Correlation Estimation, ICE) is available as developed by the US. EPA Office of Research and Development, the University of Missouri-Columbia, and the US Geological Survey (Asfaw and Mayer, 2003). At this time the Web-ICE database has over 2000 regressions with over 100 aquatic species as "surrogates" (Raimondo et al. 2007). Regressions may be made on the basis of species, families, or genera. The database also includes goodness of fit information for regressions so their suitability for a given application may be ascertained. Only statistically significant regressions are included in the database.

Using the ICE database and the following regression equation, the model can be parameterized to represent a complete food web.

$$\text{Log } LC50_{Estimated} = Intercept + Slope \cdot \text{Log } LC50_{Observed} \qquad \textbf{(410)}$$

where:

$LC50_{Estimated}$	=	estimated $LC50$ (μg/L);
$Intercept$	=	intercept for regression (μg/L);
$Slope$	=	slope of the regression equation;
$LC50_{Observed}$	=	observed $LC50$ (μg/L).

The ICE database is integrated into the AQUATOX user interface. A link is provided to the Web-based (Web-ICE) site so that the user can alternatively use the web tool. The steps that a user can take to use ICE within AQUATOX to estimate unavailable *LC50* data are as follows:

- Invoke the ICE interface from the AQUATOX "Chemical Toxicity Parameter" screen;
- Choose from the six available ICE databases (species, genus, and family by either scientific names or common names);
- Either choose a "surrogate species" that matches a species for which there is observed *LC50* data, or start with a "predicted species" that matches a species that you wish to model*;*
- The list box that you did not select from in the previous step will narrow to reflect the available surrogate or predicted species that match with your selection. Select a choice from this list box as well. If you wish to start over again, you may select the "show all" button next to this list box.
- Examine the goodness of fit for your model and evaluate whether it is appropriate for your purposes. Where there are multiple surrogates for the desired predicted species, compare the statistics and choose best surrogate/predicted pair;
- Apply the model by assigning the surrogate and predicted species to species within the chemical's toxicity record.

Experimentally derived toxicity data for individual species should be used when available. However, ICE may then be used to estimate toxicity for species that have not yet been studied given a particular chemical. There are uncertainties in this estimation procedure, but the model helps to track these uncertainties. When the ICE model is invoked, data about the goodness of fit and confidence interval are copied back into the "LC50 comment" field. Overall model uncertainty resulting from this estimation can then be numerically quantified—these goodness of fit data can be utilized within an iterative AQUATOX uncertainty analysis (see section **2.5**).

Internal Calculations

Toxicity is based on the internal concentration of the toxicant in the specified organism. Many compounds, especially those with higher octanol-water partition coefficients, take appreciable time to accumulate in the tissue. Therefore, length of exposure is critical in determining toxicity. The same principles apply to organic toxicants and to both plants and animals.

The internal lethal concentration for a given period of exposure can be computed from reported lethal toxicity data based on the simple relationship suggested by an algorithm in the FGETS model (Suárez and Barber, 1992):

$$InternalLC50 = BCF \cdot LC50 \tag{411}$$

where:

InternalLC50	=	internal concentration that causes 50% mortality;
BCF	=	bioconcentration factor (L/kg), see **(342)** to **(349)**; and
LC50	=	concentration of toxicant in water that causes 50% mortality (μg/L).

For compounds with a *LogKOW* in excess of 5 the usual 96-hr toxicity exposure does not reach steady state, so a time-dependent *BCF* is used to account for the actual internal concentration at the end of the toxicity determination. This is applicable no matter what the length of exposure (Figure 158, based on Figure 144).

Figure 158: Bioconcentration factor as a function of time and KOW
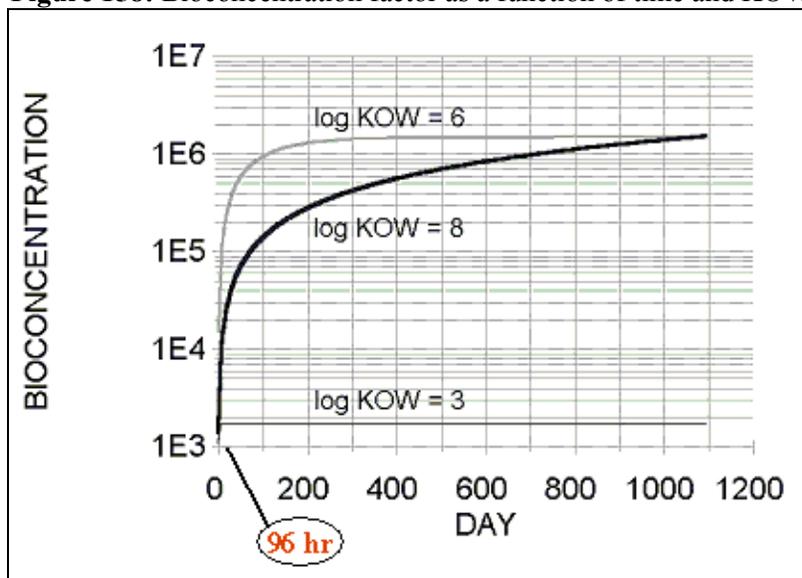
The internal concentration causing 50% mortality after an infinite period of exposure, *LCInfinite,* can be computed by:

$$LCInfinite = InternalLC50 \cdot \left(1 - e^{-k2 \bullet ObsTElapsed}\right) \tag{412}$$

where:

k2	=	elimination rate constant (1/d); and

ObsTElapsed =   exposure time in toxicity determination (h).

Essentially this equation determines the asymptotic toxicity relationship and provides the model with a constant toxicity parameter for a given compound.

The model estimates *k2*, see **(364)** and **(354)**, assuming that this *k2* is the same as that measured in bioconcentration tests; good agreement has been reported between the two (Mackay et al., 1992). The user may then override that estimate by entering an observed value. The *k2* can be calculated off-line based on the observed half-life:

$$k2 = \frac{0.693}{t_{1/2}}$$

(413)

where:
    t½   =   observed half-life.

Based on the Mancini (1983) model, the lethal internal concentration of a toxicant for a given exposure period can be expressed as (Crommentuijn et al. (1994):

$$LethalConc = \frac{LCInfinite}{1 - e^{-k2 \cdot TElapsed}}$$

(414)

where:
    LethalConc   =   tissue-based concentration of toxicant that causes 50% mortality (ppb or µg/kg);
    LCInfinite   =   ultimate internal lethal toxicant concentration after an infinitely long exposure time (ppb);
    TElapsed   =   period of exposure (d).

The longer the exposure the lower the internal concentration required for lethality.

Exposure is limited to the lifetime of the organism:

                    if *TElapsed* > *LifeSpan* then *TElapsed* = *LifeSpan*   (415)

where:
    LifeSpan   =   user-defined mean lifetime for given organism (d).

Based on an estimate of time to reach equilibrium (Connell and Hawker, 1988),

$$\text{if } TElapsed > \frac{4.605}{k2} \text{ then}$$

$$LethalConc = LCInfinite$$

(416)

The fraction killed by a given internal concentration of toxicant is best estimated using the time-dependent *LethalConc* in the cumulative form of the Weibull distribution (Mackay et al., 1992; see also Christensen and Nyholm, 1984):

$$CumFracKilled = 1 - e^{-\left(\frac{PPB}{LethalConc}\right)^{\frac{1}{Shape}}} \tag{417}$$

where:

CumFracKilled	=	fraction of organisms killed per day (g/g d),
PPB	=	internal concentration of toxicant (µg/kg), see **(310)**; and
Shape	=	parameter expressing variability in toxic response (unitless).

As a practical matter, if *CumFracKilled* exceeds 95%, then it is set to 100% to avoid complex computations with small numbers. By setting organismal loadings to very small numbers, seed values can be maintained in the simulation.

This formulation is preferable to the empirical probit and logit equations because it is simple and yet based on mechanistic relationships. The *Shape* parameter is important because it controls the spread of mortality. The larger the value, the greater the distribution of mortality over toxicant concentrations and time. Mackay et al. (1992) found that a value of 0.33 gave the best fit to data on toxicity of 21 narcotic chemicals to fathead minnows. This value is used as a default in AQUATOX, but it can be changed by the user. Although mercury is not currently modeled, data on MeHg toxicity shows that the *Shape* parameter may take a value less than 0.1 (Figure 154).

Figure 159. The effect of *Shape* in fitting the observed (McKim et al., 1976) cumulative fraction killed following continued exposure to MeHg
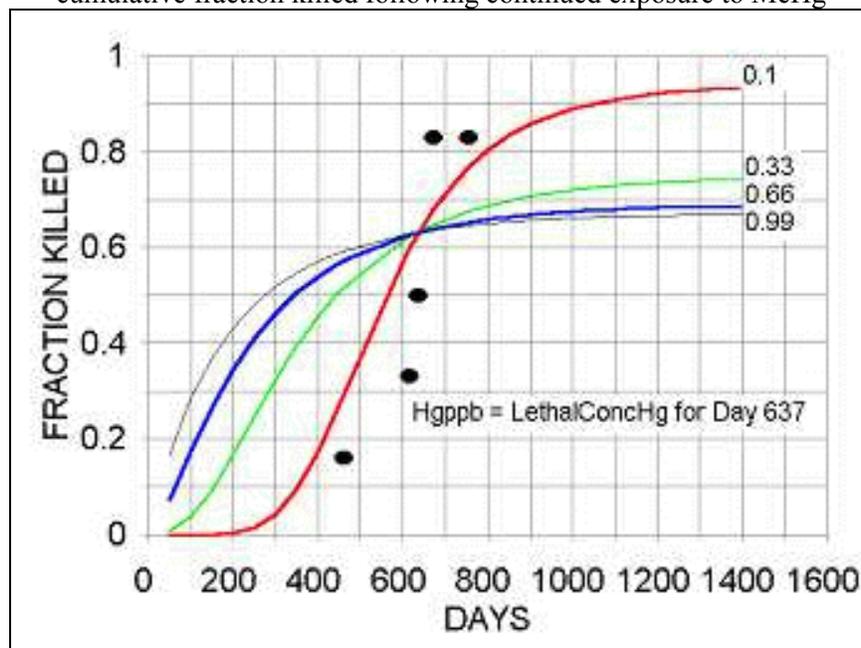
The biomass killed per day is computed by disaggregating the cumulative mortality. Think of the biomass at any given time as consisting of two types: biomass that has already been exposed to the toxicant previously, which is called *Resistant* because it represents the fraction that was not killed; and new biomass that has formed through growth, reproduction, and migration and has not been exposed to a given level of toxicant and therefore is referred to as *Nonresistant*. Then think of the cumulative distribution as being the total *CumFracKilled,* which includes the *FracKilled* that is in excess of the cumulative amount on the previous day if the internal

concentration of toxicant increases. A conservative estimate of the biomass killed at a given timeis computed as:

$$Poisoned = Resistant \cdot Biomass \cdot FracKilled + Nonresistant \cdot CumFracKill \qquad \textbf{(418)}$$

where:

Poisoned	=	biomass of given organisms killed by exposure to toxicant at given time (g/m^3 d);
Resistant	=	fraction of biomass not killed by previous exposure (frac);
FracKilled	=	fraction killed per day in excess of the previous fraction (g/g d);
Nonresistant	=	biomass not previously exposed; the biomass in excess of the resistant biomass (g/m^3) = *(1-Resistant)·Biomass*.

New biomass is considered vulnerable, ignoring the possibility of inherited tolerance. It is assumed for purposes of risk analysis that resistance is not conferred for an indefinite period. In animals elapsed exposure time is capped at the average life span, which is a parameter in the animal record. However, it is assumed that resistance persists in the population until the end of the growing season. Macrophytes can live for an entire growing season, and algae usually reproduce asexually as long as conditions are favorable. However, winter die-back does occur in most macrophytes, and many algae will switch to sexual reproduction under unfavorable conditions, especially triggered by light and temperature. As a simplifying assumption for both animals and plants, in the northern hemisphere January 1 is taken as being the date at which exposure and resistance are reset; in the southern hemisphere (denoted by negative latitude in the site record) July 1 is the reset date. On this date, the variables *Resistant, FracKilled$_{Previous}$,* and *TElapsed* are all set to zero.

9.2 Sublethal Toxicity

Organisms usually have adverse reactions to toxicants at levels significantly below those that cause death. In fact, the lethal to sublethal ratio is commonly used to quantify this relationship. The user supplies observed *EC50* values, which can then be used to compute AFs (application factors). For example:

$$AFGrowth = \frac{EC50Growth}{LC50} \qquad \textbf{(419)}$$

where:

EC50Growth	=	external concentration of toxicant at which there is a 50% reduction in growth (μg/L);
AFGrowth	=	sublethal to lethal ratio for growth (unitless); and
LC50	=	external concentration of toxicant at which 50% of population is killed (μg/L).

If the user enters an observed *EC50* value, the model provides the option of applying the resulting *AF* to estimate *EC50*s for other organisms. The computations for AFPhoto and AFRepro are similar:

$$AFPhoto = \frac{EC50Photo}{LC50} \tag{420}$$

$$AFRepro = \frac{EC50Repro}{LC50} \tag{421}$$

where:

EC50Photo	=	external concentration of toxicant at which there is a 50% reduction in photosynthesis (µg/L);
AFPhoto	=	sublethal to lethal ratio for photosynthesis (unitless);
EC50Repro	=	external concentration of toxicant at which there is a 50% reduction in reproduction (µg/L); and
AFRepro	=	sublethal to lethal ratio for reproduction (unitless).

Because of the nature of these application factors, sublethal effects cannot be calculated (using internal calculations) unless LC50 parameters are included in the model.

Similar to computation of lethal toxicity in the model, sublethal toxicity is based on internal concentrations of a toxicant. Often sublethal effects form a continuum with lethal effects and the difference is merely one of degree (Mackay et al., 1992). Regardless of whether or not the mode of action is the same, the computed factors relate the observed effect to the lethal effect and permit efficient computation of sublethal effects factors in conjunction with computation of lethal effects. Because AQUATOX simulates biomass, no distinction is made between reduction in a process in an individual and the fraction of the population exhibiting that response. The commonly measured reduction in photosynthesis is a good example: the data only indicate that a given reduction takes place at a given concentration, not whether all individuals are affected. The factor enters into the Weibull equation to estimate reduction factors for photosynthesis, growth, and reproduction:

$$FracPhoto = e^{-\left(\frac{PPB}{LethalConc \cdot AFPhoto}\right)^{1/Shape}} \tag{422}$$

$$RedGrowth = 1 - e^{-\left(\frac{PPB}{LethalConc \cdot AFGrowth}\right)^{1/Shape}} \tag{423}$$

$$RedRepro = 1 - e^{-\left(\frac{PPB}{LethalConc \cdot AFRepro}\right)^{1/Shape}} \tag{424}$$

where:

FracPhoto	=	reduction factor for effect of toxicant on photosynthesis (unitless);
RedGrowth	=	factor for reduced growth in animals (unitless);
RedRepro	=	factor for reduced reproduction in animals (unitless);
PPB	=	internal concentration of toxicant (µg/kg), see **(310)**;
LethalConc	=	tissue-based conc. of toxicant that causes mortality (µg/kg), see **(413)**;

$AFPhoto$ = sublethal to lethal ratio for photosynthesis (unitless, default of 0.10);
$AFGrowth$ = sublethal to lethal ratio for growth in animals (unitless, default of 0.10);
$AFRepro$ = sublethal to lethal ratio for reproduction in animals (unitless, default of 0.05);
$Shape$ = parameter expressing variability in toxic response (unitless, default of 0.33).

The reduction factor for photosynthesis, *FracPhoto*, enters into the photosynthesis equation (Eq. **(35)**) and it also appears in the equation for the acceleration of sinking of phytoplankton due to stress (Eq. **(69)**).

The variable for reduced growth, *RedGrowth*, is arbitrarily split between two processes, ingestion (Eq. **(91)**), where it reduces consumption by 20%:

$$ToxReduction = 1 - (0.2 \cdot RedGrowth) \tag{425}$$

and defecation (Eq. **(97)**), where it increases the amount of food that is not assimilated by 80%:

$$IncrEgest = (1 - EgestCoeff_{prey, pred}) \cdot 0.8 \cdot RedGrowth \tag{426}$$

These have indirect effects on the rest of the ecosystem through reduced predation and increased production of detritus in the form of feces.

Embryos are often more sensitive to toxicants, although reproductive failure may occur for various reasons.   As a simplification, the factor for reduced reproduction, *RedRepro*, is used only to increase gamete mortality (Eq. **(126)**) beyond what would occur otherwise:

$$IncrMort = (1 - GMort) \cdot RedRepro \tag{427}$$

By modeling sublethal and lethal effects, AQUATOX makes the link between chemical fate and the functioning of the aquatic ecosystem- a pioneering approach that has been refined over the past twenty years, following the first publications (Park et al., 1988; Park, 1990).

Sloughing of periphyton and drift of invertebrates also can be elicited by toxicants. For example, sloughing can be caused by a surfactant that disrupts the adhesion of the periphyton, or an invertebrate may release its hold on the substrate when irritated by a toxicant. Often the response is immediate so that these responses can be modeled as dependent on dissolved concentrations of toxicants with an available sublethal toxicity parameter, as in the equation for periphyton sloughing:

$$Dislodge_{Peri,Tox} = MaxToxSlough \cdot \frac{Toxicant_{Water}}{Toxicant_{Water} + EC50_{Dislodge}} \cdot Biomass_{Peri} \tag{428}$$

where:

$Dislodge_{Peri, Tox}$ = periphyton sloughing due to given toxicant (g/m^3 d);

MaxToxSlough	=	maximum fraction of periphyton biomass lost by sloughing due to given toxicant (fraction/d, 0.1);
$Toxicant_{Water}$	=	concentration of toxicant dissolved in water (µg/L); see **(300)**;
$EC50_{Dislodge}$	=	external concentration of toxicant at which there is 50% sloughing (µg/L); and
$Biomass_{Peri}$	=	biomass of given periphyton (g/m3); see **(33)**.

Likewise, drift is greatly increased when zoobenthos are subjected to stress by sublethal doses of toxic chemicals (Muirhead-Thomson, 1987), and that is represented by a saturation-kinetic formulation that utilizes an analogous sublethal toxicity parameter :

$$Dislodge_{Tox} = \sum_{tox} \frac{Toxicant_{Water} - DriftThreshold}{Toxicant_{Water} - DriftThreshold + EC50_{Growth}} \qquad \textbf{(429)}$$

where:

$Toxicant_{Water}$	=	concentration of toxicant in water (µg/L);
DriftThreshold	=	the concentration of toxicant that initiates drift (µg/L); and
$EC50_{Growth}$	=	concentration at which half the population is affected (µg/L).

These terms are incorporated in the respective periphyton washout **(72)** and zoobenthos drift **(130)** equations.

9.3 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):

$$CumFracKilled = 1 - \exp(-kz^{Eta}) \qquad \textbf{(430)}$$

where:

z	=	external concentration of toxicant (µg/L);
CumFracKilled	=	cumulative fraction of organisms killed for a given period of exposure (fraction/d), applied to equation **(417)**;
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):

$$k = \frac{-\ln(0.5)}{LC50^{Eta}} \qquad \textbf{(431)}$$

$$Eta = \frac{-2 \cdot LC50 \cdot slope}{\ln(0.5)} \qquad \textbf{(432)}$$

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

AQUATOX can assume that each chemical's dose response curve has a distinct shape, relevant to all organisms modeled. In this manner, a single "slope factor" parameter describing the shape of the Weibull curve can be entered in the chemical record rather than requiring the user to derive slope parameters for each organism modeled. (Note, this is different than the *shape* parameter used for internal toxicity.) However, animal and plant-specific slope factors may also be entered in the animal and plant chemical-toxicity databases. If these values are left blank or zero, the value from the chemical record is used. Otherwise the organism-specific factor is used. The units for this factor are the same as those for the chemical underlying data (the slope at EC50 multiplied by the EC50 in ug/L).

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. Figure 160 shows two Weibull distributions with identical shapes, but with slopes that are significantly different due to the scales of the x axes.

Figure 160. Weibull distributions with identical shapes, but different slopes.
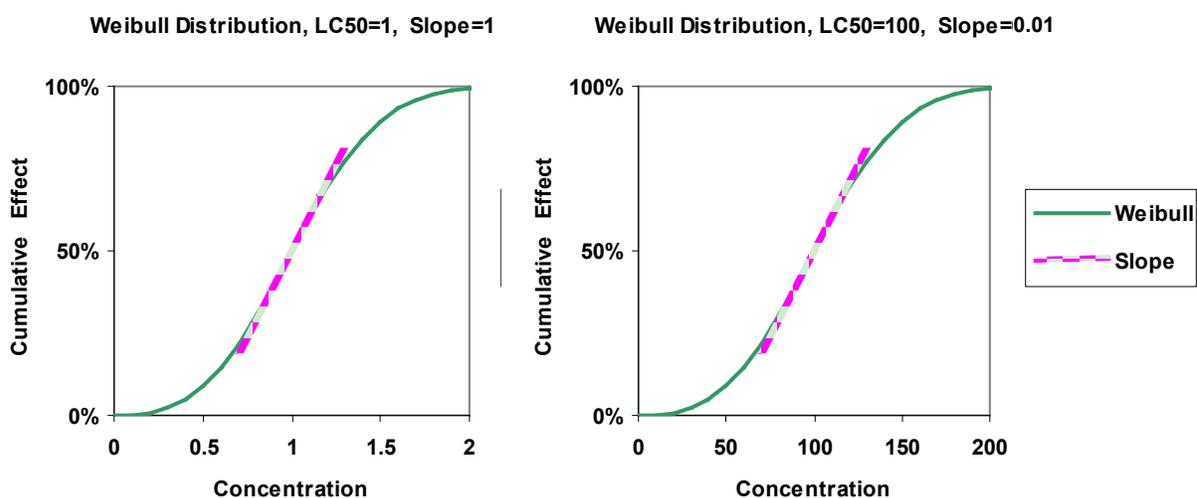
For this reason, rather than have a user enter "the slope at LC50" into the chemical record, AQUATOX asks the user to enter a "slope factor" defined as "the slope at LC50 multiplied by LC50." In the above example, the user would enter a slope factor of 1.0 and then, given an LC50 of 1 or an LC50 of 100, 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).

Unlike the internal model, application factors are not used to estimate sublethal effects when calculating external toxicity. Therefore, EC50 parameters do not need to be paired with LC50 values to calculate sublethal effects with this model.

10. ESTUARINE SUBMODEL

The estuarine version of AQUATOX is intended to be an exploratory model for evaluating the possible fate and effects of toxic chemicals and other pollutants in estuarine ecosystems. The model is not intended to represent detailed, spatially varying site-specific conditions, but rather to be used in representing the potential behavior of chemicals under average conditions.   Therefore, it is best used as a screening-level model applicable to data-poor evaluations in estuarine ecosystems. However, it can be calibrated for different estuaries.

> **AQUATOX Estuarine Submodel: Simplifying Assumptions**
>
> - Estuary is a single segment that always has two well-mixed layers
> - The estuary has freshwater inflow from upstream and saltwater inflow from the seaward end (salt-wedge)
> - Water flows at the seaward end are estimated using the salt-balance approach
> - Effects of salinity on sorption are minor and are not modeled
> - Hourly tidal fluxes are not modeled
> - Daily average volume of the estuary is assumed to remain constant over time
> - The surface area of the lower layer is the same as the upper layer
> - Nutrient concentrations in inflowing seawater are assumed to be constant
> - Possible salinity effects on microbial degradation, hydrolysis, and photolysis are ignored.

Hourly tidal fluctuations are not included in the model; the native AQUATOX time-step is one day. Because of this, the overall water volume of the estuary may be assumed to remain constant over the entire simulation.   The simplifying assumption is that the water volume of the estuary is not sensitive to the freshwater inflow. The volumes and depths of the fresh layer and the salt wedge do vary as a function of the daily average tidal range and freshwater flows.

If simulation of spatially-explicit, site-specific estuarine conditions is desired, then a multi-segment model can be implemented with flow among segments provided by an external hydrodynamic model.   The numerous effects of salinity described below in the context of the estuarine submodel are also applicable to the classic and multi-segment versions of AQUATOX.

10.1 Estuarine Stratification

As a general case, the estuarine system is assumed to always have two layers, although at times the layers may be essentially identical because of respective thicknesses and turbulent diffusion. The two layers are assumed to be a function of and to vary with freshwater loadings and daily tidal ranges. The fraction of depth in the upper layer is adjusted to account for changing volumes due to entrainment (flow of water from lower to upper layer; see section 10.4), with a value of 1.5 based on inspection of published observations. If *ResidFlow* > 0 then:

$$FreshwaterHead = \frac{ResidFlow}{Area}$$

(433)

$$FracUpper = 1.5 \cdot \frac{FreshwaterHead}{TidalAmplitude + FreshwaterHead}$$

where:

FreshwaterHead	=	height of freshwater (m/d);
ResidFlow	=	inflow residual flow of fresh water minus daily evaporation, (m^3/d) user inputs;
Area	=	area of the estuary taken at mean tide (m^2).
FracUpper	=	fraction of mean depth that is upper layer (unitless).
TidalAmplitude	=	tidal amplitude (m), see **(434)**;

If *ResidFlow* $<= 0$ then *FracUpper* is taken as having a nominal value of 0.05.

The thicknesses of the two layers, and therefore the volumes of the two layers, may be calculated as a function of *FracUpper*.

$$ThickUpper = FracUpper \cdot MeanDepth \qquad \textbf{(434)}$$
$$ThickLower = MeanDepth - ThickUpper$$
$$VolumeUpper = FracUpper \cdot Area$$
$$VolumeLower = FracLower \cdot Area$$

where:

ThickUpper	=	thickness of the upper layer (m);
FracLower	=	$1 - FracUpper$; see **(432)**;
ThickLower	=	thickness of the lower layer (m);
MeanDepth	=	mean depth of the estuary (m);
VolumeUpper	=	volume of the upper layer (m^3);
VolumeLower	=	volume of the lower layer (m^3);
Area	=	area of the estuary taken at mean tide (m^2).

As shown in the formulations above, layer thicknesses are a function of the daily predicted tidal range. Given that the estuary's average daily volume is assumed to remain constant, to maintain mass-balance of water AQUATOX moves water from one layer to the next when thicknesses change. (This same movement of water occurs when the user specifies a variable thermocline depth in a stratified lake or reservoir, see section 3.4 on "Modeling Reservoirs and Stratification Options.") In order to maintain biomass, nutrient, and toxicant mass-balance AQUATOX also transfers state variables located in the moving water from one layer to the next. This transfer can cause minor fluctuations that are visible in some estuarine-version results (e.g. wave-like patterns in fish biomass predictions.) Such fluctuation is predominantly an artifact of the simple manner in which AQUATOX models estuarine water volume.

10.2 Tidal Amplitude

Tidal amplitude is calculated using the general equation found in the *Manual of Harmonic Analysis and Prediction of Tides* (U.S. Department of Commerce 1994):

$$TidalAmplitude = \sum_{Con.} \left(\begin{array}{l} Amp_{Con.} \cdot Nodefactor_{Con.,Year} \cdot \\ \cos((Speed_{Con.} \cdot Hours) + Equil_{Con.,Year} - Epoch_{Con.}) \end{array} \right) \quad \textbf{(435)}$$

where:

$TidalAmplitude$ = one-half the range of a constituent tide (m);

$Con.$ = eight constituents of tidal range listed below;

$Amp_{Con.}$ = user-input amplitude for each constituent (m);

$Nodefactor$ = node factor for each constituent for each year, hard-wired into AQUATOX for 1970-2037 (deg.);

$Speed$ = speeds of each constituent in (deg./hour), hard-wired into AQUATOX for each relevant constituent;

$Hours$ = time since the start of the year (hours);

$Equil$ = equilibrium argument for each constituent for each year in degrees for the meridian of Greenwich, hard-wired into AQUATOX for 1970-2037 (deg.);

$Epoch$ = user input phase lag for each constituent (deg.).

AQUATOX requires *Amplitudes* and *Epochs* for the following eight constituents of tidal range for the modeled estuary, generally available for download from NOAA databases.   These "primary" constituents were found to have the largest effect on tidal range and will predict tidal range to the precision as required by the estuarine submodel:

M2 - Principal lunar semidiurnal constituent

S2 - Principal solar semidiurnal constituent

N2 - Larger lunar elliptic semidiurnal constituent

K1 - Lunar diurnal constituent

O1 - Lunar diurnal constituent

SSA - Solar semiannual constituent

SA - Solar annual constituent

P1 - Solar diurnal constituent

10.3 Water Balance

Water balance is computed using the salt balance approach (Ibáñez et al. 1999):

$$SaltwaterInflow = \frac{ResidFlow}{SalinityLower/SalinityUppper - 1}$$

(436)

$$Outflow = \frac{ResidFlow}{1 - SalinityUpper/SalinityLower}$$

(437)

where:

$SaltwaterInflow$ = water entering estuary from mouth of estuary, usually into lower level but may be into upper level if evaporation exceeds freshwater inflow (m³/d);

$Outflow$ = water leaving estuary at mouth (m³/d);

$ResidFlow$ = residual flow of fresh water; may be negative if evaporation

exceeds freshwater inflow (m^3/d);
SalinityLower   =   salinity of lower layer at mouth of estuary (psu or ‰);
SalinityUpper   =   salinity of upper layer at mouth of estuary (psu or ‰);

Programmatically, the system is modeled as a single constant-volume segment with two layers and with freshwater inflow from upstream and saltwater inflow from the seaward end. Ice cover is not assumed on top of estuaries unless the average water temperature falls below -1.8 deg.C.

10.4 Estuarine Exchange

Saltwater inflow occurs to replace water that is admixed (entrained) from one layer (usually the lower) to the other layer, producing the observed salinities of the two layers at the mouth of the estuary. (Note that this use of the term "entrainment" differs from the downstream entrainment of organisms, e.g. **(132)**.) This circulation is much greater than any longitudinal mixing (see Thomann and Mueller 1987). Therefore, effectively, entrainment is the equivalent of *SaltwaterInflow*, but its derivation is informative:

$$EntrainVel = \frac{SaltwaterInflow}{Area}$$

$$VertAdvection = EntrainVel \cdot Thick \qquad\qquad \textbf{(438)}$$

$$Entrainment = \frac{VertAdvection \cdot Area}{Thick}$$

where:
EntrainVel   =   entrainment velocity of lower layer into upper layer (m/d);
VertAdvectiveDisp =   vertical advective dispersion (m^2/d);
Entrainment   =   vertical flow as derived above (m^3/d).

Transport of suspended and dissolved substances from the lower layer to the upper layer can then be computed. In a truly stratified estuary turbulent diffusion will be minimal, so we will set the bulk mixing coefficient (*BulkMixCoeff*) to 0.1 m^2/d following the example of Koseff et al. (1993). However, when wind exceeds 3 m/s Langmuir circulation sets up with downwelling and upwelling extending to about 3 m. Therefore, if the thickness of the upper layer is less than 3 m and the wind speed is greater than 3 m/s, then bulk mixing is increased by a factor of 5. Turbulent diffusion can then be computed for each dissolved and suspended compartment:

$$TurbDiff_{upper} = \frac{BulkMixCoeff}{Volume_{upper}} \cdot Langmuir \cdot \left(Conc_{compartment,lower} - Conc_{compartment,upper}\right)$$

(439)

$$TurbDiff_{lower} = \frac{BulkMixCoeff}{Volume_{lower}} \cdot Langmuir \cdot \left(Conc_{compartment,upper} - Conc_{compartment,lower}\right)$$

If ThickUpper < 3 and Wind ≥ 3 then Langmuir = 5   else Langmuir = 1

where:

TurbDiff	=	turbulent diffusion (g/m^3-d);
BulkMixCoeff	=	bulk mixing coefficient (0.1 m^2/d);
Langmuir	=	factor for greater mixing when wind equals or exceeds 3 m/s (unitless);
Volume$_{upper}$	=	volume of the upper layer (m^3);
Volume$_{lower}$	=	volume of the lower layer (m^3);
Conc	=	concentration of given compartment in a given layer (g/m^3).

10.5 Salinity Effects

Mortality and Gamete Loss

Salinity that is less than or greater than threshold values increases mortality and gamete loss:

$$\text{if } SalMin < Salinity < SalMax \text{ then } SaltMort = 0$$

$$\text{if } Salinity < SalMin \text{ then } SaltMort = SalCoeff1 \cdot e^{SalMin - Salinity}$$

(440)

$$\text{if } Salinity > SalMax \text{ then } SaltMort = SalCoeff2 \cdot e^{Salinity - SalMax}$$

where:

SalMin	=	minimum salinity below which effect is manifested (‰);
Salinity	=	ambient salinity (‰);
SalMax	=	maximum salinity above which effect is manifested (‰);
SaltMort	=	mortality due to salinity (1/d);
SalCoeff1	=	coefficient for effect of low salinity (unitless);
SalCoeff2	=	coefficient for effect of high salinity (unitless);
e	=	the base of natural logarithms (2.71828, unitless).

SaltMort is then applied to mortality **(112)** and gamete loss **(126).** The model assumes reproduction is affected because eggs and sperm are not viable in abnormal salinities.

Other Biotic Processes

Salinity beyond the range of tolerance for a particular process, including photosynthesis, ingestion, and respiration, will reduce the process:

$$\text{if } SalMin < Salinity < SalMax \text{ then } SalEffect = 1$$

$$\text{if } Salinity < SalMin \text{ then } SalEffect = SalCoeff \, 1 \cdot e^{Salinity - SalMin} \qquad \textbf{(441)}$$

$$\text{if } Salinity > SalMax \text{ then } SalEffect = SalCoeff \, 2 \cdot e^{SalMax - Salinity}$$

where:

    $SaltEffect$ =   effect of salinity on given process (unitless).

In general, the ranges of tolerance of abnormal salinities in animals, going from least tolerant to most tolerant, affects reproduction, ingestion, respiration, and mortality in that order (Figure 161). Respiration decreases because gill ventilation is depressed. SaltEffect is applied to ingestion **(91),** respiration **(100),** and photosynthesis **(35)** as appropriate.

Figure 161. Effects of salinity on various animal processes**.**
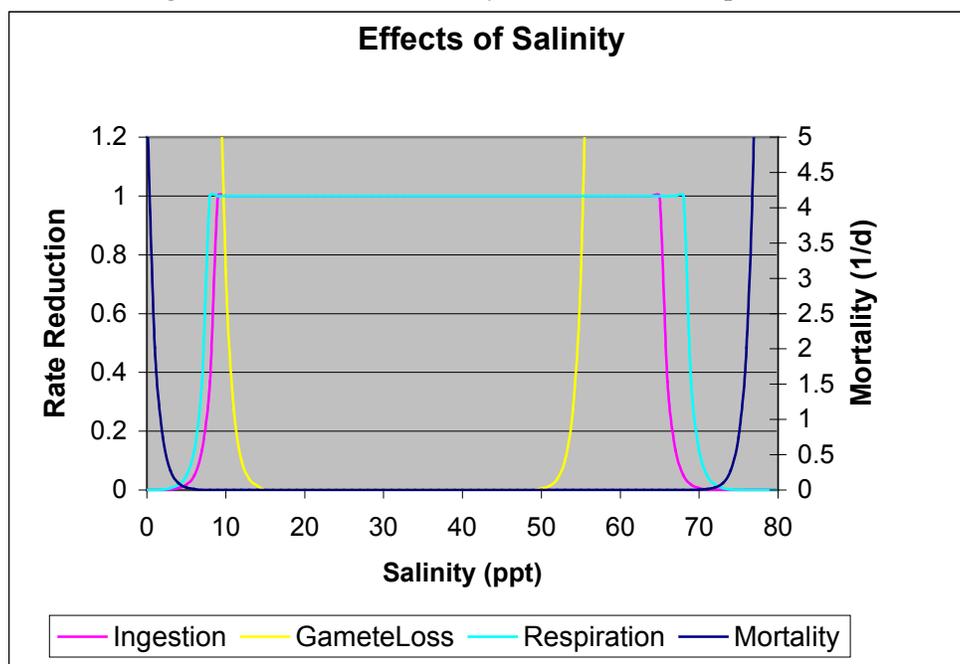
Sinking

Sinking of phytoplankton and suspended detritus also is affected by salinity, more so than by temperature (Figure 159, Figure 160). However, because ambient salinity and temperature affect sinking by controlling density, we will compute a density factor based on the effects of both compared to the salinity and temperature of the observed sinking rate (Thomann and Mueller 1987):

$$WaterDensity = 1 + \left\{ 10^{-3} \cdot \begin{bmatrix} \left(28.14 - 0.0735 \cdot Temperature - 0.00469 \cdot Temperature^2\right) \\ + \left(0.802 - 0.002 \cdot Temperature\right) \cdot \left(Salinity - 35\right) \end{bmatrix} \right\} \quad \textbf{(442)}$$

$$DensityFactor = \frac{WaterDensity_{reference}}{WaterDensity_{ambient}} \quad \textbf{(443)}$$

If salinity is not included in AQUATOX as a state variable, *DensityFactor* is set to 1.0.

$$Sink = \frac{KSed}{Thick} \cdot DensityFactor \quad \textbf{(444)}$$

where:

$WaterDensity_{reference}$	=	density of water at temperature and salinity of observed sinking rate (kg/L);
$WaterDensity_{ambient}$	=	density of water at ambient temperature and salinity (kg/L);
$Temperature$	=	temperature of water (ºC);
$DensityFactor$	=	correction factor for water densities other than those at which sinking rates were observed (unitless);
$Sink$	=	sinking rate of given suspended compartment (g/m^3-d);
$KSed$	=	intrinsic settling rate (m/d);
$Thick$	=	thickness of water layer (m).

Figure 162. Correction factor for sinking as a function of temperature.
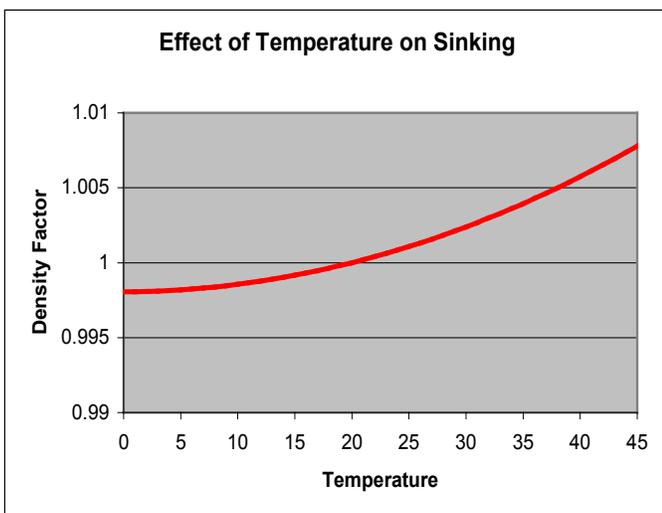
Figure 163. Correction factor for sinking as a function of salinity.
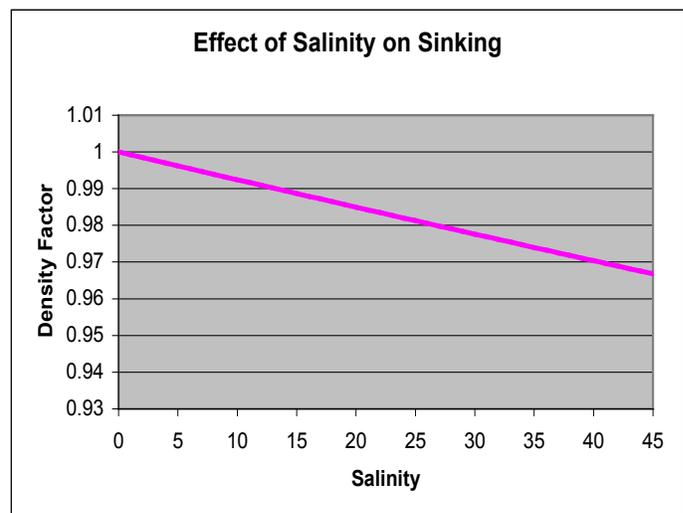
Sorption

The influence of seawater or "salting out" does not cause major changes in sorption of organic compounds (Schwarzenbach et al. 1993). It varies with the compound, with greater effect on polar compounds, but is seldom measured. Therefore, it will be ignored at the present time.

Volatilization

Volatilization is affected by salinity, and can be represented by a linear increase in the Henry's Law constant (Eqn. 330). At 35‰ salinity the average increase in the constant across tested organic compounds is 1.4 compared to that of distilled water (Schwarzenbach et al. 1993). Applying this relationship:

$$HLCSaltFactor = 1 + 0.01143 \cdot Salinity \tag{445}$$

Estuarine Reaeration

Reaeration is affected by salinity, especially through calculation of the saturation level (*O2Sat*). Salinity is included in the present formulation for *O2Sat*. Computation of the depth-averaged reaeration coefficient (*KReaer*) requires determination of the effects of both tidal velocity and wind velocity. Thomann and Fitzpatrick (1982, see also (Chapra 1997)) combine the two in one equation:

$$KReaer = 3.93 \frac{\sqrt{Velocity}}{Thick^{3/2}} + \frac{0.728 \cdot \sqrt{Wind} - 0.317 \cdot Wind + 0.0372 \cdot Wind^2}{Thick} \tag{446}$$

The daily average tidal velocity can be computed by a variation of a formulation presented by (Thomann and Mueller, 1987), substituting the spring tide harmonic for the diurnal harmonic:

$$Velocity = \frac{\left| ResidFlowVel + TidalVel \cdot \left(1 + 0.5 \cdot \sin\left(\frac{2\pi Day}{12}\right)\right) \right|}{86400} \tag{447}$$

$$ResidFlowVel = \frac{OutFlow}{XSecArea} \tag{448}$$

$$XSecArea = Depth \cdot Width \tag{449}$$

$$TidalVel = \frac{TidalPrism}{XSecArea} \qquad\qquad \textbf{(450)}$$

$$TidalPrism = 2.0 \cdot Amplitude \cdot Area \qquad\qquad \textbf{(451)}$$

where:

Velocity	=	water velocity (m/s);
Wind	=	wind velocity (m/s), see **(29)**;
ResidFlowVel	=	residual flow velocity of fresh water (m/d);
Outflow	=	water leaving estuary at mouth (m³/d), see **(436);**
TidalVel	=	mean tidal velocity (m/d);
Day	=	day of year (d);
XSecArea	=	cross-sectional area of estuary (m²);
Depth	=	mean water depth (m);
Width	=	width of estuary (m);
TidalPrism	=	the difference in water volume between low and high tides (m³);
Amplitude	=	tidal amplitude (m), see **(434)**;
Area	=	area of site (m²).

Figure 164. Daily average water velocities based on freshwater flow and tidal flow**.**
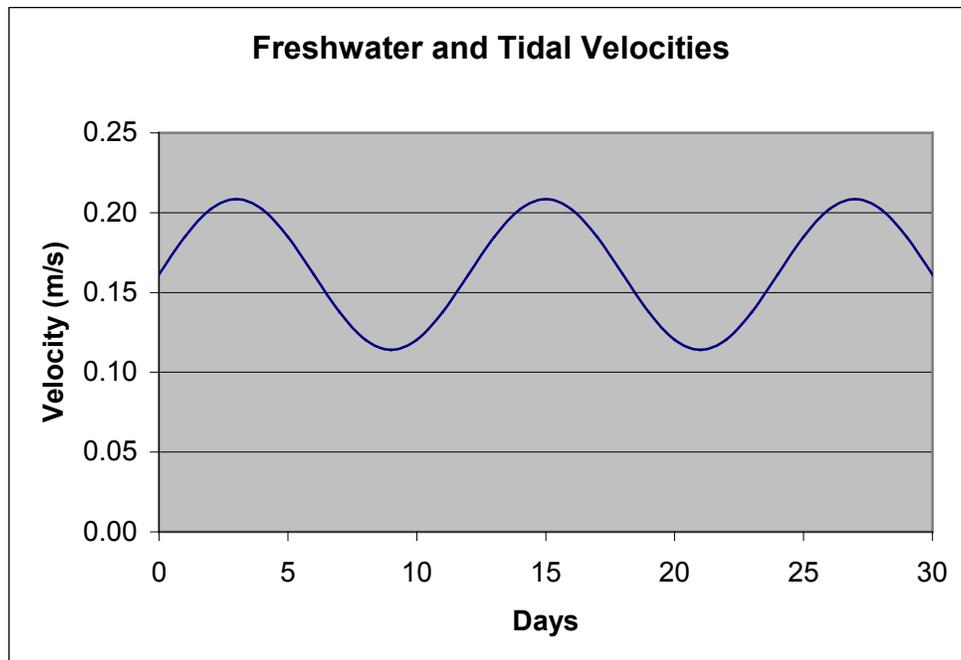
Salinity can significantly affect atmospheric exchange of carbon dioxide. For saline systems, the equilibrium parameters of the CO_2 system should be obtained using CO2SYS (Yuan, 2006) or CO2calc (USGS, 2010) and the results used as inputs for *CO2Equil* in the estuarine AQUATOX

simulation. See section 5.6 for more information about this implementation.

Migration

Fish and pelagic invertebrates will also migrate vertically when the salinity level is not favorable. Favorable salinity is defined as the range of salinity in which no ingestion effects occur for the animal (from the minimum to the maximum salinity tolerances for ingestion). If the salinity of the current segment is outside that range, and the salinity of the other segment is within the range of favorable salinity, the animal is predicted to migrate vertically to the other segment. Entrainment for pelagic invertebrates (movement due to water movement from the lower layer to the upper layer as predicted by the salt balance model, see **(437)**) will also be set to zero if the salinity in the upper layer is outside of the favorable range. This can have significant effects on shrimp populations, for example.

10.6 Nutrient Inputs to Lower Layer

Nutrient concentrations in ocean water flowing into the lower layer are set to temporally constant levels, the assumption being that the chemical composition of seawater remains relatively uniform**.** Nutrients and gasses in seawater may be edited using a button available in the initial conditions and loadings screen for each relevant variable.   The default nutrient and gas composition of seawater are set as follows:

- Ammonia: 0.02 mg/L   (Data from Galveston Bay, TX)
- Nitrate: 0.05 mg/L   (Data from Galveston Bay, TX)
- Phosphate: 0.03 mg/L   (Data from Galveston Bay, TX)
- Oxygen: 7.0   mg/L   (Default oxygen inflow to lower segment)
- CO_2 :   90.0 mg/L   (Anthoni, 2006)

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APPENDIX A. GLOSSARY OF TERMS

Taken in large part from: The Institute of Ecology. 1974. *An Ecological Glossary for Engineers and Resource Managers*. TIE Publication #3, 50 pp.

Abiotic	nonliving, pertaining to physico-chemical factors only
Adsorption	the adherence of substances to the surfaces of bodies with which they are in contact
Aerobic	living, acting, or occurring in the presence of oxygen
Algae	any of a group of chlorophyll-bearing aquatic plants with no true leaves, stems, or roots
Allochthonous	material derived from outside a habitat or environment under consideration
Algal bloom	rapid and flourishing growth of algae
Alluvial	of alluvium
Alluvium	sediments deposited by running water
Ambient	surrounding on all sides
Anaerobic	capable of living or acting in the absence of oxygen
Anoxic	pertaining to conditions of oxygen deficiency
Aphotic	below the level of light penetration in water
Assimilation	transformation of absorbed nutrients into living matter
Autochthonous	material derived from within a habitat, such as through plant growth
Benthic	pertaining to the bottom of a water body; pertaining to organisms that live on the bottom
Benthos	those organisms that live on the bottom of a body of water
Biodegradable	can be broken down into simple inorganic substances by the action of decomposers (bacteria and fungi)
Biochemical oxygen demand (BOD)	the amount of oxygen required to decompose a given amount of organic matter
Biomagnification	the step by step concentration of chemicals in successive levels of a food chain or food web
Biomass	the total weight of matter incorporated into (living and/or dead) organisms
Biota	the fauna and flora of a habitat or region
Chlorophyll	the green, photosynthetic pigments of plants
Colloid	a dispersion of particles larger than small molecules and that do not settle out of suspension
Consumer	an organism that consumes another
Copepods	a large subclass of usually minute, mostly free-swimming aquatic crustaceans
Crustacean	a large class of arthropods that bear a horny shell
Decomposers	bacteria and fungi that break down organic detritus
Detritus	dead organic matter
Diatom	any of class of minute algae with cases of silica
Diurnal	pertaining to daily occurrence

Dynamic equilibrium	a state of relative balance between processes having opposite effects
Ecology	the study of the interrelationships of organisms with and within their environment
Ecosystem	a biotic community and its (living and nonliving) environment considered together
Emergent	aquatic plants, usually rooted, which have portions above water for part of their life cycle
Environment	the sum total of all the external conditions that act on an organism
Epilimnion	the well mixed surficial layer of a lake; above the hypolimnion
Epiphytes	plants that grow on other plants, but are not parasitic
Equilibrium	a steady state in a dynamic system, with outflow balancing inflow
Euphotic	pertaining to the upper layers of water in which sufficient light penetrates to permit growth of plants
Eutrophic	aquatic systems with high nutrient input and high plant growth
Fauna	the animals of a habitat or region
Flood plain	that part of a river valley that is covered in periods of high (flood) water
Flora	plants of a habitat or region
Fluvial	pertaining to a stream
Food chain	animals linked by linear predator-prey relationships with plants or detritus at the base
Food web	similar to food chain, but implies cross connections
Forage fish	fish eaten by other fish
Habitat	the environment in which a population of plants or animals occurs
Humic	pertaining to the partial decomposition of leaves and other plant material
Hydrodynamics	the study of the movement of water
Hypolimnion	the lower layer of a stratified water body, below the well mixed zone
Influent	anything flowing into a water body
Inorganic	pertaining to matter that is neither living nor immediately derived from living matter
Invertebrate	animals lacking a backbone
Limiting factor	an environmental factor that limits the growth of an organism; the factor that is closest to the physiological limits of tolerance of that organism
Limnetic zone	the open water zone of a lake or pond from the surface to the depth of effective light penetration
Limnology	the study of inland waters
Littoral zone	the shoreward zone of a water body in which the light penetrates to the bottom, thus usually supporting rooted aquatic plants
Macrofauna	animals visible to the naked eye
Macrophytes	large (non-microscopic), usually rooted, aquatic plants
Nutrients	chemical elements essential to life
Omnivorous	feeding on a variety of organisms and organic detritus
Organic chemical	compounds containing carbon;
Overturn	the complete circulation or mixing of the upper and lower waters of a lake when temperatures (and densities) are similar
Oxygen depletion	exhaustion of oxygen by chemical or biological use
Parameter	a measurable, variable quantity as distinct from a statistic

Pelagic zone	open water with no association with the bottom
Periphyton	community of algae and associated organisms, usually small but densely set, closely attached to surfaces on or projecting above the bottom
Oxidation	a reaction between molecules, ordinarily involves gain of oxygen
Photic zone	the region of aquatic environments in which the intensity of light is sufficient for photosynthesis
Phytoplankton	small, mostly microscopic algae floating in the water column
Plankton	small organisms floating in the water
Pond	a small, shallow lake
Population	a group of organisms of the same species
Predator	an organism, usually an animal, that kills and consumes other organisms
Prey	an organism killed and at least partially consumed by a predator
Producer	an organism that can synthesize organic matter using inorganic materials and an external energy source (light or chemical)
Production	the amount of organic material produced by biological activity
Productivity	the rate of production of organic matter
Productivity, primary	the rate of production by plants
Productivity, secondary	the rate of production by consumers
Reservoir	an artificially impounded body of water
Riverine	pertaining to rivers
Rough fish	a non-sport fish, usually omnivorous in food habits
Sediment	any mineral and/or organic matter deposited by water or air
Siltation	the deposition of silt-sized and clay-sized (smaller than sand-sized) particles
Stratification	division of a water body into two or more depth zones due to temperature or density
Substrate	the layer on which organisms grow; the organic substance attacked by decomposers
Succession	the replacement of one plant assemblage with another through time
Tolerance	an organism's capacity to endure or adapt to unfavorable conditions
Trophic level	all organisms that secure their food at a common step in the food chain
Turbidity	condition of water resulting from suspended matter, including inorganic and organic material and plankton
Volatilization	the act of passing into a gaseous state at ordinary temperatures and pressures
Wastewater	water derived from a municipal or industrial waste treatment plant
Wetlands	land saturated or nearly saturated with water for most of the year; usually vegetated
Zooplankton	small aquatic animals, floating, usually with limited swimming capability

APPENDIX B. USER-SUPPLIED PARAMETERS AND DATA

The model has many parameters and internal variables. Most of these are linked to data structures such as ChemicalRecord, SiteRecord, and ReminRecord, which in turn may be linked to input forms that the user accesses through the Windows environment. Although consistency has been a goal, some names may differ between the code, the user interface, and the technical documentation

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
	ChemicalRecord	**Chemical Underlying Data**	**For each chemical simulated, the following Parameters are required**	
Chemical	ChemName	N / A	Chemical's Name. Used for Reference only.	N / A
CAS Registry No.	CASRegNo	N / A	CAS Registry Number. Used for Reference only.	N / A
Molecular Weight	MolWt	MolWt	Molecular weight of pollutant	g/mol
Dissociation Constant	pka	pKa	Acid dissociation constant	negative log
Solubility	*Solubility*	*N / A*	*Not utilized as a parameter by the code.*	*ppm*
Henry's Law Constant	Henry	Henry	Henry's law constant	atm m^3 mol-^{1}
Vapor Pressure	*VPress*	*N / A*	*Not utilized as a parameter by the code.*	*mm Hg*
Octanol-water partition coefficient	LogKow	LogKow	Log octanol-water partition coefficient	unitless
KPSED	KPSed	KPSed	Detritus-water partition coefficient	L/kg OC
KOM$_{RefrDOM}$	KOMRefrDOM	KOM$_{RefrDOM}$	Reftractory DOM to Water Partition Coefficient	L/kg OM
Uptake Rate (K1) Detritus	K1Detritus	K1$_{Detr}$	Uptake rate constant for organic matter, default of 1.39	L/kg dry day
Cohesives K1	CohesivesK1	K1	Uptake rate constant for cohesives	L/kg dry day
Cohesives K2	CohesivesK2	K2	Depuration rate constant for cohesives	day^{-1}
Cohesives Kp	CohesivesKp	Kp	Partition coefficient for cohesives	L/kg dry
Non-Cohesives K1	NonCohK1	K1	Uptake rate constant for non-cohesives class 1	L/kg dry day
Non-Cohesives K2	NonCohK2	K2	Depuration rate constant for non-cohesives class 1	day^{-1}
Non-Cohesives Kp	NonCohKp	Kp	Partition coefficient for non-cohesives class 1	L/kg dry

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
Non-Cohesives2 K1	NonCoh2K1	K1	Uptake rate constant for non-cohesives class 2	L/kg dry day
Non-Cohesives2 K2	NonCoh2K2	K2	Depuration rate constant for non-cohesives class 2	day^{-1}
Non-Cohesives2 Kp	NonCoh2Kp	Kp	Partition coefficient for non-cohesives class 2	L/kg dry
Activation Energy for Temperature	En	En	Arrhenius activation energy	cal/mol
Rate of Anaerobic Microbial Degradation	KMDegrAnaerobic	KAnaerobic	Decomposition rate at 0 g/m3 oxygen	1/d
Max. Rate of Aerobic Microbial Degradation	KMDegrdn	KMDegrdn	Maximum (microbial) degradation rate	1/d
Uncatalyzed hydrolysis constant	KUnCat	KUncat	The measured first-order reaction rate at ph 7	1/d
Acid catalyzed hydrolysis constant	KAcid	KAcid	Pseudo-first-order acid-catalyzed rate constant for a given ph	L/mol · d
Base catalyzed hydrolysis constant	KBase	KBase	Pseudo-first-order rate constant for a given ph	L/mol · d
Photolysis Rate	PhotolysisRate	KPhot	Direct photolysis first-order rate constant	1/d
Oxidation Rate Constant	*OxRateConst*	*N / A*	*Not utilized as a parameter by the code.*	*L/ mol d*
Weibull Shape Parameter	Weibull_Shape	Shape (Internal Model)	Parameter expressing variability in toxic response; default is 0.33	unitless
Weibull Slope Factor	WeibullSlopeFactor	Slope Factor (External Model)	Slope at EC50 multiplied by EC50	slope · ug/L
Chemical is a Base	ChemIsBase	Compound is a base	True if the compound is a base	True/False
This Chemical is a PFA	IsPFA	Compound is a PFA	True if the compound is a perfluorinated surfactant	True/False
Type of PFA	PFAType	carboxylate / sulfonate	Sulfonate group and carboxylate group	carboxylate / sulfonate
Perfluoralkyl Chain Length	PFAChainLength	ChainLength	Length of perfluoroalkyl chain	Integer
Kom for Sediments (PFA)	PFASedKom	Kom for Sediments	Organic matter partition coefficient for the PFA	L/kg

USER INTERFACE	INTERNAL	TECH DOC	Description	UNITS
BCF for Algae (PFA)	PFAAlgBCF	BCF for Algae	Bioconcentration Factor for the PFA to algae	L/kg
BCF for Macrophytes (PFA)	PFAMacroBCF	BCF for Macrophytes	Bioconcentration Factor for the PFA to macrophytes	L/kg
Use BCF to Estimate Uptake	BCFUptake			

	SiteRecord	**Site Underlying Data**	**For each water body simulated, the following Parameters are required**	
Site Name	SiteName	N / A	Site's Name. Used for Reference only.	N / A
Max Length (or reach)	SiteLength	Length	Maximum effective length for wave setup	km
Vol.	Volume	Volume	Initial volume of site (must be copied into state var.)	m^3
Surface Area	Area	Area	Site area	m^2
Estuary Site Width	SiteWidth	Width	Width of estuary	m
Mean Depth	ZMean	ZMean	Mean depth, (initial condition if dynamic mean depth is selected)	M
Maximum Depth	ZMax	ZMax	Maximum depth	M
Ave. Temp. (epilimnetic or hypolimnetic)	TempMean	TempMean	Mean annual temperature of epilimnion (or hypolimnion)	°C
Epilimnetic Temp. Range (or hypolimnetic)	TempRange	TempRange	Annual temperature range of epilimnion (or hypolimnion)	°C
Latitude	Latitude	Latitude	Latitude	Deg, decimal
Altitude (affects oxygen sat.)	Altitude	Altitude	Site specific altitude	m
Average Light	LightMean	LightMean	Mean annual light intensity	Langleys/day
Annual Light Range	LightRange	LightRange	Annual range in light intensity	Langleys/day
Total Alkalinity	*AlkCaCO3*	*N / A*	*Not utilized as a parameter by the code.*	*mg/L*
Hardness as CaCO3	*HardCaCO3*	*N / A*	*Not utilized as a parameter by the code.*	*mg CaCO3 / L*
Sulfate Ion Conc	*SO4Conc*	*N / A*	*Not utilized as a parameter by the code.*	*mg/L*

Total Dissolved Solids	*TotalDissSolids*	*N / A*	*Not utilized as a parameter by the code.*	*mg/L*
USER INTERFACE	**INTERNAL**	**TECH DOC**	**DESCRIPTION**	**UNITS**
Enclosure Wall Area	EnclWallArea	EnclWallArea	Area of experimental enclosures walls; only relevant to enclosure	m^2
Mean Evaporation	MeanEvap	MeanEvap	Mean annual evaporation	inches / year
Extinct. Coeff Water	ECoeffWater	ExtinctH2O	Light extinction of wavelength 312.5 nm in pure water	1/m
Extinct. Coeff Sediment	ECoeffSed	ECoeffSed	Light extinction due to inorganic sediment in water	$1/(m{\cdot}g/m^3)$
Extinct. Coeff DOM	ECoeffDOM	ECoeffDOM	Light extinction due to dissolved organic matter in water	$1/(m{\cdot}g/m^3)$
Extinct. Coeff POM	ECoeffPOM	ECoeffPOM	Light extinction due to particulate organic matter in water	$1/(m{\cdot}g/m^3)$
Baseline Percent Embeddedness	BasePercentEmbed	baseline embeddedness	Observed embeddedness that is used as an initial condition	percent (0-100)
Minimum Volume Frac.	Min_Vol_Frac	Minimum Volume Frac.	Fraction of initial condition that is the minimum volume of a site	frac. of Initial Condition
Auto Select Eqn. for reaeration	UseCovar	Covar	Boolean to determine whether user is entering reaeration coefficient	boolean
Enter KReaer	KReaer	KReaer	Depth-averaged reaeration coefficient	1/d
Total Length	TotalLength	TotLength	Total river length for calculating Nhytoplankton retention	km
Watershed Area	WaterShedArea	WaterShed	Watershed area for estimating total river length (above)	km^2
Fractal Dimension	FractalD	FractalDMarsh	Fractal dimension of marsh-water interface for the site.	unitless
Fractal D. Refuge Coefficient	FD_Refuge_Coeff	Coeff	Fractal dimension *Refuge* coefficient (-0.5 to 100 with the lowest values providing the strongest *Refuge* effect).	unitless
Half Sat Oyster Refuge	HalfSatOysterRefuge	HalfSat (eqn. 95)	Half-saturation constant for oysters in terms of providing refuge from feeding	g/m^2
M2, Amplitude & Epoch	amplitude1, k1	M2	Estuary Only - principal lunar semidiurnal constituent	m, deg. Local Siderial Time (LST)
S2, Amplitude & Epoch	amplitude2, k2	S2	Estuary Only - principal solar semidiurnal constituent	m, deg. LST
N2, Amplitude & Epoch	amplitude3, k3	N2	Estuary Only - larger lunar elliptic semidiurnal constituent	m, deg. LST
K1, Amplitude & Epoch	amplitude4, k4	K1	Estuary Only - lunar diurnal constituent	m, deg. LST

O1, Amplitude & Epoch	amplitude5, k5	O1	Estuary Only - lunar diurnal constituent	m, deg. LST
SSA, Amplitude & Epoch	amplitude6, k6	SSA	Estuary Only - solar semiannual constituent	m, deg. LST
SA, Amplitude & Epoch	amplitude7, k7	SA	Estuary Only - solar annual constituent	m, deg. LST
P1, Amplitude & Epoch	amplitude8, k8	P1	Estuary Only - solar diurnal constituent	m, deg. LST

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
	SiteRecord (Stream-Specific)	**Site Underlying Data**	**For each stream simulated, the following Parameters are required**	
Channel Slope	Channel_Slope	Slope	Slope of channel	m/m
Maximum Channel Depth Before Flooding	Max_Chan_Depth	Max_Chan_Depth	Depth at which flooding occurs	m
Sediment Depth	SedDepth	SedDepth	Maximum sediment depth	m
Stream Type	StreamType	Stream Type	Concrete channel, dredged channel, natural channel	Choice from List
use the below value	UseEnteredManning		Do not determine Manning coefficient from streamtype	true/false
Mannings Coefficient	EnteredManning	Manning	Manually entered Manning coefficient.	$s / m^{1/3}$
Percent Riffle	PctRiffle	Riffle	Percent riffle in stream reach	%
Percent Pool	PctPool	Pool	Percent pool in stream reach	%
	SiteRecord (Sand-Silt-Clay Specific)	**Site Underlying Data**	**For each stream with the inorganic sediments model included, the following Parameters are required**	
Silt: Critical Shear Stress for Scour	ts_silt	TauScourSed	Critical shear stress for scour of silt	kg/m^2

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
Silt: Critical Shear Stress for Deposition	tdep_silt	TauDepSed	Critical shear stress for deposition of silt	kg/m^2
Silt: Fall Velocity	FallVel_silt	VTSed	Terminal fall velocity of silt	m/s
Clay: Critical Shear Stress for Scour	ts_clay	TauScourSed	Critical shear stress for scour of clay	kg/m^2
Clay: Critical Shear Stress for Deposition	tdep_clay	TauDepSed	Critical shear stress for deposition of clay	kg/m^2
Clay: Fall Velocity	FallVel_clay	VTSed	Terminal fall velocity of clay	m/s

	ReminRecord	**Remineralization Data**	**For each simulation, the following Parameters are required (pertaining to organic matter)**	
Max. Degrdn Rate, labile	DecayMax_Lab	DecayMax	Maximum decomposition rate	g/g·d
Max Degrdn Rate, Refrac	DecayMax_Refr	ColonizeMax	Maximum colonization rate under ideal conditions	g/g·d
Temp. Response Slope	*Q10*	*Q10*	*Not utilized as a parameter by the code.*	
Optimum Temperature	TOpt	TOpt	Optimum temperature for degredation to occur	°C
Maximum Temperature	TMax	TMax	Maximum temperature at which degradation will occur	°C
Min. Adaptation Temp	*TRef*	*TRef*	*Not utilized as a parameter by the code.*	°C
Min pH for Degradation	pHMin	pHMin	Minimum ph below which limitation on biodegradation rate occurs.	pH
Max pH for Degradation	pHMax	pHMax	Maximum ph above which limitation on biodegradation occurs.	pH
KNitri, Max Rate of Nitrif.	KNitri	KNitri	Maximum rate of nitrification	1/day
KDenitri Bottom (max.)	KDenitri_Bot	$KDenitri_{Bottom}$	Maximum rate of denitrification at the sed/water interface	1/day
KDenitri Water (max.)	KDenitri_Wat	$KDenitri_{Water}$	Maximum rate of denitrification in the water column	1/day
P to Organics, Labile	P2OrgLab	P2OrgLab	Ratio of phosphate to labile organic matter	fraction dry weight
N to Organics, Labile	N2OrgLab	N2OrgLab	Ratio of nitrate to labile organic matter	fraction dry weight

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
P to Organics, Refractory	P2OrgRefr	P2OrgRefr	Ratio of phosphate to refractory organic matter	fraction dry weight
N to Organics, Refractory	N2OrgRefr	N2OrgRefr	Ratio of nitrate to refractory organic matter	fraction dry weight
P to Organics, Diss. Labile	P2OrgDissLab	P2OrgDissLab	Ratio of phosphate to dissolved labile organic matter	fraction dry weight
N to Organics, Diss. Labile	N2OrgDissLab	N2OrgDissLab	Ratio of nitrate to dissolved labile organic matter	fraction dry weight
P to Organics, Diss. Refr.	P2OrgDissRefr	P2OrgDissRefr	Ratio of phosphate to dissolved refractory organic matter	fraction dry weight
N to Organics, Diss. Refr.	N2OrgDissRefr	N2OrgDissRefr	Ratio of nitrate to dissolved refractory organic matter	fraction dry weight
O2 : Biomass, Respiration	O2Biomass	O2Biomass	Ratio of oxygen to organic matter	unitless ratio
CBODu to BOD5 conversion factor	BOD5_CBODu	*N / A*	*Not utilized as a parameter by the code.*	unitless ratio
O2: N, Nitrification	O2N	O2N	Ratio of oxygen to nitrogen	unitless ratio
Detrital Sed Rate (KSed)	KSed	KSed	Intrinsic sedimentation rate	m/d
Temperature of Obs. KSed	KSedTemp	Temperature$_{Reference}$	Reference temperature of water for calculating detrital sinking rate	deg. c
Salinity of Obs. KSed	KSedSalinity	Salinity$_{Reference}$	Reference salinity of water for calculating detrital sinking rate	‰
PO4, Anaerobic Sed.	*PSedRelease*	*N / A*	*Not utilized as a parameter by the code.*	$g/m^2 \cdot d$
NH4, Aerobic Sed.	*NSedRelease*	*N / A*	*Not utilized as a parameter by the code.*	$g/m^2 \cdot d$
Wet to Dry Susp. Labile	Wet2DrySLab	Wet2DrySLab	Wet weight to dry weight ratio for suspended labile detritus	ratio
Wet to Dry Susp. Refr	Wet2DrySRefr	Wet2DrySRefr	Wet weight to dry weight ratio for suspended refractory detritus	ratio
Wet to Dry Sed. Labile	Wet2DryPLab	Wet2DryPLab	Wet weight to dry weight ratio for particulate labile detritus	ratio
Wet to Dry Sed. Refr.	Wet2DryPRefr	Wet2DryPRefr	Wet weight to dry weight ratio for particulate refractory detritus	ratio
KD, P to CaCO3	KDPCalcite	KD_P_Calcite	Partition coefficient for phosphorus to calcite	L / kg
	ZooRecord	**Animal Underlying Data**	**For each animal in the simulation, the following Parameters are required**	
Animal	AnimalName	N / A	Animal's Name. Used for Reference only.	N / A
Animal Type	Animal_Type	Animal Type	Animal type (fish, pelagic invert, benthic invert, benthic insect)	Choice from List
Taxonomic Type or Guild	Guild_Taxa	Taxonomic type or guild	Taxonomic type or trophic guild	Choice from List

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USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
Toxicity Record	ToxicityRecord	N / A	Associates animal with appropriate toxicity data	Choice from List
Half Saturation Feeding	FHalfSat	FHalfSat	Half-saturation constant for feeding by a predator	g/m^3
Maximum Consumption	CMax	CMax	Maximum feeding rate for predator	g/g·d
Min Prey for Feeding	BMin	BMin	Minimum prey biomass needed to begin feeding	g/m^3 or g/m^2
Sorting: selective feeding	Sorting	Sorting	Fractional degree to which there is selective feeding	Unitless
BurrowIndex	Burrow_Index	BurrowIndex	animal-specific parameter with 0 representing no burrowing refuge;	Unitless
CanSeekRefuge	CanSeekRefuge	Can Seek Refuge	can this animal, as prey, seek refuge in macrophytes, seagrass, or oyster bed?	Boolean
Is a Visual Feeder	Visual_Feeder	Is a Visual Feeder	Does this animal feed based on vision, thereby being impeded by animals seeking refuge in macrophytes, etc.?	Boolean
Susp. Sed. Affect Feeding	SuspSedFeeding	Option to use eqn.	Does suspended sediment affect feeding	Boolean
Slope for Sed. Response	SlopeSSFeed	SlopeSS	Slope for sediment response	Unitless
Intercept for Sed. Resp.	InterceptSSFeed	InterceptSS	Intercept for sediment response	Unitless
Temp Response Slope	Q10	Q10	Slope or rate of change in process per 10°C temperature change	Unitless
Optimum Temperature	TOpt	TOpt	Optimum temperature for given process	°C
Maximum Temperature	TMax	TMax	Maximum temperature tolerated	°C
Min Adaptation Temp	TRef	TRef	Adaptation temperature below which there is no acclimation	°C
Endogenous Respiration	EndogResp	EndogResp	Basal respiration rate at 0° C for given predator	day^{-1}
Specific Dynamic Action	KResp	KResp	Proportion assimilated energy lost to specific dynamic action	Unitless
Excretion:Respiration	KExcr	KExcr	Proportionality constant for excretion:respiration	Unitless
N to Organics	N2OrgInit	N2Org	Fixed ratio of nitrate to organic matter for given species	fraction dry weight
P to Organics	P2OrgInit	P2Org	Fixed ratio of phosphate to organic matter for given species	fraction dry weight
Wet to Dry	Wet2Dry	Wet2Dry	Ratio of wet weight to dry weight for given species	Ratio
Gamete : Biomass	PctGamete	PctGamete	Fraction of adult predator biomass that is in gametes	Unitless
Gamete Mortality	GMort	GMort	Gamete mortality	1/d

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
Mortality Coefficient	KMort	KMort	Intrinsic mortality rate	1/d
Sensitivity to Sediment	SensToSediment	Sensitivity Categories	Which equation to use for mortality due to sediment	"Zero," "Tolerant," "Sensitive," "Highly Sensitive"
Ortanism is Sensitive to Percent Embeddedness	SenstoPctEmbed	N / A	If this checkbox is checked then the organism will be sensitive to the sites calculated embeddedness as a function of TSS	Boolean
Percent Embeddedness Threshold	PctEmbedThreshold	embeddedness threshold value	If the site's calculated embeddedness exceeds this value, mortality for the organism is set to 100%	percent (0-100)
Carrying Capacity	KCap	KCap	Carrying capacity	g/m^2
Average Drift	AveDrift	Dislodge	Fraction of biomass subject to drift per day	fraction / day
Trigger: Deposition Rate	Trigger	Trigger	deposition rate at which drift is accelerated	kg/m^2 day
Frac. in Water Column	FracInWaterCol	$Frac_{WaterColumn}$	Fraction of organism in water column, differentiates from pore-water uptake if the multi-layer sediment model is included	Fraction
VelMax	VelMax	VelMax	Maximum water velocity tolerated	cm/s
Removal due to Fishing	Fishing_Frac	fraction fished	Daily loss of organism due to fishing Pressure	Fraction
Mean lifespan	LifeSpan	LifeSpan	Mean lifespan in days	Days
Fraction that is lipid	FishFracLipid	LipidFrac	Fraction of lipid in organism	g lipid/g org. Wet
Mean Wet Weight	MeanWeight	WetWt	Mean wet weight of organism	g wet
Low O_2: Lethal Conc	O2_LethalConc	$LCKnown_{duration}$	Concentration where there is a known mortality over 24 hours	mg/L (24 hour)
Low O_2: Pct. Killed	O2_LethalPct	$PctKilled_{Known}$	The percentage of the organisms killed at the lcknown level above.	Percentage
Low O_2: EC50 Growth	O2_EC50growth	$EC50_{duration}$	Concentration where there is 50% reduction in growth over 24 hours	mg/L (24 hour)
Low O_2: EC50 Reproduction	O2_EC50repro	$EC50_{duration}$	Concentration where there is 50% reduction in reproduction over 24 hours	mg/L (24 hour)
Ammonia Toxicity: LC50, Total Ammonia (pH=8)	Ammonia_LC50	$LC50_{t,8}$	$LC50_{total\ ammonia}$ at 20 degrees centigrade and ph of 8	mg/L (ph=8)
Salinity Ingestion Effects	Salmin_Ing, SalMax_Ing, Salcoeff1_Ing, Salcoeff2_Ing	SalMin, SalMax, SalCoeff1, SalCoeff2	Parameters used to calculate the effects of the current level of salinity on ingestion for the given animal	‰, ‰, unitless, unitless

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
Salinity Gamete Loss Effects	Salmin_Gam, SalMax_Gam, Salcoeff1_Gam, Salcoeff2_Gam	SalMin, SalMax, SalCoeff1, SalCoeff2	Parameters used to calculate the effects of the current level of salinity on gamete loss for the given animal	‰, ‰, unitless
Salinity Respiration Effects	Salmin_Rsp, SalMax_Rsp, Salcoeff1_Rsp, Salcoeff2_Rsp	SalMin, SalMax, SalCoeff1, SalCoeff2	Parameters used to calculate the effects of the current level of salinity on respiration for the given animal	‰, ‰, unitless, unitless
Salinity Mortality Effects	Salmin_Mort, SalMax_Mort, Salcoeff1_Mort, Salcoeff2_Mort	SalMin, SalMax, SalCoeff1, SalCoeff2	Parameters used to calculate the effects of the current level of salinity on mortality of the given animal	‰, ‰, unitless, unitless
Percent in Riffle	PrefRiffle	PreferenceHabitat	Percentage of biomass of animal that is in riffle, as opposed to run or pool	%
Percent in Pool	PrefPool	PreferenceHabitat	Percentage of biomass of animal that is in pool, as opposed to run or riffle	%
Fish spawn automatically, based on temperature range	AutoSpawn		Does AQUATOX calculate Spawn Dates	true/false
Fish spawn of the following dates each year	SpawnDate1..3		User entered spawn dates	Date
Fish can spawn an unlimited number of times...	UnlimitedSpawning		Allow fish to spawn unlimited times each year	true/false
Use Allometric Equation to Calculate Maximum Consumption	UseAllom_C		Use allometric consumption equation	true/false
Intercept for weight dependence	CA		Allometric consumption parameter	real number
Slope for weight dependence	CB		Allometric consumption parameter	real number
Use Allometric Equation to Calculate Respiration	UseAllom_R		Use allometric consumption respiration	true/false
RA	RA		Intercept for species specific metabolism	real number
RB	RB		Weight dependence coefficient	real number

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
Use "Set 1" of Respiration Equations	UseSet1		Use "Set 1" of Allometric Respiration Parameters	true/false
RQ	RQ	RQ	Allometric respiration parameter	real number
RTL	RTL	RTL	Temperature below which swimming activity is an exponential function of temperature	°C
ACT	ACT	ACT	Intercept for swimming speed for a 1g fish	cm/s
RTO	RTO	RTO	Coefficient for swimming speed dependence on metabolism	s/cm
RK1	RK1	RK1	Intercept for swimming speed above the threshold temperature	cm/s
BACT	BACT	BACT	Coefficient for swimming at low temperatures	1/ °C
RTM	RTM		Not currently used as a parameter by the code	
RK4	RK4	RK4	Weight-dependent coefficient for swimming speed	real number
ACT	ACT		Intercept of swimming speed vs. Temperature and weight	real number
Preference (ratio)	TrophInt.Pref[ ]	Prefprey,pred	Initial preference value from the animal parameter screen	Unitless
Egestion (frac.)	TrophInt.Egest[ ]	EgestCoeffprey,pred	Fraction of ingested prey that is egested	Unitless

	PlantRecord	Plant Underlying Data	For each Plant in the Simulation, the following Parameters are required	
Plant	PlantName		Plant's name. Used for reference only.	N / A
Plant Type	PlantType	Plant Type	Plant type: (Phytoplankton, Periphyton, Macrophytes, Bryophytes)	Choice from List
Plant is Surface Floating	SurfaceFloating	SurfaceFloating	Is this plant surface floating and therefore subject to a shallowlight climate as well as excluded from the hypolimnion.	Boolean
Macrophyte Type	Macrophyte_Type	Macrophyte Type	Benthic, rooted floating, free-floating	Choice from List
Taxonomic Group	Taxonomic_Type	Taxonomic Group	Taxonomic group	Choice from List
Toxicity Record	ToxicityRecord	N / A	Associates plant with appropriate toxicity data	Choice from List

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
Saturating Light	LightSat	LightSat	Light saturation level for photosynthesis	ly/d
Use Adaptive Light	UseAdaptiveLight	Adaptive Light	Choice whether to use adaptive light construct	Boolean
Max. Saturating Light	MaxLightSat	user-entered maximum	Maximum light saturation allowed from adaptive light equation	ly/d
Min. Saturating Light	MinLightSat	user-entered minimum	Minimum light saturation allowed from adaptive light equation	ly/d
P Half-saturation	KPO4	KP	Half-saturation constant for phosphorus	gP/m^3
N Half-saturation	KN	KN	Half-saturation constant for nitrogen	gN/m^3
Inorg C Half-saturation	KCarbon	KCO2	Half-saturation constant for carbon	gC/m^3
Temp Response Slope	Q10	Q10	Slope or rate of change per 10°C temperature change	Unitless
Optimum Temperature	TOpt	TOpt	Optimum temperature	°C
Maximum Temperature	TMax	TMax	Maximum temperature tolerated	°C
Min. Adaptation Temp	TRef	TRef	Adaptation temperature below which there is no acclimation	°C
Max. Photosynthesis Rate	PMax	PMax	Maximum photosynthetic rate	1/d
Photorespiration Coefficient	KResp	KResp	Coefficient of proportionality between. Excretion and photosynthesis at optimal light levels	Unitless
Resp Rate at 20 deg. C	Resp20	Resp20	Respiration rate at 20°C	g/g·d
Mortality Coefficient	KMort	KMort	Intrinsic mortality rate	g/g·d
Exponential Mort Coeff	EMort	EMort	Exponential factor for suboptimal conditions	g/g·d
P to Photosynthate	P2Org	P2Org	Initial ratio of phosphate to organic matter for given species	fraction dry weight
N to Photosynthate	N2Org	N2Org	Initial ratio of nitrate to organic matter for given species	fraction dry weight
Light Extinction	ECoeffPhyto	EcoeffPhyto	Attenuation coefficient for given alga	$1/m\text{-}g/m^3 w$
Wet to Dry	Wet2Dry	Wet2Dry	Ratio of wet weight to dry weight for given species	Ratio
Fraction that is lipid	PlantFracLipid	LipidFrac	Fraction of lipid in organism	g lipid/g org. Wet
N Half-saturation Internal	NHalfSatInternal	$NHalfSat_{Internal}$	half-saturation constant for intracellular nitrogen	gN / gAFDW
P Half-saturation Internal	PHalfSatInternal	$PHalfSat_{Internal}$	half-saturation constant for intracellular phosphorus	gP / gAFDW

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
N Max Uptake Rate	MaxNUptake	MaxNUptake	the maximum uptake rate for nitrogen	gN / gAFDW·d
P Max Uptake Rate	MaxPUptake	MaxPUptake	the maximum uptake rate for phosphorus	gP / gAFDW·d
Min N Ratio	Min_N_Ratio	MinNRatio	the ratio of intracellular nitrogen at which growth ceases	gN / gAFDW
Min P Ratio	Min_P_Ratio	MinPRatio	the ratio of intracellular phosphorus at which growth ceases	gP / gAFDW
Phytoplankton: C:Chlorophyll *a*	Plant_to_Chla	CToChla	ratio of carbon to chlorophyll *a*	g carbon/g chl. *a*
Phytoplankton: Sedimentation Rate (KSed)	KSed	KSed	Intrinsic settling rate	m/d
Phytoplankton: Temperature of Obs. KSed	KSedTemp	$Temperature_{Reference}$	Reference temperature of water for calculating Nhytoplankton sinking rate	deg. C
Phytoplankton: Salinity of Obs. KSed	KSedSalinity	$Salinity_{Reference}$	Reference salinity of water for calculating Nhytoplankton sinking rate	‰
Phytoplankton: Exp. Sedimentation Coeff	ESed	ESed	Exponential settling coefficient	Unitless
Macrophytes: Carrying Capacity	Carry_Capac	KCap	Macrophyte carrying capacity, converted to g/m^3 and used to calculate washout of free-floating macrophytes	g/m^2
Macrophytes: VelMax	Macro_VelMax	VelMax	Velocity at which total breakage occurs	cm/s
Periphyton: Reduction in Still Water	Red_Still_Water	RedStillWater	Reduction in photosynthesis in absence of current	Unitless
Periphyton: Critical Force (FCrit)	FCrit	FCrit	Critical force necessary to dislodge given periphyton group	newtons (kg m/s^2)
Percent Lost in Slough Event	PctSloughed	FracSloughed	Fraction of biomass lost at one time	%
Percent in Riffle	PrefRiffle	PrefRiffle	Percentage of biomass of plant that is in riffle, as opposed to run or pool	%
Percent in Pool	PrefPool	PrefPool	Percentage of biomass of plant that is in pool, as opposed to run or riffle	%
Salinity Photosyn. Effects	Salmin_Phot, SalMax_Phot, Salcoeff1_Phot, Salcoeff2_Phot	SalMin, SalMax, SalCoeff1, SalCoeff2	Parameters used to calculate the effects of the current level of salinity on photosynthesis for the given plant	‰, ‰, unitless, unitless
Salinity Mortality Effects	Salmin_Mort, SalMax_Mort, Salcoeff1_Mort,	SalMin, SalMax, SalCoeff1, SalCoeff2	Parameters used to calculate the effects of the current level of salinity on mortality for the given plant	‰, ‰, unitless,

	Salcoeff2_Mort			unitless

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
	AnimalToxRecord	**Animal Toxicity Parameters**	**For each Chemical Simulated, the following Parameters are required for each animal simulated**	
LC50	LC50	LC50	Concentration of toxicant in water that causes 50% mortality	µg/L
LC50 exp time (h)	LC50_exp_time	ObsTElapsed	Exposure time in toxicity determination	H
K2 Elim rate const	K2	K2	Elimination rate constant	1/d
K1 Uptake const	K1	K1	Uptake rate constant, only used if "Enter K1" option is selected	L / kg dry day
BCF	BCF	BCF	Bioconcentration factor, only used if "Enter BCF" option is selected	L / kg dry
Biotrnsfm rate	BioRateConst	BioRateConst	Percentage of chemical that is biotransformed to Specific daughter products	1/d
EC50 growth	EC50_growth	EC50Growth	External concentration of toxicant at which there is a 50% reduction in growth	µg/L
Growth exp (h)	Growth_exp_time	ObsTElapsed	Exposure time in toxicity determination	H
EC50 repro	EC50_repro	EC50Repro	External concentration of toxicant at which there is a 50% reduction in reprod	µg/L
Repro exp time (h)	Repro_exp_time	ObsTElapsed	Exposure time in toxicity determination	H
Mean wet weight (g)	Mean_wet_wt	WetWt	Mean wet weight of organism	G
Lipid Frac	Lipid_frac	LipidFrac	Fraction of lipid in organism	g lipid/g wet wt.
Drift Threshold (µg/L)	Drift_Thresh	Drift Threshold	Concentration at which drift is initiated	µg/L
LC50 Slope	LC50_Slope	Slope Factor (External Model)	Animal-specific Slope at LC50 multiplied by LC50. If left blank or zero, the value from the chemical record is used.	slope · ug/L
	TPlantToxRecord	**Plant Toxicity Parameter**	**For each Chemical Simulated, the following Parameters are required for each plant simulated**	
EC50 photo	EC50_photo	EC50Photo	External concentration of toxicant at which there is 50% reduction in photosynthesis	µg/L

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
EC50 exp time (h)	EC50_exp_time	ObsTElapsed	Exposure time in toxicity determination	H
EC50 dislodge	EC50_dislodge	EC50Dislodge	For periphyton only: external concentration of toxicant at which there is 50% dislodge of periphyton	µg/L
K2 Elim rate const	K2	K2	Elimination rate constant	1/d
K1 Uptake const	K1	K1	Uptake rate constant, only used if "Enter K1" option is selected	L / kg dry day
BCF	BCF	BCF	Bioconcentration factor, only used if "Enter BCF" option is selected	L / kg dry
Biotrnsfm rate	BioRateConst	BioRateConst	Percentage of chemical that is biotransformed to Specific daughter products	1/d
LC50	LC50	LC50	Concentration of toxicant in water that causes 50% mortality	µg/L
LC50 exp.time (h)	LC50_exp_time	ObsTElapsed	Exposure time in toxicity determination	H
Lipid Frac	Lipid_frac	LipidFrac	Fraction of lipid in organism	g lipid/g org. Wet
LC50 Slope	LC50_Slope	Slope Factor (External Model)	Plant-specific Slope at LC50 multiplied by LC50. If left blank or zero, the value from the chemical record is used.	slope · ug/L
	TChemical	**Chemical Parameters**	**For each Chemical to be simulated, the following Parameters are required**	
Initial Condition	InitialCond	Initial Condition	Initial Condition of the state variable	µg/L
Gas-phase conc.	Tox_Air	Toxicantair	Gas-phase concentration of the pollutant	g/m3
Loadings from Inflow	Loadings	Inflow Loadings	Daily loading as a result of the inflow of water	µg/L
Loadings from Point Sources	Alt_Loadings[Pointsource]	Point Source Loadings	Daily loading from point sources	g/d
Loadings from Direct Precipitation	Alt_Loadings[Direct Precip]	Direct Precipitation Load	Daily loading from direct precipitation	g/m^2 ·d
Nonpoint-source Loadings	Alt_Loadings[NonPointsource]	Non-Point Source Loading	Daily loading from non-point sources	g/dTox_AirGas-phase concentrationg/m3
Biotransformation	BioTrans[ ]	Biotransform	Percentage of chemical that is biotransformed to specific daughter products	%

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
	TRemineralize	**Nutrient Parameters**	**For each Nutrient to be simulated, O2 and CO_2, the following Parameters are required**	
Initial Condition	InitialCond	Initial Condition	Initial Condition of the state variable (TotP or TotN optional)	mg/L
	Loadings	Inflow Loadings	Daily loading as a result of the inflow of water (TotP or TotN optional)	mg/L
Loadings from Point Sources	Alt_Loadings[Pointsource]	Point Source Loadings	Daily loading from point sources	g/d
Loadings from Direct Precipitation	Alt_Loadings[Direct Precip]	Direct Precipitation Loa	Daily loading from direct precipitation	$g/m^2 \cdot d$
Non-point source loadings	Alt_Loadings[NonPointsource]	Non-Point Source Loading	Daily loading from non-point sources	g/d
Fraction of Phosphate Available	FracAvail		Fraction of phosphate loadings that is available versus that which is tied up in minerals	Unitless
	TSedDetr	**Sed. Detritus Parameters**	**For the Labile and Refractory Sedimented Detritus compartments, the following Parameters are required**	
Initial Condition	InitialCond	Initial Condition	Initial Condition of the labile or refractory sedimented detritus	g/m^2
Initial Condition	TToxicant.InitialCond	Toxicant Exposure	Initial Toxicant Exposure of the state variable, for each chemical	µg/kg
Loadings from Inflow	Loadings	Inflow Loadings	Daily loading of the sedimented detritus as a result of the inflow of water	mg/L
(Toxicant) Loadings	TToxicant.Loads	Tox Exposure of Inflow L	Daily parameter; Toxicant Exposure of each type of inflowing detritus, for each chemical	µg/kg

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
	TDetritus	**Susp & Dissolved Detritus**	**For the Suspended and Dissolved Detritus compartments, the following Parameters are required**	
Initial Condition	InitialCond	Initial Condition	Initial Condition of suspended & dissolved detritus, as organic matter, organic carbon, or biochemical oxygen demand	mg/L
Initial Condition: % Particulate	Percent_Part_IC		Percent of Initial Condition that is particulate as opposed to dissolved detritus	Percentage
Initial Condition: % Refractory	Percent_Refr_IC		Percent of Initial Condition that is refractory as opposed to labile detritus	Percentage
Inflow Loadings	Loadings	Inflow Loadings	Daily loading as a result of the inflow of water	mg/L
Dissolved / Particulate Breakdown	Percent_Part	Percent Particulate Inflow, Point Source, Non-Point Source	Three constant or time-series parameters; % of each type of loading that is particulate as opposed to dissolved detritus	Percentage
Labile / Refractory Breakdown	Percent_Refr	Percent Refractory Inflow, Point Source, Non-Point Source	Three constant or time-series parameters; % of each type of loading that is refractory as opposed to labile detritus	Percentage
Loadings from Point Sources	Alt_Loadings[Pointsource]	Point Source Loadings	Daily loading from point sources	$g_{organic\ matter}/d$
Nonpoint-source Loadings (Associated with Organic Matter)	Alt_Loadings	Non-Point Source Loading	Daily loading from non-point sources	$g_{organic\ matter}/d$
(Toxicant) Initial Condition	TToxicant.InitialCond	Toxicant Exposure	Initial Toxicant Exposure of the suspended and dissolved detritus	μg/kg
(Toxicant) Loadings (associated with Organic Matter)	TToxicant.Loads	Tox Exposure of Inflow Loading	Daily parameter; Toxicant Exposure of each type of inflowing detritus, for each chemical	μg/kg

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
	TBuried Detritus	**Buried Detritus**	**For Each Type of Buried Detritus, the following Parameters are required**	
Initial Condition	InitialCond	Initial Condition	Initial Condition of the labile and refractory buried detruitus	Kg/cu. m
(Toxicant) Initial Condition	TToxicant.InitialCond	Toxicant Exposure	Initial Toxicant Exposure of the labile and refractory buried detritus , for each chemical simulated	Kg/cu. m
	TPlant	**Plant Parameters**	**For each plant type simulated, the following Parameters are required**	
Initial Condition	InitialCond	Initial Condition	Initial Condition of the plant	mg/L or g/m^2 dry
Loadings from Inflow	Loadings	Inflow Loadings	Daily loading as a result of the inflow of water	mg/L or g/m^2 dry
(Toxicant) Initial Condition	TToxicant.InitialCond	Toxicant Exposure	Initial Toxicant Exposure of the plant	µg/kg
(Toxicant) Loadings	TToxicant.Loads	Tox Exposure of Inflow L	Daily parameter; Toxicant exposure of the Inflow Loadings, for each chemical simulated	µg/kg
	TAnimal	**Animal Parameters**	**For each animal type simulated, the following Parameters are required**	
Initial Condition	InitialCond	Initial Condition	Initial Condition of the animal	mg/L or g/sq.m also expressed as g/m^2
Loadings from Inflow	Loadings	Inflow Loadings	Daily loading as a result of the inflow of water	mg/L or g/sq. m
(Toxicant) Initial Condition	Ttoxicant.InitialCond	Toxicant Exposure	Initial Toxicant Exposure of the animal	µg/kg
(Toxicant) Loadings	TToxicant.Loads	Tox Exposure of Inflow L	Daily parameter; toxic exposure of the Inflow Loadings, for each chemical simulated	µg/kg
Preference (ratio)	TrophIntArray.Pref	Prefprey, pred	For each prey-type ingested, a preference value within the matrix of preferences	Unitless
Egestion (frac.)	TrophIntArray.ECoeff	EgestCoeff	For each prey-type ingested, the fraction of ingested prey that is egested	Unitless

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
	TVolume	**Volume Parameters**	**For each segment simulated, the following water flow parameters are required**	
Initial Condition	InitialCond	Initial Condition	Initial Condition of the water volume .	m^3
Water volume	Volume	Volume	Choose method of calculating volume; choose between Manning's equation, constant volume, variable depending upon inflow and discharge, or use known values	cu. M
Inflow of Water	InflowLoad	Inflow of Water	Inflow of water; daily parameter, can choose between constant and dynamic loadings	m^3/d cu m/d
Discharge of Water	DischargeLoad	Discharge of Water	Discharge of water; daily parameter, can choose between constant and dynamic loadings	m^3/d
	Site Characteristics	**Site Characteristics**	**The following Parameters are required**	
Site Type	SiteType	Site Type	Site type affects many portions of the model.	Pond, Lake, Stream, Reservoir, Enclosure, Estuary
Frac. of Site that is Shaded	Shade	user input shade	Fraction of site that is shaded, time-series	Fraction
Water Velocity	DynVelocity	user entered velocity	Optional, time series of run velocities	cm/s
Site Mean Depth	DynZMean	user entered mean depth	Optional, time series of mean depth for site	M
	Temperature	**Temperature**	**Temperature Parameters Required**	
Initial Condition	InitialCond	Initial condition	Initial temperature of the segment or layer (if vertically stratified	°C
Could this system stratify			could system vertically stratify	true/false
Valuation or loading			Temperature of the segment. Can use annual means for each stratum and constant or dynamic values	°C

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
	Wind	**Wind**	**Wind parameters required**	
Initial Condition	InitalCond		Initial wind velocity 10 m above the water	m/s
Mean Value	MeanValue		Mean wind velocity	m/s
Wind Loading	Wind	Wind	Daily parameter; wind velocity 10 m above the water; l, can choose default time series, constant or dynamic loadings	m/s
	Light	**Light**	**Light Parameters Required**	
Initial Condition	Light	Light		ly/d
Loading	Loadsrec		Daily parameter; avg. light intensity at segrment top; can choose annual mean, constant loading or dynamic loadings	
Photoperiod	Photoperiod	Photoperiod	Fraction of day with daylight; optional, can be calculated from latitude	hr/d
	pH	**pH**	**pH Parameters Required**	
Initial Condition	InitialCond		Initial pH value	pH
State Variable Valuation	pH	pH	pH of the segment; can choose constant or daily value.	pH
Mean alkalinity	alkalinity	alkalinity	mean Gran alkalinity (if dynamic pH option selected)	µeq CaCO3/L
Sand / Silt / Clay	**TSediment**	**Inorganic Sediment Parameters**	**If the inorganic sediments model is included in AQUATOX, the following Parameters are required for sand, silt, and clay**	
Initial Susp. Sed.	InitialCond	Initial Condition	Initial Condition of the sand, silt, or clay	mg/L
Frac in Bed Seds	FracInBed	FracSed	Fraction of the bed that is composed of this inorganic sediment. Fractions of sand, silt, and clay must add to 1.0	Fraction
Loadings from Inflow	Loadings	Inflow Loadings	Daily sediment loading as a result of the inflow of water	mg/L

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
Loadings from Point Sources	Alt_Loadings[Pointsource]	Point Source Loadings	Daily loading from point sources	g/d
Loadings from Direct Precipitation	Alt_Loadings[Direct Precip]	Direct Precipitation Loa	Daily loading from direct precipitation	Kg ·d
Non-point source loadings	Alt_Loadings[NonPointsource]	Non-Point Source Loading	Daily loading from non-point sources	g/d
Multi-Layer Sediment Model	**Global SedData**	**Multi-layer Sediment Parameters**	**If the multi-layer sediment model is included in AQUATOX, the following general parameters are required**	
Densities [Organic and Inorganic Components]	Densities	Density$_{Sed}$	Density of each organic and inorganic component of the sediment bed.	g/cm^3
Multi-Layer Sediment Model	**Active Layer SedData**	**Multi-layer Parameters**	**If the multi-layer sediment model is included these parameters are required *for the active layer only***	
Max Thickness of Active Layer	MaxUpperThick	user defined maximum thickness	Maximum thickness of the active layer before it becomes split into multiple layers	M
Min Thickness of Active Layer	BioTurbThick	user defined minimum thickness	Minimum thickness of active layer before it is added to the layer below it	M
Cohesives, NonCohesives, Daily Scour	LScour	Erode$_{Sed}$	Scour of this sediment to the water column above	g/d
Cohesives, NonCohesives, Daily Deposition	LDeposition	Deposit$_{Sed}$	Deposit of this sediment from the water column	g/d
Cohesives only, Erosion Velocity	LErodVel	ErodeVel	User input time-series of cohesives erosion velocities, used to calculate scour of organics	m/d
Cohesives only, Deposition Velocity	LDepVel	DepVel	User input time-series of cohesives deposition velocities, used to calculate deposition of organics	m/d
Multi-Layer Sediment Model	**Each Layer SedData**	**Multi-layer Parameters**	**If the multi-layer sediment model is included these parameters are required *for each layer modeled***	
Thickness	BedDepthIC	thickness	Initial thickness of each modeled layer	M
Diffusion Coefficient for top of sediment layer	UpperDispCoeff	DiffCoeff	Dispersion coefficient	m^2/d

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
Pore Water Init. Cond.	TPoreWater.InitialCond	$Conc_{sed}$ Initial Cond.	Concentration of pore water initial condition	m^3 water / m^2
RDOM, LDOM PoreW, Initial Cond	TDOMPorewater.InitialCond	$Conc_{sed}$ Initial Cond.	Concentration of refractory or labile DOM in pore water, initial condition	g/m^3
Cohesives, NonCohesives, Initial Cond	TBottomSediment.InitialCond	$Conc_{sed}$ Initial Cond.	Concentration of inorganic sediments in the layer, initial condition	$g\ m^2$
R Detr Sed, L Detr Sed, Initial Cond	TBuriedSed.InitialCond	$Conc_{sed}$ Initial Cond.	Concentration of refractory and labile organic sediments in the layer, initial condition	g/m^2 dry
Chemical Exposures	[Component]Tox.InitialCond	$Toxicant_{BottomSed}$ Initial Cond.	Concentration of relevant toxicant in element of sediment layer	µg/L pore water, ug/kg solids
Trophic Interactions, BCFs for Shorebirds	**Gull Parameters**	**Shorebirds**	**If the shorebird model is included in a simulation, the following Parameters are required**	
Preference (ratio)	GullPref	$Pref_{prey,\ pred}$	For each prey-type ingested, a preference value within the matrix of preferences	Unitless
Biomagnification Factor	GullBMF	BMF_{Tox}	Biomagnification factor for this chemical in gull	Unitless
Clearance Rate	GullClear	$Clear_{Tox}$	Clearance rate for the given toxicant in gulls	day^{-1}
Link Between Two Segments	**TSegmentLink**	**Multi-Segment Model**	**If the multi-segment model is used for a simulation, the following Parameters are required for each link between segments**	
Type of Link	LinkType	two types of linkages	Indicates whether linkage is unidirectional or bidirectional	"cascade" or "feedback"
Link Name	Name		Used for the user to keep track of linkages	String
FromSeg, ToSeg	FromID, ToID		Used for the model to keep track of linkages	existing segments
Characteristic Length	CharLength	CharLength	Characteristic mixing length, feedback links only	M
Water Flow Data	WaterFlowData	Discharge	Time-series of water flow from one segment to the next	m^3/d
Dispersion Coeff.	DiffusionData	$Diffusion_{ThisSeg}$	Time-series of dispersion coefficients between two segments, feedback links only	m^2/d

USER INTERFACE	INTERNAL	TECH DOC	DESCRIPTION	UNITS
XSection of Boundary	XSectionData	Area	Time-series of cross sectional areas between two segments, feedback links only	m^2
BedLoad$_{Inroganics}$	BedLoad	Bedload$_{Upstreamlink}$	Time-series of bedload from the upstream segment to the downstream segment	g/d