AQUATOX Short Course

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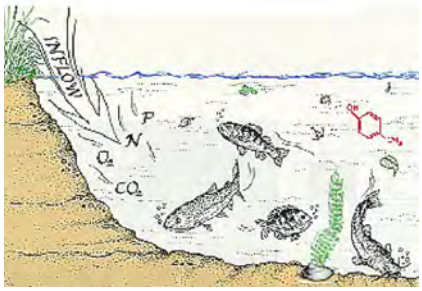
Richard A. Park, Eco Modeling, Diamondhead MS
dickpark@CableOne.net
Jonathan S. Clough, Warren Pinnacle Consulting, Warren VT
jclough@warrenpinnacle.com
Marjorie Coombs Wellman, Office of Water, US EPA, Washington DC
wellman.marjorie@epamail.epa.gov



Introduction to Course, Organization

- Schedule and administrative details
- CD organization
  - Directory Setup
  - For those with laptops, files to look at during the day

Overview: What is AQUATOX?

- Simulation model that links pollutants to aquatic life
- Integrates fate & ecological effects
  - nutrient & eutrophication effects
  - fate & bioaccumulation of organics
  - food web & ecotoxicological effects
- Predicts effects of multiple stressors
  - nutrients, organic toxicants
  - temperature, suspended sediment, flow
- Can be evaluative (with "canonical" or representative environments) or site-specific
- Peer reviewed by independent panels and in several published model reviews
- Distributed by US EPA, Open Source code

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 et al., 1988; 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). Release 1 from the U.S. Environmental Protection Agency (US EPA) was improved with the addition of constructs for chronic effects and uncertainty analysis, making it a powerful tool for probabilistic risk assessment (US EPA, 2000a, b, c). Release 1.1 (US EPA 2001a, b) provided a much enhanced periphyton submodel and minor enhancements for macrophytes, fish, and dissolved oxygen. Release 2, which had a number of major enhancements including the ability to model up to 20 toxic chemicals and more than twice as many biotic compartments and linkage to the BASINS system, was released in early 2004. Significant enhancements resulted in Release 2.1 in October, 2005; Release 2.2 is coming out this summer. Release 3 is a powerful version, which can model linked segments, layered sediments, and estuaries, with significantly improved graphing capabilities.

Why AQUATOX?

- A truly integrated eutrophication, contaminant fate and effect model
  - "is the most complete and versatile model described in the literature" (Koelmans et al. 2001)
  - CATS-5 (Traas et al. 2001) is similar; models microcosms
  - CASM (Bartell et al. 1999) models toxic effects but not fate
- Can simulate many more types of organisms with more realism than most other water quality models
  - WASP6 models total phytoplankton and "benthic algae" (Wool et al. 2004); zooplankton are just a grazing term
  - QUAL2K models phytoplankton and "bottom algae" (Chapra and Pelletier 2003); no animals
- Very comprehensive bioaccumulation model

Bartell, Steven M., Guy Lefebvre, Gregoire Kaminski, Michel Carreau, and Kym Rouse Campbell. 1999. An Ecological Model for Assessing Ecological Risks in Quebec Rivers, Lakes, and Reservoirs. Ecological Modelling **124**:43-67.

Chapra, Steve, and Greg Pelletier. 2003. QUAL2K: A Modeling Framework for Simulating River and Stream Water Quality: Documentation and Users Manual. Medford MA: Civil and Environmental Engineering Dept., Tufts University.

Imhoff, John C., Jonathan S. Clough, Richard A. Park, and Andrew Stoddard. 2004. Evaluation Of Chemical Bioaccumulation Models of Aquatic Ecosystems: Final Report. Athens GA: U.S. Environmental Protection Agency.

Koelmans, A.A., , A. Van der Heidje, , L.M. Knijff, , and R.H. Aalderink. 2001. Integrated Modelling of Eutrophication and Organic Contaminant Fate & Effects in Aquatic Ecosystems. A Review. *Water Research* 35 (15):3517-3536.

Traas, Theo P., J.H. Janse, P.J. Van den Brink, and T. Aldenberg. 2001. A Food Web Model for Fate and Effects of Toxicants and Nutrients in Aquatic Mesocosms. Model Description. Bilthoven, The Netherlands: RIVM.

Wool, Tim A., Robert B. Ambrose, James L. Martin, and Edward A. Comer. 2004. Water Quality Analysis Simulation Program (WASP) Version 6.0 DRAFT: User's Manual. Atlanta GA: US Environmental Protection Agency – Region 4.

Acceptance of AQUATOX

- Has gone through 2 EPA-sponsored peer reviews (following quotes from 2008 review):
  - "model enhancements have made AQUATOX one of the most exciting tools in aquatic ecosystem management"
  - "this is the first model that provides a reasonable interface for scientists to explore ecosystem level effects from multiple stressors over time"
  - "the integration of ICE data into AQUATOX makes this model one of the most comprehensive aquatic ecotoxicology programs available"
  - it "would make a wonderful textbook for an ecotoxicology class"
- Is gradually appearing in open literature

Mauriello, D.A., and R.A. Park. 2002. An adaptive framework for ecological assessment and management. In: Integrated Assessment and Decision Support (A. E. Rizzoli and A.J. Jakeman, eds.) International Environmental Modeling and Software Society, Manno, Switzerland. pp. 509-514.

Rashleigh, B. 2003. Application of AQUATOX, a process-based model for ecological assessment, to Contentnea Creek in North Carolina. *Journal of Freshwater Ecology* 18 (4): 515- 522.

Carleton, J. N., M. C. Wellman, P. A. Cocca, A. S. Donigian, R. A. Park, J. T. Love, and J. S. Clough. 2005. Nutrient Criteria Development with a Linked Modeling System: Methodology Development and Demonstration. *TMDL 2005*. Water Environment Federation, Alexandria, Virginia, pp. 1-25.

Park, R. A., J. S. Clough, M. C. Wellman, and A. S. Donigian. 2005. Nutrient Criteria Development with a Linked Modeling System: Calibration of AQUATOX Across a Nutrient Gradient. *TMDL 2005*. Water Environment Federation, Alexandria, Virginia, pp. 885-902.

Rashleigh, B., M.C. Barber, and D.M. Walters. 2005. Foodweb modeling for PCBs in the Twelvemile Creek Arm of Lake Hartwell. Pages 301-304 *in*: K.J. Hatcher (Ed.), Proceedings of the Georgia Water Resources Conference, April 25-27, Athens, Georgia.

Rashleigh, B. 2007. Assessment of lake ecosystem response to toxic events with the AQUATOX model. Pages 293–299 in: I.E. Gonenc, V.

Park, R. A., J. S. Clough, and M. C. Wellman. 2008. AQUATOX: Modeling environmental fate and ecological effects in aquatic ecosystems. *Ecological Modelling* 213: 1-15 (24 April 2008)

Koutitonsky, B. Rashleigh, R. A. Ambrose, and J. P. Wolfin (eds) 2007. *Assessment of the fates and effects of toxic agents on water resources.* Springer, Dordrecht, The Netherlands.

Sourisseau, S, A. Basser s, F. Perie, T. Caquet. 2007. *Calibration, validation and sensitivity analysis of an ecosystem model applied to artificial streams.* Water Research (in press).

Park, R. A., J. S. Clough, and M. C. Wellman. 2008. AQUATOX: Modeling environmental fate and ecological effects in aquatic ecosystems. *Ecological Modelling* 213: 1-15 (24 April 2008)

Potential Applications for AQUATOX

- Many waters are impaired biologically as well as chemically
- Managers need to know:
  - Which of several stressors is causing the impairment?
  - Will proposed pollution control actions reach their goals?
    - restoration of desirable aquatic community
    - improved chemical water quality
  - Will there be any unintended consequences?
  - How long will recovery take?

Although much progress has been made in controlling water pollution in our Nation's waters since the advent of the Clean Water Act, there is still a long way to go. Under sections 303(d) and 305(b) of the CWA, States are required to identify waterbodies that don't fully support the aquatic life uses as designated in their state water quality standards.

According to the 2002 National Water Quality Inventory, 45% of river reaches, 47% of lake acreage, and 32% of estuarine areas that were assessed are impaired for one or more of their designated uses. Commonly reported causes of impairment included nutrients, siltation,, organic enrichment, and pesticides. Many impaired waters are subjected to multiple stressors. The relative importance of each stressor to the observed biological impairment is not always evident, but the first step in corrective action is to know what stressor (or combination of stressors) is causing the impairment.

Regulatory Endpoints Modeled

- nutrient and toxicant concentrations
- biomass
  - plant, invertebrate, fish
- chlorophyll a
  - phytoplankton, periphyton, moss
- total suspended solids, Secchi depth
- dissolved oxygen
  - daily min. and max. in Rel. 3
- biochemical oxygen demand
- bioaccumulation factors
- half-lives of organic toxicants

AQUATOX has many kinds of output, many of which may be used in a regulatory context.

Potential Applications
nutrients

- Develop nutrient targets for rivers, lakes and reservoirs subject to nuisance algal blooms
- Evaluate which factor(s) is controlling algae levels
  - nutrients, suspended sediments, grazing, herbicides, flow
- Using the linkage to BASINS, evaluate effects of agricultural practices
  - Will target chlorophyll *a* concentrations be attained after BMPS are implemented?
  - Will land use changes from agriculture to residential use increase or decrease eutrophication effects?

Using a process-based model such as AQUATOX can help to provide a mechanistic link between nutrients and the algal responses. This can be used in conjunction with other efforts and approaches to establish nutrient targets. We'll explore this in greater detail later.

Potential Applications of AQUATOX *toxic substances*

- Ecological risk assessment
  - Will non-target organisms be harmed?
    - Will sublethal effects cause game fish to disappear?
  - Will there be disruptions to the food web?
    - Will reduction of zooplankton reduce the food supply for beneficial fish?
    - Or will it lead to nuisance algae blooms?
- Calculate bioaccumulation factors and tissue concentrations
- Estimate time until fish are safe to eat following remediation

Potential Applications
aquatic life support

- Estimate recovery time for fish or invertebrates after reducing pollutant loads
- Evaluate potential ecosystem responses to invasive species and mitigation measures
  - Will native species disappear?
  - Will there be changes in ecosystem “services”?
  - What are the potential effects and half-life of a biocide?
- *Coordinate with biological criteria program*
  - *Estimate biological metrics*
  - *Simulate reference conditions where none exist*
  - *Evaluate biological potential*

The last item is in italics to reflect the fact that this is an area we are just beginning to explore.

Comparison of Dynamic Risk Assessment Models

State Variables & 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			
SABS 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

Park, R. A., J. S. Clough, and M. C. Wellman. 2008. AQUATOX: Modeling environmental fate and ecological effects in aquatic ecosystems. *Ecological Modelling* 213: 1-15 (24 April 2008)

Comparison of Bioaccumulation Models: Biotic State Variables

Table 3.2. Comparison of Bioaccumulation State Variables

BIOTIC STATE VARIABLES	AQUATOX Release 2	BASS v 2.1	Biotic Ligand 1.0.0	Ecofate 1.001, Gobas	EMCM 1.0	RAMAS Ecosystem	QEAFDCHN 1.0	TRIM.FaTE v 3.3
Plants								
Single Generalized Water Column Algal Species	★	7		★	★			★
Multiple Generalized Water Column Algal Species	★							
Green Algae	★							
Blue-green Algae	★							
Diatoms	★							
Single Generalized Benthic Algal Species	★	7						
Multiple Generalized Benthic Algal Species	★							
Periphyton	★	7			★			
Macrophytes	★				★			★
Animals								
Generalized Compartments for Invertebrates or Fish						★	★	
Generalized Zooplankton Species	★	7		★	★		★	
Detritivorous Invertebrates	★			★	4		★	
Herbivorous Invertebrates	★		3	★			★	★
Predatory Invertebrates	★						★	
Single Generalized Fish Species	★	★		★	★		★	
Multiple Generalized Fish Species	★	★		★	★		★	
Bottom Fish	★	★		★	★		★	★
Forage Fish	★	★	3	★	★		★	★
Small Game Fish	★	★		★	★		★	★
Large Game Fish	★	★	3	★	★		★	★
Fish Organ Systems			6					
Age / Size Structured Fish Populations	★	★		★	★	5	★	
Marine Birds	★			★				★
Additional Mammals								★

Imhoff et al. 2004

AQUATOX has a very complete coverage of plants and animals with the capability to model Diatoms, Greens, Blue-greens, and Macrophytes along with a generalized "other algae" compartment. AQUATOX animal compartments are separated into shredders, sediment feeders, suspended feeders, clams, grazers, snails, predatory invertebrates, forage fish, bottom fish, and game fish.

Many models incorporate a complex animal food-web but very few have the capability to model plants with the complexity of AQUATOX.

What AQUATOX does *not* do

- It does not model metals
  - **Hg was attempted, but unsuccessful**
- It does not model bacteria or pathogens
  - **microbial processes are implicit in decomposition**

We have no immediate plans to add metals. Several years ago we added a mercury fate and bioaccumulation submodel. However, a test with independent data did not meet our criteria for a satisfactory fit. The problem seems to be that there is no general algorithm for methylation under varying site conditions. It has been suggested that we just use the bioaccumulation portion of the model and drive it with observed methyl mercury concentrations, and we may eventually do that.

Release 3 has the capability of modeling with a 1-hour time step, thus allowing representation of diel oxygen and time-dependent mortality due to low oxygen levels.

Nutrient release from bottom sediments is represented only to the extent that the nutrients contained in animals, plants, and detritus are released as decomposition progresses. However, the Di Toro sediment diagenesis model is available as an option in Release 3, though it does require additional parameters.

Di Toro, D. M. 2001. Sediment Flux Modeling. Wiley-Interscience, New York.

AQUATOX Structure

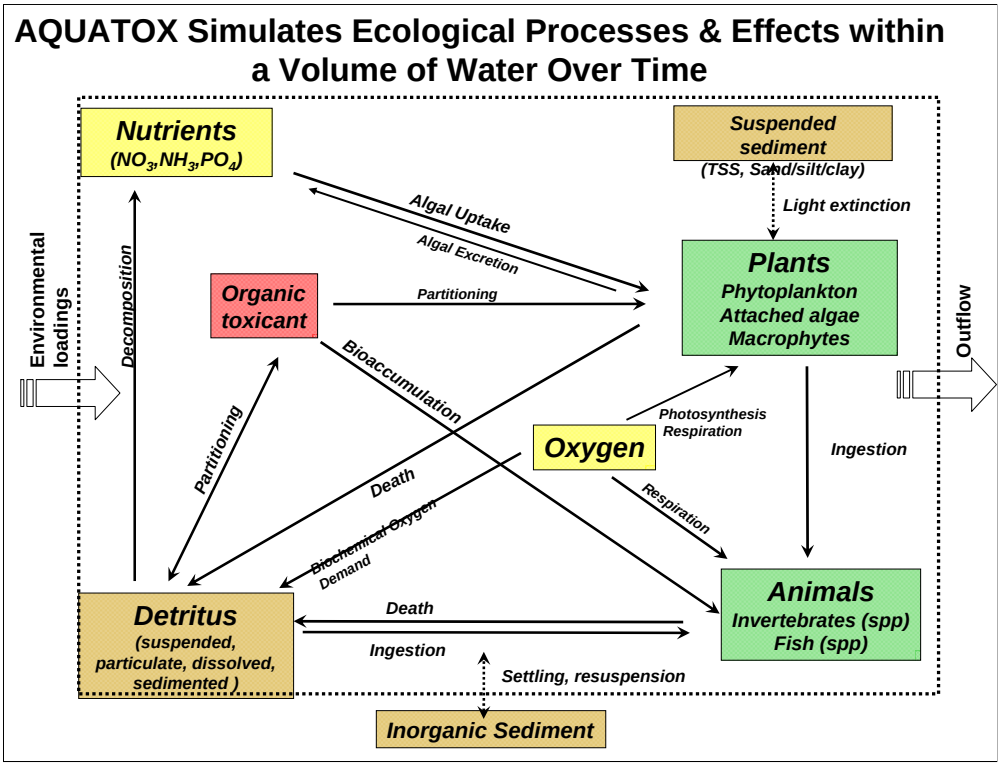
- Time-variable
  - variable-step 4th-5th order Runge-Kutta
    - usually daily reporting time step
    - can use hourly time-step and reporting step in Rel. 3
- Spatially simple unless linked to hydrodynamic model
  - thermal stratification
  - salinity stratification (based on salt balance in Rel 3)
- Modular and flexible
  - written in object Pascal (Delphi)
  - model only what is necessary (flask to river)
  - multi-threaded, multiple document interface
- Control vs. perturbed simulations

AQUATOX varies the time step of the differential equation solver in order to achieve specified accuracy. It may cut down the step to 15 minutes or less to step past a discontinuity. However, it will never increase to more than a day so that pulsed loadings can be detected. The reporting time step is usually a day, but it may be less and it can be as long as 200 days. The results are integrated over the specified time period.

Stratification with two layers can be modeled based on temperature differences or specified dates.

State variables can be added or deleted easily because of the object-oriented Pascal. We have even modeled a flask without any biota to check the chemical fate part of the model against lab results.

The model can simulate conditions with and without a perturbation in order to distinguish impacts. This means that a simulation doesn't have to be perfectly calibrated to evaluate an impact.

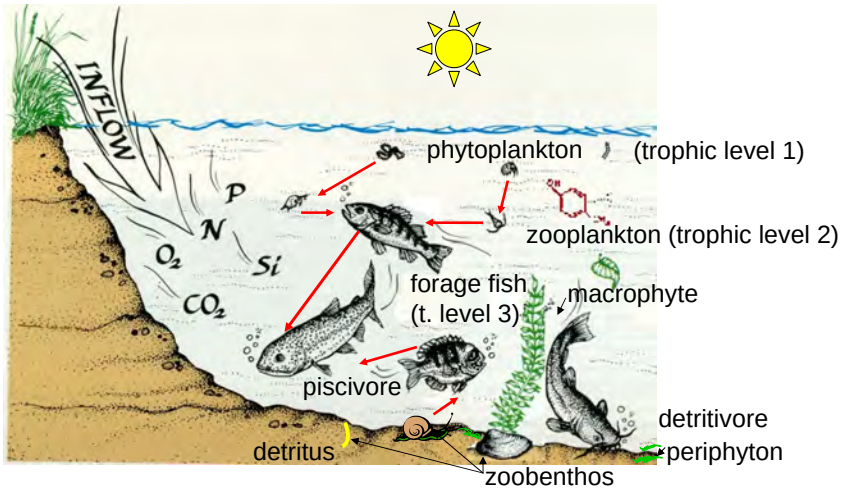

AQUATOX Simulates Ecological Processes & Effects within a Volume of Water Over Time
Nutrients
(NO3,NH3,PO4)
Suspended sediment
(TSS, Sand/silt/clay)
Light extinction
Algal Uptake
Algal Excretion
Plants
Phytoplankton
Attached algae
Macrophytes
Environmental loadings
Decomposition
Organic toxicant
Partitioning
Outflow
Bioaccumulation
Partitioning
Photosynthesis
Respiration
Oxygen
Ingestion
Death
Respiration
Biochemical Oxygen Demand
Animals
Invertebrates (spp)
Fish (spp)
Detritus
(suspended, particulate, dissolved, sedimented)
Death
Ingestion
Settling, resuspension
Inorganic Sediment

Processes Simulated

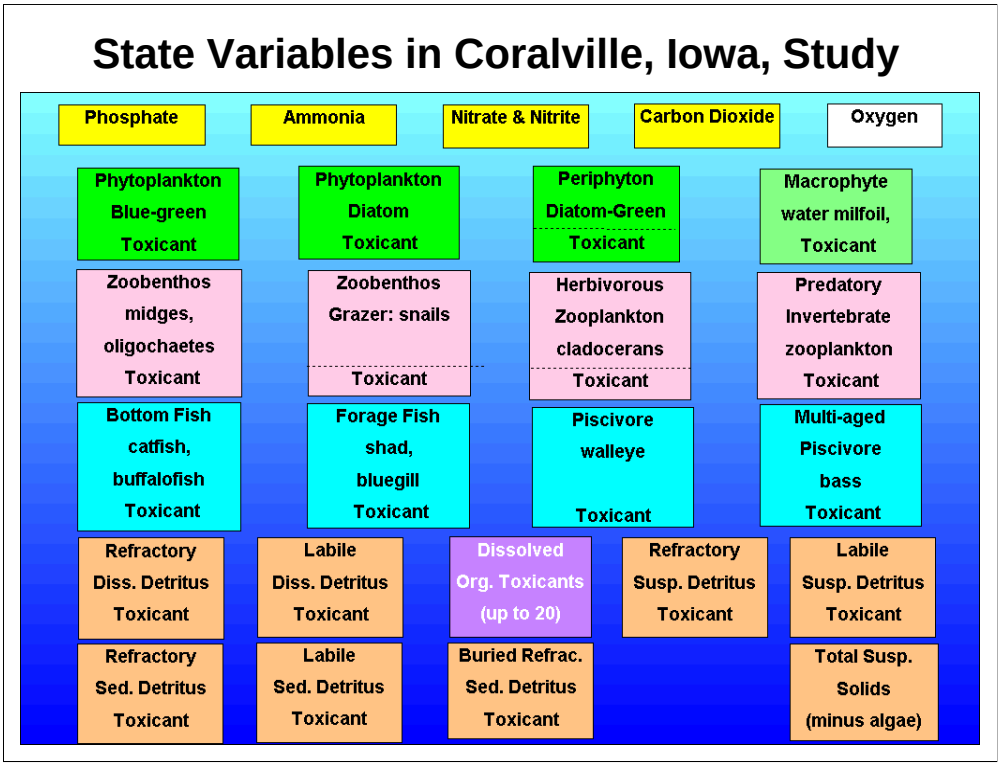
- **Bioenergetics**
  - **feeding, assimilation**
  - **growth, promotion, emergence**
  - **reproduction**
  - **mortality**
  - **trophic relations**
  - **toxicity (acute & chronic)**
- **Environmental fate**
  - **nutrient cycling**
  - **oxygen dynamics**
  - **partitioning to water, biota & sediments**
  - **bioaccumulation**
  - **chemical transformations**
  - **biotransformations**
- **Environmental effects**
  - **direct & indirect**

Both biotic and chemical processes are modeled. Because the model is a eutrophication model combined with a chemical fate model, and includes ecotoxicology, it can represent both direct and indirect effects of various pollutants. For example, it can simulate the combined effects of nutrients and pesticides in agricultural runoff, with representation of eutrophication and simultaneous removal of grazing pressure.

Ecosystem components

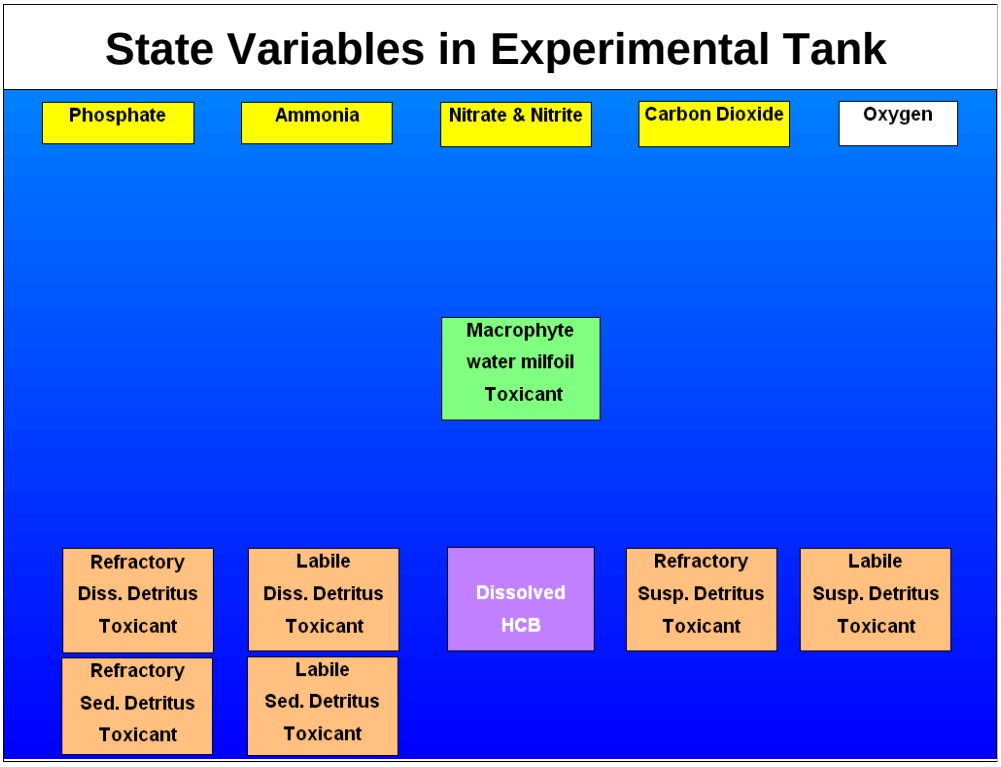


The ecosystem consists of abiotic and biotic components. Phytoplankton, periphyton, and macrophytes are the primary producers, fixing organic matter from nutrients and sunlight. As such they are the first trophic level. Zooplankton and many zoobenthos are primarily herbivores, thus they are the second trophic level. They and the higher trophic levels are consumers. However, usually there isn't a simple food chain with one trophic level feeding on another; most systems have complex food webs with organisms feeding at several trophic levels. Furthermore, animals may feed on both plants and detritus. Animals that feed on fish are termed "piscivores' and animals that feed on detritus are "detritivores." AQUATOX allows a user to specify preferences at multiple levels, thus modeling complex food webs.



Here is an example of a typical set of compartments used in simulating a eutrophic reservoir. The model can represent complex food webs with ease. Up to 20 organic toxicants can be simulated; however, a toxicant is associated with each compartment, so the total number of state variables may be quite large, slowing down the simulation.

Several detrital compartments are modeled, providing more realistic dynamics for detrital feeding and for decomposition and oxygen demand. Labile detritus is nutritious and decomposes rapidly; refractory detritus is not assimilated and decomposes slowly. Detrital compartments also differ in their sorptive capacity for organic chemicals.



You can simulate as few state variables as you wish. These are the state variables used in simulating an experimental tank (aquarium) with a toxicant and a macrophyte. The absolute minimal simulation consists of detritus, nutrients, and oxygen; AQUATOX will not let you delete those.

AQUATOX Capabilities

(*Release 3 in red)*

- **Ponds, lakes, reservoirs, streams, rivers, estuaries**
- **Riffle, run, and pool habitats for streams**
- **Completely mixed, thermal stratification, or salinity stratification**
- **Linked segments, tributary inputs**
- **Multiple sediment layers with pore waters**
- **Sediment Diagenesis Model**
- **Diel oxygen and low oxygen effects, ammonia toxicity**
- **Interspecies Correlation Estimation (ICE) toxicity database**
- **Variable stoichiometry, nutrient mass balance, TN & TP**
- **Dynamic pH**
- **Biota represented by guilds, key species**
- **Constant or variable loads**
- **Latin hypercube uncertainty, nominal range sensitivity analysis**
- **Wizard & help files, multiple windows, task bar**
- **Links to HSPF and SWAT in BASINS**

Because you may have been using an earlier version of the model, it is instructive to highlight the capabilities of successive versions. Release 2 was issued by the US EPA in April 2004. Release 2.1 was issued in October, 2005, and Release 2.2 October 2006. Release 3 is a much more powerful version, which can model linked segments, layered sediments, and estuaries. It has recently undergone a very favorable peer review and will be issued on the EPA web site in early 2009. A pre-release version may be obtained from `http://www.warrenpinnacle.com/prof/AQUATOX/howcani1.html`

Demonstration 1

How is AQUATOX used? Overview of user-friendly graphical interface

- ❑ Installation Considerations
- ❑ The “APS” file unit
- ❑ Looking at a few Parameters
- ❑ Libraries of Parameters
- ❑ Looking at Model Output vs. Observed
- ❑ Setup Screen
- ❑ Integrated Help-File and Users Manual

This demonstration is not intended to describe the functionality of any of these screens in particular, but rather to get you used to navigating through AQUATOX and provide an overview of model and interface design. We will start by loading **FarmPond MO Esfenvalerate.aps** into AQUATOX as a basis for exploring these screens.

Questions to answer on your own as we examine these screens:

•What period is simulated?

•What rates are being saved?

•What is the mean temperature for the site?

•What is the mean light?

•What is the pH?

•What is the ammonia loading?

•What is the nitrate loading? Source?

•Does water volume vary?

•What is mean wind speed?

•What is the source of the esfenvalerate loadings?

•How long would it take for esfenvalerate to reach equilibrium (in fish)?

What are the Analytical Capabilities?

- Graphical Analysis
  - Comparison of model results to Observed Data
  - Graph types and graph libraries
- Control-Perturbed Comparisons
- Process Rates
- Sensitivity Analysis
- Uncertainty Analysis

Release 1 from the U.S. Environmental Protection Agency (US EPA) was improved with the addition of constructs for chronic effects and uncertainty analysis, making it a powerful tool for probabilistic risk assessment (US EPA, 2000a, b, c). Release 1.1 (US EPA 2001a, b) provided a much enhanced periphyton submodel and minor enhancements for macrophytes, fish, and dissolved oxygen. Release 2, which had a number of major enhancements including the ability to model up to 20 toxic chemicals and more than twice as many biotic compartments and linkage to the BASINS system, was released in early 2004. Release 2.1 was issued in October, 2005, and Release 2.2 October 2006. Release 3 is a much more powerful version, which can model linked segments, layered sediments, and estuaries.

The Many Types of AQUATOX Output

(in order of output list)

- Concentrations of State Variables
  - toxicants in water
  - nutrients and gasses
  - organic matter, plants, invertebrates, fish
- Physical Characteristic State Variables
  - water volume, temperature, wind, light, pH
- Mass of Toxicants within State Variables (normalized to water vol.)
  - T1-T20 in organic matter, plants, invertebrates, and fish
- Additional Model Calculations
  - Secchi depth, chlorophyll *a*, velocity, TN, TP
- Toxicant PPB
  - T1-T20 (PPB) in organic matter, plants, invertebrates, and fish
- Nitrogen and Phosphate Mass Tracking Variables
- Bioaccumulation Factors

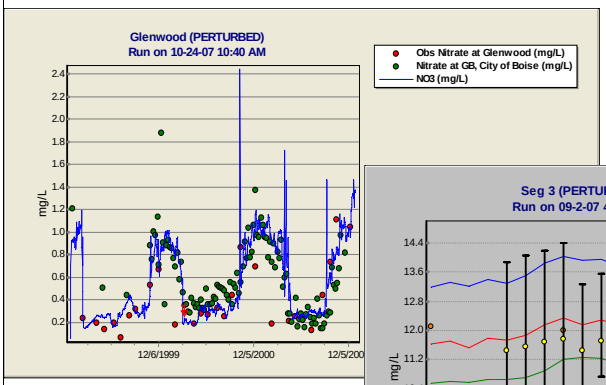
State variables are organized in order of trophic level, starting with organic matter and working upward through plants, invertebrates, and fish.

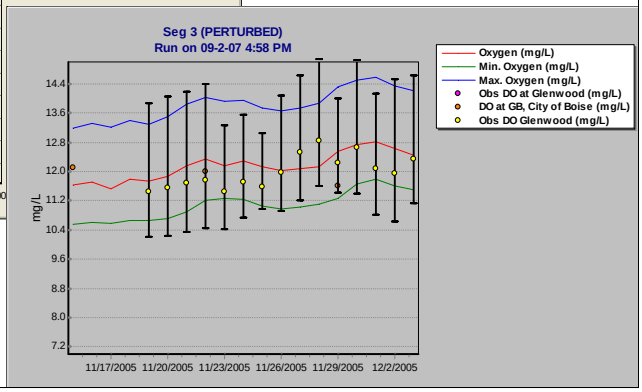
When a toxicant is included in a simulation, the amount of output in a simulation more than triples. Additional chemical output includes the toxicant dissolved in water, the mass of toxicants in state variables normalized to the water volume (units of μg/L), the concentration of toxicants in state variables (PPB), and bioaccumulation factors for organisms.

Because there are so many types of AQUATOX output you may use the "filter" option whenever looking through this list to reduce the amount of output. Try filtering on units ("mg/L" or "g/m2") or on partial state variable names ("peri" "phyto"). Only state variables that include your sub-string will be displayed making it far easier to find the output you wish to graph.

Graphical Analysis

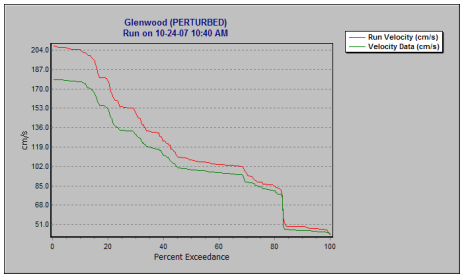
Compare observed data to model output

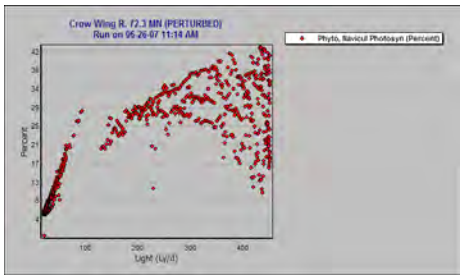




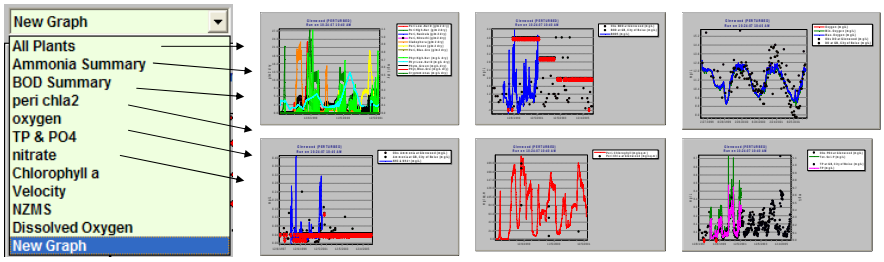
Graphical Analysis

Percent exceedance, duration, scatter plots, log-scale graphs





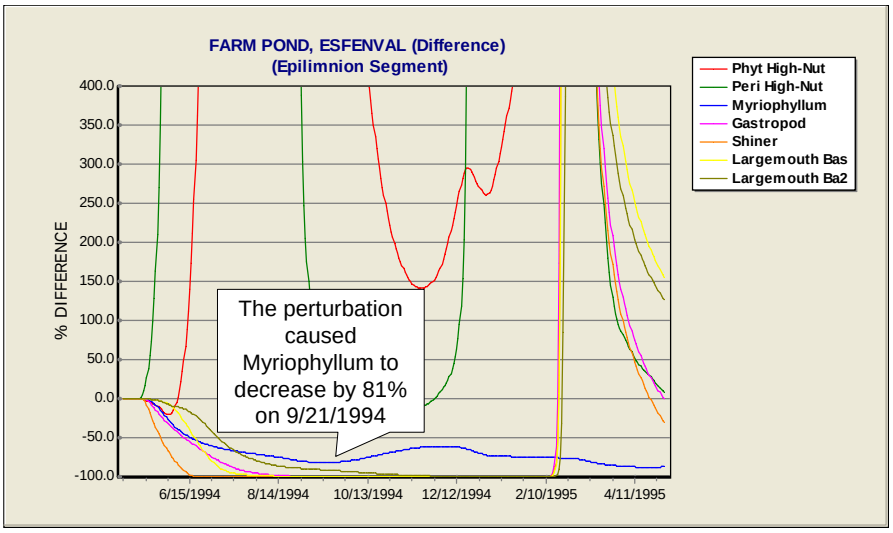
Graph Library saved within simulation



Comparing Scenarios: the "Difference" Graph

Difference graph designed to capture the percent change in results due to perturbation:

$$\%\ Difference = \left(\frac{Result_{Perturbed} - Result_{Control}}{Result_{Control}} \right) \cdot 100$$



The equation shown calculates the percent difference that the perturbation causes from the control simulation. By this formulation a 100% difference means that the perturbation caused the state variable to double. A negative 50% difference means that the perturbation caused the state variable to halve.

We will first examine a difference graph of all of the macrophytes, the invertebrates, and fish in the simulation (graph above). Note that the animals go extinct. Why do you suppose the macrophyte *Myriophyllum* declines?

The difference graph is especially useful when comparing differences in fairly stable sets of results such as fish biomass. As an example of a different type of difference graph, graph the difference in periphyton biomass between control and perturbed.

Care should be taken when interpreting spikes of short duration in a difference graph, this could simply be the result of a short (and potentially unimportant) difference in the timing of events. Also note that when biomass values fall to very low values in both simulations, large differences could be unimportant.

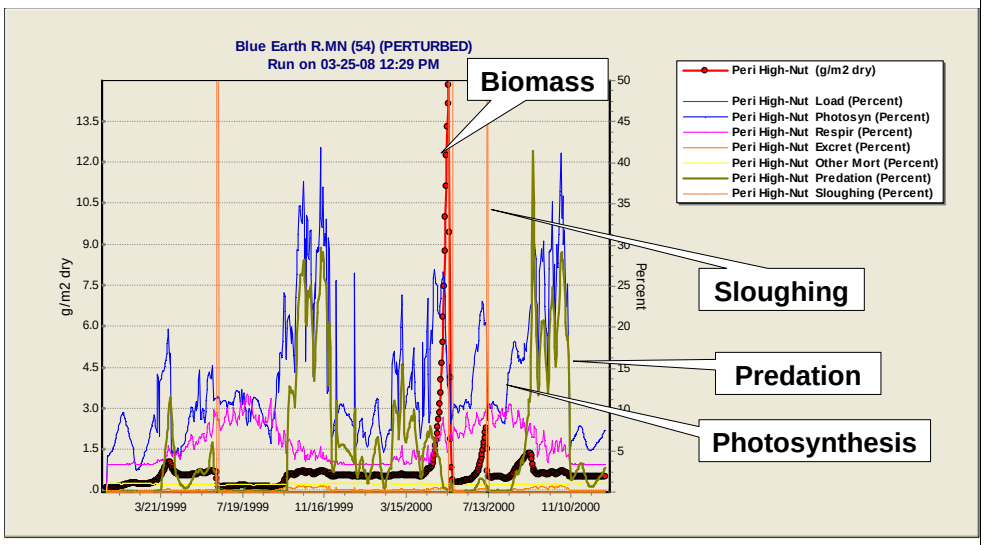
Process Rates

- concentrations of state variables are solved using partial differential equations (Tech. Doc.)
- e.g. the equation for periphyton concentrations is

$$\frac{dBiomass_{Peri}}{dt} = Loading + Photosynthesis - Respiration - Excretion - Mortality - Predation + Sed_{Peri}$$

- individual components of these equations may be saved internally, and graphed to understand the basis for various predictions

Rates Plot Example: Periphyton



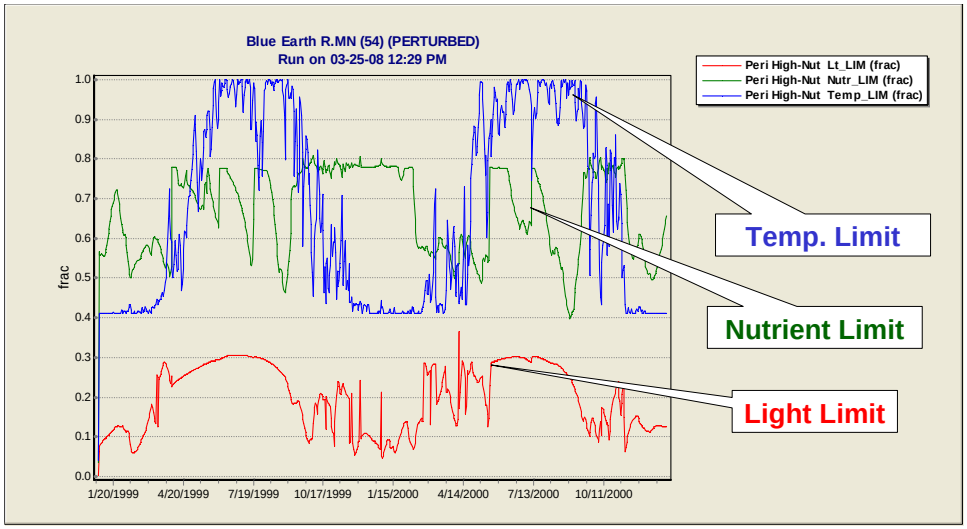
The red line with red circles represents the biomass. The user may wonder why there is such a large bloom of periophyton predicted in the second year. The answer maybe ascertained by examining the rates.

The answer is not explained by photosynthesis rates, in blue, which remain cyclical but consistent over the course of the simulation.

The answer is explained by predation which drops down dramatically in the second year.

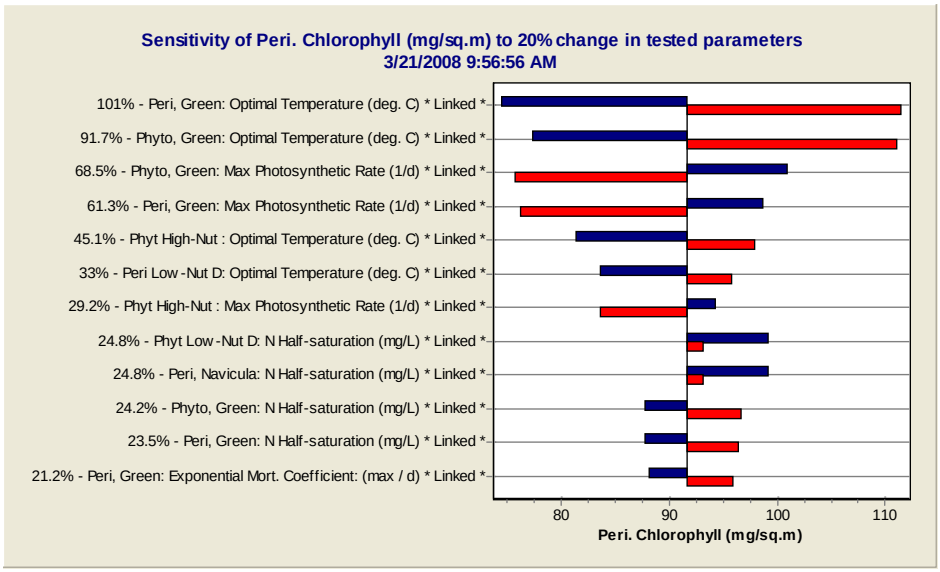
There are also three sloughing events, worth noting in which periphyton is sloughed and moves downstream.

Limitations to Photosynthesis May also be Graphed

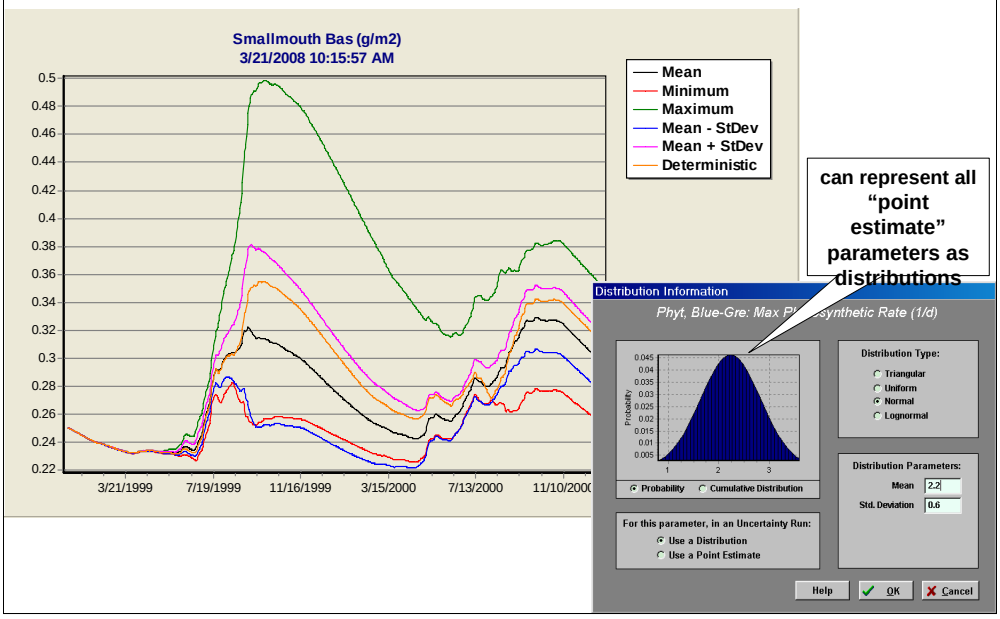


Light limitation means that the plant photosynthesis rate is less than one third of the PMax. The temperature limitation reduces photosynthesis during winter months.

Integrated Nominal Range Sensitivity Analysis with Graphics



Integrated Latin Hypercube Uncertainty Analysis with Graphics



These model results represent summary statistics for each time-step of the simulation based on the Monte-Carlo analysis. The deterministic line plotted represents a single scenario run with "point estimate" values replacing each distribution. All other lines are statistics derived from all of the scenarios run during the analysis.

Applications in Nutrient Analysis

- Lake Onondaga, NY
- Rum, Blue Earth, Crow Wing Rivers, MN
- Cahaba River, AL
- Lower Boise River, ID
- Lake Tenkiller, OK

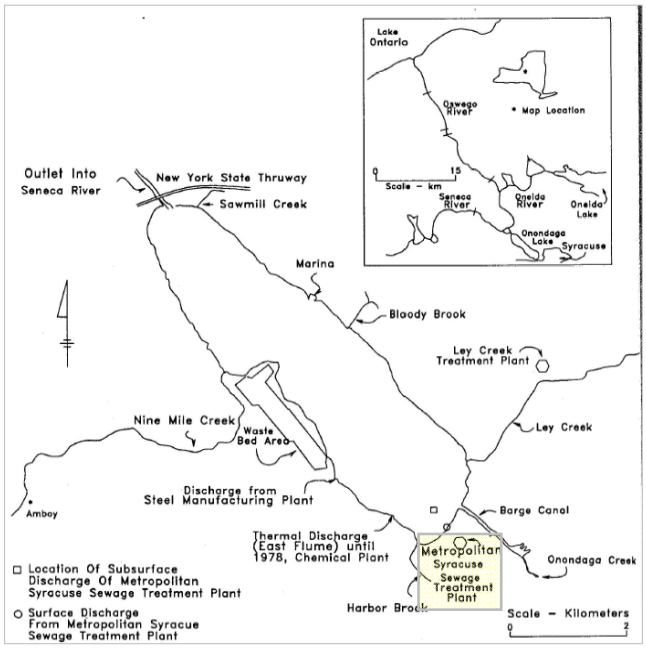
Lake Onondaga, NY

- AQUATOX Validation Site
- "Most polluted lake in U.S."
  - nutrient inputs from wastewater treatment plant ("Metro") & combined sewers
  - successive algal blooms
  - hypoxia in hypolimnion
  - build-up of organic sediments in bottom
  - high mercury levels (not modeled at present)
  - high salinity

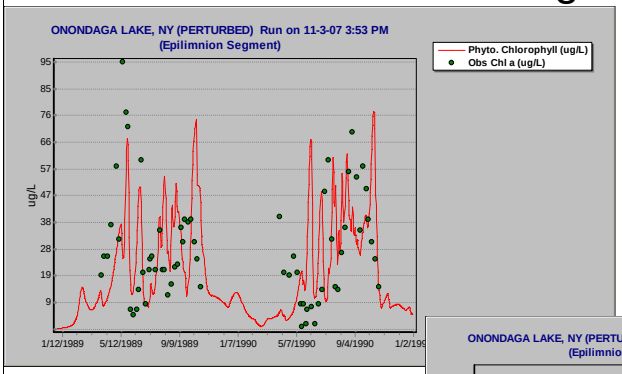
"Lake Onondaga is arguably the most polluted lake in the United States" according to Effler (1996) in the preface to his comprehensive book, which serves as the primary reference for the following information and data on the lake. The shore of this lake in central New York State was industrialized before 1800, and over the last hundred years at least thirty different chemicals were produced from nearby salt and limestone deposits. Unfortunately, the lake was a convenient dumping ground for waste products. Production of soda ash resulted in waste beds as much as 21 m deep and 8.1 km^2 in area along 30% of the lake shore; the wastes include NaCl and $CaCl_2$ that easily leach into the lake. The salinity of the lake was around 3‰ (parts per thousand) prior to closure of the soda ash plant in 1986; by 1990 the salinity had decreased to 1.3‰. Nevertheless, this salinity creates unusual density gradients and intense stratification of the lake. A chlor-alkali plant produced NaOH and Cl by electrolysis, using Hg as the cathode. From 1946 to 1970 as much as 75,000 kg of Hg were discharged into the lake. Aside from an advisory against eating fish from the lake, the high mercury levels may have adversely affected the functioning of the lake ecosystem.

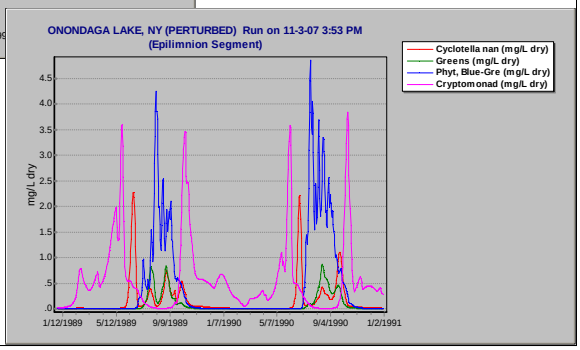
The lake has been a receptacle for most of the domestic waste and urban runoff from Syracuse and the surrounding area. Prior to 1960 untreated and poorly treated sewage was discharged directly to the lake. In 1960 the Metropolitan Sewer District (METRO) primary treatment plant was completed; in 1979 it was upgraded to secondary treatment; and in 1981 tertiary treatment (removal of phosphorus) was instituted. By design, there is little reduction in ammonia in the sewage effluent. At present nearly 20% of the annual inflow into the lake is from METRO. Most troubling are the combined sewer overflows (CSOs) that carry storm water and raw sewage into tributary creeks about 50 times a year.

Lake Onondaga NY, heavily polluted



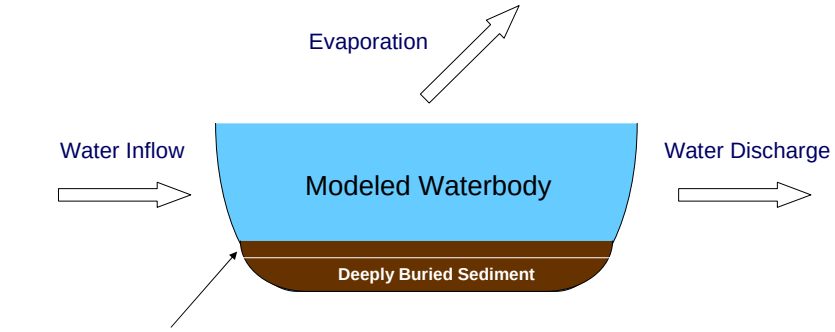
Lake Onondaga is very productive with succession of algal groups





Physical Characteristics of a Site

Water Balance and Sediment Structure

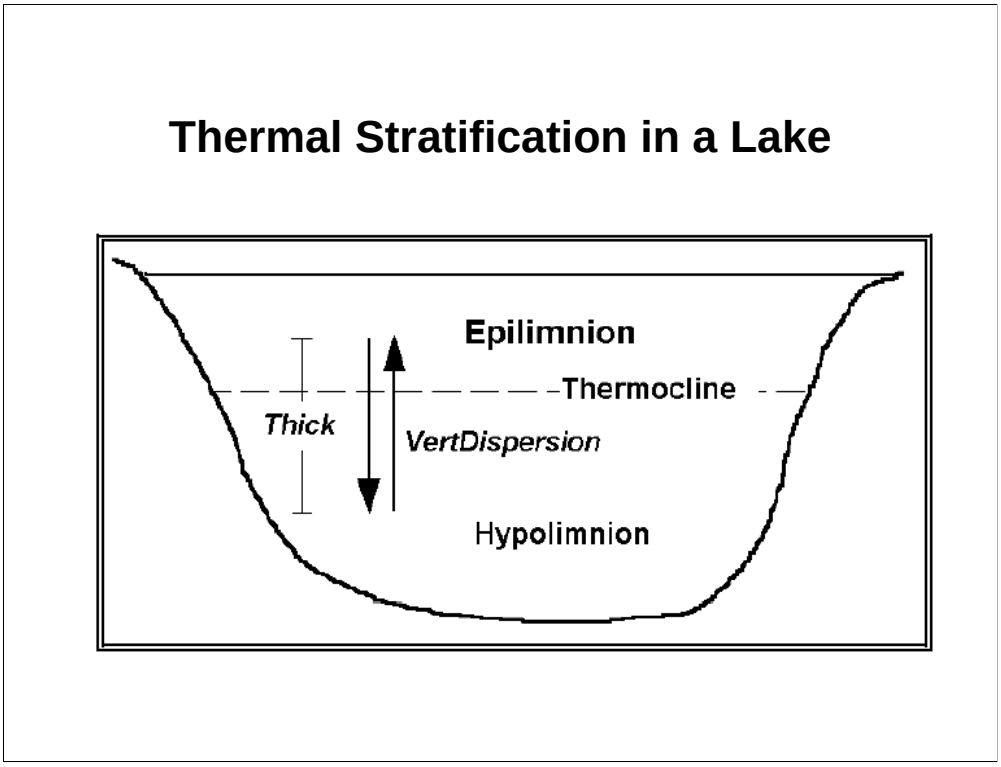


Water balance is defined as a function of inflow, evaporation, and discharge. We will discuss the various mechanisms for modeling water balance in a future slide. The modeled waterbody or river segment is assumed to be well mixed. Evaporation is a function of the site's surface area and the mean annual evaporation at the site.

Nutrients, plankton, and organics wash in and out of the system along with the flow of water.

The bottom sediment includes an active layer and a deeply buried sediment layer that is not reactive with the overlying water unless scour reduces the active layer and the deeply buried sediment is exposed.

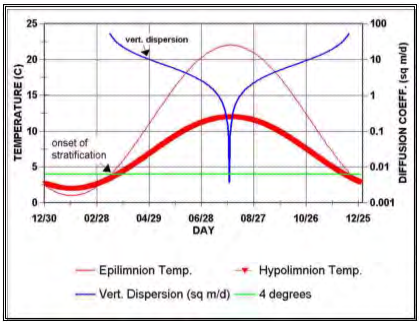
This information covered in Section 3 of the **Technical Documentation**.



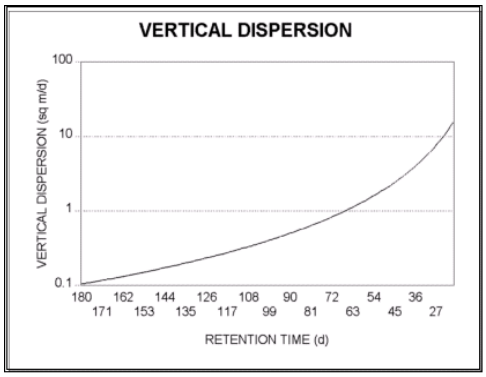
Thermal stratification is handled in the simplest form consistent with the goals of forecasting the effects of nutrients and toxicants. Lakes and reservoirs are considered in the model to have two vertical zones: epilimnion and hypolimnion; the metalimnion zone that separates these is ignored. Instead, 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). As a default, the onset of stratification is considered to occur when the mean water temperature exceeds 4° and the difference in temperature between the epilimnion and hypolimnion exceeds 3°; overturn occurs when this temperature difference is less than 3°, usually in the fall. However, stratification dates may also be specified by the user. Similarly, a temporally constant thermocline depth may be calculated or a time-series of thermocline depths may be specified by the user.

Stratification is a Function of Temperature Differences

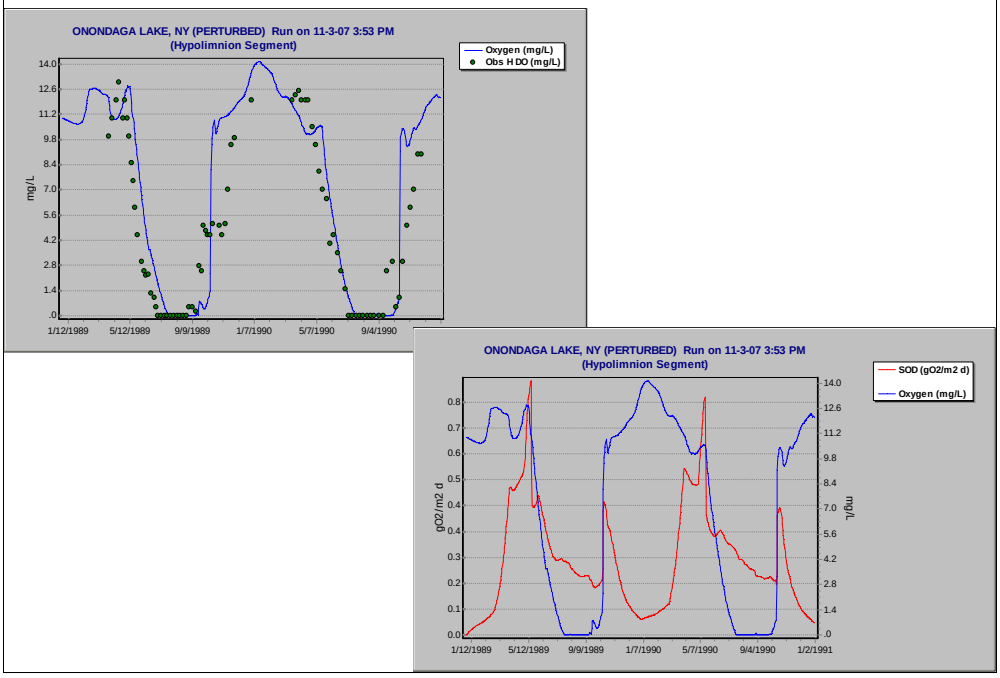


Stratification is also a Function of Discharge

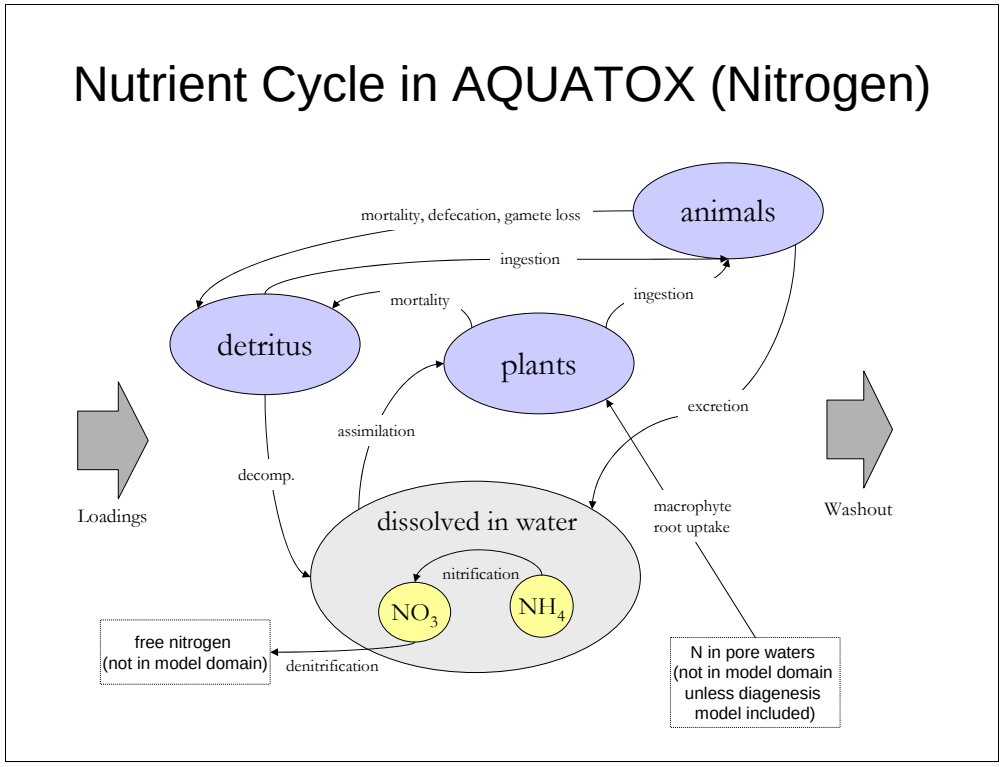


Diffusion between the epilimnion and hypolimnion is a function of the temperature differential. The user specifies the temperatures (or mean and range) for each layer and the model computes when stratification occurs and how much turbulent diffusion occurs.

Hypolimnion goes anoxic with high SOD



Observed data are shown as circles in the above graph while the AQUATOX simulation is the blue line.

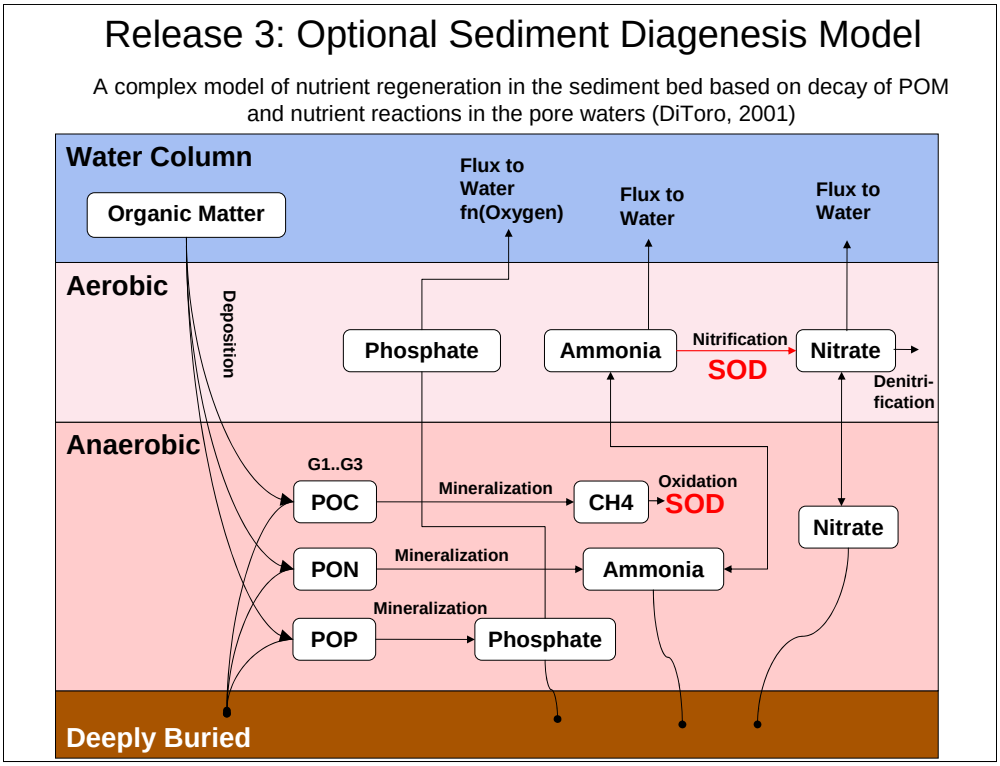


•While this graph looks complex, there is really a fairly straightforward cyclical nature to the movement of nutrients within AQUATOX. Nutrients are taken up into higher organisms through ingestion and assimilation , nutrients are released back into the water column through mortality, defecation, and gamete loss.

•Nutrients from animals and plants break down into various forms of detritus and then are returned to the water column through detrital decomposition.

•Un-ionized ammonia (NH3) is not modeled as a separate state variable but is estimated as a fraction of ammonia.

•The un-ionized form of ammonia 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, NH4+, and the proportion is determined by pH and temperature



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.

Key Points: Diagenesis Model

- Two sediment layers: thin aerobic and thicker anaerobic
- When oxygen is present, the diffusion of phosphorus from sediment pore waters is limited
  - Strong P sorption to oxidated ferrous iron in the aerobic layer (iron oxyhydroxide precipitate)
  - Under conditions of anoxia, phosphorus flux from sediments dramatically increases.
- Sediment oxygen demand (SOD) a function of specific chemical reactions following the decomposition of organic matter
  - methane or sulfide production
  - nitrification of ammonia

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

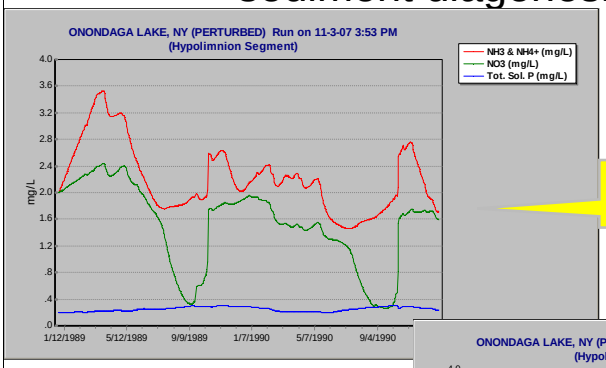
• Model is best suited to represent predominantly anaerobic sediments.

• Deposition of particulate organic matter moves directly into Layer 2.

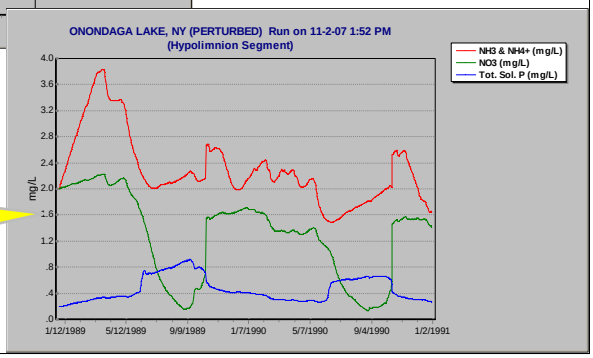
• The fraction of POP and PON within defecated or sedimented matter is assumed equal to the ratio of phosphate or nitrate to organic matter for given species.

• All methane is oxidized or lost.

Hypolimnion PO_4 is better modeled by sediment diagenesis model



"Classic" AQUATOX model

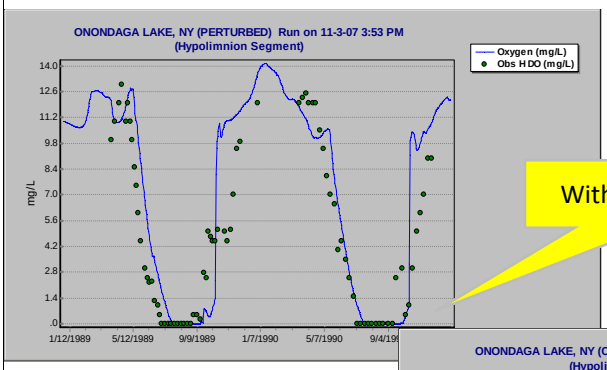


Sediment diagenesis model

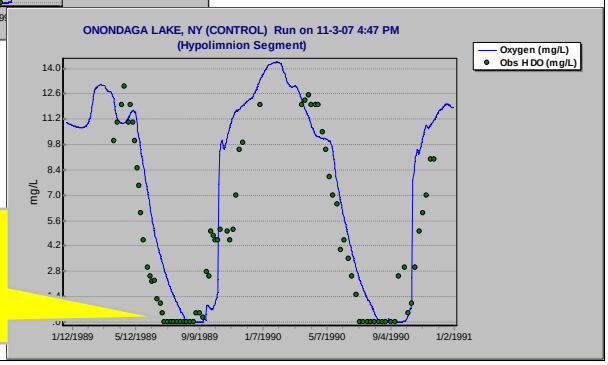
Nutrient Effects on Simulations

- Direct effects on algal growth rates
  - Maximum growth rates often limited by nutrients
  - Degree of limitation may be tracked and plotted
- Indirect repercussions throughout the foodweb due to bottom-up effects
- Light climate changes due to algal blooms
- Algal composition will be affected
- Decomposition of organic matter affects oxygen concentrations

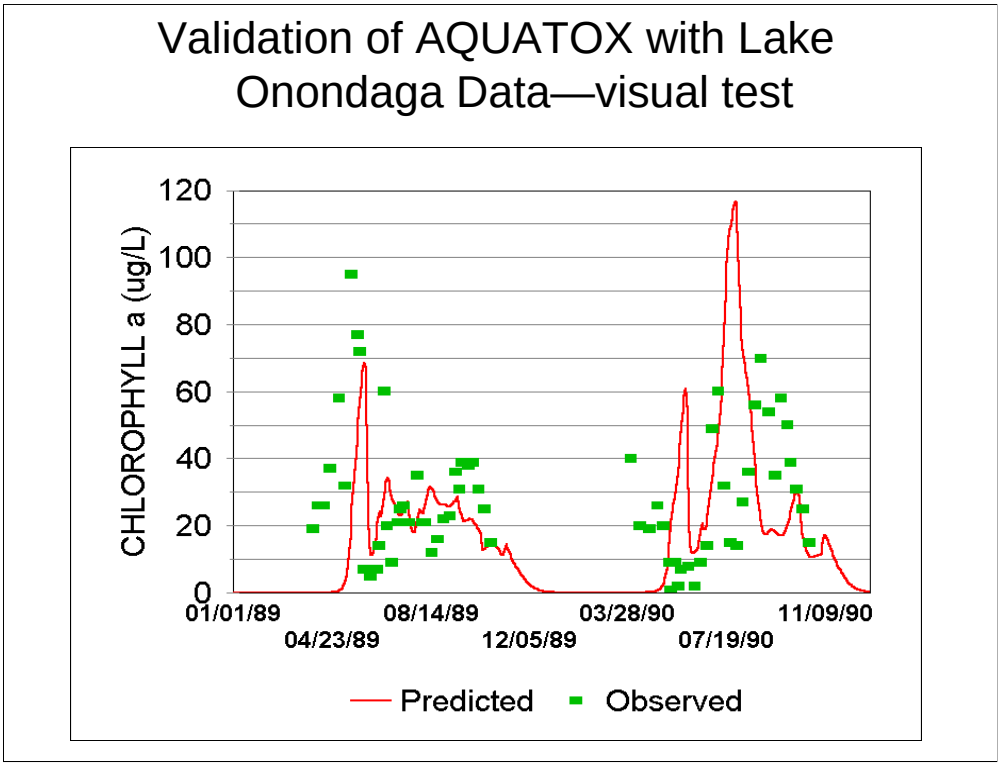
What if Metro WWTP effluent were diverted?



With Metro effluent

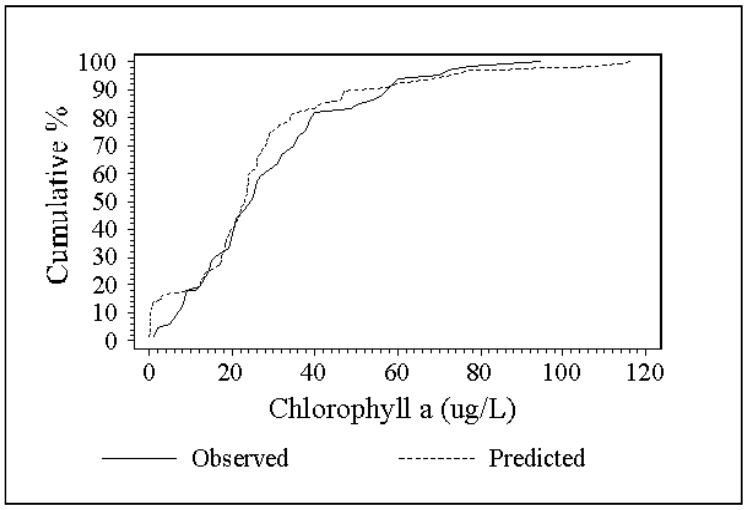


With Metro diversion, in first 2 years anoxia is delayed 1 month



U.S. Environmental Protection Agency. 2000. AQUATOX for Windows: A Modular Fate and Effects Model for Aquatic Ecosystems-Volume 3: Model Validation Reports. Washington, DC.

Validation with chlorophyll a in Lake Onondaga, NY



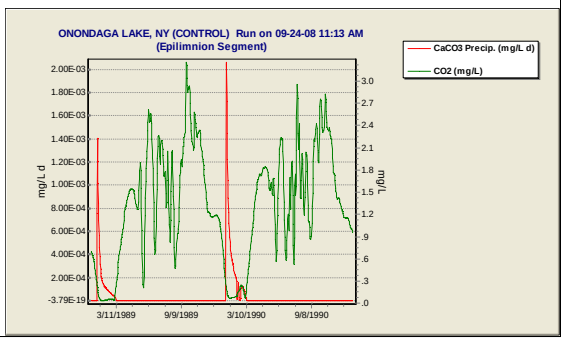
Kolmogorov-Smirnov p statistic = 0.319 (not sign. different)

U.S. Environmental Protection Agency. 2000. AQUATOX for Windows: A Modular Fate and Effects Model for Aquatic Ecosystems-Volume 3: Model Validation Reports. Washington, DC.

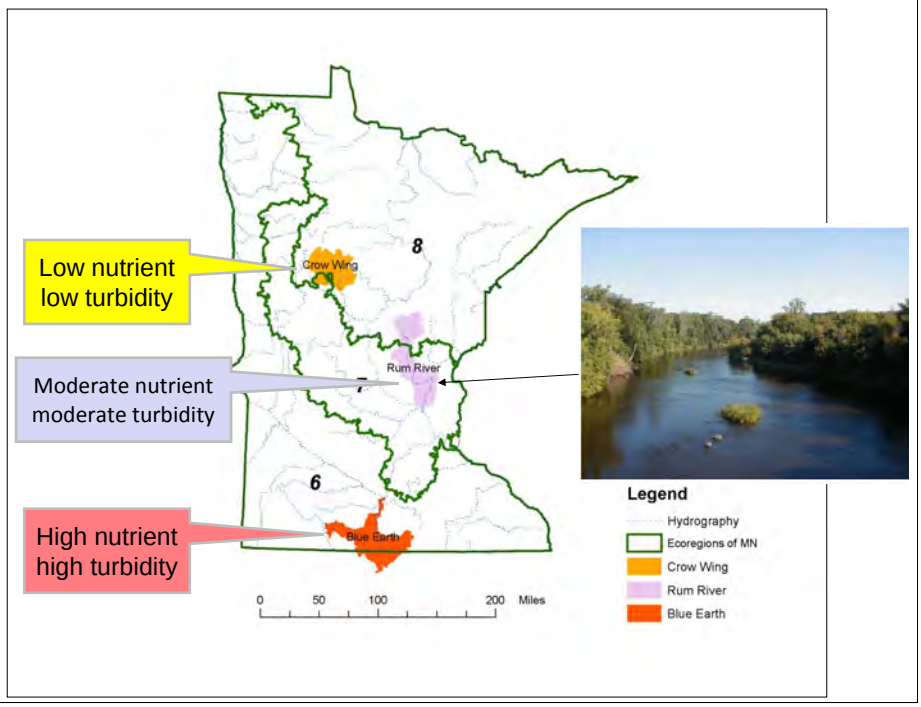
The Kolmogorov-Smirnov statistic is a non-parametric test of whether two datasets differ significantly based on their cumulative distributions. It implied fairly good agreement between the predicted and observed distributions of the chlorophyll *a* values.

Release 3 Addition: Calcium Carbonate Precipitation

- Predicted as a function of pH and algae type
  - When pH exceeds 8.25, precipitation is predicted
  - Precipitation rate is dependent on photosynthesis rate in precipitating algae
- $CaCO_3$ sorbs phosphate from the water column



Minnesota Nutrient Sites



Calibration Strategy for Minnesota Rivers

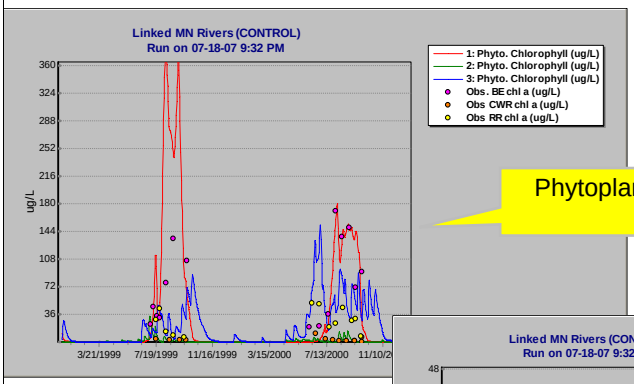
- Must be able to simulate *changing* conditions!
- Add plants and animals representative of both low- (Crow Wing) and high-nutrient (Blue Earth) rivers
- Iteratively calibrate key parameters for each site and cross-check to make sure they still hold for other site
- When goodness-of-fit is acceptable for both sites, apply to an intermediate site (Rum River) and reiterate calibration across all three sites
- Parameter set was validated with Cahaba River AL data

First the model was calibrated against observed data for the Blue Earth River, then the same parameter set was used to simulate the Crow Wing River. Adjustments were made to parameters, especially for the low-nutrient algae, until a suitable fit was obtained, and then the new values were used to simulate the Blue Earth River, and further adjustments were made. This iterative approach proceeded until both sites were suitably represented by the same parameter set.

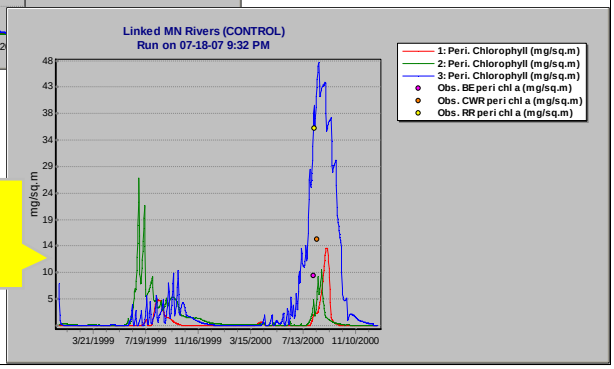
The next step was to attempt to validate the two-site calibration with data from the Rum River. HSPF was not run for the Rum River basin; a stand-alone implementation was used with the same parameter set. However, the fit was not satisfactory. A combination of moderate nutrients and low turbidity seems to favor green algae in ways not predicted by the experience with the low- and high-nutrient sites, and additional calibration was indicated. So, rather than using the site for validation, the decision was made to calibrate across all three sites.

To avoid reentering parameter values between sites and to speed up the calibration, a modification was made to AQUATOX Release 3, which is in beta test now. Release 3 represents linked segments sharing a common parameter set. The model was made more general so that separate, unlinked sites could be simulated simultaneously with a common parameter set. Thus, the effect of a change in a parameter value could be evaluated across all three sites and changed accordingly. The procedure is not only efficient, it facilitates comparisons among the three sites.

Chlorophyll *a* Trends in MN Rivers



Phytoplankton follow nutrient trend



Periphyton reach maximum in Rum River with moderate nutrients and turbidity

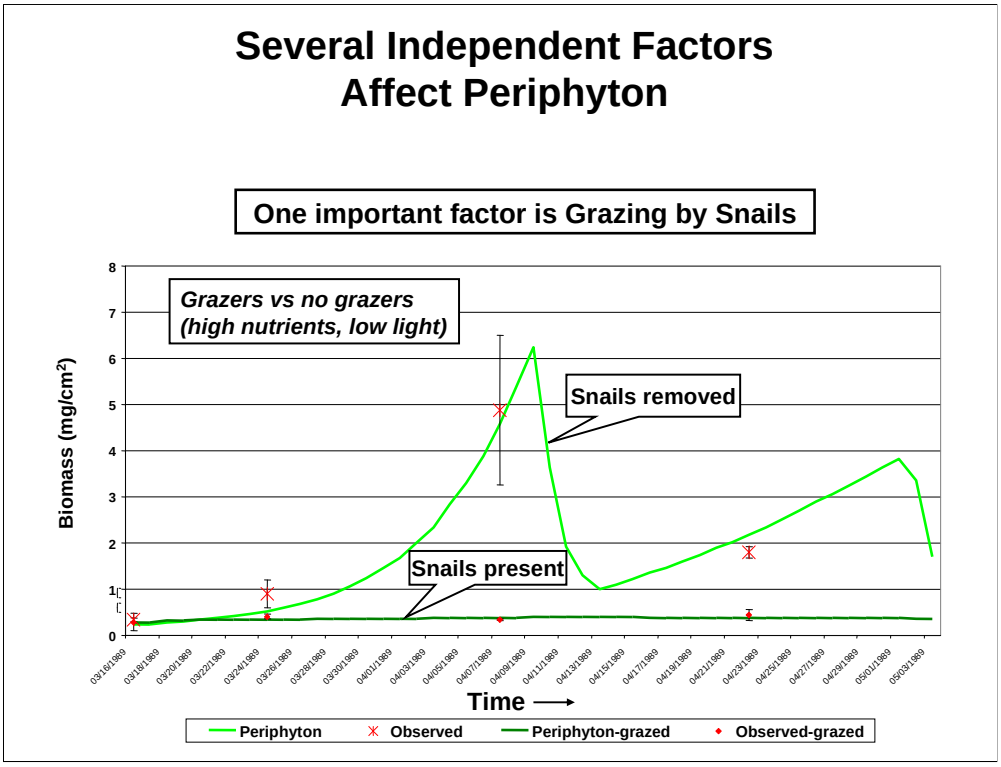
Modeling Phytoplankton

- Phytoplankton may be greens, blue-greens, diatoms or “other algae”
- Subject to sedimentation, washout, and turbulent diffusion
- In stream simulations, assumptions about flow and upstream production are important

Because the phytoplankton (and zooplankton) in a particular reach may have washed in from upstream, residence time in the upstream reaches is important. However, phytoplankton usually experience a longer residence time than the mainstem water because of growing in backwater eddies. Therefore, one should usually use an effective length of upstream river that is twice or even three times the actual length. AQUATOX uses a simple empirical relationship to compute length based on watershed area; that can be used in the absence of information on the actual length.

Modeling Periphyton

- Periphyton are not simulated by most water quality models
- Periphyton are difficult to model
  - include live material and detritus
  - stimulated by nutrients
  - snails & other animals graze it heavily
  - riparian vegetation reduces light to stream
  - build-up of mat causes stress & sloughing, *even at relatively low velocity*
- Many water body impairments due to periphyton



This and the following graph were the result of a model validation exercise utilizing a comprehensive dataset from a series of experiments that manipulated nutrient levels, ambient light and grazing pressure by snails Rosemond, 1993). The model was calibrated using the experimental results, and then validated against ambient stream conditions.

Rosemond, A. D. 1993. Seasonality and Control of Stream Periphyton: Effects of Nutrients, Light, and Herbivores. Pages 185. Vanderbilt University, Nashville, Tenn.

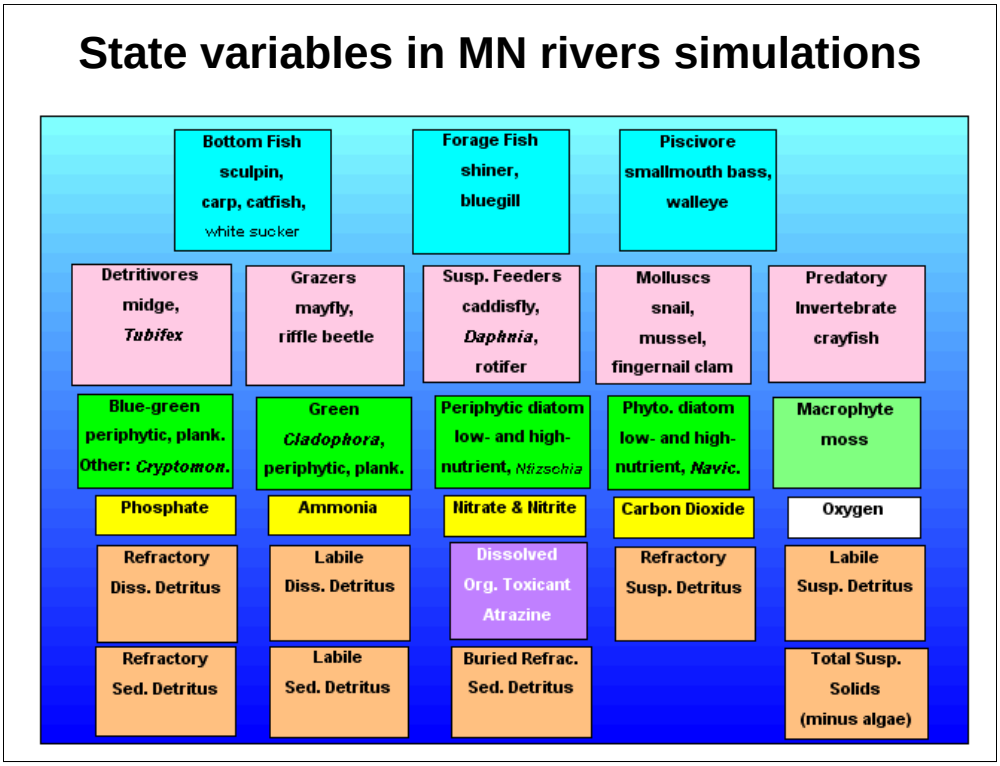
Modeling Macrophytes

- Macrophytes may be specified as benthic, rooted-floating, or free-floating
- Macrophytes can have significant effect on light climate and other algae communities
- Root uptake of nutrients is assumed and mass balance tracked
- May act as refuge from predation for animals
- Moss are a special category

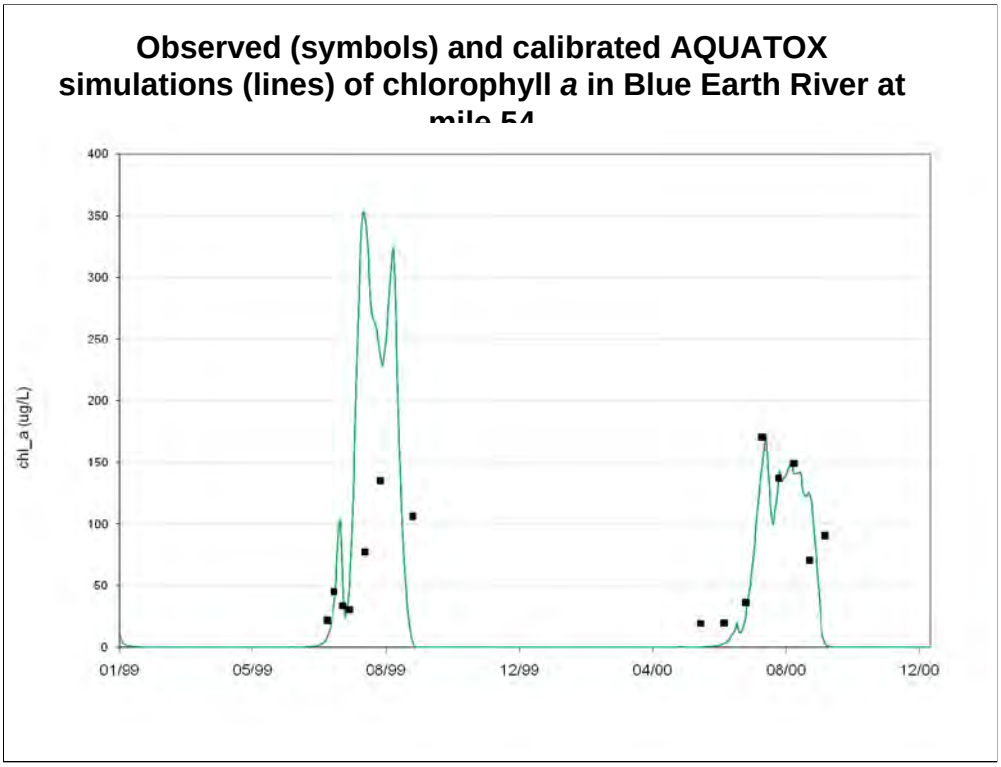
The macrophyte leaves can provide significant surface area for periphyton growth

Calibration of Plants

- algae are differentiated on basis of:
  - nutrient half-saturation values
  - light saturation values
  - maximum photosynthesis
- MN project has developed new parameter sets that span nutrient, light, and PMax
- phytoplankton sedimentation rates differ between running and standing water
- critical force for periphyton scour and TOpt may need to calibrated for other sites

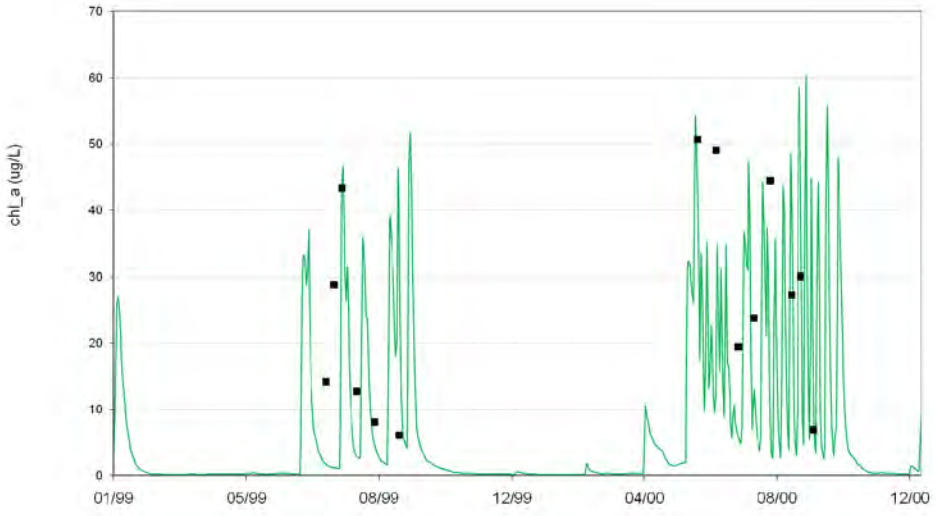


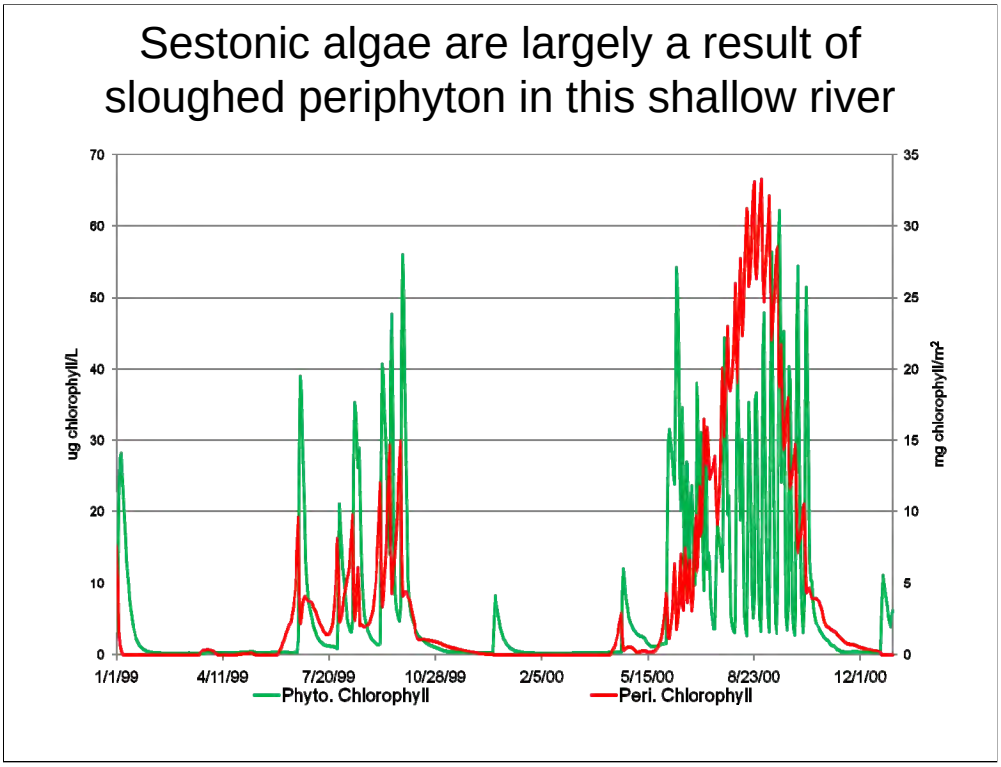
State variables were chosen to represent both the nutrient-poor, clear-water Crow Wing River and the nutrient-enriched, turbid Blue Earth River. Sculpin, a cold-water fish, was included although conditions in the Blue Earth River are too warm for its continued survival. Because the objective was to obtain a set of state variables that would span the conditions on the Minnesota rivers, the number of state variables is larger than if a single river with static conditions were being simulated. In fact, the number of algal groups is almost double that required if the model were calibrated for present conditions in a single river.



Note the order-of-magnitude range in scale between this and the following figure.

Observed (symbols) and calibrated AQUATOX simulations (lines) of chlorophyll *a* in Rum River at mile

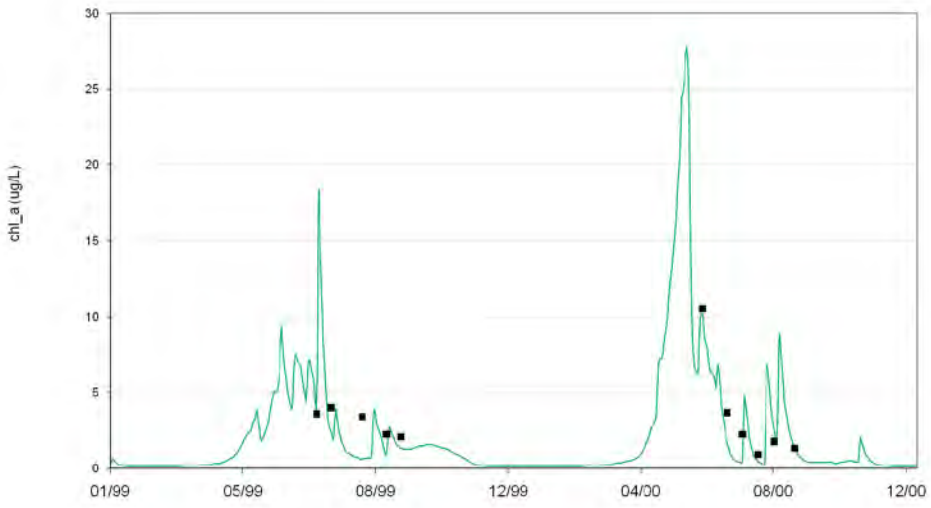




Periphyton may slough or be physically scoured, contributing to the suspended algae; this may be reflected in the chlorophyll *a* observed in the water column. Periphyton may be linked to a phytoplankton compartment so that sestonic chlorophyll *a* results reflect the results of periphyton sloughing.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

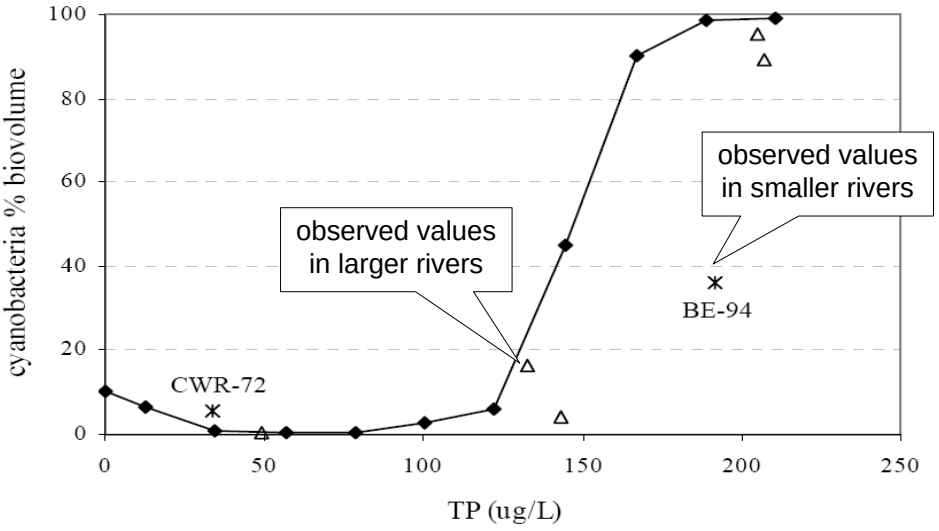
Additionally, when phytoplankton undergoes sedimentation it will now be incorporated into the linked periphyton layer if such a linkage exists.

Observed (symbols) and calibrated AQUATOX simulations (lines) of chlorophyll *a* in Crow Wing at mile 72

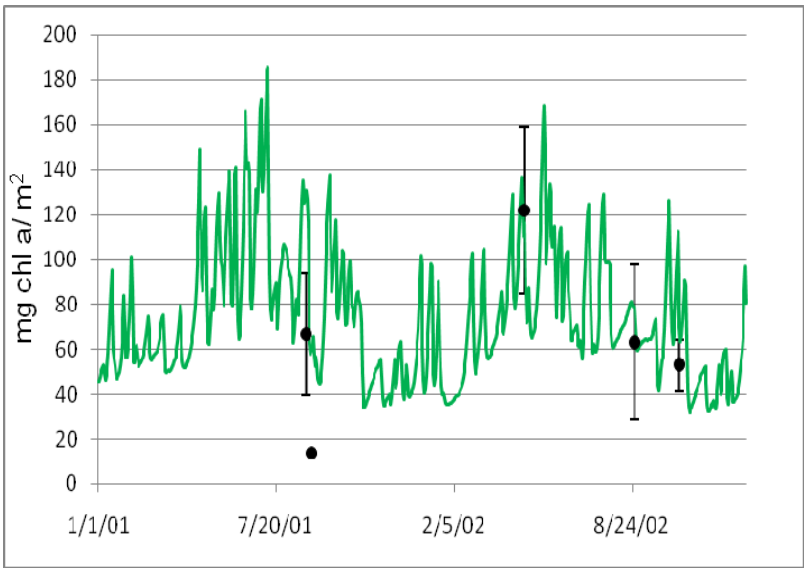


Note scale in comparison with earlier figures

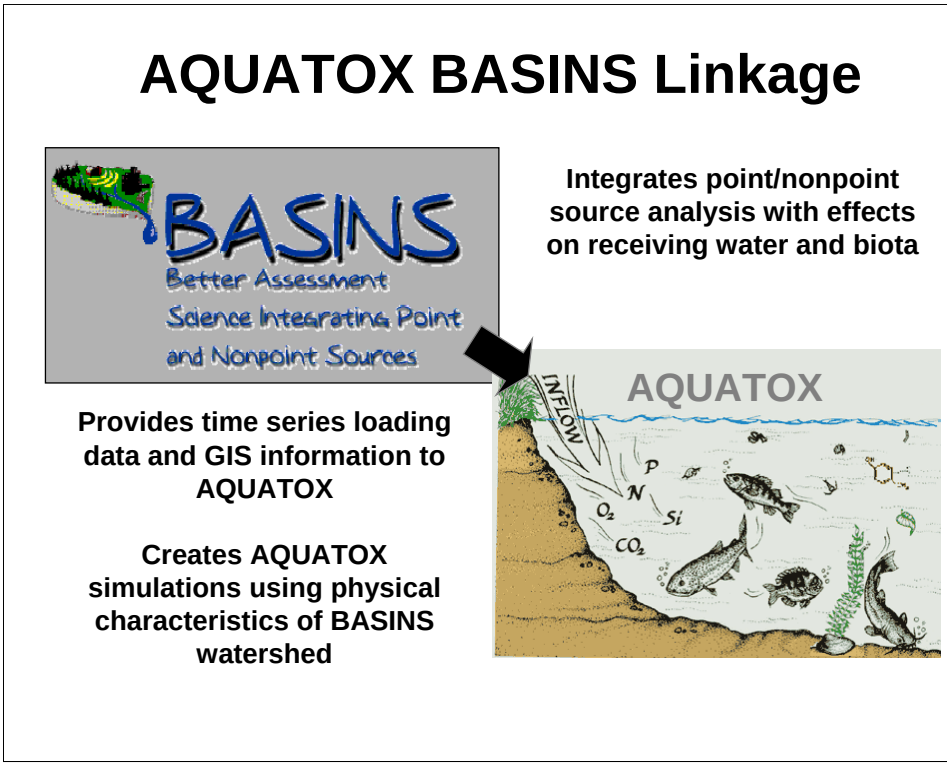
Summer mean percent Phytoplankton composed of cyanobacteria-- BE-54 simulations with fractional multipliers on TP, TN, and TSS



Validation: observed (symbols) and AQUATOX simulation (line) of periphytic chlorophyll *a* in Cahaba River AL

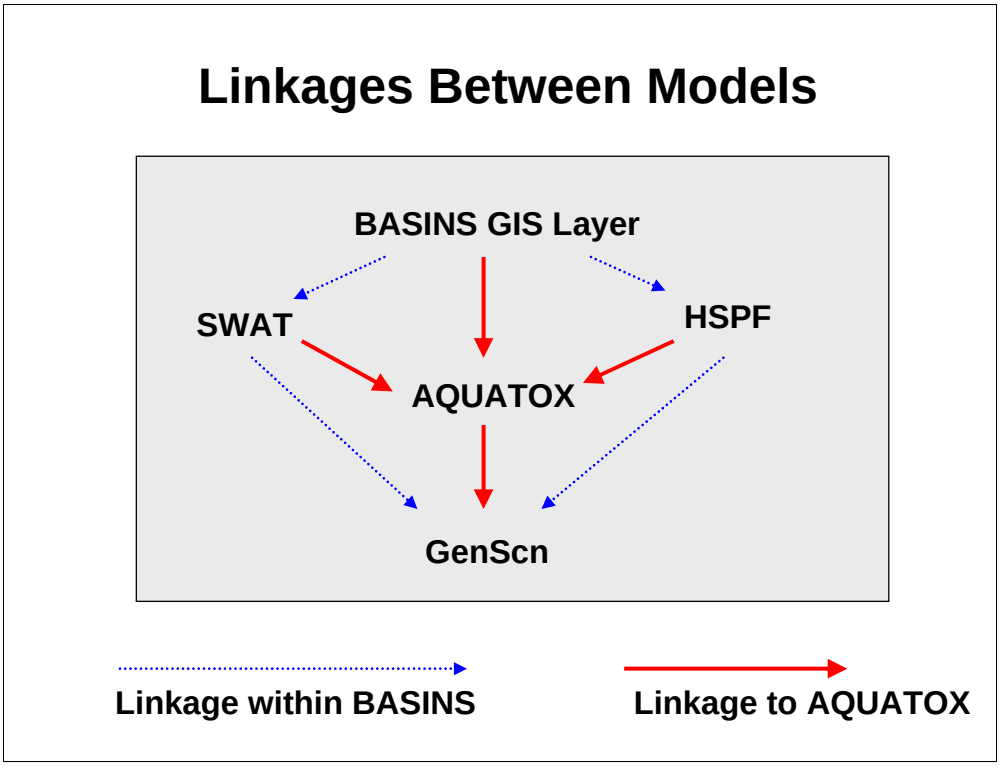


The MN parameter set was used with only a couple modifications. The critical force for periphyton scour was changed based on the bedrock riffles, and the optimum temperature was changed for two groups based on the difference in temperature between MN and AL. Therefore, this is considered a good partial validation.



BASINS is a multipurpose environmental analysis system for use by regional, state, and local agencies in performing watershed and water quality based studies. BASINS makes it possible to quickly assess large amounts of point source and nonpoint source data in a format that is easy to use and understand. BASINS combines GIS technology, environmental data, watershed and water quality models and other tools. More information can be found on the BASINS web site at http://www.epa.gov/waterscience/basins/.

BASINS 3.1 and 4 are able to link with AQUATOX. The GIS – based data and watershed models provide input data (pollutant loads, flow, and water body or channel characteristics to AQUATOX.



These are the specific data that are passed with the various AQUATOX/BASINS linkages:

- BASINS GIS to AQUATOX
  - Channel geometry (length, depth, slope)
- HSPF to AQUATOX
  - Geometry
  - Time series: flow, water quality (nutrients, BOD, temperature, sand/silt/clay)
- SWAT to AQUATOX
  - Geometry
  - Time series: flow, water quality (nutrients, BOD, pesticides, TSS)
- AQUATOX to GenScn
  - All time series output
  - Note that many of the graphing capabilities of GenScn are now available within AQUATOX

The linkage program takes the rather voluminous output from SWAT or HSPF and formats correctly it for AQUATOX, potentially a huge time savings for the user.

Use of AQUATOX in development of water quality criteria

- 2008 peer review suggests AQUATOX is suited to support existing approaches used to develop water quality standards and criteria
  - One tool among many that should be used in a weight of evidence approach
- AQUATOX enables the evaluation of multiple stressor scenarios
  - What is the most important stressor driving algal response?
- Go beyond chlorophyll *a* to evaluate quality, not just quantity, of algal responses (e.g., reduction of blue-green algae blooms)

The application of AQUATOX to the development of water quality criteria and the WQS process is in its early stages, but has great potential, particularly with regard to linking chemical and physical water quality and its ability to support designated aquatic life uses.

We will focus on nutrient criteria, and discuss it in the context of the Minnesota rivers modeling.

Use analytical power of AQUATOX to analyze what factors are driving algal response:

Suspended sediments & light? (we have already seen how sensitive the algae are to light regime)

Nutrients?

Organic loads

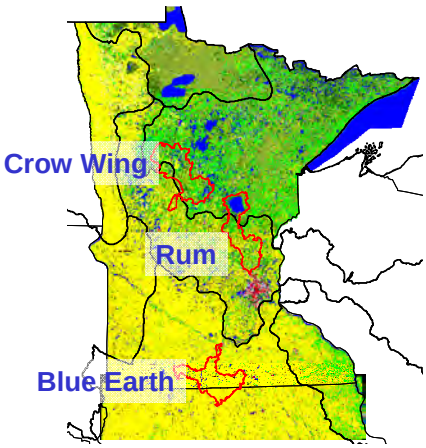
Flow regime

Herbicides?

Combination of factors

Modeling Case Study: Minnesota

- **MPCA collected monitoring data from rivers in different ecoregions:**
  - **nutrients, BOD, water clarity, chlorophyll a**
  - **phytoplankton, periphyton, fish & invertebrate IBI scores.**



For this exercise, we made use of some chemical and biological data that MPCA had collected from medium sized rivers in Minnesota. These watersheds are in different ecoregions and have different mixes of land uses. This shows the locations of the watersheds for the three rivers we modeled, on top of 1992 NLCD (land cover database): the yellow color is row crop agriculture, and the green colors are forested land. The nutrient concentrations in these rivers span roughly an order of magnitude, increasing generally in a N-S direction from the Crow Wing to the Blue Earth, as the land becomes increasingly dominated by agriculture.

Example Nutrient Analyses from MN

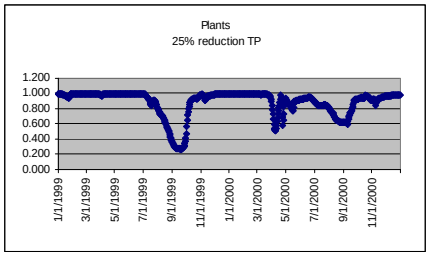
- Calibrated AQUATOX across nutrient gradient
- Set up HSPF, linked loadings to AQUATOX
- Ran iterative simulations with various nutrient reductions
- Applied 2 ways of developing nutrient target
  - Accept the ecoregion chl *a* target, use AQUATOX to get corresponding TP level
  - Use AQUATOX to develop chl *a* and TP target based on algal species composition
- Ran HSPF with various likely pollutant reductions from BMPs
  - Will chl *a* and/or TP target be achieved under any of these scenarios?

Although this discussion presents some alternatives to existing EPA recommendations for nutrients, our intent is NOT to undercut them, but rather to illustrate a technique to supplement and enhance the process of determining appropriate nutrient concentrations in our nation's waters.

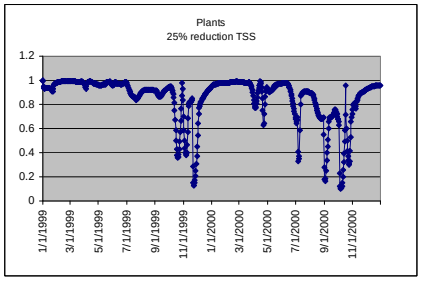
We are working on a project to investigate how AQUATOX, coupled with the watershed modeling capabilities in BASINS, can be used as a tool in the analysis of potential WQC. The project also looks at whether reasonable management practices and load reductions could be expected to lead to attainment of the criteria. The illustrations here were developed for the purposes of the workshop and are based on preliminary model simulations, and are subject to change. I hope also to illustrate how several of the tools in AQUATOX can be used.

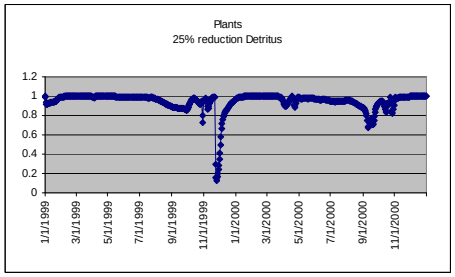
With AQUATOX calibrated across a gradient of nutrient concentrations in similarly sized rivers, we have reasonable confidence in our ability to predict mean responses to hypothetical reductions in nutrient concentrations in the high nutrient system. This exercise focused on the Blue Earth river as an example of a water body in which nutrient reductions might be desired. We asked the question what sort of nutrient reductions might be needed to bring chlorophyll *a* in that river down to some predefined acceptable level, i.e. possible response variable criterion.

Steinhaus Similarity Indices show changes in algal community



Differences in TSS and TP loadings have significant effects on algal community; BOD appears to have some effect, though of much shorter duration





First we used one tool in AQUATOX to reduce the number of stressors considered in the analysis.

Steinhaus community similarity indices can be calculated easily by AQUATOX; the model calculates the similarity between the control and perturbed runs for plants, invertebrates, fish, and all animals. 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. See Sec 4.4 of the Addendum to Release 2 Technical Documentation addendum for more information.

TSS and TP had significant effects on the Steinhaus values; BOD had only transitory effects, and NH3 and NO3 had almost no effect (not shown). For purposes of the exercise, we focused, therefore, on TP and TSS reductions.

What reductions in TP will result in attainment of long term chl. *a* target?

Start with reference condition chl. a value (7.85 ug/L)

Parameter	Reported min	Reported max	25th Percentile (all seasons)	AQUATOX 6-yr average
TP (ug/L)	11.25	1720	**118.13**	**268**
Chl a (ug/L)	3.76	90.6	**7.85**	**18.3**

We used the model to explore the question of what sort of nutrient reductions would be required to achieve mean chlorophyll *a* in the Blue Earth river at or below hypothetical criteria concentrations. We did this analysis for two different hypothetical chl_a numbers. The first was simply the 304(a) value, shown in red in this table.

The ecoregional recommendations are 118.13 ug/L for TP, and 7.85 ug/L chl a. The 6-year averages calculated by AQUATOX at baseline conditions were 268 ug/L and 18.3 ug/L, respectively.

Effect of Load Reductions on Blue Earth Mean Chlorophyll *a*

TP/TSS multiplier	TP (ug/L)	Mean chl_*a* (ug/L)
1.0	268	18.3
0.8	214	11.0
0.6	161	9.5
0.4	107	8.2
0.2	54	8.0
0.0	0*	0.2

7.85 ug/L

We ran Blue Earth River AQUATOX model simulations with fractional multipliers applied to the influent TP loadings from the linked HSPF simulation. This table shows the resulting mean chlorophyll *a* concentrations from these runs.

These results suggest that >80 percent reduction in TP would be required to bring the mean chlorophyll *a* in the Blue Earth River down to 7.85 ug/L. By contrast, the 304a TP value (118.13 ug/L) corresponds with only a 56 percent reduction.

We used reductions of TSS as well as TP because most of the management measures that control P would also reduce TSS, though not necessarily 1:1, as we have assumed here.

Target Development
Method #1

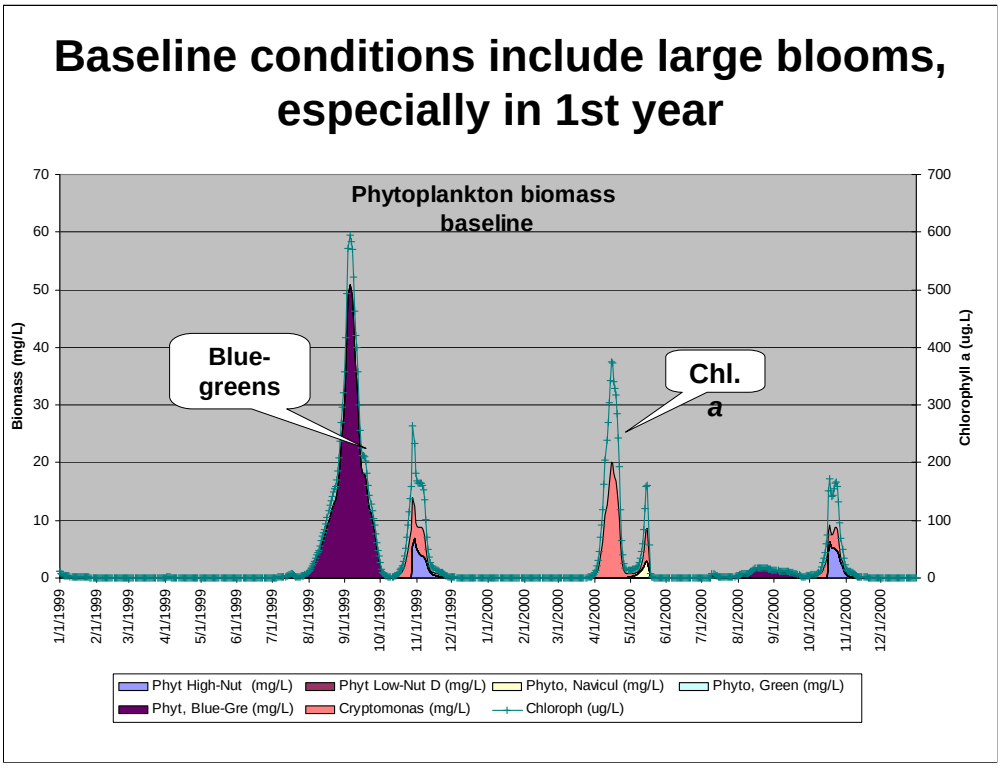
- Model results suggest that **> 80%** reduction of TP (coupled with TSS reductions) required to attain 7.85 ug/L
- 304(a) recommendations suggest a **56%** reduction of TP would be necessary

Target Development Method #2

- Focus on specific algal response, not just total chl a
  - Especially blue greens, as blooms can be noxious and cause taste & odor problems
  - At what levels do blue greens reach an "acceptable" proportion of total algae?
- Where do there appear to be shifts in species composition?

If the State wishes to consider the composition of the algal community as well as the total chlorophyll *a* value, AQUATOX provides a way to do so.

Obviously, what percentage of blue-green is "acceptable" is subject to debate. There is some work being done on developing this kind of metric, but to our knowledge, no one has adopted one.



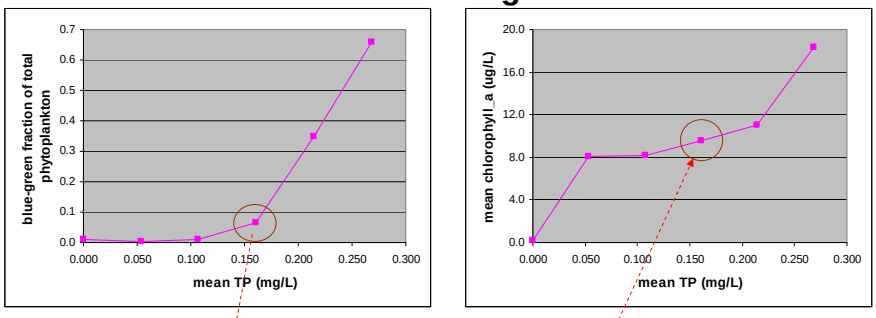
Blue Earth River had reports of severe blooms of blue-green algae in some years.

The model simulated very high chl a peaks (almost 600 ug/L) for 1999. Largest bloom (in the fall) is dominated by blue-greens, and lasts almost 2 months; later bloom by cryptomonads, plus some hi-nutrient diatom.

Note that there is no spring bloom in 1999, probably due to light limitation or washout; it was a very high flow year.

Target Development

- **<u>Method 2</u>: Use AQUATOX to estimate chl_*a* concentration associated with a shift in dominance between blue-greens and more desirable algae.**



<u>Inflection point</u> – corresponds with 9.5 ug/L mean chl_a, 0.161 mg/L TP, and blue-greens <10% of total water column phytoplankton.
Represents ~40% reduction in TP and TSS.

In the second example, we used the AQUATOX runs to estimate a chl *a* concentration that corresponds with the point where a shift between dominance of blue-greens and more desirable algal species occurs. The left figure shows blue-greens as a fraction of total water column phytoplankton, and the right shows mean chl *a* concentrations. Both are plotted as functions of mean TP, in increments of 20% reduction on the horizontal axis.

The left figure shows an inflection point at a approximately 0.161 mg/L, a 40 percent decrease in TP below existing concentrations. The inflection point occurs at a blue-green fraction of slightly less than 10% total phytoplankton; it also corresponds with mean chl *a* of 9.5 ug/L (on the right). The chl *a* value is slightly higher than the 304(a) number, and the TP value is substantially higher than the 304a value. So if the management goal focuses on the % blue-greens rather than chl *a* per se, and if "less than 10% blue-greens" is an acceptable target, 9.5 ug/L would be as our second hypothetical chlorophyll *a* criterion.

So we had two different hypothetical criteria values for chl_a: the reference condition 304a number itself, and a slightly higher number corresponding with the inflection point in the left figure. The corresponding TP values, are rather different between the 2 methods using AQUATOX, and between them and the 304(a) recommendations.

Method #2 Target

- Results suggest that a 40% reduction of TP, if coupled with a corresponding reduction in TSS as well, would result in an algal community with a much reduced proportion of noxious blue green algae

Summary of Minnesota Analysis

- **Stressor-response linkage: Algal responses linked quantitatively with TP and TSS concentrations.**
- **Criteria development: Derived alternative hypothetical criteria, one based on ecologically meaningful endpoint (e.g. blue-green fraction of total phytoplankton).**
- **Attainability: Results suggest both 304(a) and hypothetical criteria in Blue Earth river may be very difficult to achieve, even with heavy use of BMPs.**

So to summarize, we used mechanistic modeling to quantitatively link nutrient stressor and response variables in three Minnesota rivers. We identified TP and TSS as the most important stressors controlling instream phytoplankton concentrations, though not necessarily downstream conditions. Using these model results we derived an example of a hypothetical chl_a criterion based on a biological metric that we came up purely with for illustrative purposes. And we used a linked watershed model to assess the attainability of this hypothetical criterion, as well the ecoregion 304a criteria, by adding BMPs at various densities into the watershed model and simulating their impact on water quality.

Other Possible Analyses to Support Development of Water Quality Targets

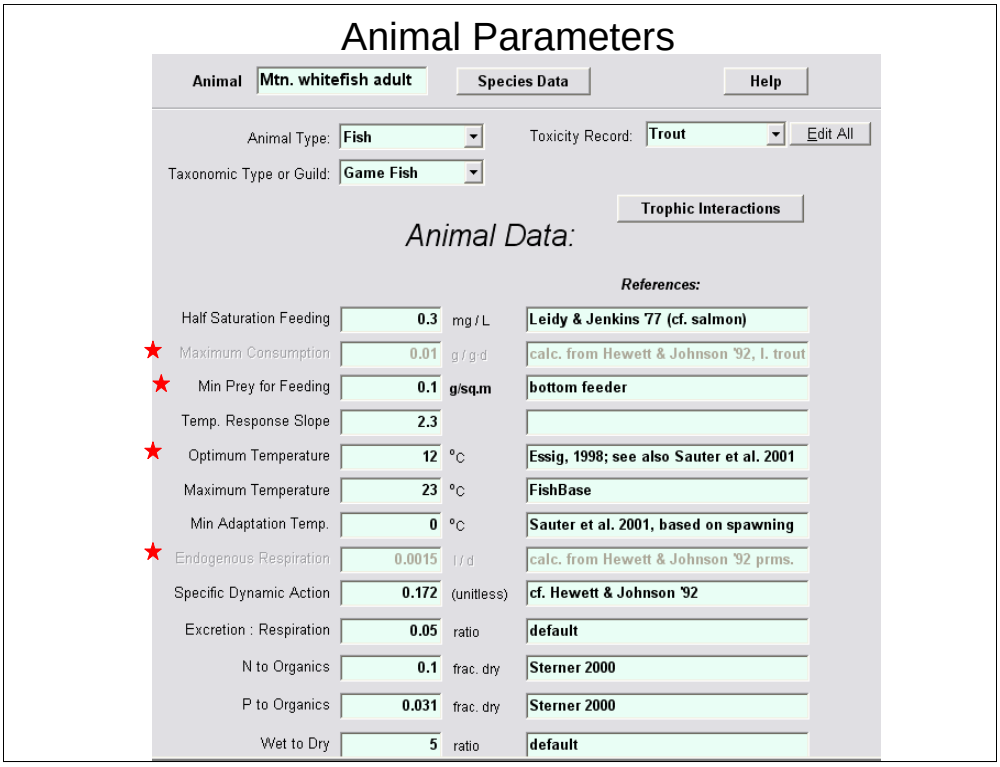
- For different target concentrations you could compare differences in:
  - Duration of hypoxia or anoxia in hypolimnion
  - Duration of algal blooms
  - Secchi depth
  - Fish and invertebrate species composition

Modeling Animals with AQUATOX

- Overview
- Parameters
- Zooplankton
- Zoobenthos
- Fish
- Trophic Interaction Matrices

Animal Modeling Overview

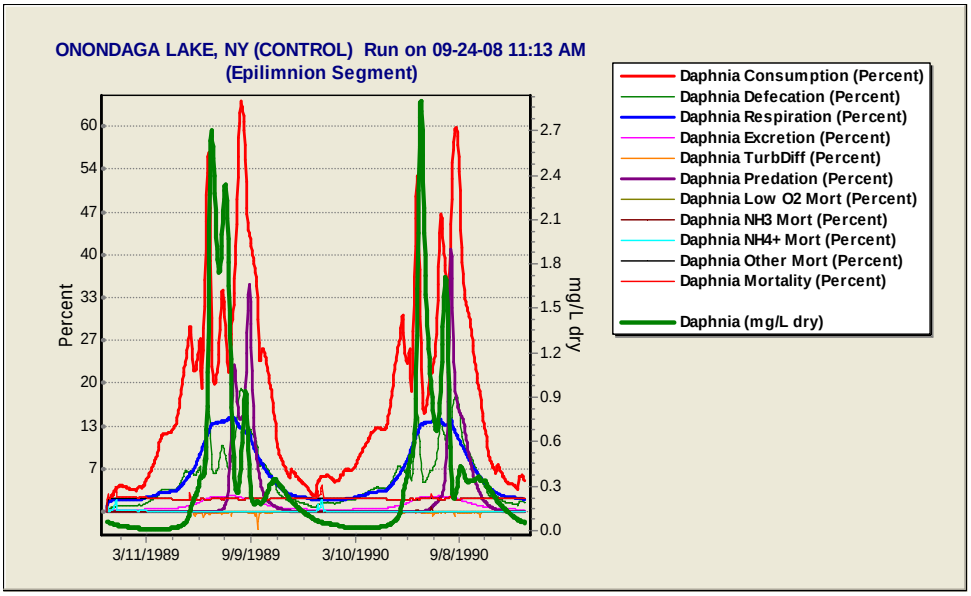
- Animal biomasses calculated dynamically
  - **Gains** due to consumption and boundary-condition loadings
  - **Losses** due to defecation, respiration, excretion, mortality, predation, boundary condition losses
- Careful specification of feeding preferences required
- Bioenergetic modeling for fish



Sensitive parameters include maximum consumption rate and respiration rate if not calculated based on weight using the Wisconsin bioenergetic parameters (Hanson et al. 1997).

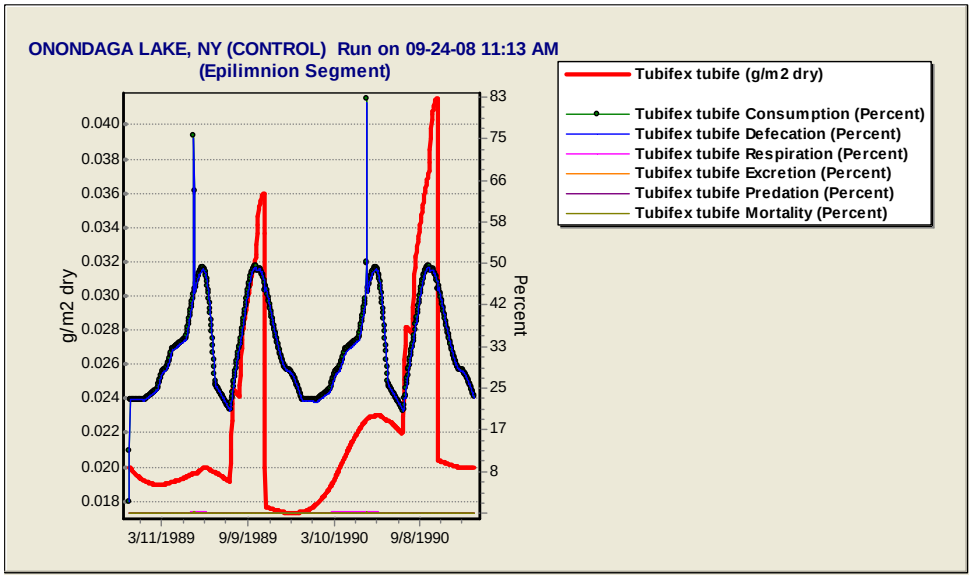
Hanson, P. C., T. B. Johnson, D. E. Schindler, and J. F. Kitchell. 1997. Fish Bioenergetics 3.0. Center for Limnology, University of Wisconsin, Madison.

Zooplankton consumption is tied to phytoplankton productivity



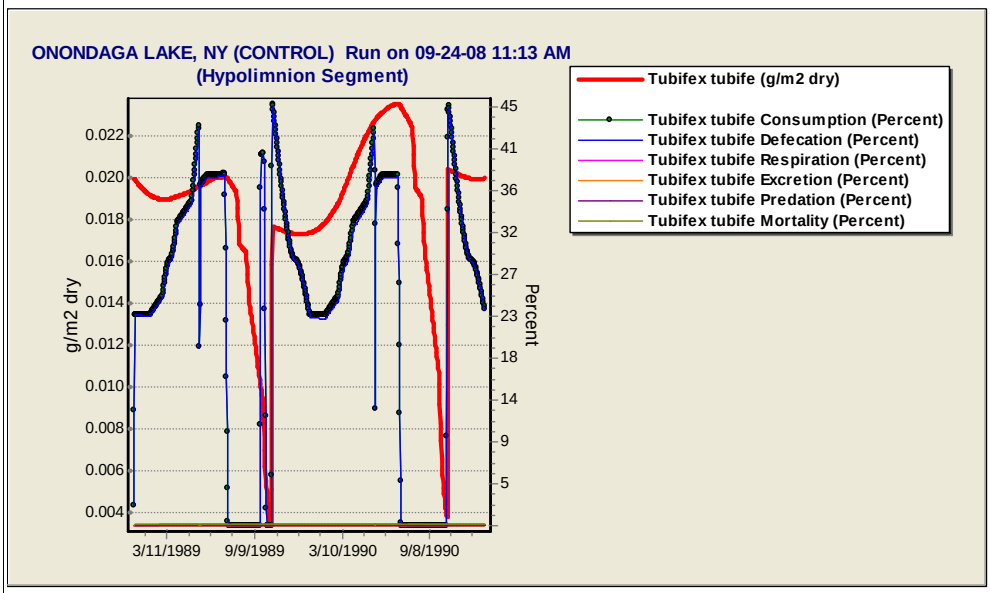
In Onondaga Lake consumption is heaviest during phytoplankton blooms, although detritus is a secondary source of food. (Without detritus as an alternate food source zooplankton would not be sustained.) Predation offsets high consumption in late summer.

Benthic invertebrates are also tied to phytoplankton productivity through detritus



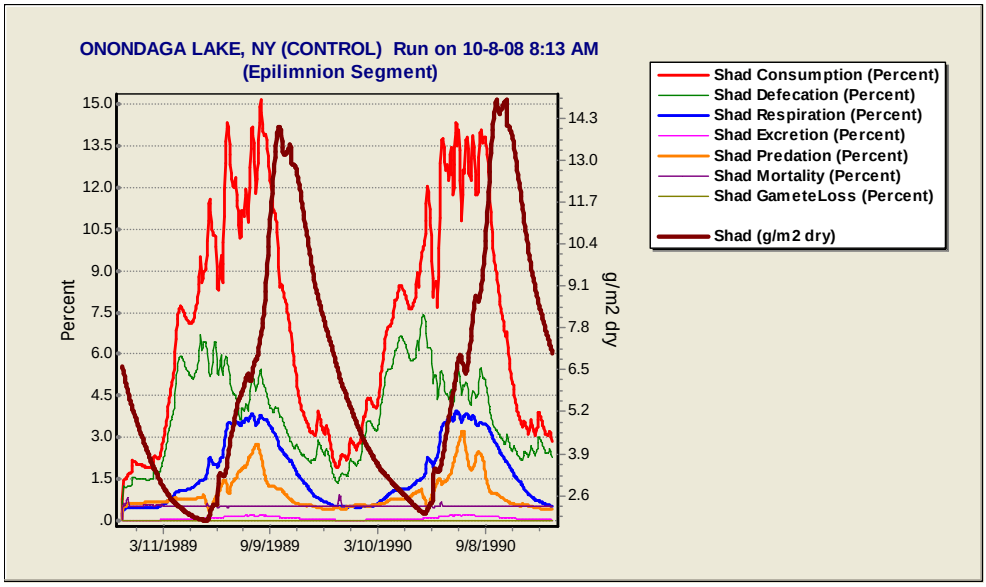
High consumption occurs when algal blooms crash and detritus settles to the bottom.

Tubifex in hypolimnion are tolerant of anoxia but stop feeding and slowly decline



The pattern between the epilimnion (previous slide) and the hypolimnion is quite different. *Tubifex* stops feeding with anoxic conditions. The rebound is actually the combination of biomasses when the epilimnion and hypolimnion are combined at overturn.

Fish exhibit seasonal patterns based on food availability and temperature



Shad feed on plankton, so they too show a seasonal pattern of growth and decline.

Foodweb Model specified as Trophic Matrix

Interactions are normalized to 100%

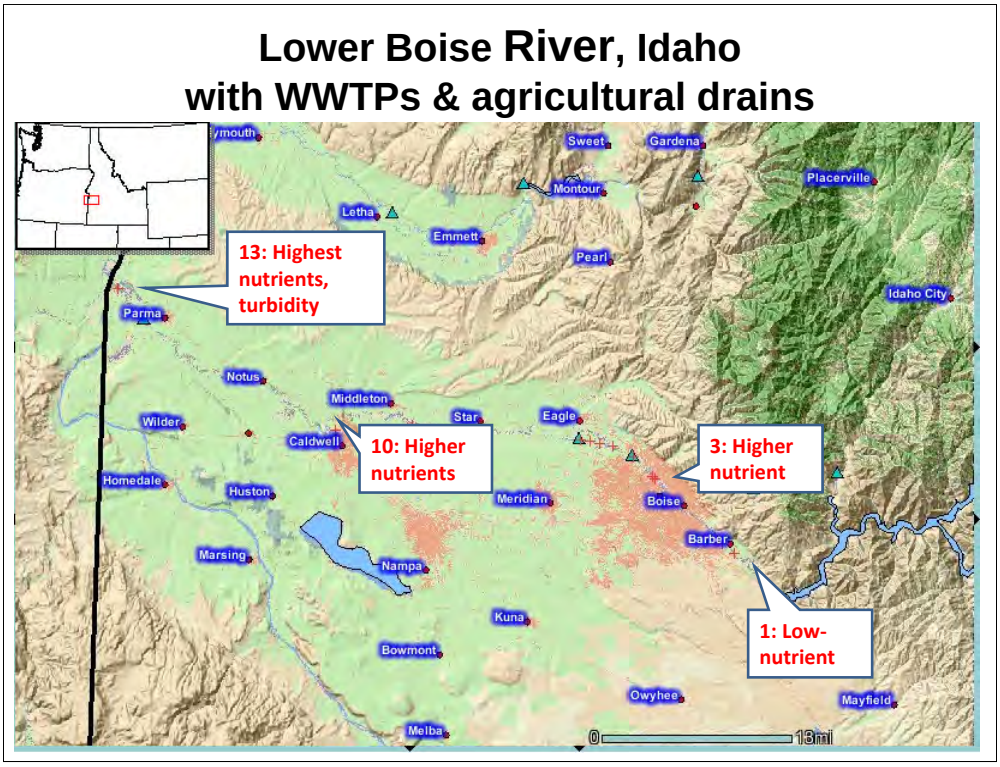
AQUATOX - Trophic Interaction Matrix

Preference percentages are initially normalized to 100% based on species in the simulation. Renormalize

Show Preferences | Show Egestion Coefficients | Show Comments

	Tubifex tubi	Daphnia	Rotifer, Brac	Predatory Z	Shad	Bluegill	White Perch	Catfish	Largemouth	Largemouth	Walleye
R detr sed	50.0							1.2			
L detr sed	50.0							4.7			
R detr part					12.5				2.1		
L detr part		30.0	40.0		12.5	3.9	0.5		2.1		
Cyclotella nan		35.0	5.0		12.5						
Greens		30.0	5.0		12.5						
Phyt, Blue-Gre					12.5						
Cryptomonad		5.0	50.0								
Tubifex tubife						9.5	29.8	46.5	40.4	0.3	1.0
Daphnia				50.0	12.5	15.7	29.9	2.9	27.7	0.3	
Rotifer, Brach				50.0	12.4	15.7					
Predatory Zoop					12.5	7.9	29.9	2.9	27.7	38.2	1.6
Shad						15.8		20.9		44.3	23.1
Bluegill										2.9	
White Perch						15.7	10.0	20.9		10.1	24.8
Catfish											24.8
Largemouth Bas						15.7					24.8
Largemouth Ba2											
Walleye										3.9	

AQUATOX models **prey switching** based on prey biomasses: during each time-step of the simulation, prey species are assessed to see if they exceed the minimum prey threshold (BMIN). If there is insufficient prey for feeding, that compartment is zeroed out and the normalization to 100% continues with other existing species.



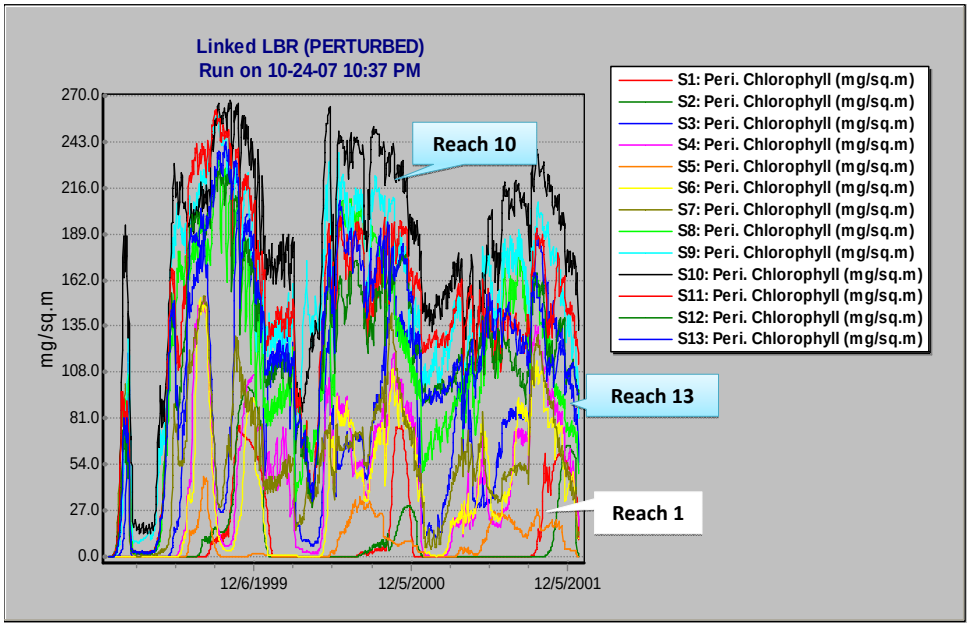
The Lower Boise River is a shallow river that is heavily managed for irrigation. In fact, segment 10 has the lowest flow; below that reach, drains bring in nutrient- and sediment-laden return flow.

Lower Boise River in Boise, Idaho

Complex Linked Model

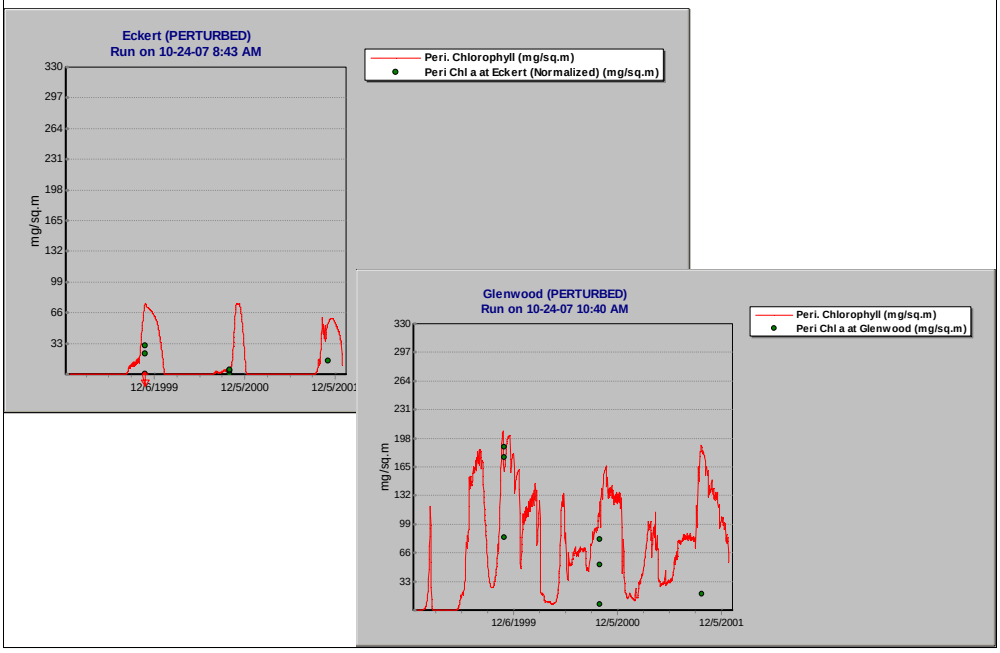
- 13 main-stem segments modeled
- 26 “tributary inputs”
  - Groundwater inputs
  - Waste Water Treatment Facilities
  - Input drains and tributaries
- Extensive water withdrawals
- Complex water-balance model
- Nutrients are integrated within main-stem

LBR Downstream Periphyton Trend



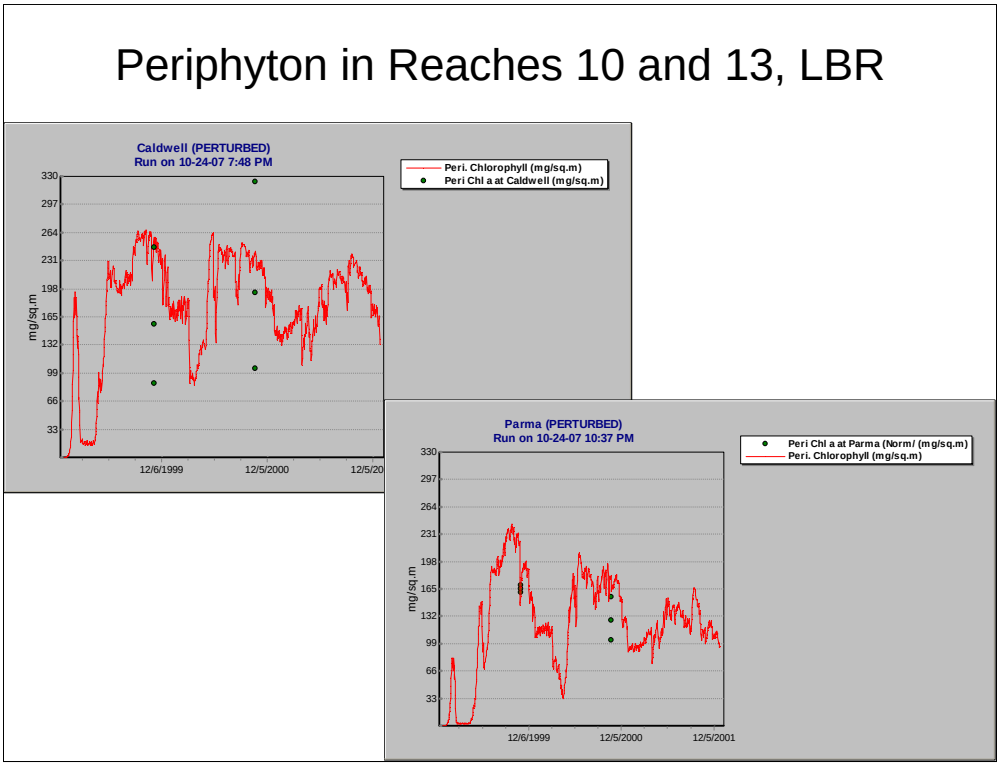
Nutrient-poor Reach 1 has the lowest periphyton biomass. Reach 10 with nutrient-rich clear water has the highest periphyton.

Periphyton in Reaches 1 and 3, LBR



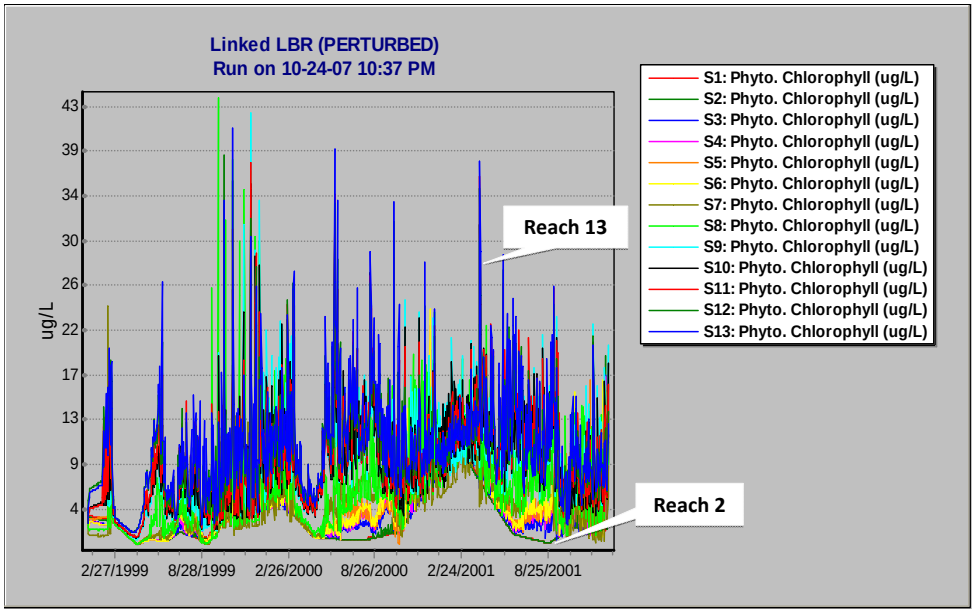
All four graphs have the same scale.

Periphyton in Reaches 10 and 13, LBR



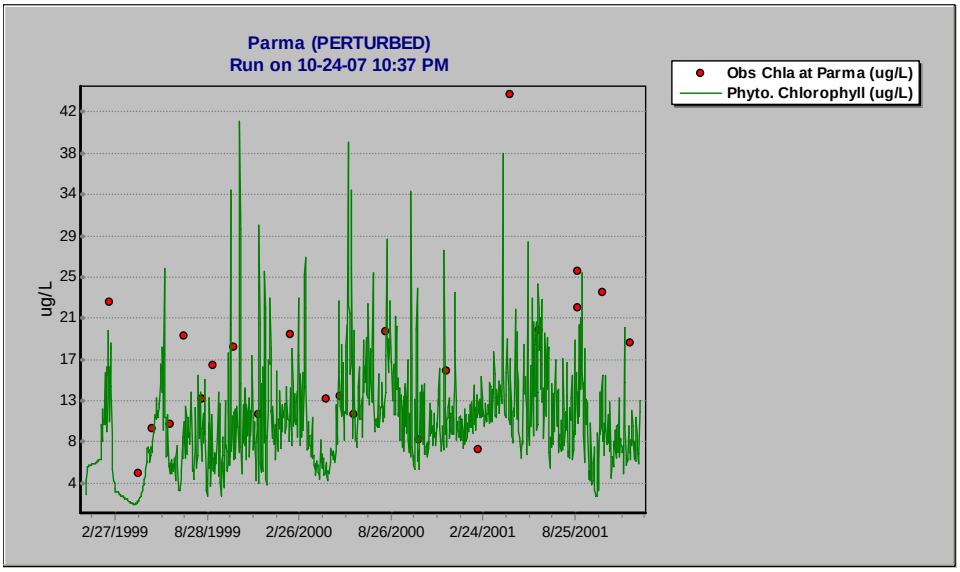
All four graphs have the same scale.

LBR Downstream Phytoplankton Trend

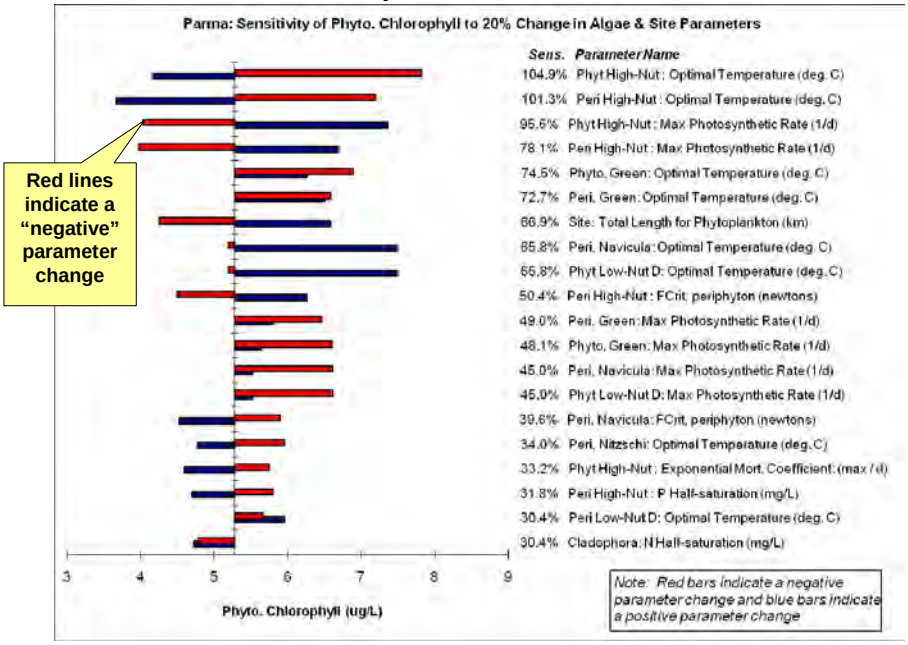


Sestonic algae include sloughed periphyton upstream and true phytoplankton downstream.

Sestonic algae at Parma (Reach 13), both upstream loadings and periphyton sloughing



Phytoplankton Sensitivity, Parma LBR could choose parameters for better fit



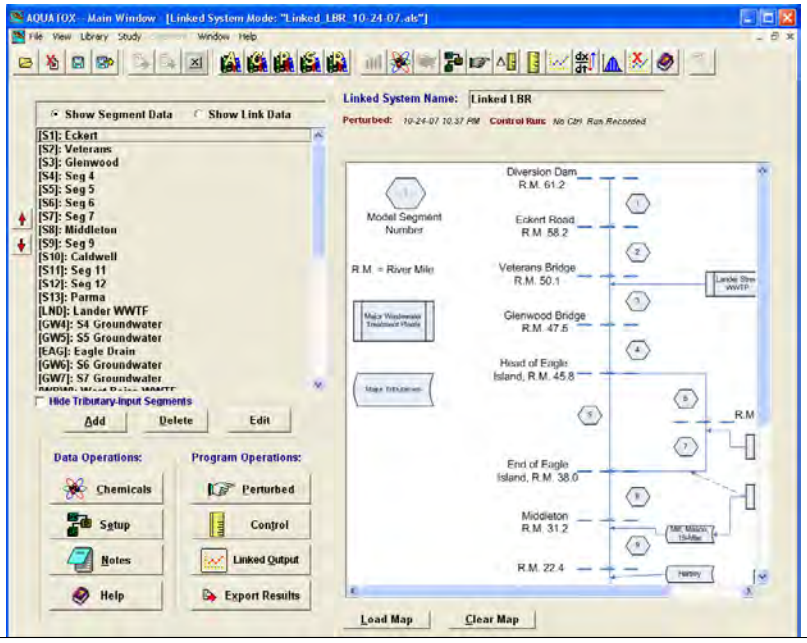
Nominal range sensitivity analysis can be performed easily with AQUATOX.

Demonstration 2: Linked Segment Version

- Developed as part of a Superfund project; now part of Release 3
- Allows the capability to model multiple linked segments--converting AQUATOX into a two dimensional model
- State variables move from one linked segment to the next through water flow, diffusion, bed-load, and migration.

Migration of fish into and out of the model's spatial domain (e.g. spawning runs) is not modeled.

Segmented Version can Represent Dynamically Linked Multiple Segments



In this example main-stem reaches, tributary agricultural drains, groundwater, and waste water treatment effluents are linked in simulating 61 miles of the Lower Boise River, Idaho.

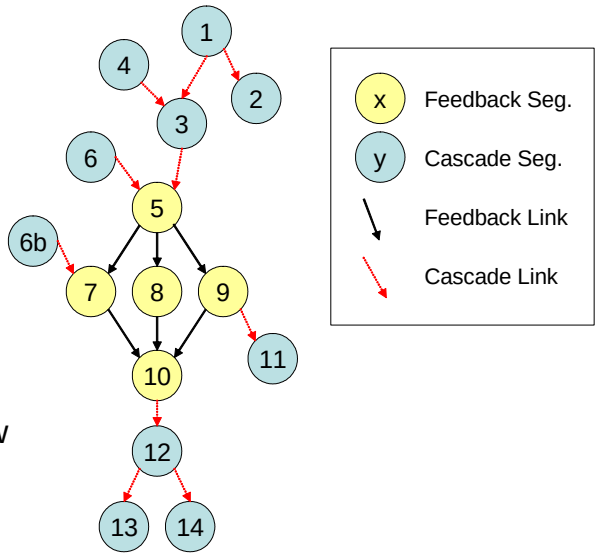
Cascade & Feedback Linkages

Cascade Linkages:

One-way linkages with no backwards flow or diffusion across segment boundaries

Feedback Linkages:

Two-way linkages that allow for backwards flow and diffusion



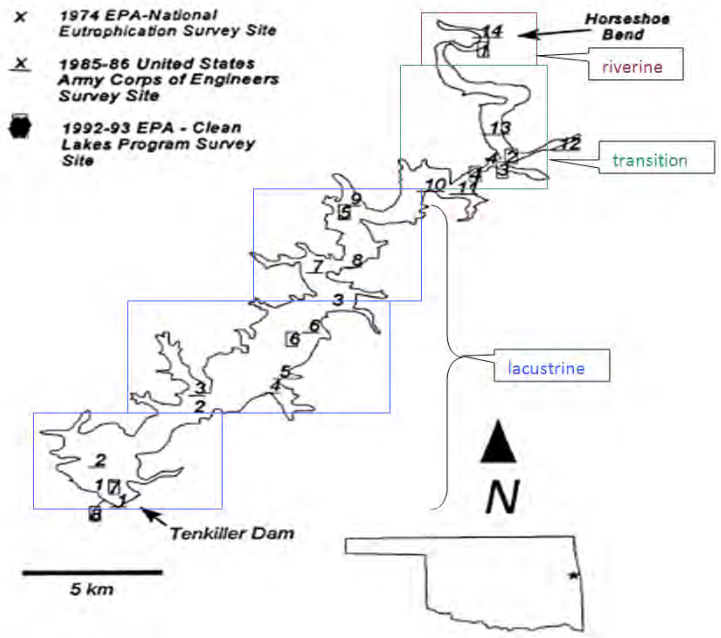
- After cascade and feedback linkages are defined, note that the purpose of this is to allow for slower running segments (i.e. segments with rapid water flow) to solve independently of other segments.
- In the diagram shown AQUATOX would first run the "upper cascade" segments. Those being 1, 2, 3, 4, 6, and 6b.
- AQUATOX would use the loadings from the "upper cascade" run to run the "feedback" segments. Those being 5, 7, 8, 9, and 10.
- Finally, AQUATOX would use the loadings from the feedback run to run the "lower cascade" segments. Those being 11, 12, 13, and 14.
- Mass balance of water, toxicants, nutrients, organisms is maintained through a complex system such as this one.

Linked Segment Model Data Requirements

- Water flows between segments
- Initial conditions for all state variables for each segment modeled
- Inflows, point-sources and non-point-source loadings for each segment
- Tributary or groundwater inputs and/or any withdrawals

Interface Demonstration to follow

Tenkiller Lake, OK



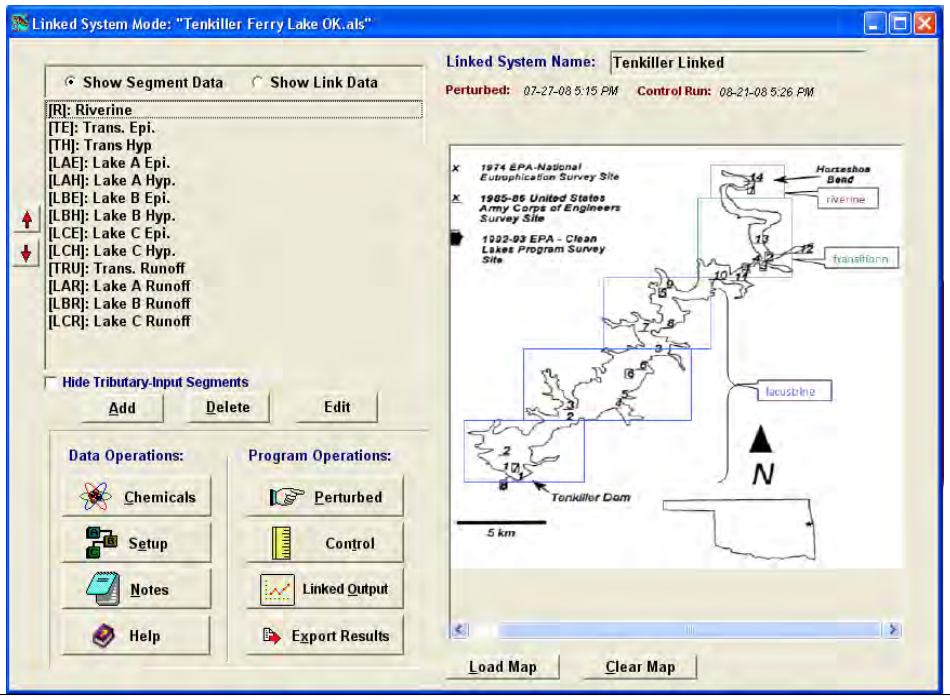
Tenkiller Lake Background

- Reservoir in eastern Oklahoma formed by the damming of the Illinois River (1947-1952)
- Identified on Oklahoma's 1998 303(d) list as impaired (nutrients)
- High-priority target for TMDL development
- 1996 Clean Lakes Study: nutrient concentrations and water clarity are indicative of eutrophic conditions

Tenkiller Lake Application

- Linked Model application includes nine segments
  - Riverine segment
  - Vertically stratified transitional segment
  - Three vertically stratified lacustrine segments
- Model linkage to HSPF (watershed) and EFDC (in-lake hydrology) models
- Model can predict chlorophyll *a* levels based on nutrient loadings (BMPs)

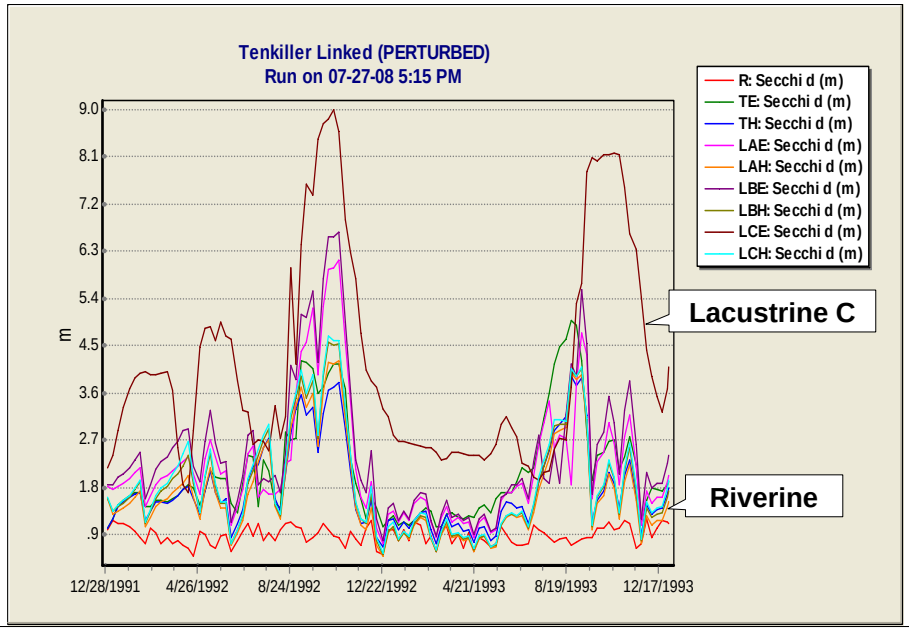
Tenkiller Lake OK



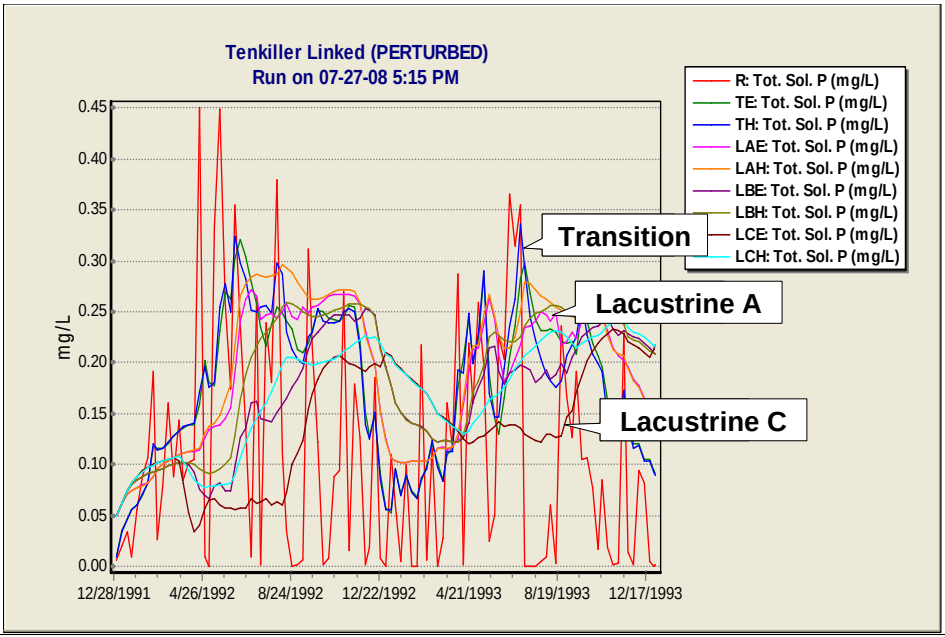
Storm-water plume, algae-rich riverine segment

duckweed (*Lemna* sp.) forms surface scum at the interface

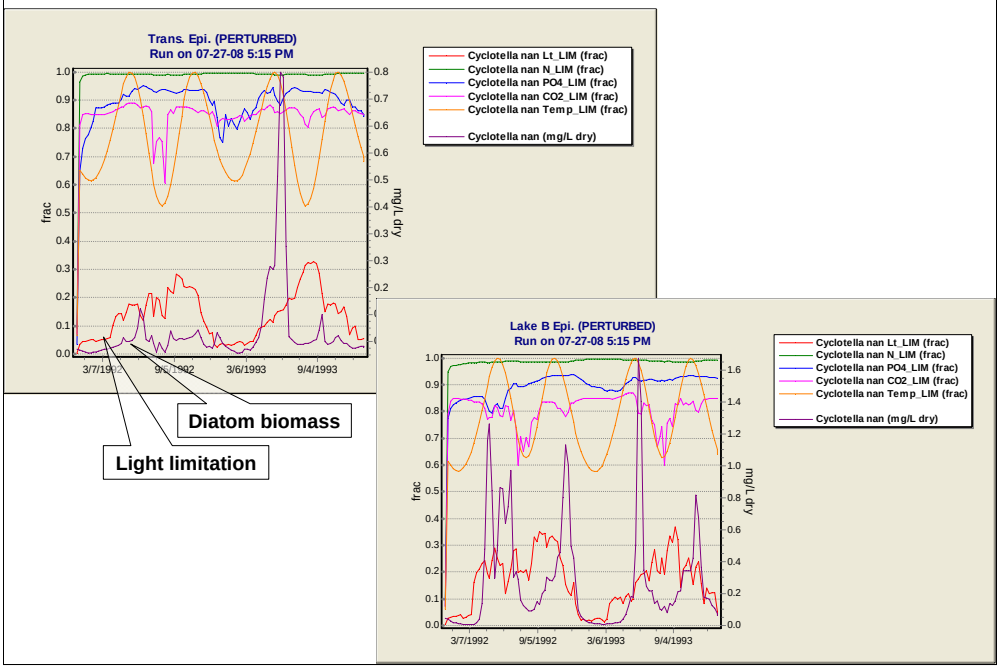
Known for its clarity, Tenkiller Lake Secchi depth increases down reservoir



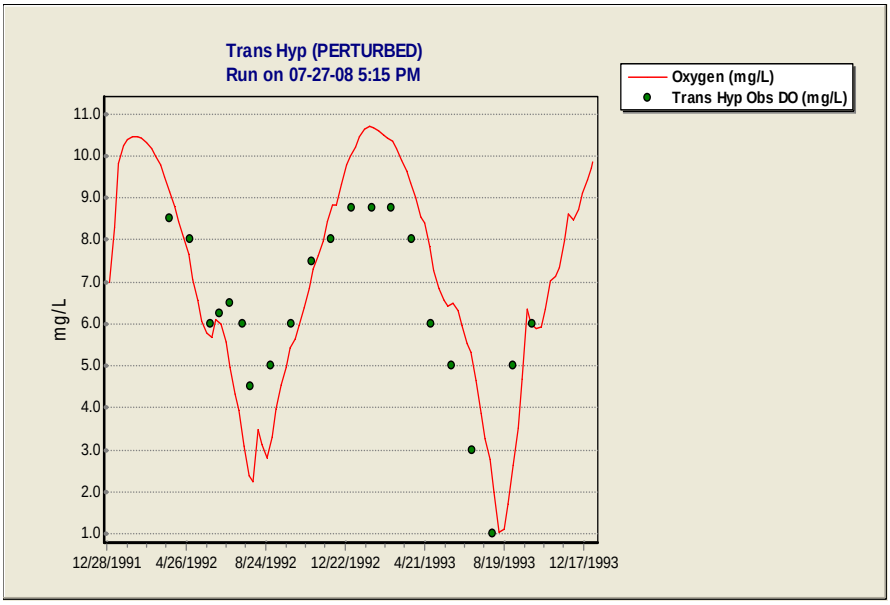
Peak phosphorus decreases down reservoir



Transition diatoms suppressed by turbidity



Transition hypolimnion exhibits hypoxia



AQUATOX– Chemical Fate Overview

- Can model up to twenty chemicals simultaneously
- Fate processes:
  - ionization
  - volatilization
  - hydrolysis
  - photolysis
  - sorption
  - microbial degradation
- Biotransformation—can model daughter products
- Bioaccumulation

The chemical fate module of AQUATOX predicts the partitioning of a compound between water, sediment, and biota, and estimates the rate of degradation and loss of the compound. Microbial degradation, biotransformation, photolysis, hydrolysis, and volatilization are modeled in AQUATOX.

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).

Chemical fate clarified using half-Lives and DT95

Time-to-loss Estimated Using Loss Rates at a given time

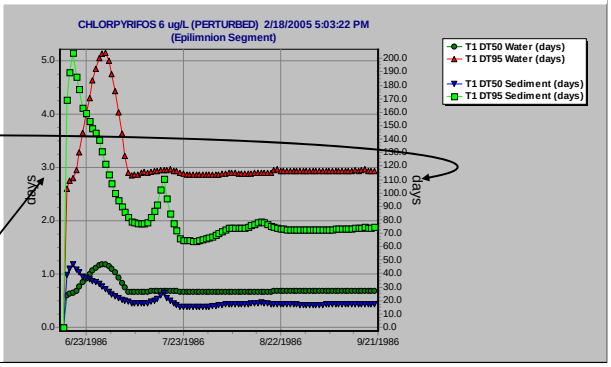
$$Loss_{Water} = \frac{Hydrolysis_{Water} + Photolysis + Microbial_{Water} + Washout + Volat. + Sorption}{Mass_{Water}}$$

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

For this Chlorpyrifos Study:

Half-life in Sediment of roughly 20 days
DT95 of roughly 75 days

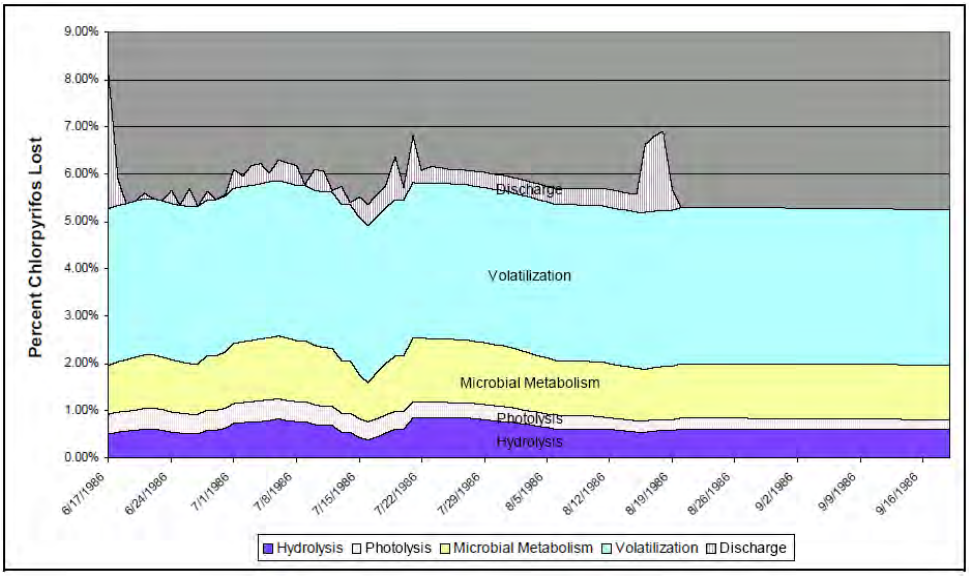
Half-life in water of roughly 16 hours, DT95 in water is roughly 3 days



AQUATOX estimates 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.

Chemical rates may be tracked

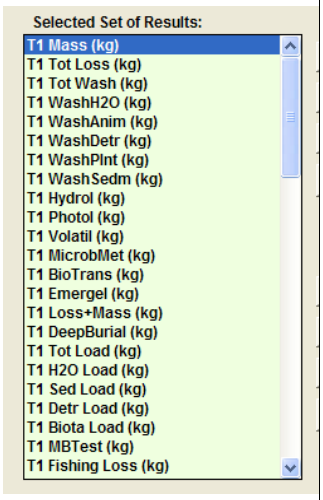
Predicted In-situ Degradation Rates for Chlorpyrifos in Pond



Chlorpyrifos is moderately persistent; however, according to the simulation about 3% per day is lost due to volatilization, about 1% due to microbial degradation, and another 1% due to hydrolysis and photolysis.

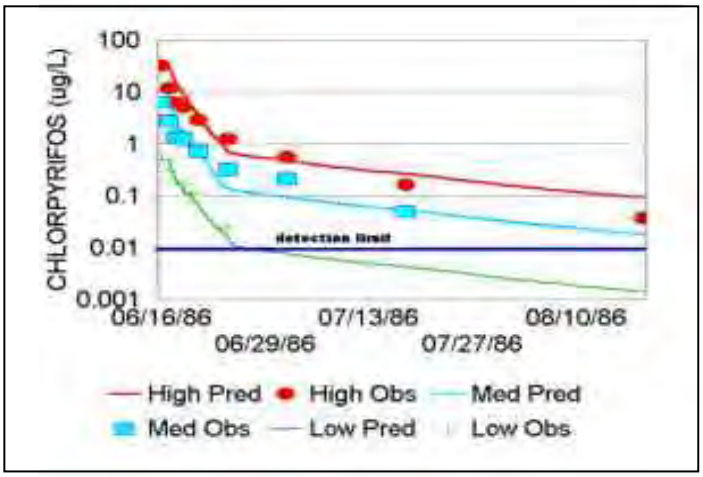
Toxicant mass balance tracking

- Extensive set of model outputs
- Provides mass accounting of total toxicant loadings to and total toxicant losses from the system
- Provides accounting of toxicants within the system at a given time
- Provides assurance of model mass balance throughout the complex cycling processes



Fate of Chlorpyrifos in the Duluth MN Pond was Predicted Successfully

Multiple Dosing Levels

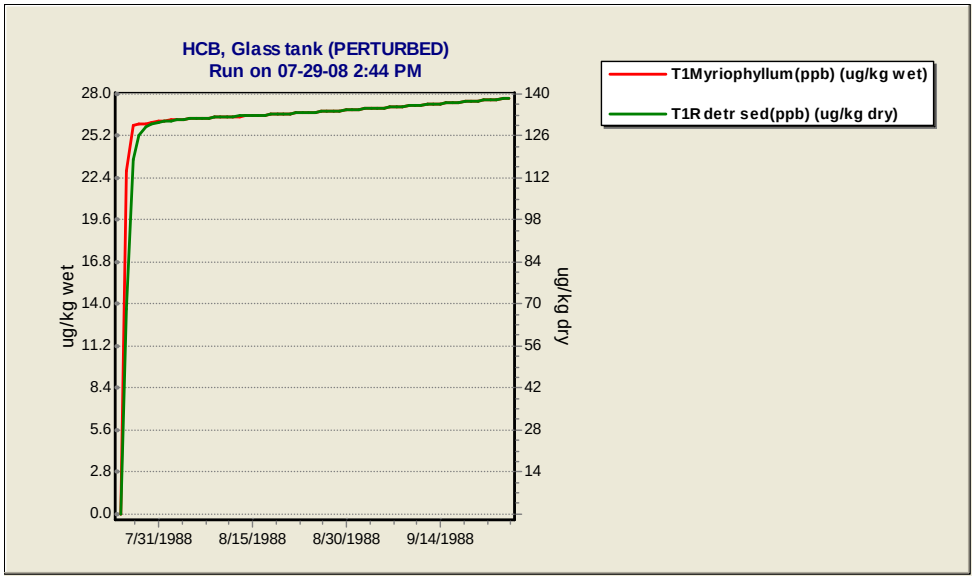


In a validation study several years ago, three levels of chlorpyrifos in a pond were predicted and compared to observed data.

HCB in tank

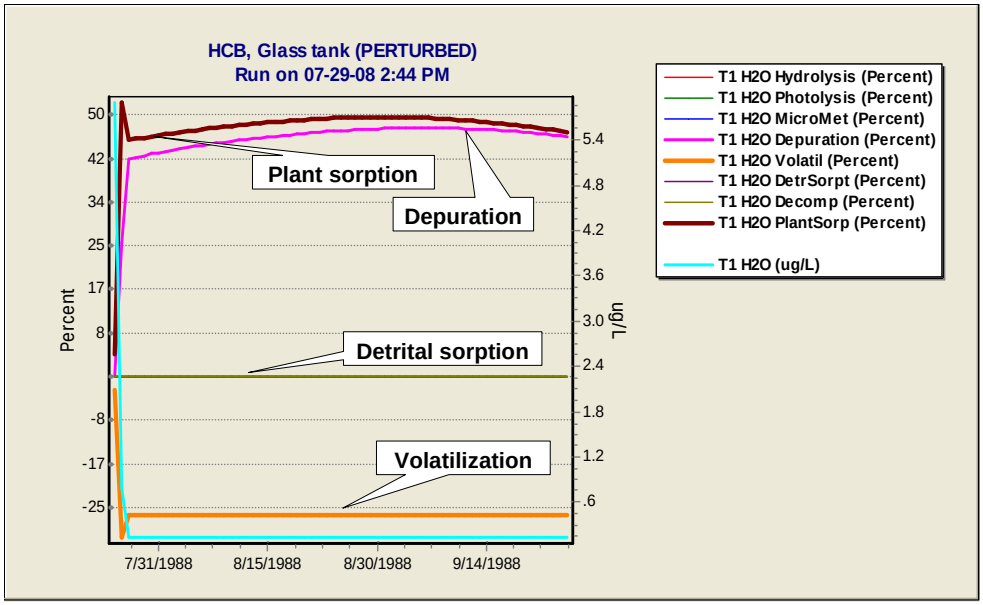
- Reproduces experimental results (Gobas) in which macrophytes are enclosed in an aquarium tank
- A single dose of hexachlorobenzene is applied at the beginning of the simulation
- Simplest type of AQUATOX model setup

HCB is taken up rapidly by macrophyte and by organic sediments



Given the differences in scales, hexachlorobenzene is taken up similarly by the macrophyte *Myriophyllum* and by sediments. In fact, with a wet:dry ratio of 5, the scales are comparable. Also note that the macrophytes are the source of detritus.

HCB loss rates can be plotted, showing that sorption to detritus is negligible (due to mass)

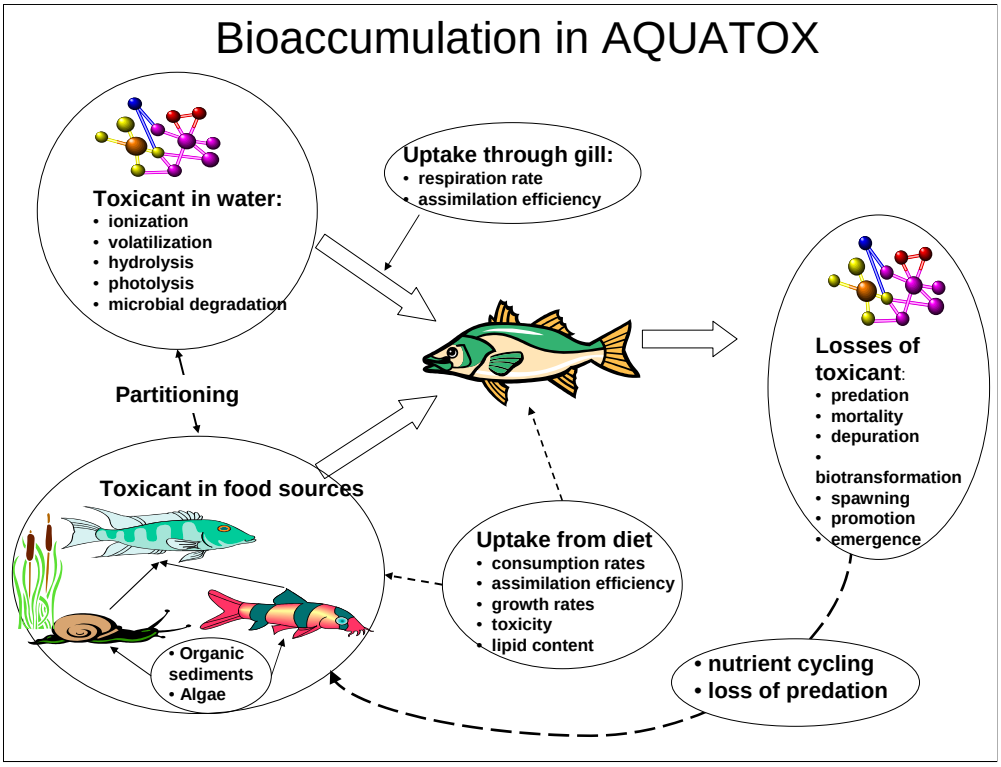


The rates plot indicate that the only significant processes in the tank are sorption by plants and volatilization. As we saw on the previous slide, the rate of sorption by detritus is almost the same as for plants; however the amount of detritus is so small that it accounts for only a fraction of a percent of the HCB in the water. The macrophytes, on the other hand, have a very large biomass in the tank, so much of the mass of HCB is taken up by the plants.

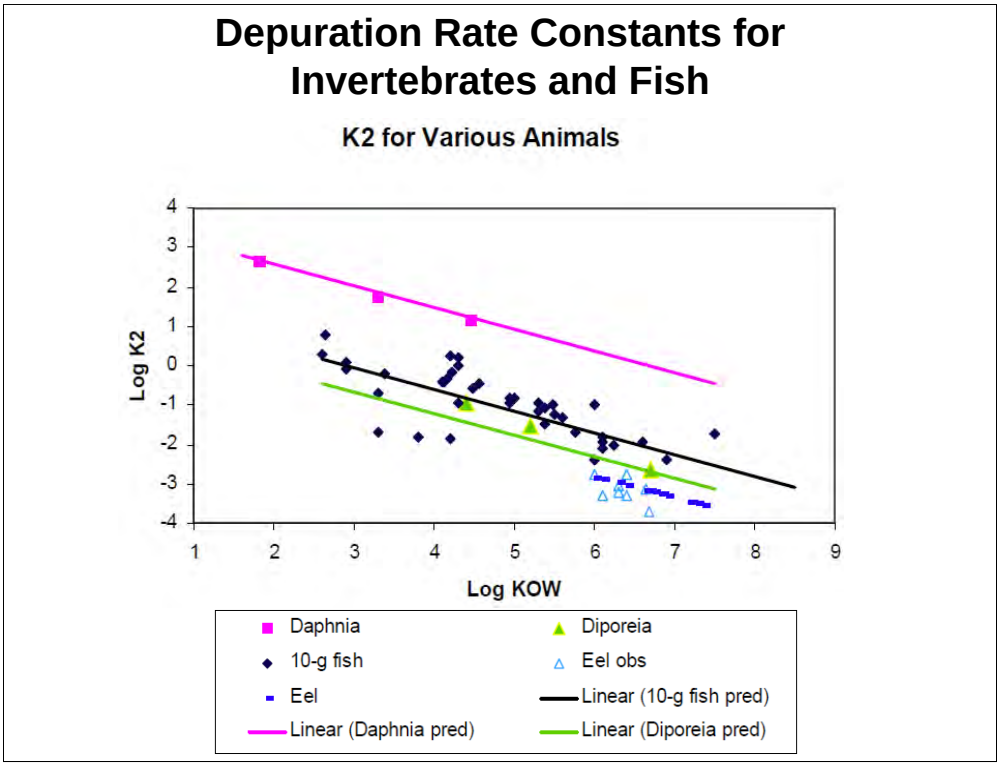
Note that volatilization is a negative when there is loss from the water into air (transfer through the water-air interface can be in either direction).

Chemical Bioaccumulation Overview

- Kinetic model of uptake and depuration
  - Uptake through gill
  - Uptake through diet
    - Consumption rate
    - Assimilation efficiency
  - Loss through depuration, biotransformation, growth dilution (implicit)
- Alternative (simple) BCF model available



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.



K2 can be estimated based on size, lipid content, and the LogKow of the chemical being modeled.

Alternative Chemical Uptake Model

The user may enter two of the three factors defining uptake (BCF, K1, K2) and the third factor is calculated:

$$BCF\ (\text{L/kg}) = \frac{K1\ (\text{L/kg} \cdot \text{d})}{K2\ (\text{1/d})}$$

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

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

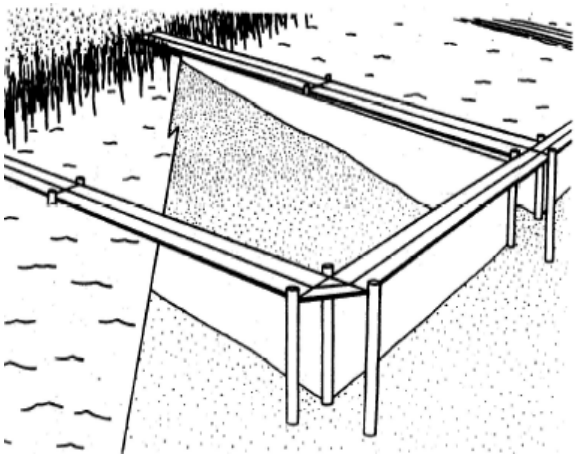
When performing bioaccumulation calculations, the default behavior of the AQUATOX model is to allow the user to enter elimination rate constants (K2) for all plants and animals for a particular organic chemical. K2 values may also be estimated based on the $\text{Log}K_{OW}$ of the chemical, as shown earlier. Uptake in plants and gill uptake in animals is a function of K_{OW} in plants and respiration to chemical uptake efficiency in animals. While the AQUATOX default model works well for a wide variety of organic chemicals, some chemicals with different physical characteristics are not effectively modeled using these relationships.

For this reason, an alternative uptake model based on equilibrium relationships among K1, K2, and BCF is provided to the user.

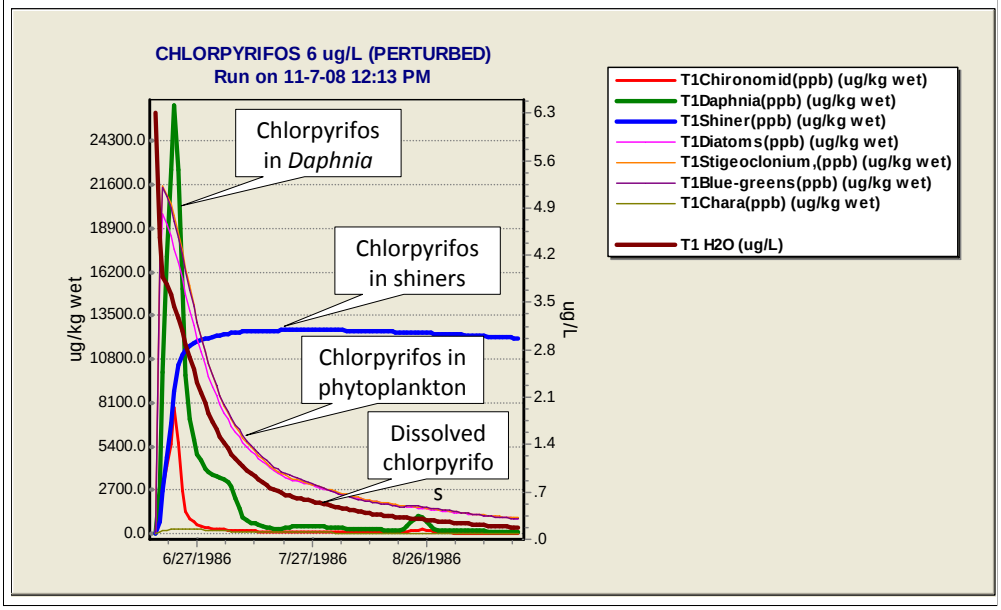
Chlorpyrifos in Pond

- Pond enclosure dosed with chlorpyrifos at EPA Duluth lab
- A single dose of chlorpyrifos is applied at the beginning of the simulation
- Additional biotic compartments
  - diatoms, greens, invertebrates,
  - sunfish, shiner

Chlorpyrifos-dosed pond enclosures at Duluth MN used to validate fate and effects model



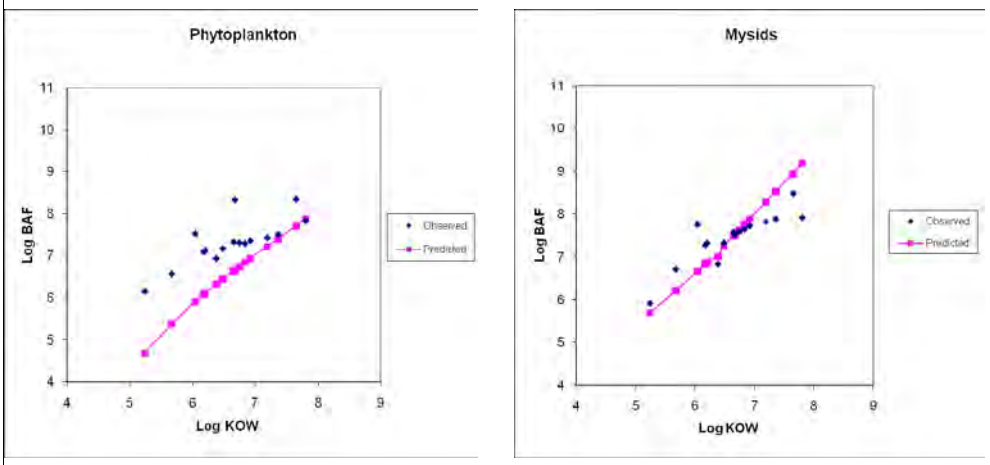
Can trace how the toxicant is partitioned in the biota



The fate depends in part on the effects: shiners (minnows) are tolerant of chlorpyrifos but *Daphnia* and chironomids aren't. Sunfish (not shown) aren't either, but a very small, resistant population remains and the concentration of chlorpyrifos continues to build up.

Lake Ontario Bioaccumulation

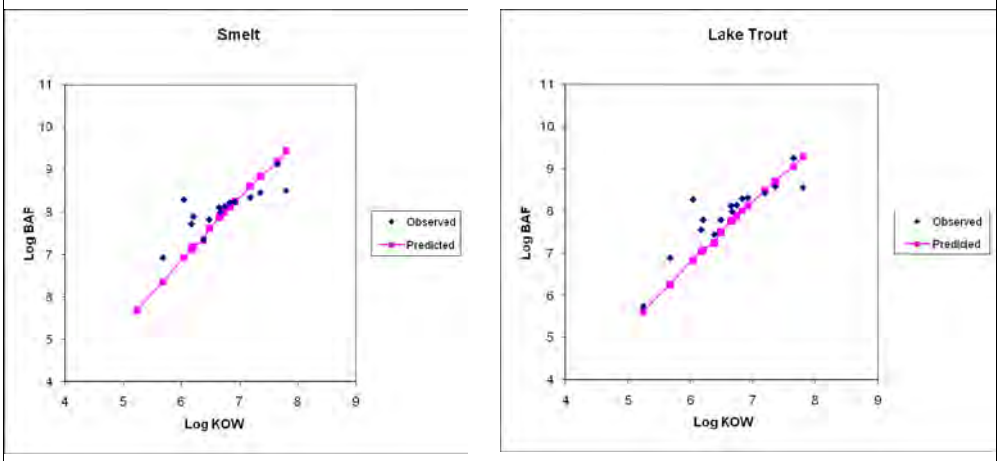
Observed and predicted lipid-normalized and freely dissolved BAFs for PCBs in Lake Ontario ecosystem components.



Phytoplankton BAFs are under-predicted, but observed values include zooplankton.

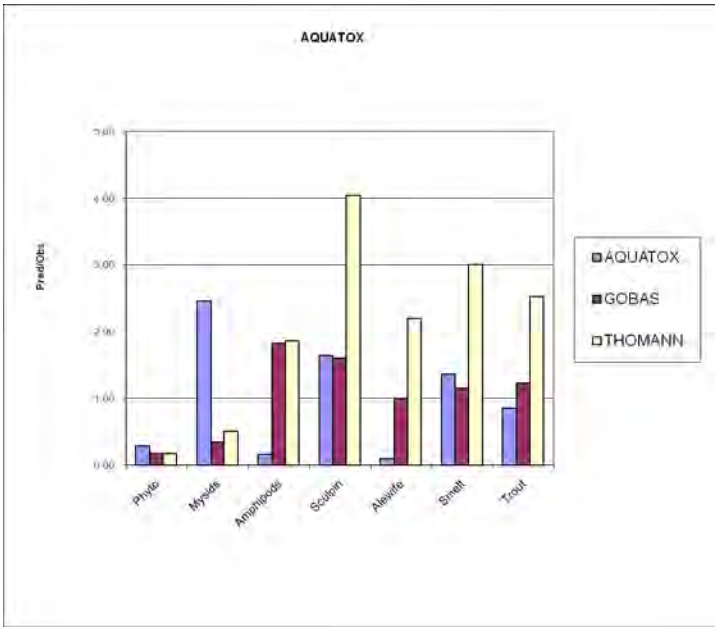
Lake Ontario Bioaccumulation

Observed and predicted lipid-normalized and freely dissolved BAFs for PCBs in Lake Ontario ecosystem components.



These are the best fits to observed data

Lake Ontario BAF model comparison



AQUATOX under-predicts amphipod and alewife BAFs, for reasons that we are still investigating; phytoplankton BAFs are also under-predicted, but that is in comparison to combined phytoplankton and zooplankton BAFs. Mysids are over-predicted. The model compares favorably with the Gobas and Thomann models as applied by Burkhard (1998).

Burkhard, L. P. 1998. Comparison of Two Models for Predicting Bioaccumulation of Hydrophobic Organic Chemicals in a Great Lakes Food Web. Environmental Toxicology and Chemistry **17:383-393.**

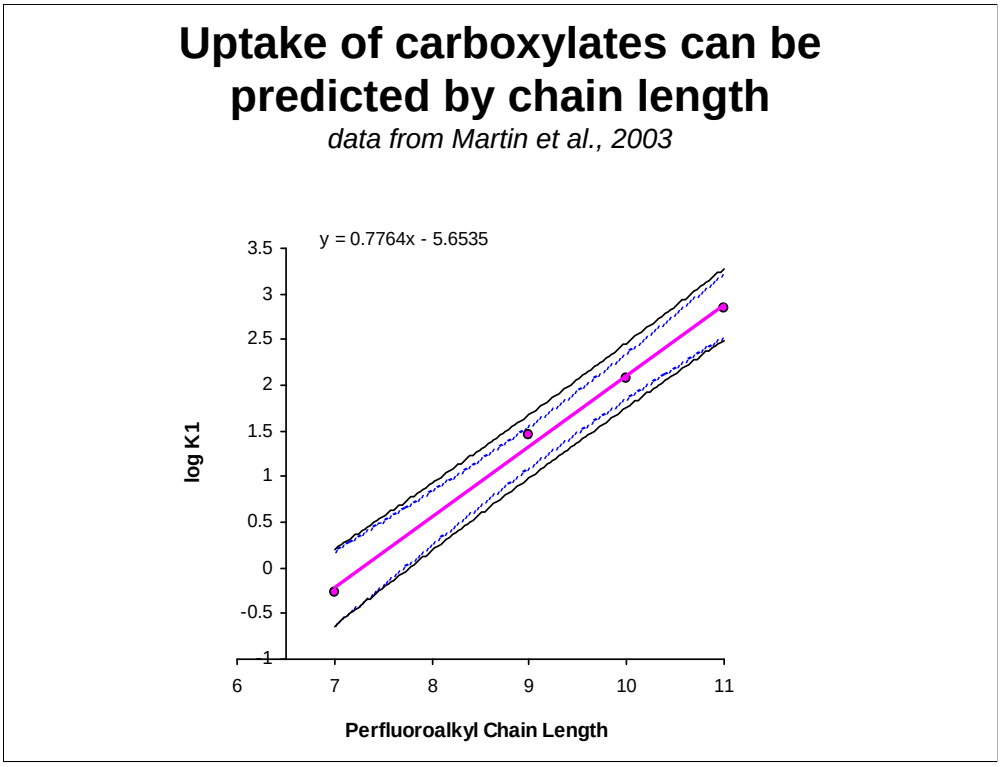
Perfluorinated Surfactants (PFAs)

- Originally developed as part of estuarine model
  - Sorption modeled using empirical approach
  - Animal Uptake/Depuration a function of chain length and PFA type (sulfonate/ carboxylate)
  - Biotransformation can be modeled

The addition of code specifically developed for perfluorinated surfactants is an example of how AQUATOX can be modified to evaluate unusual chemicals.

EPA recently evaluated the bioaccumulation and effects of a group of chemicals known as perfluorinated surfactants. There are two major types of perfluorinated surfactants: perfluoroalkanesulfonates and perfluorocarboxylates. Perfluoroctane sulfonate (PFOS) belongs to the perfluoroalkanesulfonate group and Perfluorooctanoic acid (PFOA) belongs to the perfluorocarboxylate group. These persistent chemicals have been found in humans, fish, birds, marine and terrestrial animals throughout the world. PFOS has an especially high bioconcentration factor in fish. At present there is increasing public concern about PFOA, which is associated with the manufacture of Teflon (see, for example, an article in the August 8, 2004, NY Times).

Park, R. A., and J. S. Clough. 2003. AQUATOX for Windows: A Modular Fate and Effects Model for Aquatic Ecosystems: Perfluoroalkylated Surfactant and Estuarine Versions, Addendum to Release 2 Technical Documentation (Unpublished report). U.S. Environmental Protection Agency, Washington, D.C.



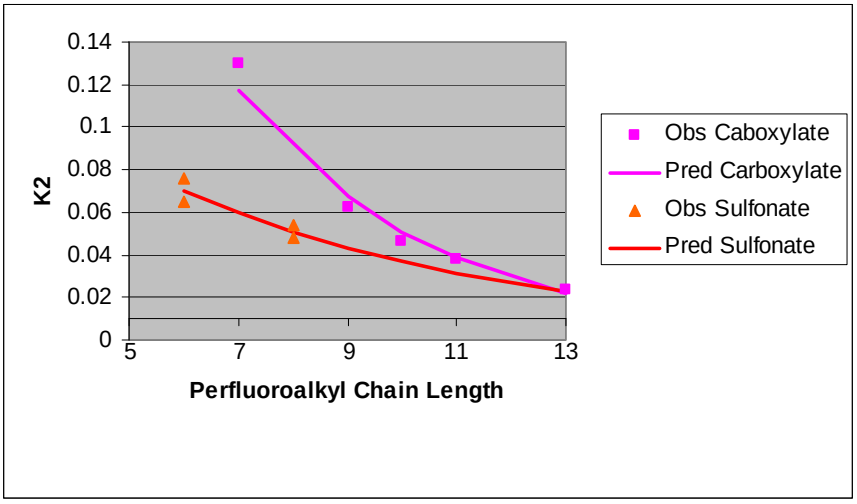
Because PFAs behave differently from most bioaccumulative compounds it was necessary to program estimation procedures for uptake and depuration specific to them. Fortunately, papers documenting such estimation procedures appeared just as we embarked on this project:

Martin, Jonathan W., Scott A. Mabury, Keith R. Solomon, and Derek C.G. Muir. 2003. Bioconcentration and Tissue Distribution of Perfluorinated Acids in Rainbow Trout (*Oncorhyncus mykiss*). *Environmental Toxicology and Chemistry* 22 (1):196-204.

Martin, Jonathan W., Scott A. Mabury, Keith R. Solomon, and Derek C.G. Muir. 2003. Dietary Accumulation of Perfluorinated Acids in Juvenile Rainbow Trout (*Oncorhynchus mykiss*). *Environmental Toxicology and Chemistry* 22 (1):189-195.

Depuration rate is also a function of chain length

data from Martin et al., 2003



Martin, Jonathan W., Scott A. Mabury, Keith R. Solomon, and Derek C.G. Muir. 2003. Bioconcentration and Tissue Distribution of Perfluorinated Acids in Rainbow Trout (*Oncorhyncus mykiss*). *Environmental Toxicology and Chemistry* 22 (1):196-204.

Martin, Jonathan W., Scott A. Mabury, Keith R. Solomon, and Derek C.G. Muir. 2003. Dietary Accumulation of Perfluorinated Acids in Juvenile Rainbow Trout (*Oncorhynchus mykiss*). *Environmental Toxicology and Chemistry* 22 (1):189-195.

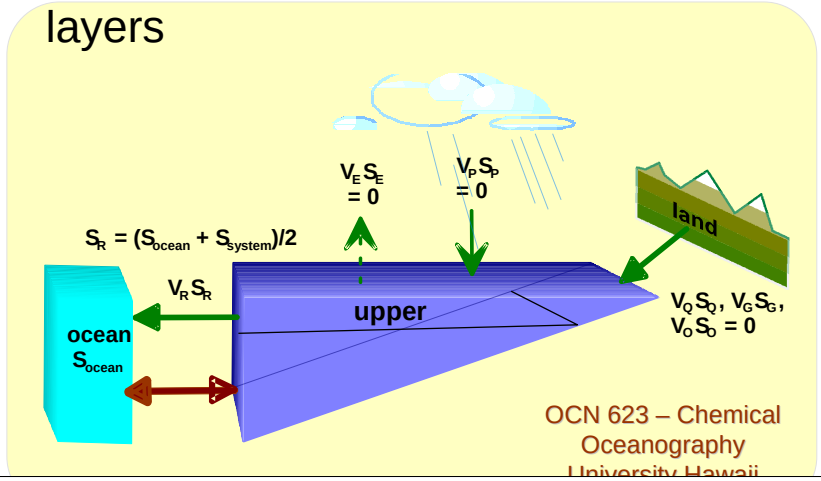
Estuarine version applied to Galveston Bay, Texas, to evaluate toxicants

Photo Courtesy NASA Johnson Space Center

AQUATOX includes an estuarine module. It was calibrated and partially verified using Galveston Bay, Texas.

Estuarine Features

- Stratification – salt wedge
- Water Balance – salt balance approach
- Entrainment Process – lower to upper layers



- Estuaries are considered to be permanently stratified, though at times the extent of turbulent diffusion will essentially mean that they are well mixed.
- Salt balance approach: salt water inflow and outflow at the estuary mouth is a function of salinity and residual flow.
- Entrainment, water movement from the lower level to the upper level, transports suspended and dissolved substances from one layer to the next.

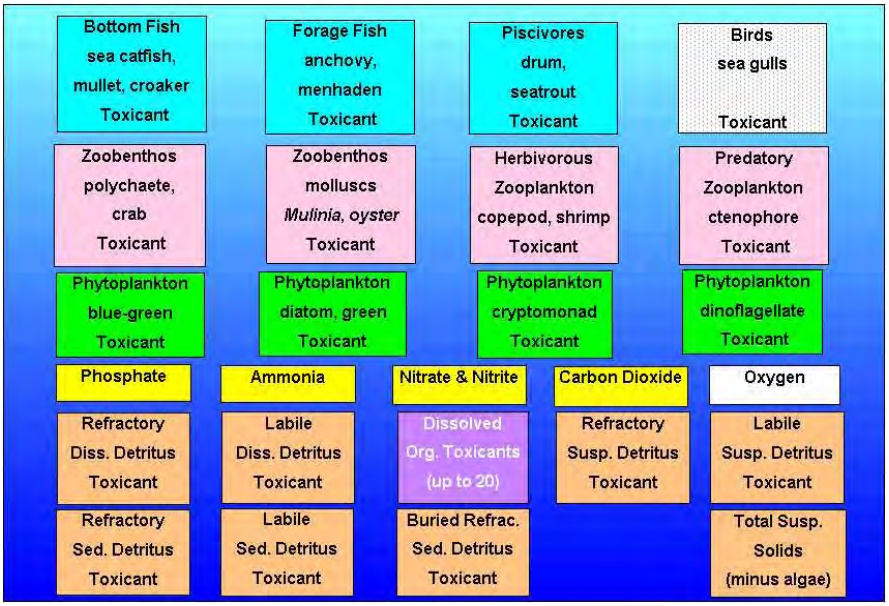
Estuary Model Data Requirements

- Time series of “Upper Layer” and “Lower Layer” salinities at mouth for Salt Wedge Model
- Tidal range model parameters
  - “harmonic constants”, often available from NOAA website
- Estuary site width
- Loadings of freshwater inflow

The website to load tide prediction parameters (harmonic constants) within the United States is:

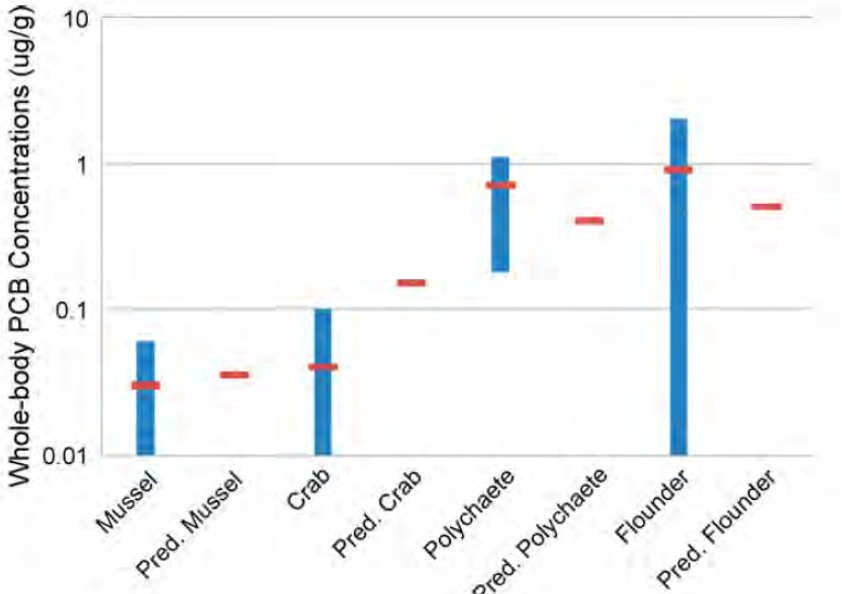
http://tidesandcurrents.noaa.gov/

Galveston Bay, Texas, compartments



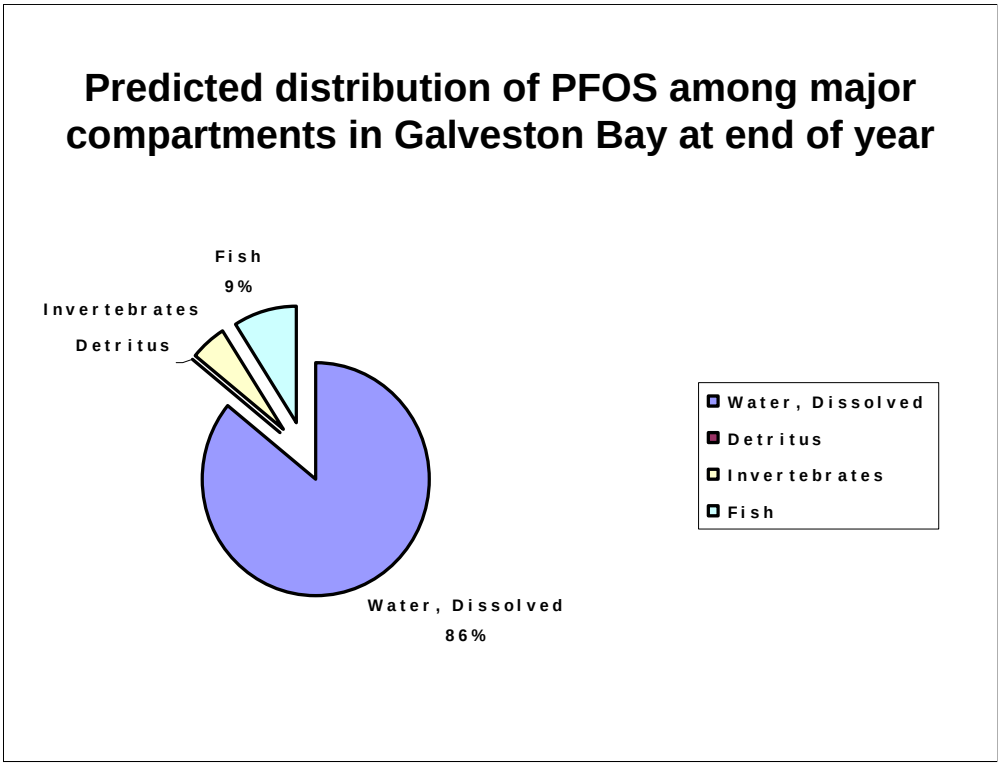
Most commercial species are represented, as well as other critical food web components. Birds are a bioaccumulative endpoint; concentration of chemical is function of given BAFs weighted by food preference.

Validation: New Bedford Harbor MA, observed & predicted PCB values are comparable



Park et. al, 2008, Figure 7, data from Connolly, 1991

PCB concentrations in New Bedford Harbor, MA, water and sediments were imported into Galveston Bay TX simulation. The results were comparable between observed and predicted mean whole-body concentrations.



The estuarine version was used to predict the fate and bioaccumulation of PFOS and other PFAs in the nearshore environment. Because of the volume of water, most of the mass resides in the dissolved phase.

Modeling Toxicity of Chemicals

- Lethal and sublethal effects are represented
- Chronic and acute toxicity are both represented
- Effects based on total internal concentrations
- Uses the critical body residue approach (McCarty 1986, McCarty and Mackay 1993)
- Can also model external toxicity
  - Useful if uptake and depuration are very fast (as with herbicides)

Sublethal effects include reduction in photosynthesis, ingestion, and reproduction, and increased egestion, drift, and sloughing of periphyton.

From Wikipedia, the free encyclopedia:

Chronic toxicity is a property of a substance that has toxic effects on a living organism, when that organism is exposed to the substance continuously or repeatedly.

Acute Toxicity is a property of a substance that has toxic effects on a living organism, when that organism is exposed to a lethal dose of a substance once. In other words, basically a short-term version of chronic toxicity.

AQUATOX models time-varying toxicity—both chronic and acute.

McCarty, L.S., G.W. Ozburn, A.D. Smith, and D.G. Dixon. 1992. Toxicokinetic Modeling of Mixtures of Organic Chemicals. *Environmental Toxicology and Chemistry*, 11:1037-1047.

Mackay, D., H. Puig, and L.S. McCarty. 1992. An Equation Describing the Time Course and Variability in Uptake and Toxicity of Narcotic Chemicals to Fish. *Environmental Toxicology and Chemistry*, 11:941-951.

Toxicity Models within Bioaccumulation Models

Table 3.5. Toxicity Models

	AQUATOX Release 2	BASS v 2.1	Biotic Ligand 1.0.0	RAMAS Ecosystem
Domain of Toxicity Models				
Acute Toxicity	★	★	★	★
Chronic Toxicity	★	★		★
Sub-Lethal Effects	★			
Toxicity Effects Feed Back to Bioconcentration Model	★	★		★
Toxicity Mechanisms				
Based on Total Internal Concentrations	★	★		★
Based on Concentrations in Organs			★	
User Input Required				
LC50 values	★	★		
EC50 values	★			★
Weibull Shape Parameter	★			★

Imhoff et al. 2004

Many bioaccumulation models do not include toxicity models, and of those, few include sub-lethal effects (such as toxicity-induced drift and periphyton sloughing).

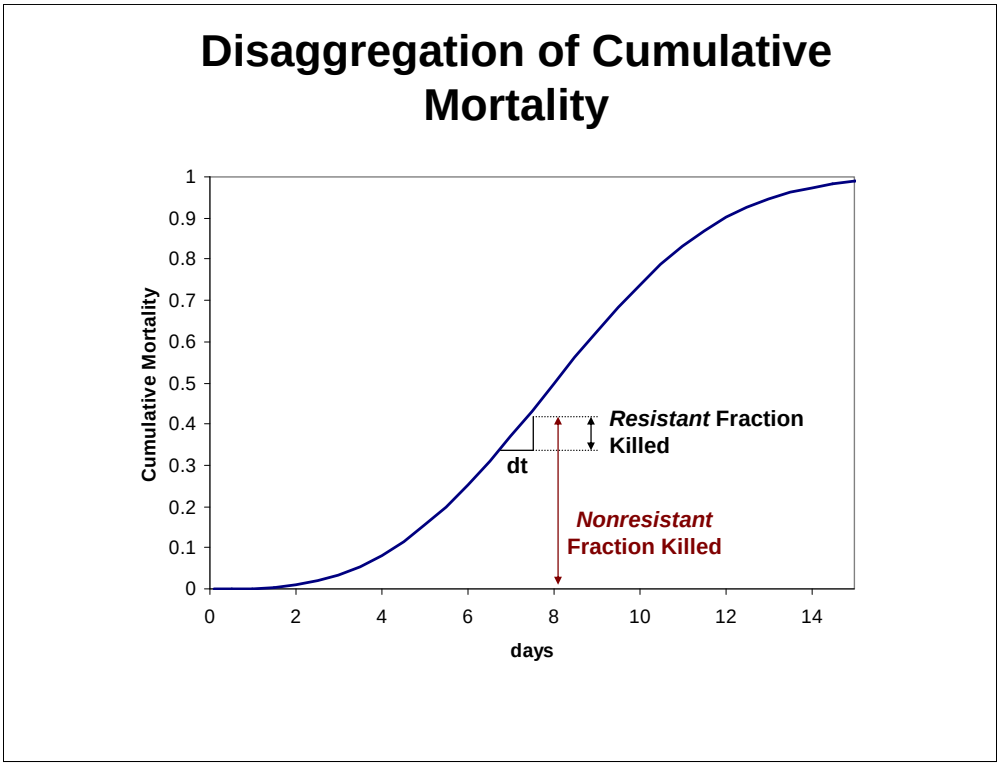
Imhoff, John C., Jonathan S. Clough, Richard A. Park, and Andrew Stoddard. 2004. Evaluation Of Chemical Bioaccumulation Models of Aquatic Ecosystems: Final Report. Athens GA: U.S. Environmental Protection Agency.

Steps Taken to Estimate Toxicity

- Enter LC_{50} and EC_{50} values
  - LC_{50} estimators are available for species
- Compute internal LC_{50}
- Compute infinite LC_{50} (time-independent)
- Compute t-varying internal lethal concentration
- Compute cumulative mortality
- Compute biomass lost per day by disaggregating cumulative mortality
- Sublethal toxicity is related to lethal toxicity through an application factor
- Option has been added to use external concentration.

The details are covered in Chapter 8 of the *Technical Documentation*.

By entering both LC_{50} and EC_{50} values for a species the application factor can be computed.



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*.

New Option to Model with External Concentrations

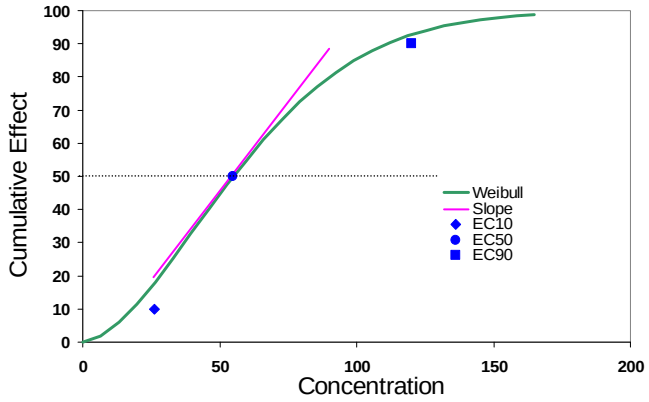
Two-parameter Weibull distribution as in Christiensen and Nyholm (1984)

$$CumFracKilled = 1 - \exp(-kz^{\eta})$$

Two Required Parameters:

LC50 (or EC50)

"Slope Factor" = Slope at LC50 multiplied by LC50



Rather than require the user to fit toxicological bioassay data to determine the parameters for ***k*** and ***η***, 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). (See *Technical Documentation Addendum*.)

AQUATOX assumes that each chemical's dose response curve has a distinct shape, relevant to all organisms modeled. In this manner, a single parameter describing the shape of the Weibull parameter can be entered in the chemical record rather than requiring the user to derive slope parameters for each organism modeled. However, as shown in the slide above, 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. For this reason, rather than have a user enter "the slope at LC50" into the chemical record, AQUATOX asks that the user enter a "slope factor" defined as "the slope at LC50 multiplied by LC50." In the above example, the user would enter a slope factor of 1.0 and then, given an LC50 of 1 or an LC50 of 100, the above two curves would be generated.

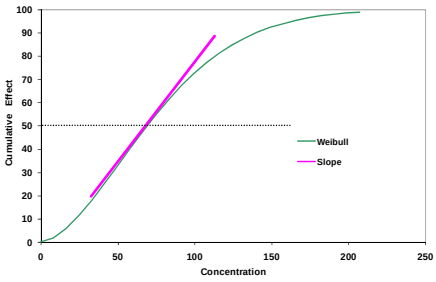
When modeling toxicity based on external concentrations, organisms are assumed to come to equilibrium with external concentrations (or the toxicity is assumed to be based on external effects to the organism).

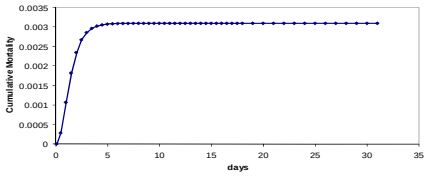
Spreadsheet Demo

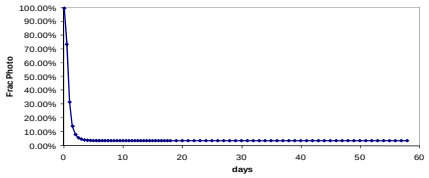
AQUATOX is distributed with two spreadsheets useful in understanding the model's toxicity components

AQUATOX_Internal_Toxicity_Model.xls

AQUATOX_External_Toxicity_Model.xls

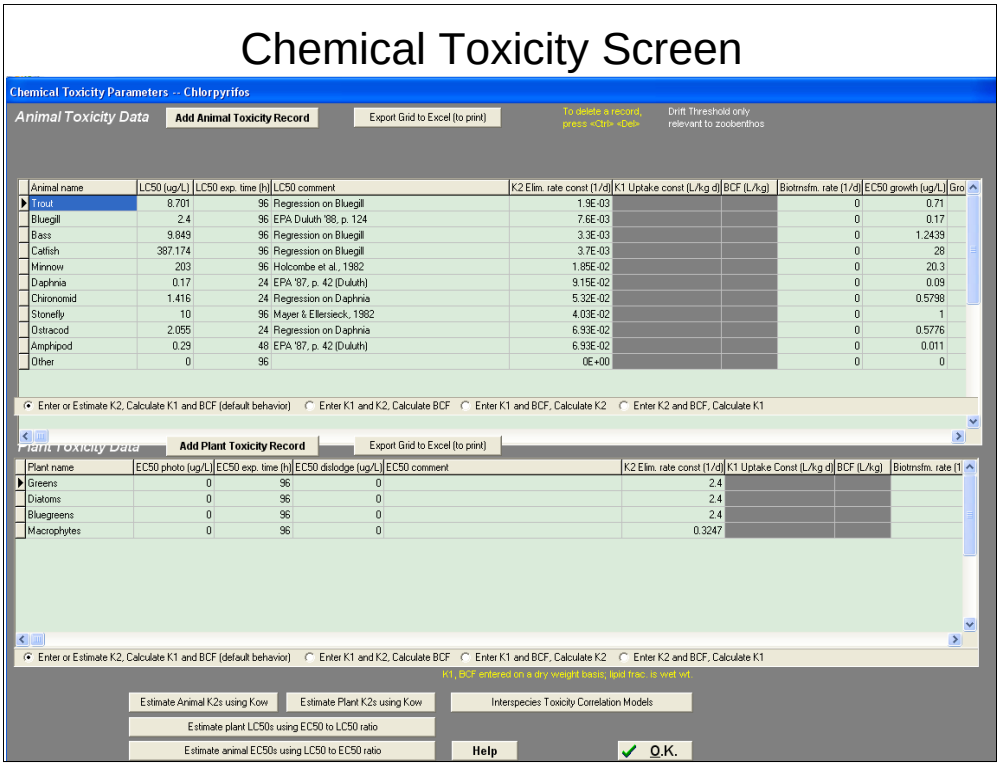






These Excel spreadsheets are located in the STUDIES directory of your AQUATOX installation location.

Chemical Toxicity Screen



This screen is where all of the important chemical toxicity parameters are located. To get to this screen go to Chemical Underlying Data and select the "Toxicity Data" button.

There are multiple options for entering uptake rate constant (k1), the elimination rate constant (k2) and the bioconcentration factor (BCF) or allowing the model to calculate these parameters (BCF=k1/k2)

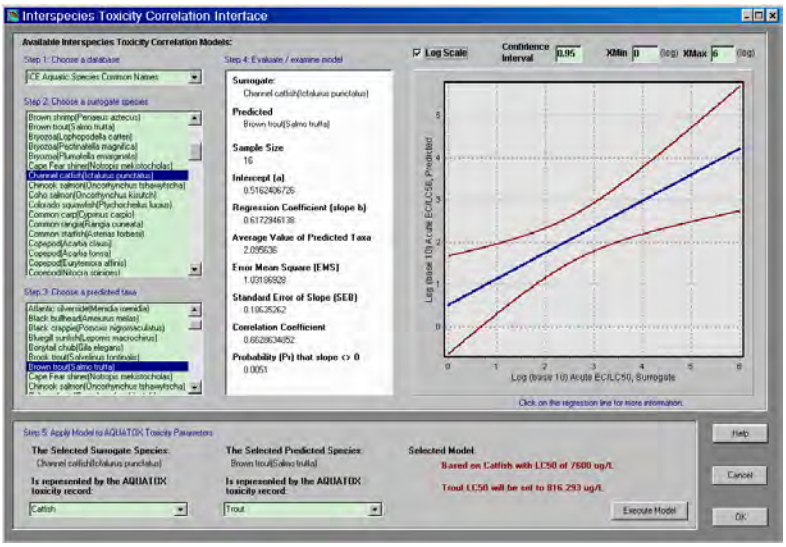
Additionally, elimination rates may be estimated using the octanol water partition coefficient (Kow).

Fish and invertebrate regressions are available for many organisms using the ICE database (see next slide).

As explained previously, by entering both LC_{50} and EC_{50} values for a species the application factor can be computed. The user has the option of applying that same ratio to the rest of the species in the animal or plant toxicity screen using the buttons **Estimate animal LC50s**... and **Estimate plant EC50s...**.

Release 3: Additional Toxicity Features

- Integration with ICE: a large EPA database of toxicity regressions



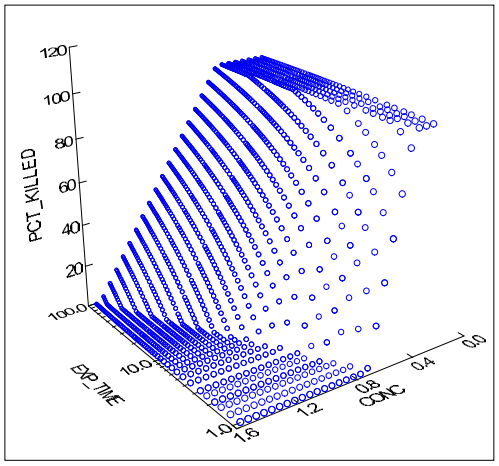
http://www.epa.gov/ceampubl/fchain/webice/index.htm

Release 3: Additional Toxicity Features

- Integration with ICE: a large EPA database of toxicity regressions
- DO effects

A 3D model of effects that is a function of exposure time and oxygen concentration.

Includes non-lethal effects on consumption and reproduction



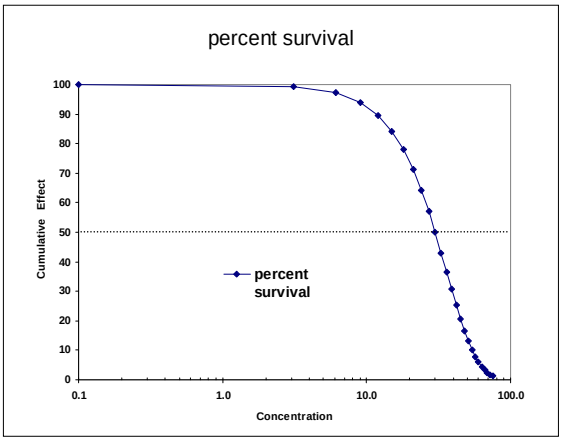
Release 3: Additional Toxicity Features

- Integration with ICE: a large EPA database of toxicity regressions
- DO effects
- Ammonia effects

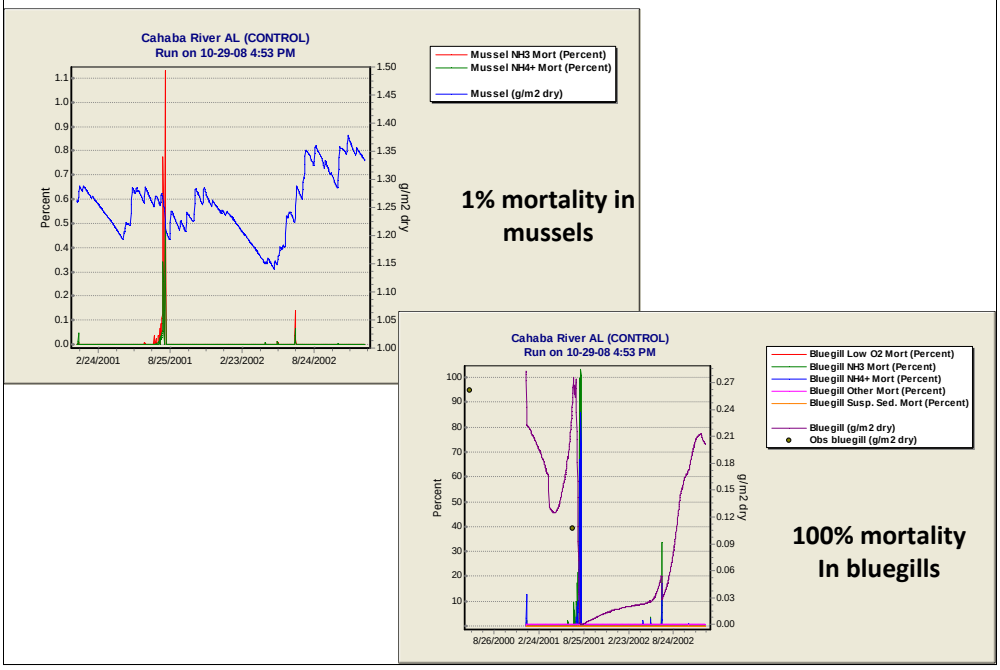
External Toxicity Model Utilized

Effects from un-ionized and

ionized ammonia are additive

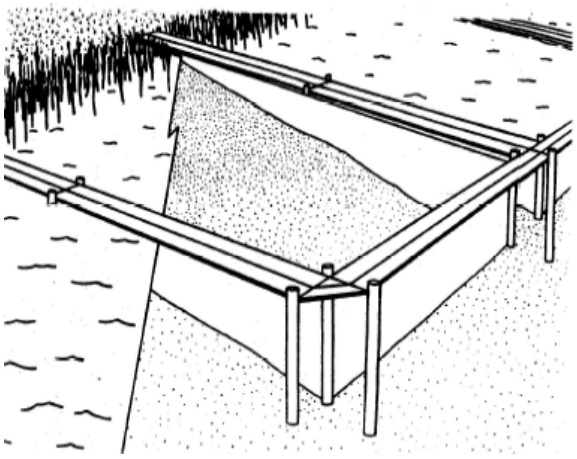


Predicted ammonia toxicity in Cahaba River AL

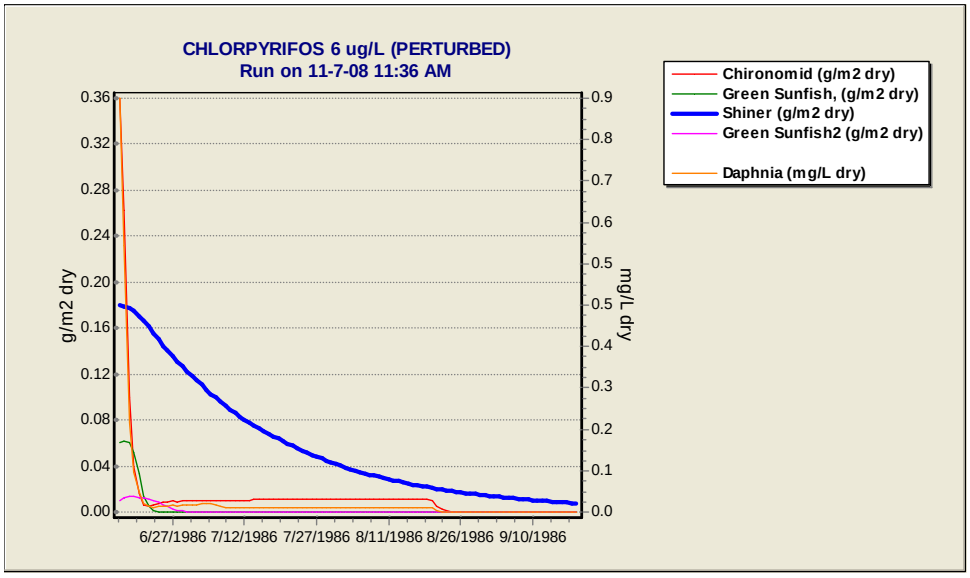


Young mussels are very sensitive to ammonia (LC50 = 0.165), but adults appear to be tolerant (LC50 = 17 mg/L), so the default of 10 mg/L was used for mussels. Bluegill LC50 = 0.62 mg/L.

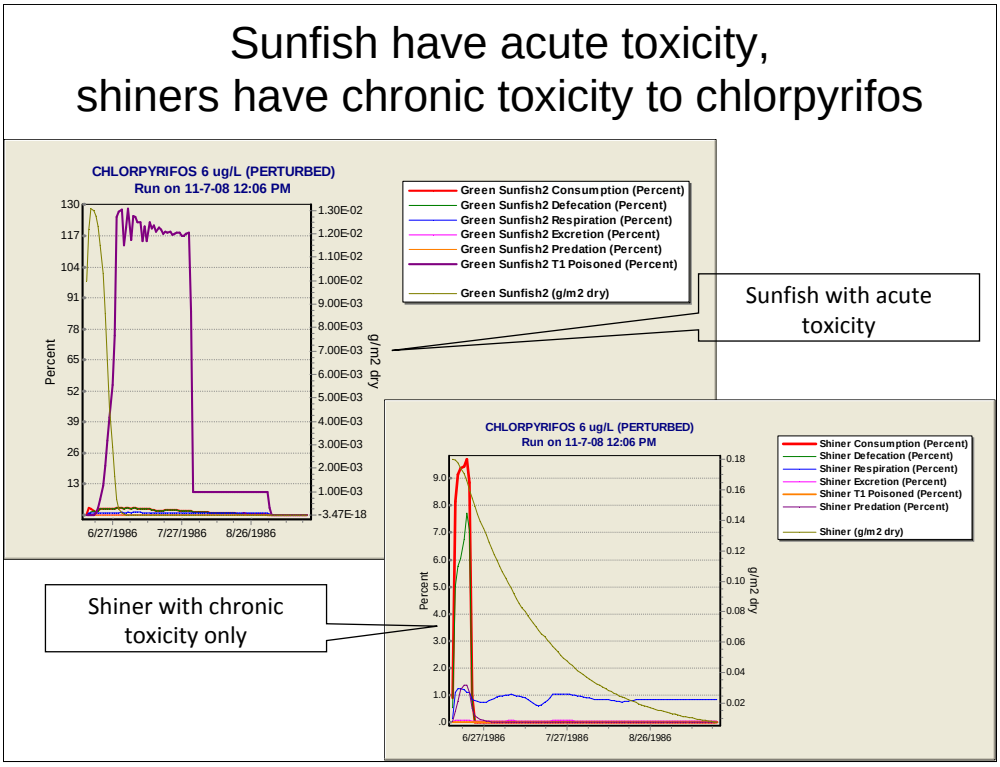
Returning to the Limnocorral in Duluth MN . . .



Animals all decline at varying rates following a single initial dose of chlorpyrifos

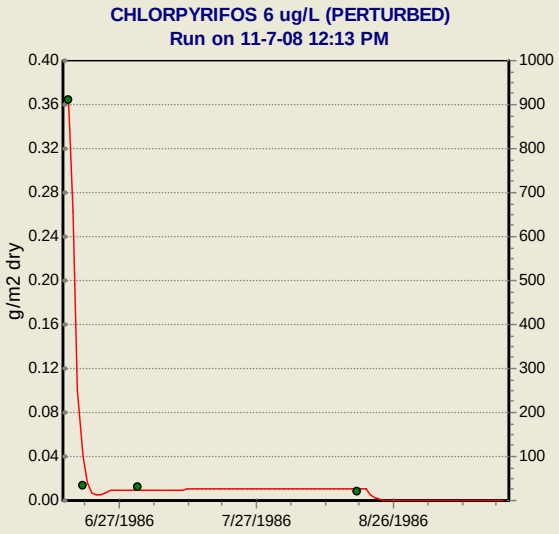


Shiners are most tolerant to chlorpyrifos according to toxicity data. Chironomids and *Daphnia* are most sensitive.



Sunfish have a low tolerance to chlorpyrifos (LC50 = 2.4 ug/L), so bioaccumulation is followed by acute toxicity with gradual recovery. Shiners are tolerant of chlorpyrifos (LC50 =203 ug/L) and exhibit no mortality with an initial dose of 6 ug/L chlorpyrifos; they do exhibit chronic toxicity in the form of decreased consumption and assimilation; loss of forage is a predicted indirect effect. Predicted recovery of sunfish eventually leads to high predation of shiners.

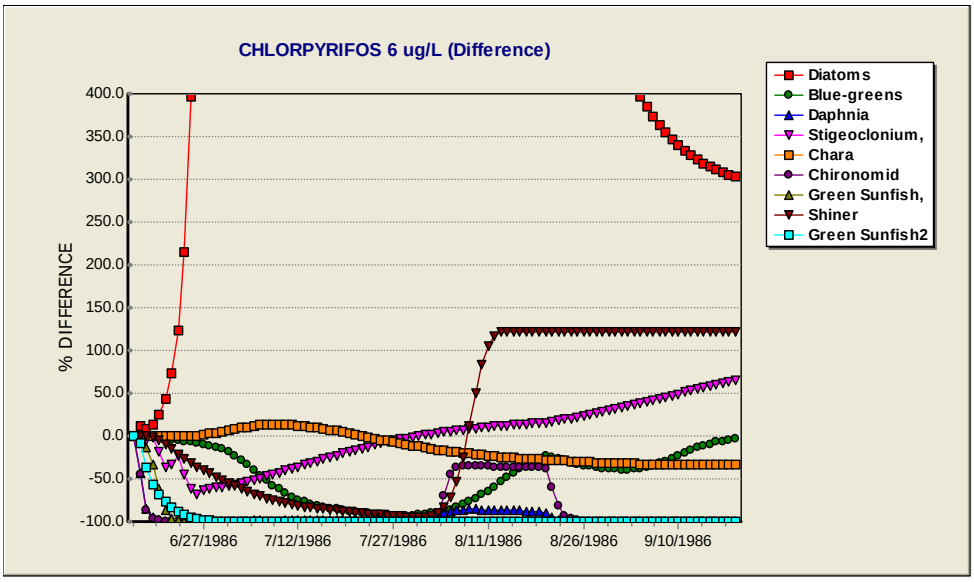
Toxic effects of Chlorpyrifos in Duluth pond



Predicted biomass and observed numbers of insect larvae in a Duluth, Minnesota, pond dosed with 6 ug/L chlorpyrifos

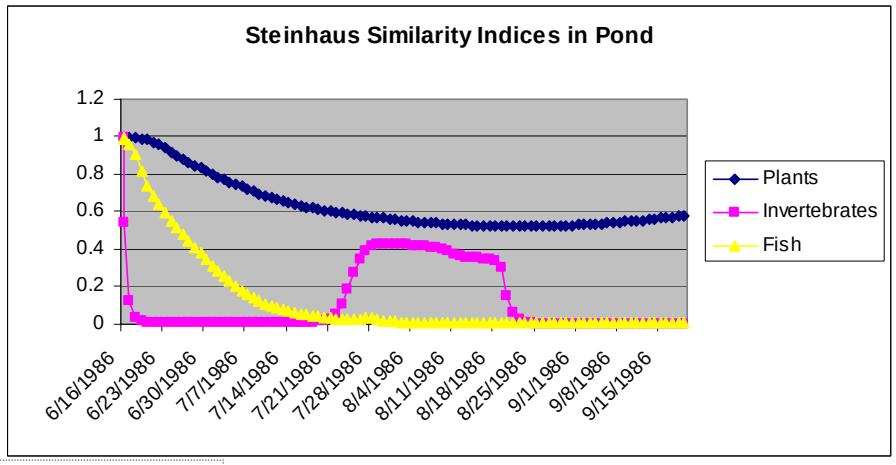
In a validation study 6 ug/L initial dose of chlorpyrifos in a pond resulted in a decline in predicted insect biomass, which compared favorably to decline in observed numbers of insects.

% Difference Graph shows differences in species response to toxicant



An initial 6 ug/L chlorpyrifos in the pond has an immediate impact on the invertebrates and sunfish. Removal of predation causes an explosive increase in diatoms; shiners recover, partly in response to chironomid recovery half way through the simulation period.

Steinhaus Indices show ecosystem impacts predicted by the model



$$S = \frac{2 * \sum_{k=1}^{n} Min(a_{1,k}, a_{2,k})}{\sum_{k=1}^{n} a_{1,k} + \sum_{k=1}^{n} a_{2,k}}$$

Coefficients of similarity are used to determine whether the composition of two communities is similar. The Steinhaus coefficient or similarity index (S) is based on the species abundances (in this case indicated by the species specific daily biomass) common to two communities, where $a_{i,k}$ is abundance of species k in sample I.

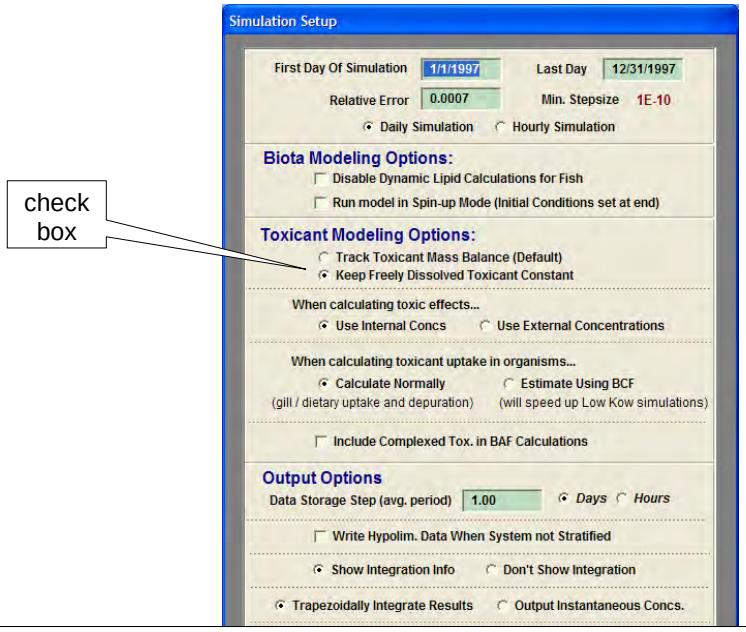
Chlorpyrifos in Stream

Objective: analyze direct and indirect ecotoxicological effects with model

- Assessment of chlorpyrifos in a generic stream
  - small stream in corn belt
  - exposure to constant level of Chlorpyrifos assessed (0.4 ug/L)

Set exposure to a constant in Study Setup

Set “Control Setup” to omit toxicants from “control” results

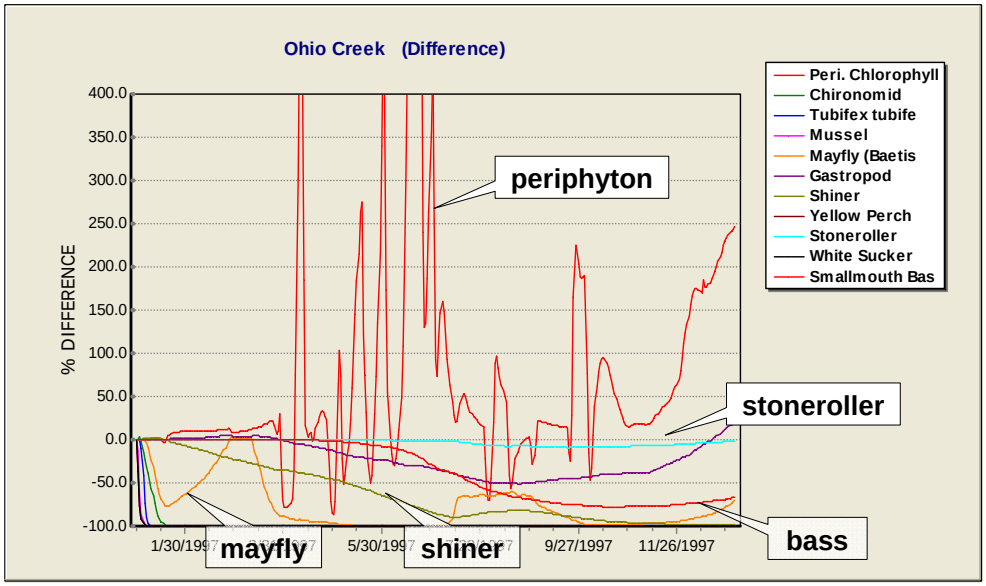


If you wish to try this yourself, open a study with a chemical attached. Then, in Main Screen click on **Study Setup**

Check box **Keep Freely Dissolved Contaminant Constant**

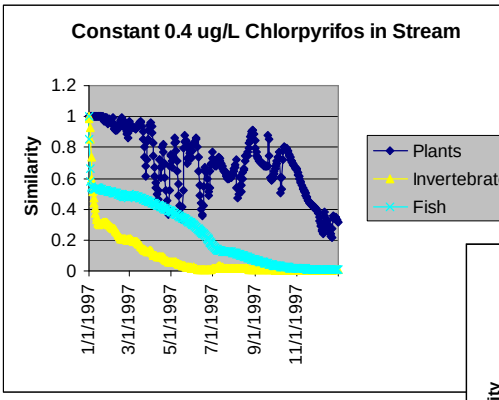
To compare control (with no toxicant) to perturbed with constant dose, in **Control Setup** check **All Organic Toxicants** boxes (so Control will not have chlorpyrifos)

Impacts of constant chlorpyrifos are dramatic: animals decline, algae increase (less herbivory)

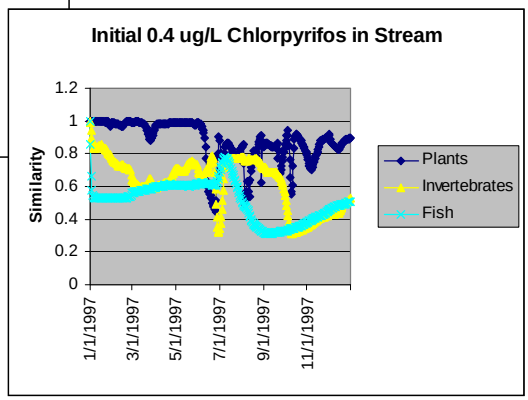


The best indication of the impacts are to be seen in a **Difference** graph that compares the perturbed with the control. To get this you have to run the simulations for the same period. Note that most of the invertebrates disappear quickly, followed by the fish. Shiners and stonerollers share the same toxicity record (Minnow), so the relative decline of shiners is due to loss of invertebrate food base and not direct toxicity whereas stonerollers, which graze periphyton, are unaffected.

Plot of Steinhaus indices shows lasting impacts predicted by the model



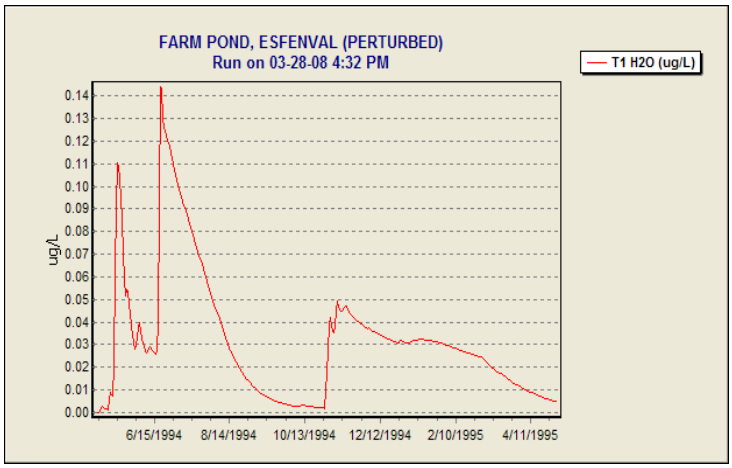
$$S = \frac{2 * \sum_{k=1}^{n} Min(a_{1,k}, a_{2,k})}{\sum_{k=1}^{n} a_{1,k} + \sum_{k=1}^{n} a_{2,k}}$$



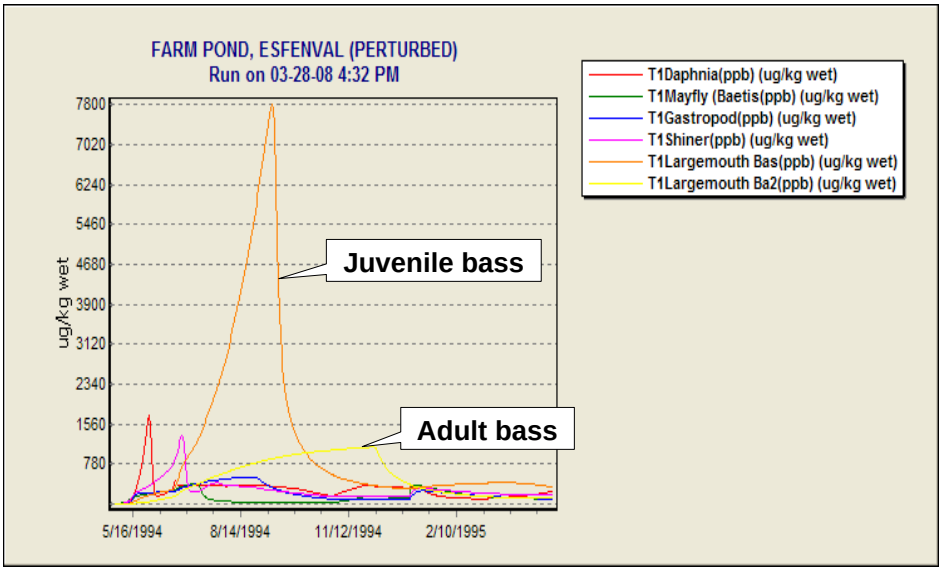
Coefficients of similarity are used to determine whether the composition of two communities is similar. The Steinhaus coefficient or similarity index (S) is based on the species abundances (in this case indicated by the species specific daily biomass) common to two communities, where $a_{i,k}$ is abundance of species k in sample I.

Farm Pond MO, Esfenvalerate

- Loadings from PRIZM for adjacent cornfield
- 20% of worst case scenario for runoff of pesticide predicted by PRZM

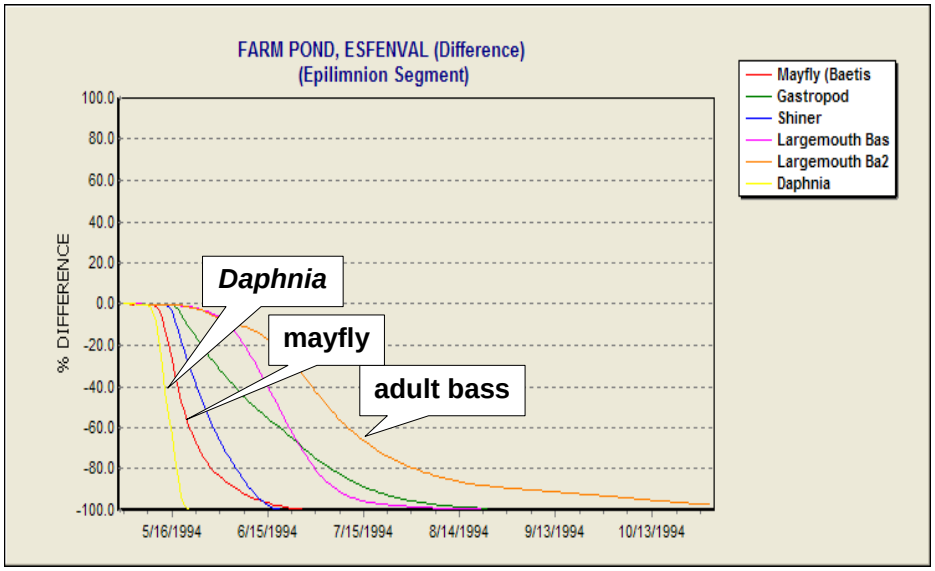


Farm Pond, Esfenvalerate
Chemical Uptake in animals



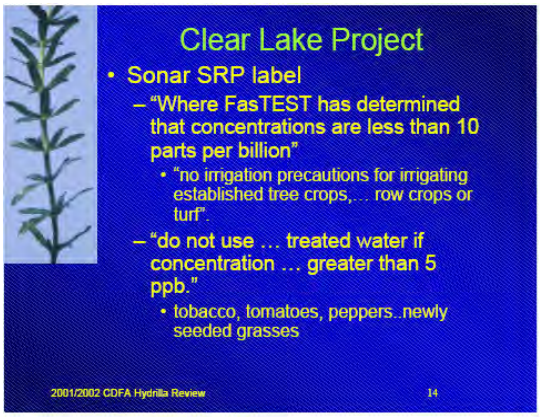
Juvenile bass are predicted to bioaccumulate esfenvalerate quickly because of bioenergetics; adult bass are predicted to bioaccumulate more slowly and, because of loss of forage base, not as much.

Farm Pond, Esfenvalerate Difference Graph

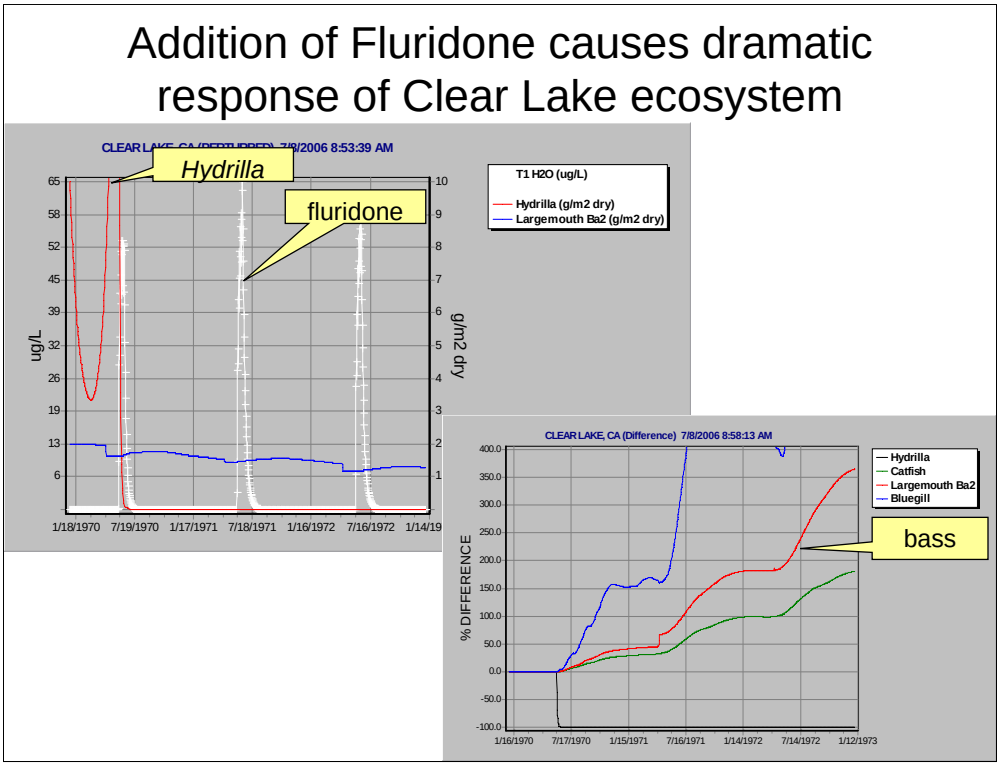


Fluridone (Sonar) used to eradicate *Hydrilla* in Clear Lake CA

- Six doses
  - 20 ppb dose
- What is impact on non-target organisms?
- What is recovery of Clear Lake ecosystem?
- Impact on DO from death of large *Hydrilla* biomass?



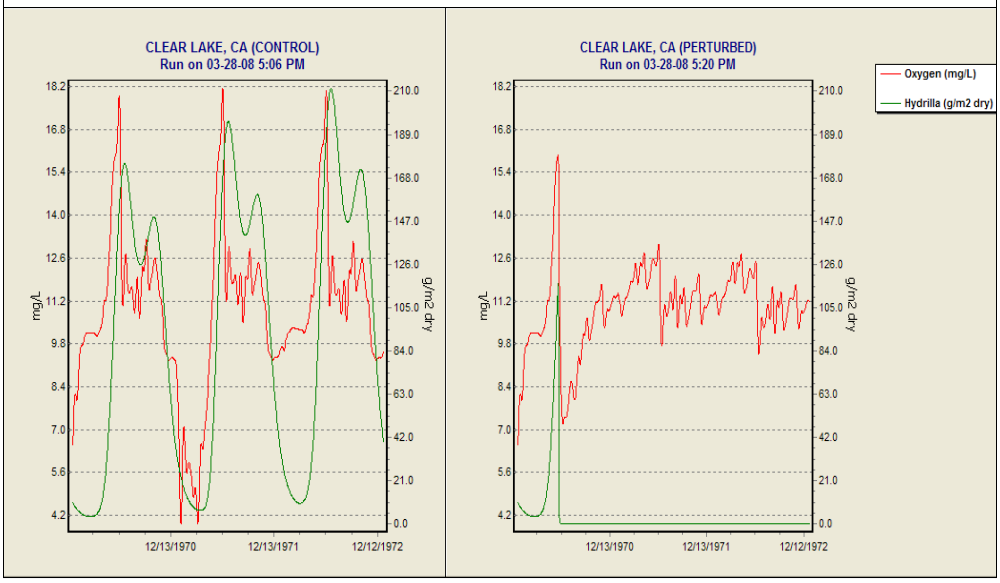
Sonar (fluridone) has been used successfully in Clear Lake to eradicate *Hydrilla*. Although *Hydrilla* did not appear until 1994, we will use the study set up with 1970-1971 data. Note that the fluridone loadings are for 1971 but without bracketing the simulation period with 0 loadings, the loadings are repeated in each of the three years. You can easily change this in the supplied study if you wish. Also note that we are modeling the entire lake for convenience; in reality, *Hydrilla* spread slowly, so only selected areas needed to be treated; our simulation is, therefore, a worst-case scenario.



Fluridone kills off *Hydrilla*, leading to predicted recovery of fisheries.

Indirect Effects Captured

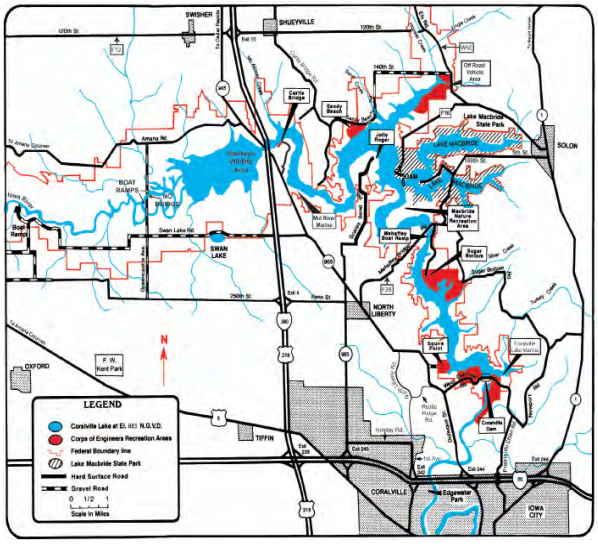
e.g. Impact on DO levels is negligible



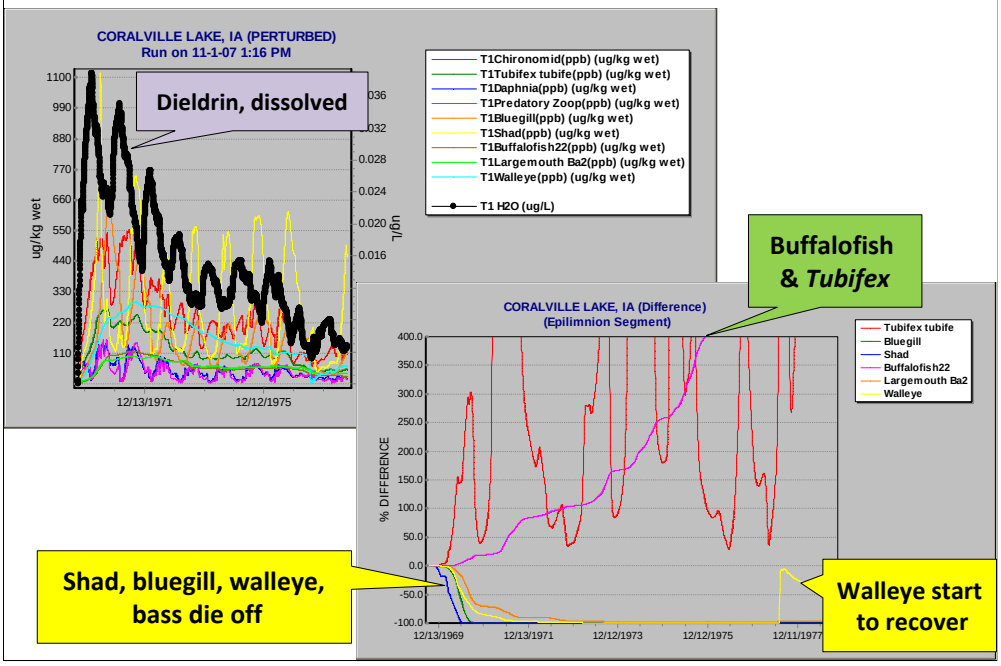
Death of *Hydrilla* is not predicted to have serious impact on dissolved oxygen. Production of detritus by *Hydrilla* is predicted to impact DO more with seasonal dieoff.

Coralville Reservoir Iowa
long-term contamination with dieldrin

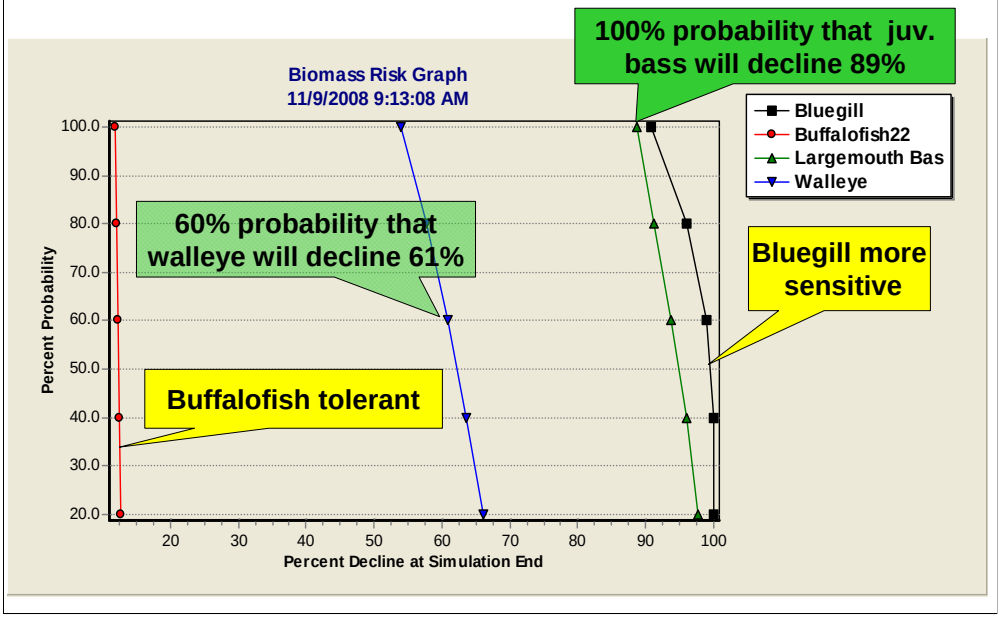
- Run-of-river
- Flood control
- 90% of basin in agriculture
  - Nutrients
  - Pesticides
  - Sediment



Dieldrin bioaccumulates & declines over 20 years with fish mortality, but tolerant buffalofish, *Tubifex* prosper



Probability of decline in biomass (end of 1st year) can be estimated based on uncertainty



AQUATOX can estimate probability of decline, which is a very powerful tool for risk assessment. In this example, using a distribution of loadings of dieldrin, we see that bluegill are the most sensitive to dieldrin and buffalofish are the least sensitive. Walleye are of intermediate sensitivity, as suggested by their recovery shown in the previous slide.

Uncertainty and Sensitivity Analysis

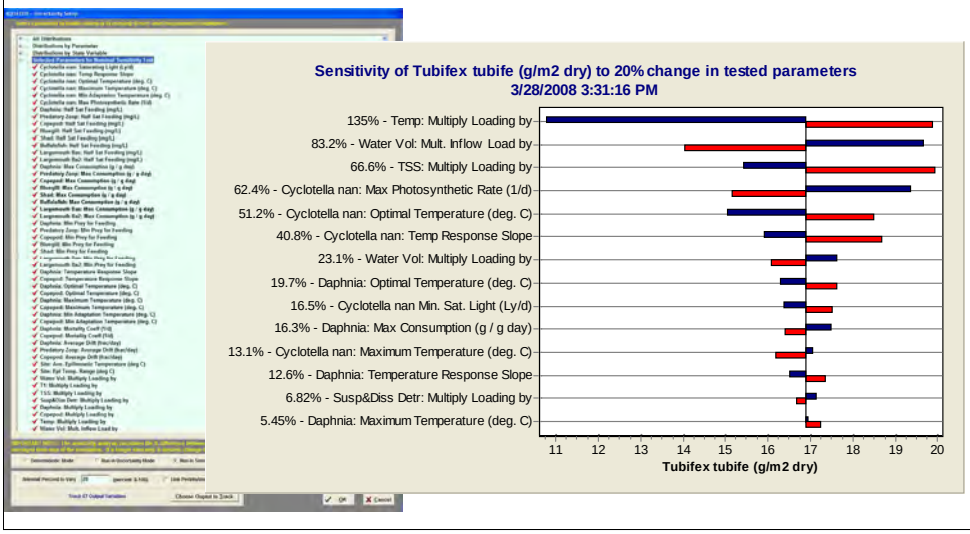
- "Sensitivity" refers to the variation in output of a mathematical model with respect to changes in the values of the model inputs (Saltelli, 2001).
- Sensitivity analysis provides a ranking of the model input assumptions with respect to their relative contribution to model output variability or uncertainty (EPA, 1997).
- A comprehensive sensitivity analysis of AQUATOX is currently being performed for diverse sites.

EPA (U.S. Environmental Protection Agency). 1997. *Guiding Principles for Monte Carlo Analysis*. Risk Assessment Forum, U.S. Environmental Protection Agency. EPA/630/R-97/001. March 1997.

Saltelli, A. 2001. Unpublished manuscript. Sensitivity Analysis for Importance Assessment. Proceedings of a workshop held June 11-12, 2001, at North Carolina State on "Sensitivity Analysis Methods." Joint Research Centre of the European Communities in Ispra. 36 http://www.ce.ncsu.edu/risk/pdf/saltelli.pdf

Coralville Sensitivity Analysis Demo

Demonstration of inputs and outputs from Coralville analysis



Uncertainty Analysis

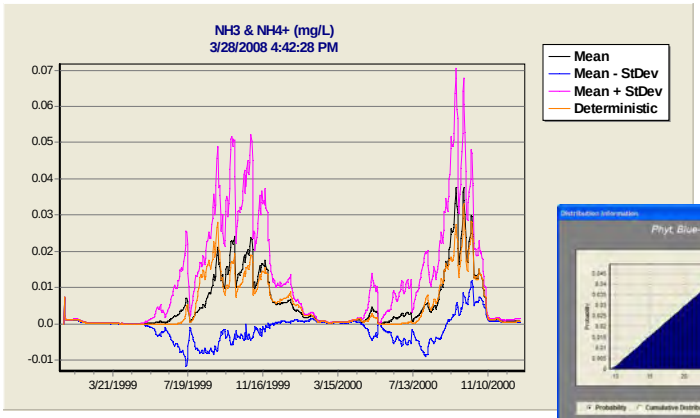
- Uncertainty analyses describe sources of incertitude and variability
- There are many sources of uncertainty e.g.
  - parameter uncertainty
  - model uncertainty due to necessary simplification of real-world processes
- Monte Carlo analysis is a statistical sampling technique that allows us to obtain a probabilistic approximation to the effects of parameter uncertainty
- AQUATOX Utilizes Monte Carlo analysis with efficient “Latin Hypercube Sampling” (reduces required iterations)

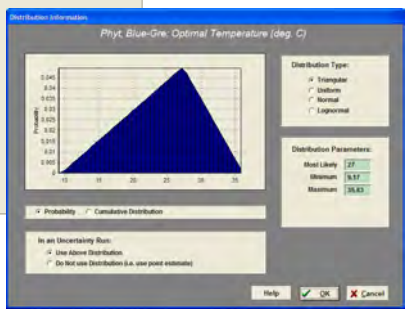
EPA (U.S. Environmental Protection Agency). 1997. *Guiding Principles for Monte Carlo Analysis*. Risk Assessment Forum, U.S. Environmental Protection Agency. EPA/630/R-97/001. March 1997.

A formal uncertainty analysis often follows a sensitivity analysis as the modelers may limit the parameters they are varying to those that have proven to be sensitive over the range of uncertainty.

Blue Earth Uncertainty Analysis Demo

Demonstration of inputs and outputs from Blue Earth River, MN

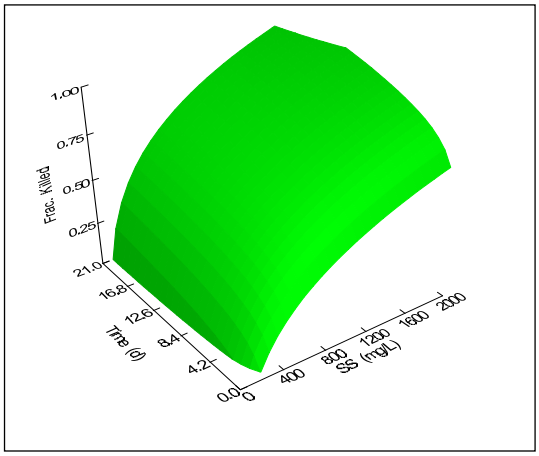




Sediment Effects Overview

- Suspended and bedded sediment effects
  - Mortality

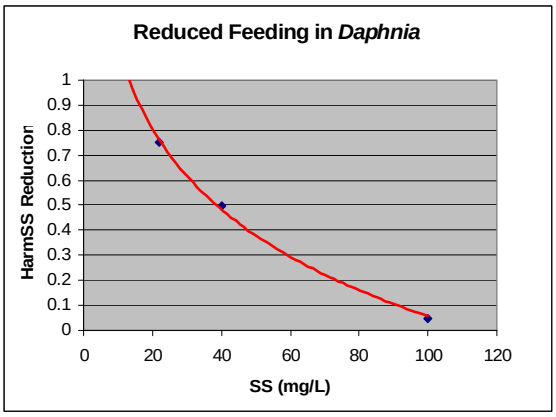
- Highly Sensitive
- Sensitive
- Tolerant
- Intolerant



Sediment Effects Overview

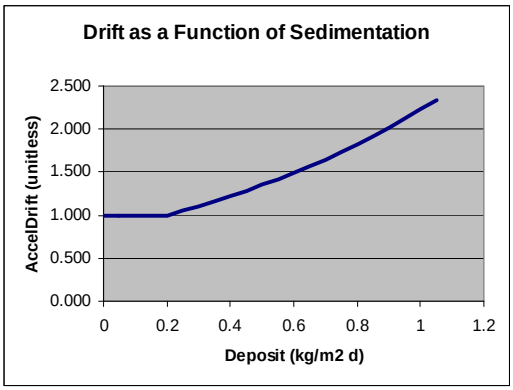
- Suspended and bedded sediment effects
  - Mortality
  - Reduced Feeding

- Dilution effect
- Direct effects due to clogging of filter feeding apparatus



Sediment Effects Overview

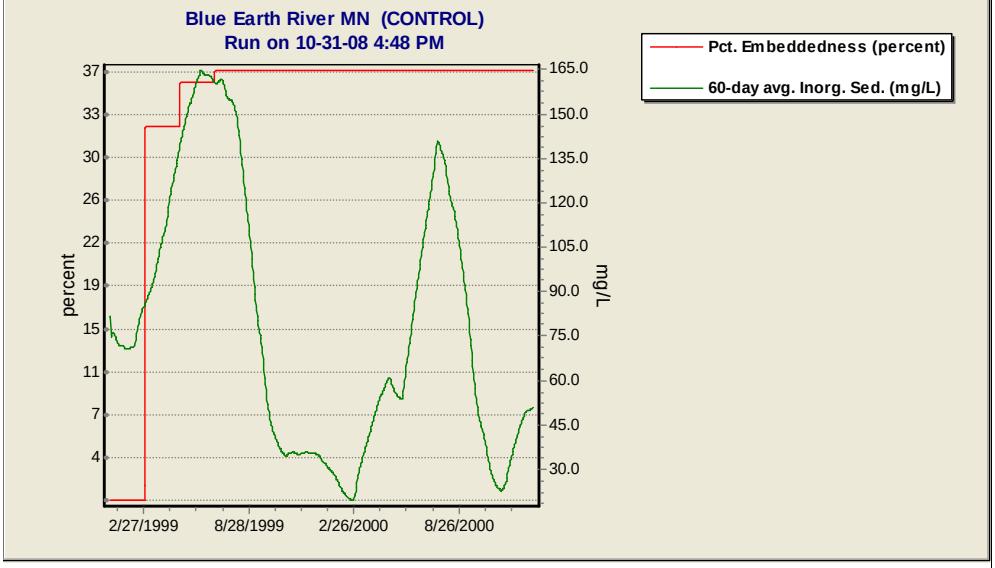
- Suspended and bedded sediment effects
  - Mortality
  - Reduced Feeding
  - Increased drift of grazers due to sedimentation



Sediment Effects Overview

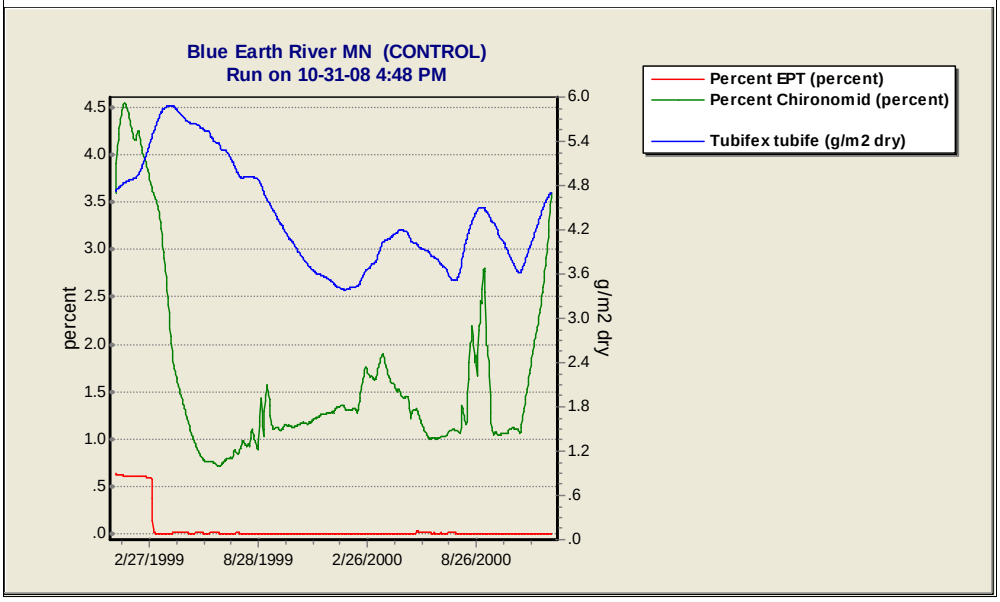
- Suspended and bedded sediment effects
  - Mortality
  - Reduced Feeding
  - Increased drifting of grazers due to sedimentation
  - Deposition of fines and affect on invertebrates and salmonid reproduction
    - Percent Embeddedness calculated as a function of 60-day average TSS

Percent embeddedness is computed from 60-day deposition rate (a function of TSS)

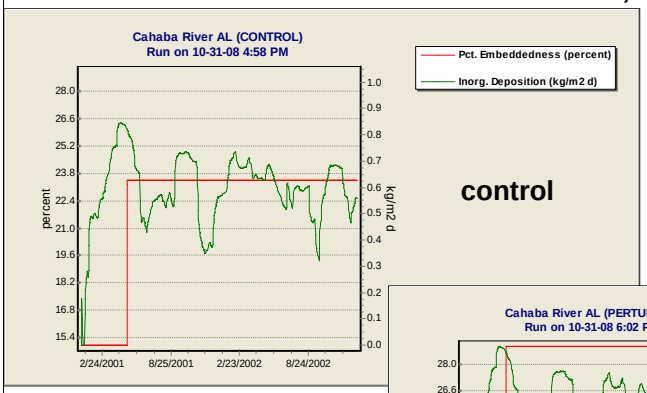


Percent Embeddedness = % sediment surrounding pebbles

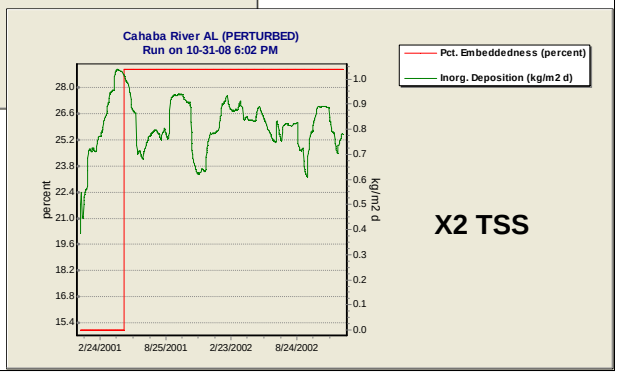
Mayflies, stoneflies, & caddisflies (EPT) are sensitive to embeddedness, chironomids aren't



Doubling TSS increases embeddedness in Cahaba River, AL

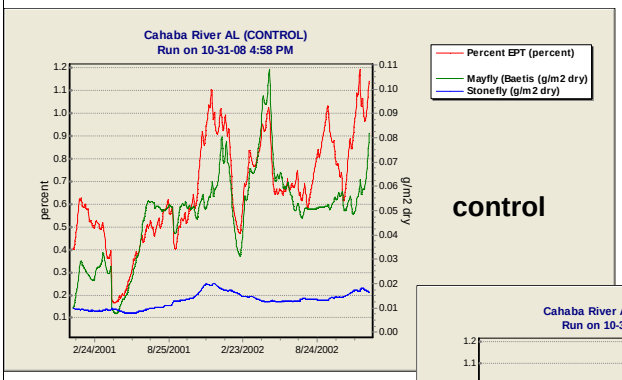


control

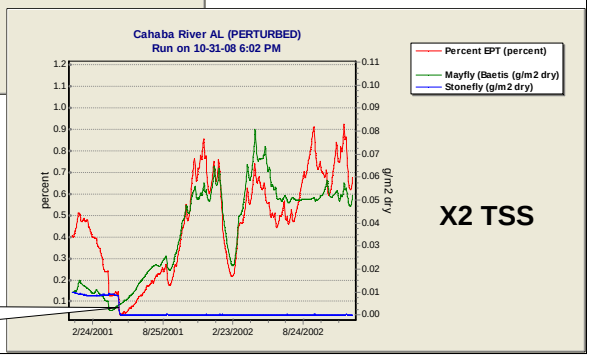


X2 TSS

Doubling TSS loadings adversely impacts insect community in Cahaba River, AL



control



X2 TSS

stoneflies crash

Closure

- Topics not yet covered (time-permitting)
  - Diel Oxygen
  - Sand-Silt-Clay model
  - Multi-layer sediment model
- Final Q&A

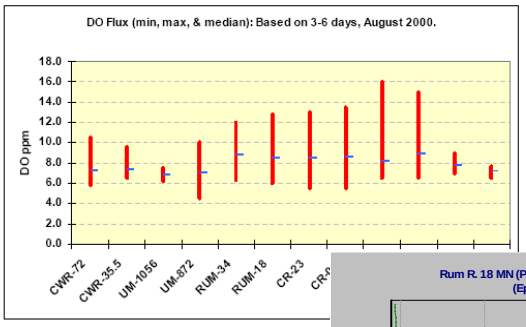
Please Keep in Touch!

- Applications help drive enhancements, example studies and data libraries
- Growing user community builds robustness and confidence
- Continued model and user support
  - One-on-one technical support is available
  - AQUATOX listserver
- Visit the AQUATOX web site
  - http://epa.gov/ost/models/aquatox/

Listserver URL:
http://www.epa.gov/waterscience/models/aquatox/listserv.html

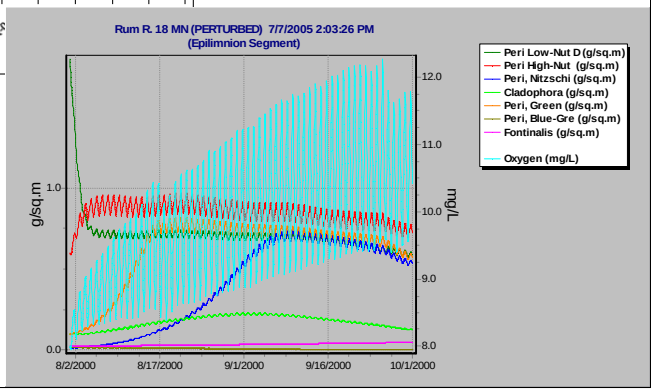
Diel Oxygen, Light; Hourly time-step

Figure 4. Dissolved oxygen flux based on continuous measurement.



AQUATOX can now run with an hourly time-step including hourly light inputs. This results in a simulation of oxygen concentrations on an hourly basis

Monitoring data indicate that oxygen levels fluctuate daily

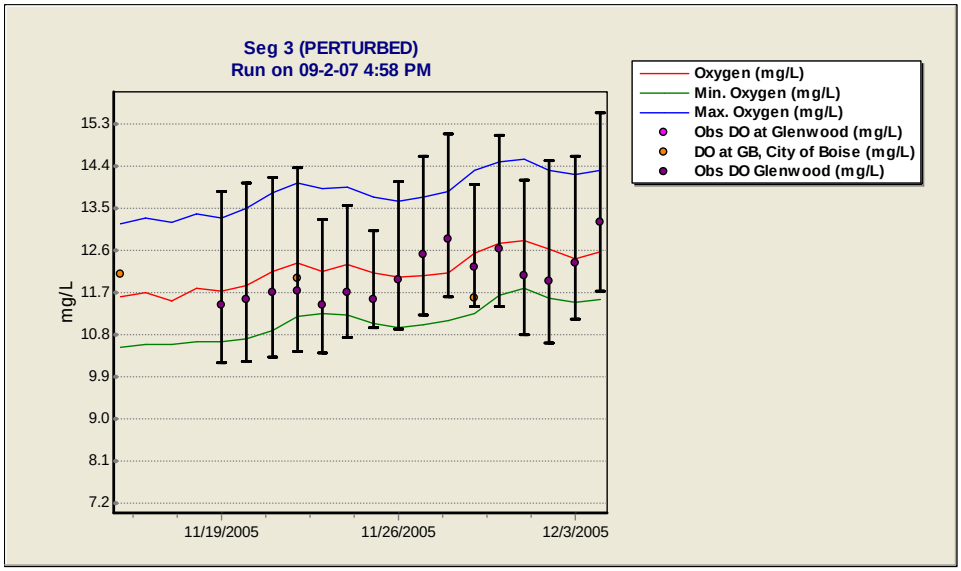


Photosynthesis can be calculated on an hourly basis.

The Light Limitation calculation is modified during hourly simulation to remove the now irrelevant photoperiod.

Stress due to low light conditions remains calculated with an average daily light value.

Diel Oxygen, Light; Hourly time-step



Predicted and observed diel dissolved oxygen at Glenwood Bridge, Lower Boise River, Idaho.

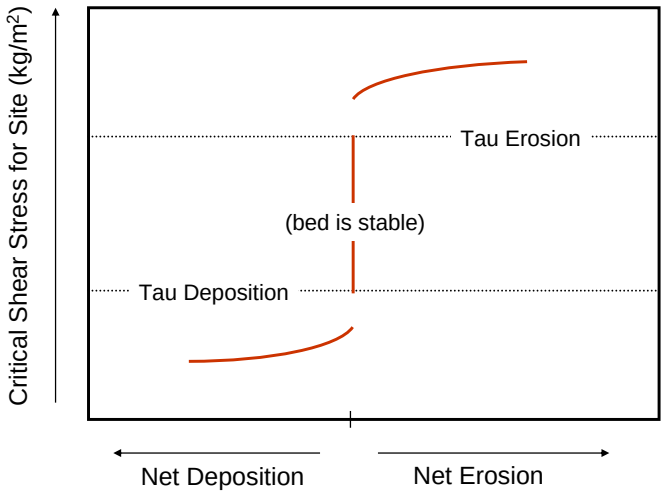
Modeling Inorganic Sediments (sand, silt, and clay)

- Stream simulations only
- Scour, deposition and transport of sediments
- River reach assumed short and well mixed
- Daily average flow regime determines shear stresses
- Feedback to biota through light limitation, sequestration of chemicals

The sediment transport component of 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: 1) sand, with particle sizes between 0.062 to 2.0 millimeters (mm), 2) silt (0.004 to 0.062 mm), and 3) 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. At present, inorganic sediments in standing water are computed based on total suspended solids loadings.

Output variables resulting from the inclusion of sand/silt/clay include suspended sand, silt,and clay, bed sheer, and bed depth.

Critical Shear Stress for Erosion and Deposition Key Parameters

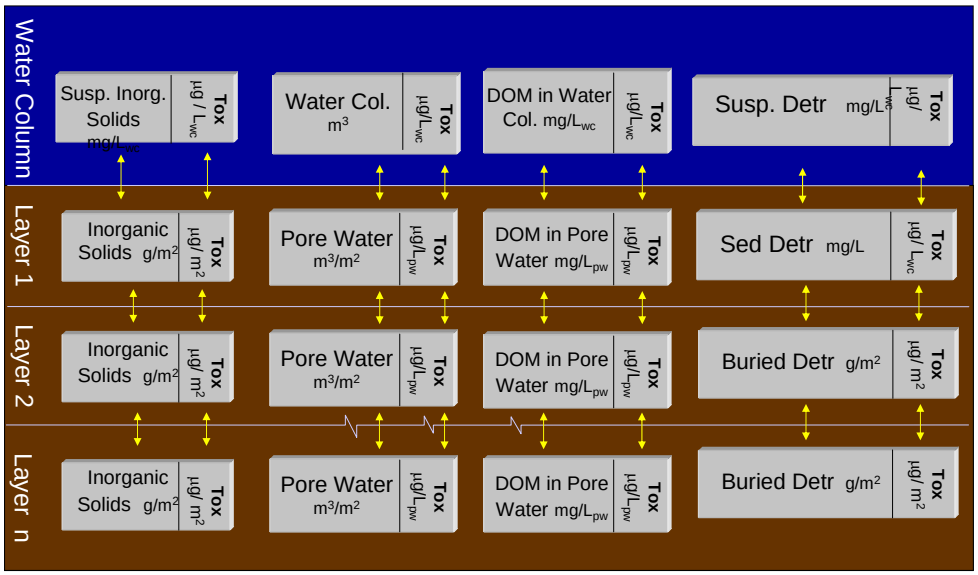


These two parameters are specified for silt and clay and can be found in the Stream section of the Site underlying data. This section of model is identical to HSPF. These parameters can be highly site-specific and are usually used as calibration parameters when calibrating the HSPF inorganic sediment model.

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.

When the inorganic sediments model is included in a stream simulation, particulate detritus moves to and from the bed to and from the water column along with the deposition and resuspension of the Cohesives compartment.

AQUATOX Multi-Layer Sediment Model based on the IPX module (Velleux et al. 2000)



- From left to right each sediment layer is composed of inorganic solids, water, dissolved organic matter, and organic solids. Each category can have toxicant sorbed to it, or in the case of water, dissolved within it.
- In this case the top layer (Layer 1) is the active layer and interacts with the water column through scour, deposition and diffusion. This layer changes height and if it gets too big it is split into two layers; if it gets too small it is joined with the layer below it.
- Lower layers only interact through pore-water diffusion.

Velleux, M., S. Westenbroek, J. Ruppel, M. Settles, and D. Endicott. 2000. A User's Guide to IPX, The In-Place Pollutant Export Water Quality Modeling Framework, Version 2.7.4. US Environmental Protection Agency, Grosse Ile, MI.