AQUATOX Training Workshop (Day 2)

Web Training Materials, August 2012

Based on Workshop Given for EPA Region 6, Dallas, Texas, December 2010 and Columbia River Intertribal Fish Commission, November 2011

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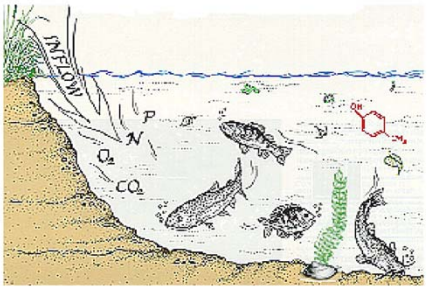


Lab 4: Application to Minnesota Rivers

Objectives:

- familiarization with using model as forecasting tool
- analyzing impacts of development on pristine and moderately impacted rivers

If bank erosion along the Rum River doubled TSS, what would be the impacts? Use **Lab4_Rum R MN.aps.**

If summer houses with septic tanks doubled TP in the Crow Wing River, what would be the impacts? Use **Lab4_Crow Wing R MN.aps.**

You can set up the simulations and let them run during the next lecture, then we will discuss the results.

The Rum River is a wild and scenic waterway with smallmouth bass and walleye fishing within commuting distance to St. Paul. Dairy farms are predominant.

The Crow Wing River is a broad, shallow river that is popular for float trips. The watershed is forested with numerous small lakes.

*If the simulations take too long to run, open **Lab4_Rum R MN 2X TSS.aps** and **Lab4_Crow Wing R 2X TP. MN.aps.***

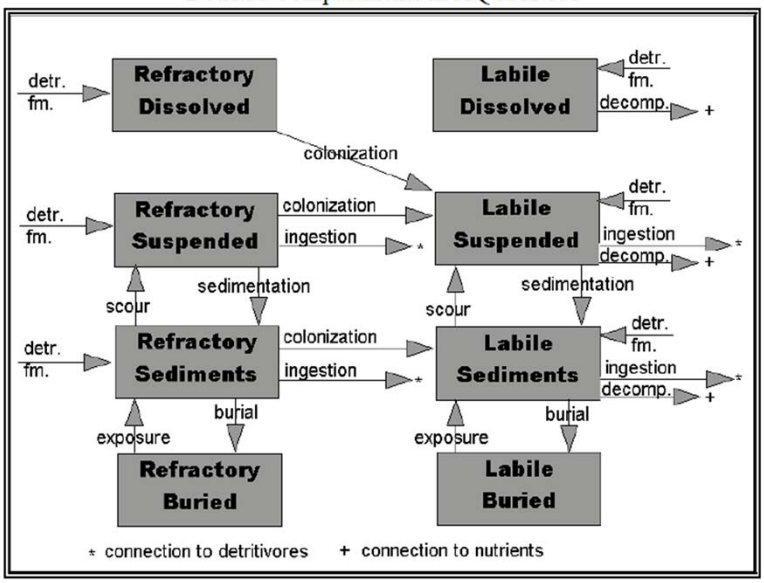
Remineralization

- Detritus
- Variable stoichiometry
- Nutrients
- Variable pH
- Dissolved oxygen and anoxia

Remineralization is covered in detail in Chapter 5 of the Technical Documentation.

Detritus Compartments in AQUATOX

Figure 54
Detritus Compartments in AQUATOX



Remineralization Discussion:

Detritus is formed in several ways: through mortality, gamete loss, sinking of phytoplankton, excretion and defecation.

A fraction of mortality, including breakage of leaves from macrophytes, is assumed to go to refractory detritus; a much larger fraction goes to labile detritus.

Labile detritus decomposes quickly; refractory much more slowly.

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

Variable Stoichiometry

- Ratios of elements in organic matter are editable on an organism by organism basis as well as for detrital state variables.
- Stoichiometry can vary among compartments but is constant within a compartment
- Nutrient mass balance tracked to machine accuracy (nitrogen & phosphorus).
- Nutrient fate can be tracked as well as mass of nutrients dissolved in water, in detritus, in animals, and in plants.

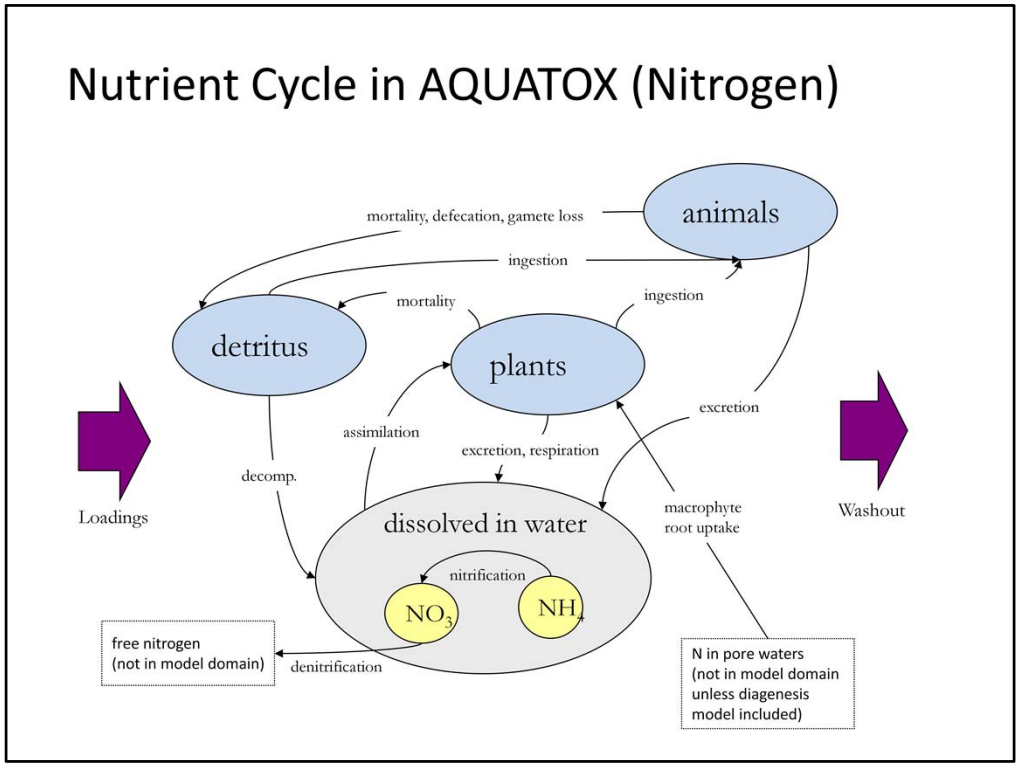
Default Nutrient to Organic Matter Ratios

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

- The actual values are not particularly important in this slide, the slide is just being shown for a couple of reasons:
  - It shows that AQUATOX comes with default values.
  - It indicates the type of data that can be entered into AQUATOX if available, specifically the N to Organic Matter and P to Organic Matter ratios.

Sterner, R. W., and N. B. George. 2000. Carbon, Nitrogen, and Phosphorus Stoichiometry of Cyprinid Fishes. *Ecology* 81: 127-140.

Sterner, R. W., and J. J. Elser. 2002. *Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere*. Princeton University Press, Princeton NJ.

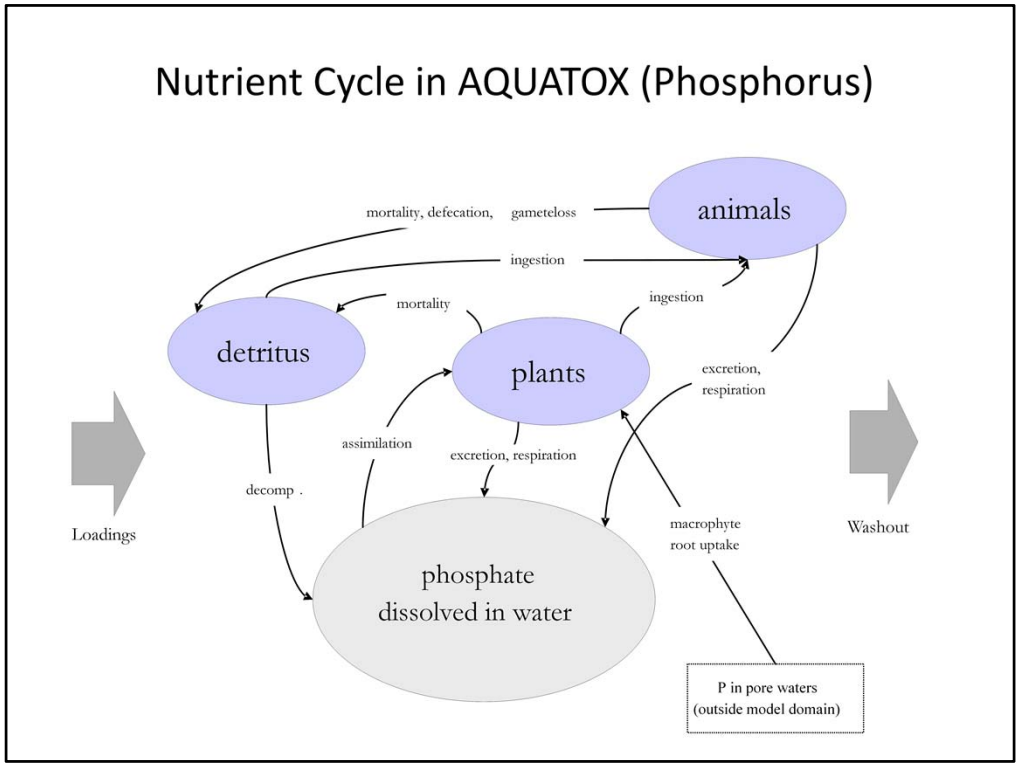


•While this graph looks complex, there is really a fairly straightforward cyclical nature to the movement of nutrients within AQUATOX. Nutrients are taken up into higher organisms through ingestion and assimilation , nutrients are released back into the water column through mortality, defecation, and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

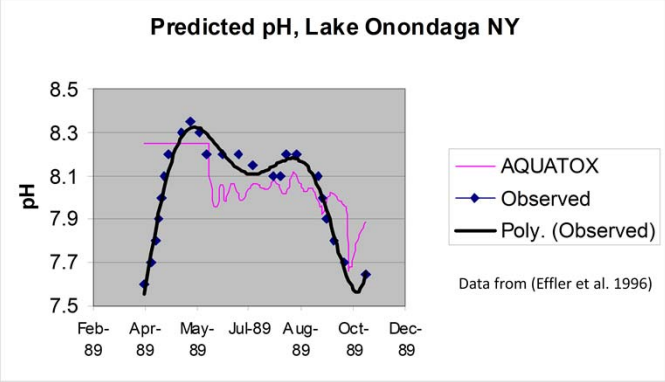
•The un-ionized form of ammonia is toxic to invertebrates and fish. Therefore, it is often singled out as a water quality criterion. Un-ionized ammonia is in equilibrium with the ammonium ion, NH4+, and the proportion is determined by pH and temperature



In addition to the pathways shown, AQUATOX Release 3 can simulate precipitation of $CaCO_3$ with sedimentation of sorbed P.

Dynamic pH also added to variable stoichiometry version:

semi-empirical computation employed for simplicity as in (Small and Sutton 1986; Marmorek et al. 1996) :



Dynamic pH is important in simulations for several reasons:
• pH affects the ionization of ammonia and potential resulting toxicity;
• pH affects the hydrolysis and ionization of organic chemicals which potentially has effects on chemical fate and the degree of toxicity;
• pH also affects the decay of organic matter and denitrification of nitrate which could eventually feed back to the animals;
• if pH exceeds 7.5, calcite precipitation can take place which has a significant effect on the food-web

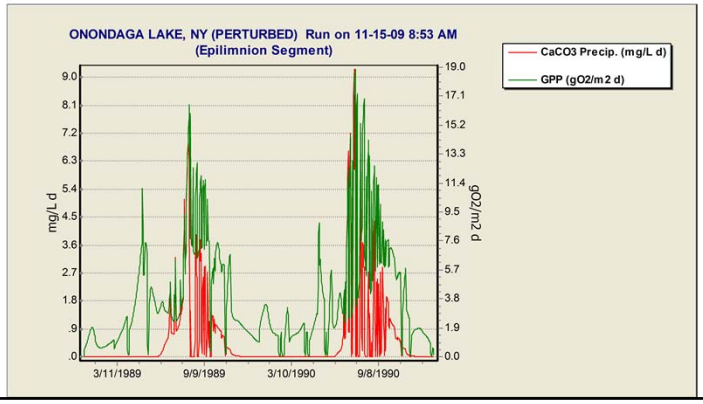
Many models follow the example of Stumm and Morgan (1996) and solve simultaneous equations for pH, alkalinity, and the complete carbonate-bicarbonate equilibrium system.

- There are several reasons to go with a simpler pH formulation rather than the more complex formulation:
    - often detailed data are not available;
    - the iterative solution of the simultaneous chemical equations entails an additional computational burden;
    - precision of complex chemical models is unnecessary for ecosystem models.
- Only additional parameter required for AQUATOX to model pH in this manner is total alkalinity.
- This construct is applicable to pH 3.75 – 8.25.

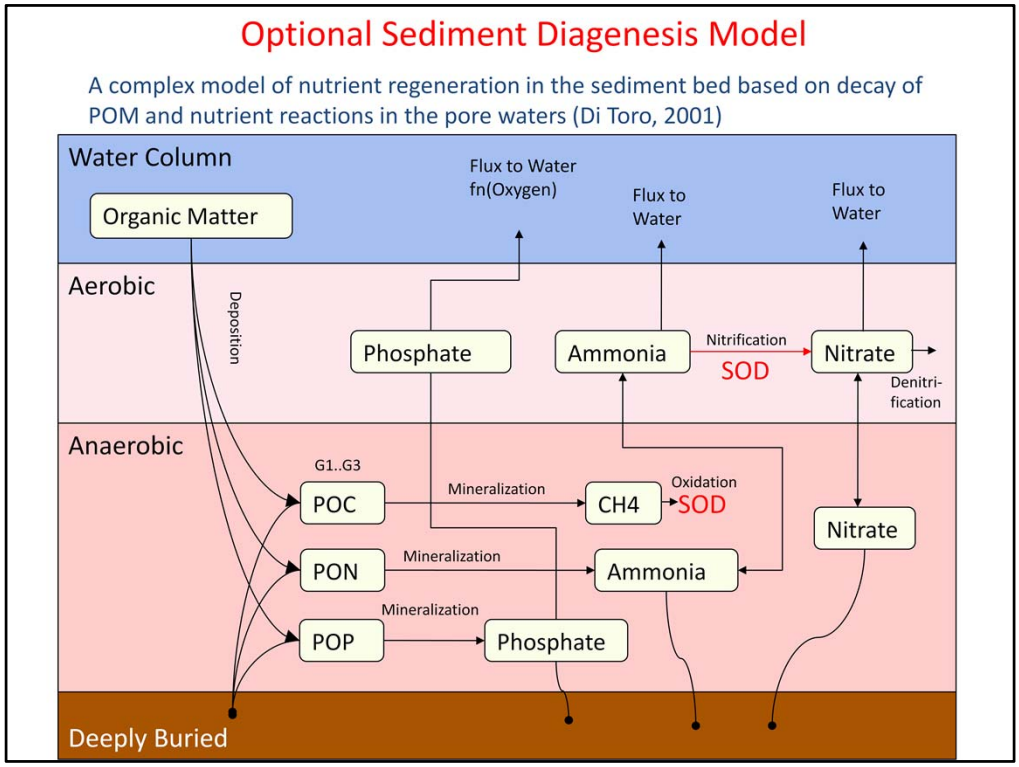
For more info. see Marmorek et al., 1996; Small and Sutton, 1986; Stumm et al., 1996.

Calcium Carbonate Precipitation

- Predicted as a function of pH and algal type
  - When pH >=7.5, precipitation is predicted
  - Precipitation rate is dependent on photosynthesis rate (gross primary production) in some, but not all, plants
- $CaCO_3$ sorbs phosphate from the water column



At high pH CaCO3 comes out of solution, precipitates, and takes PO4 along with it. This process is mediated by algae, so precipitation parallels photosynthesis (shown here as Gross Primary Production).



AQUATOX has been modified to include a representation of the sediment bed as presented in Di Toro's book on 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 most likely to occur.

Key Points: Diagenesis Model

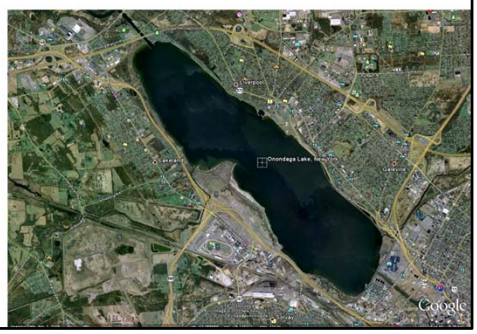
- Two sediment layers: thin aerobic and thicker anaerobic
- When oxygen is present, the diffusion of phosphorus from sediment pore waters is limited
  - Strong P sorption to oxidized ferrous iron in the aerobic layer (iron oxyhydroxide precipitate)
  - Under conditions of anoxia, phosphorus flux from 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
- Steady-state mode dramatically reduces execution time

Sediment Diagenesis Model: Simplifying Assumptions

- Model assumes a depositional environment (no scour is modeled).
- Two layers of sediment are modeled.
- Aerobic (top) layer is 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.

Sediment Diagenesis Demo

- Lake Onondaga, NY
  - Significant nutrient inputs from wastewater treatment plant; combined sewers
  - successive algal blooms
  - hypoxia in hypolimnion
  - build-up of organic sediments in bottom
  - More details to follow!



I will start by taking an existing simulation without sediment diagenesis included and modifying it to show the effects / capabilities of this model.

Feel free to follow along during this demo or to play different games with this simulation.

1. Open **Onondaga NY.aps** or **Onondaga NY Results.aps** to open a version that has been run already.
2. Run the model as-is as "control."
3. Examine results briefly. Oxygen and chlorophyll *a* predictions could improve.
4. Look at the sediment bed setup (L-Detr-Sed & R-Detr-Sed Initial Conditions of 37.2 g/m^2 and 3683 g/m^2 respectively)
5. Add the sediment diagenesis model. Note that the refractory detritus compartments disappeared.

Sediment Bed Initialization

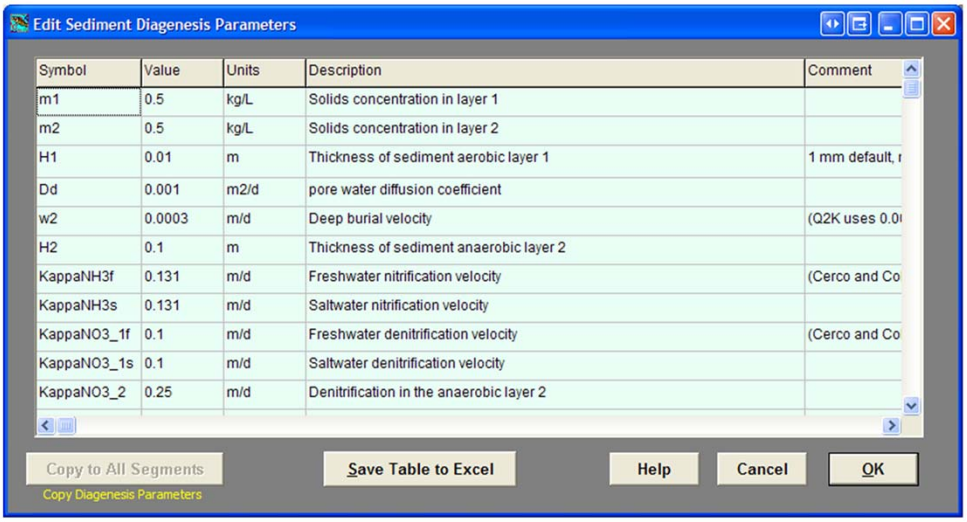
AQUATOX_Sed_Bed_Inputs.xls

INPUTS			AQUATOX "CLASSIC" PARAMS			SED-DIAGENESIS PARAMS		
Name	*Value*	*Units*	*Name*	*Value*	*Units*	*Name*	*Value*	*Units*
foc	0.01	frac OC	L Detr Sed	37.2	g/m2	POC G1	196	g C/m3
depth	0.1	meters	R Detr Sed	3683	g/m2	POC G2	38766	g C/m3
sed dens.	3720	kg/m3				POC G3	196	g C/m3
frac. Labile	0.01							
						PON G1	29	g N/m3
Diagenesis Only:						PON G2	147	g N/m3
frac G3 (nonreactive)	0.01					PON G3	0.7	g N/m3
						POP G1	6.7	g P/m3
Diagenesis Assumptions:						POP G2	14.7	g P/m3
						POP G3	0.07	g P/m3
P to Org, Refr	0.0002	frac dry						
N to Org, Refr	0.002	frac dry						
P to Org, Labile	0.018	frac dry						
N to Org, Labile	0.079	frac dry						
C to Org, All	0.526	frac dry						

This spreadsheet, which is included in the “STUDIES” directory of every AQUATOX installation provides useful tools for initializing the AQUATOX “Classic” sediment bed or alternatively the nine input parameters required for the Sediment Diagenesis model. We will explore this spreadsheet and its use to set model initial conditions.

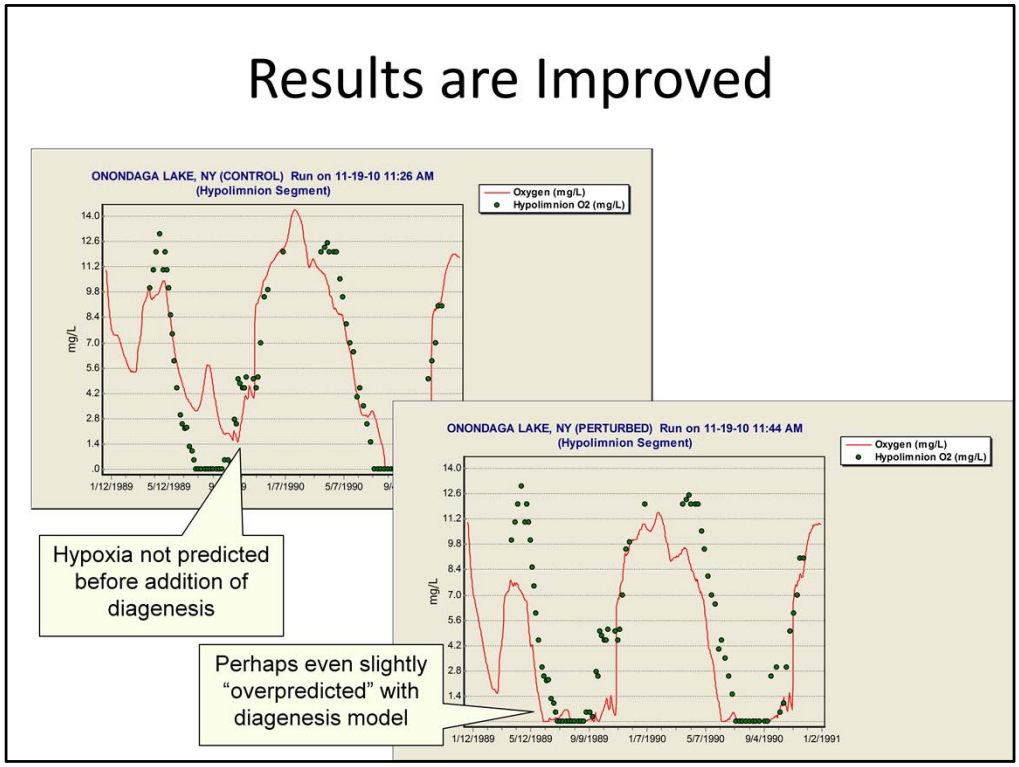
Sediment Diagenesis initial conditions for carbon, nitrogen, and phosphorus will be set to the values as shown above.

Sediment Diagenesis Parameters



The thickness of sediment aerobic layer 1 is an important determinant of model execution speed. We rarely run this model with an aerobic layer of less than 1 cm. We are working on a version in which the aerobic layer is solved with a steady-state formulation that will remove this sensitivity. In the short run, though, it was much easier to integrate the differential equations within this layer into the AQUATOX solver. This also enabled the maintenance of nutrient and organic matter mass balance within the simulation.

DiToro states, p 363: "*For phosphorus [parameters], however, the variation is extreme (Table 15.4). The aerobic layer partition coefficients vary from 30000 to 10000 to the low 400 for the MERL nutrition experiment. By contrast the anaerobic layer partition coefficient varies from 100 to 1000 an order of magnitude. The variables that affect phosphate partitioning include pH, sediment composition, and solution ionic strength.*"



After re-running the model we see that results for all three categories have improved (epilimnion oxygen, hypolimnion oxygen, and chl-*a*).

Will spend a moment with percent exceedance graphs to get a better sense of these improvements.

Also, graphs of POC Concentrations, POC deposition, SOD, P. Diagenesis flux will be created and examined.

Full results and graphs are available as **Onondaga NY Diagenesis Lab.aps**

AQUATOX also simulates:

- Diel oxygen
- Effects of low dissolved oxygen
- Ammonia toxicity

These will be covered later this afternoon

AQUATOX as a Part of BASINS

Integration of tools

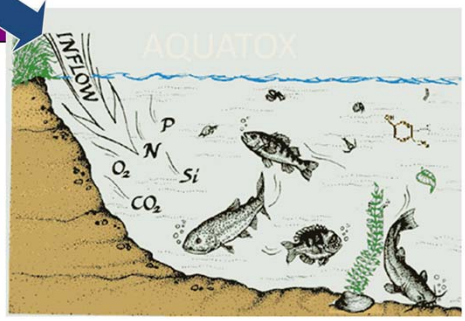
AQUATOX BASINS Linkage

BASINS
Better Assessment Science Integrating Point and Nonpoint Sources

Integrates point/nonpoint source analysis with effects on receiving water and biota

Provides time series loading data and GIS information to AQUATOX

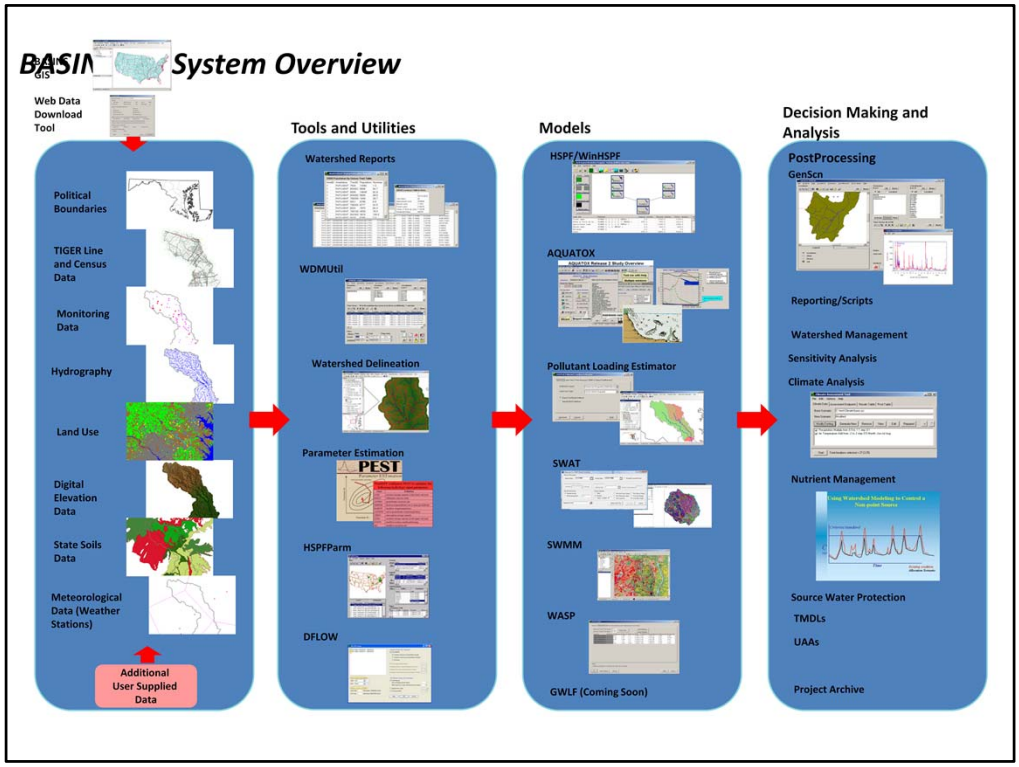
Creates AQUATOX simulations using physical characteristics of BASINS watershed



Originally introduced in 1996 with subsequent releases in 1998, 2001, and 2004, BASINS is a multipurpose environmental analysis system designed for use by regional, state, and local agencies in performing watershed and water quality-based studies. This system makes it possible to quickly assess large amounts of point source and non-point source data in a format that is easy to use and understand. Installed on a personal computer, BASINS allows the user to assess water quality at selected stream sites or throughout an entire watershed. This invaluable tool integrates environmental data, analytical tools, and modeling programs to support development of cost-effective approaches to watershed management and environmental protection, including TMDLs.

More information can be found on the BASINS web site at http://water.epa.gov/scitech/datait/models/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.

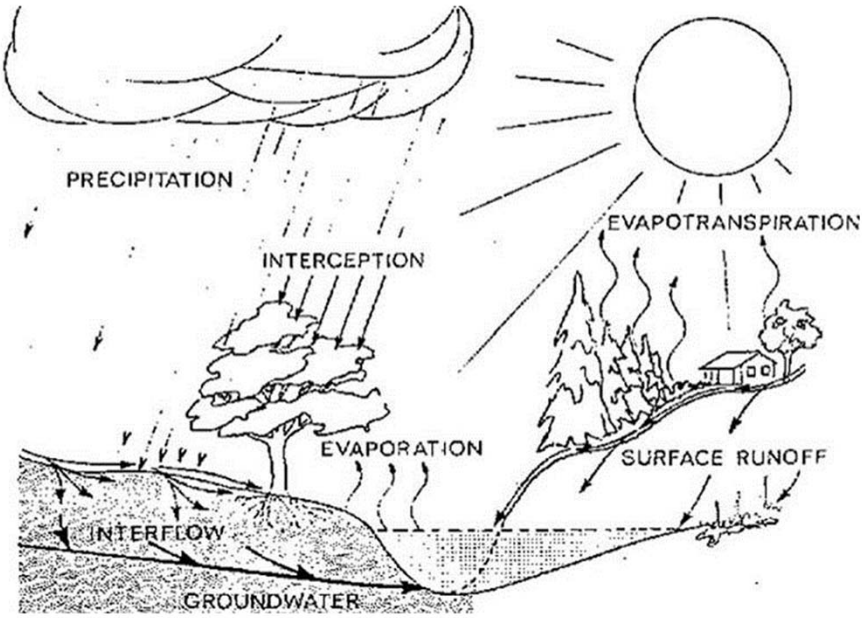


BASINS is a watershed analysis and modeling system that contains basic GIS data, data management and analytical tools, watershed and receiving water models, and a “download tool” for obtaining data from the Web. It is designed to be modular, and therefore customizable, so that each user can work with just the tools he or she needs. It is also designed for straightforward incorporation of additional models and tools.

The biggest change in BASINS 4.0 over 3.1 is the switch to open source GIS software and the ability to transfer and share GIS standard data (shapefile, dbf, and GeoTiff) between other licensed GIS software. Also new to BASINS 4 is a Windows-based Climate Assessment Tool (CAT), for assessing potential impacts of changing climate on stream flows and pollutant loads has been added as a "plug-in" program which interfaces with WinHSPF.

The components of BASINS that are pertinent to AQUATOX are WinHSPF, SWAT and GenScn. WinHSPF is the Windows interface to HSPF Version 12, a watershed model. SWAT is another watershed model specifically for agricultural watersheds. GenScn is a model post processing and scenario analysis tool that is used to analyze output from HSPF, SWAT and AQUATOX.

Simplified Hydrologic Model

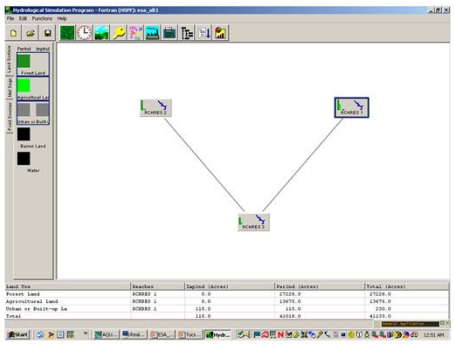


This is a very simplified representation of the hydrologic processes that watershed loading models simulate. The ability to link watershed models directly to AQUATOX can enable analysis of potential effects of changes in the watershed on the stream biota.

WinHSPF

Hydrologic **S**imulation **P**rogram–**F**ORTRAN

- Predicts loadings in mixed land use settings for bacteria, metals, ***sediments, nutrients, algae as Chlorophyll a***
- Considers point source and nonpoint source loadings
- Natural and developed watersheds and water systems
- Continuous simulation, hourly meteorology
- Lumped parameters by landuse/watershed
- **AQUATOX 3.1 will include a link to HSPF (external to BASINS)**



Note: red indicates parameter that may be loaded into AQUATOX

The first watershed model in BASINS is HSPF; the version within BASINS is named WinHSPF. HSPF evolved from the old Stanford Watershed Model from the 1960s. The model's greatest strength is probably its versatility. It can be used to simulate runoff and transport of nutrients, general pollutants including pesticides and metals, and eroded sediments. HSPF is a lumped parameter model where the watershed is broken into multiple sub-basins that contain one impervious segment, and up to several pervious segments that each represent different land use types. "Lumped parameter" means that the physical processes simulated are assumed to be uniform within each sub-basin; exact location on the land is not tracked.

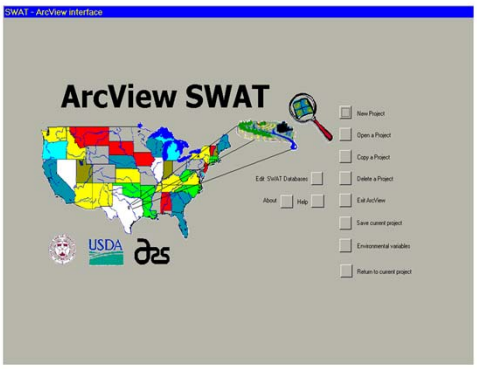
HSPF has a long history of nonpoint source modeling for TMDLs and many other purposes. It generally requires significant flow data from stream gages. HSPF outputs are time series (generally hourly, but as frequently as 15 minutes) of flow and water quality (concentrations). WinHSPF does in-stream WQ simulation for some parameters, and AQUATOX will perform the simulations for other parameters.

WinHSPF does not have the full capabilities of HSPF; AQUATOX Release 3.1 (and the draft version you are working with) includes the ability to link to HSPF external to the BASINS framework.

SWAT

Soil and Water Assessment Tool

- Physically-based, watershed scale model
- Predicts impacts of land management practices on water, sediment, and agricultural chemical yields in large complex watersheds
- Models *water and sediment movement, nutrient cycling,* crop growth, metals, pesticides, etc.
- *Current AQUATOX linkage only to SWAT in BASINS 3.1, due to different SWAT version in BASINS 4*

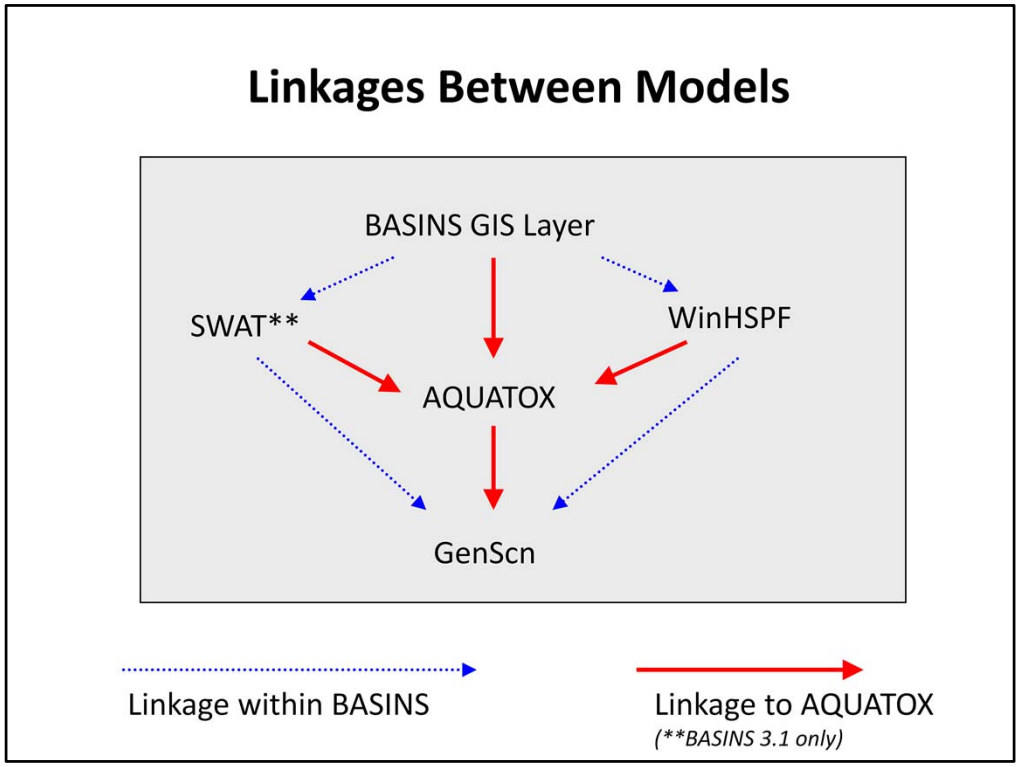


Note: red indicates parameter that can be loaded into AQUATOX

The other main watershed model in BASINS is USDA's SWAT model.

SWAT is also a lumped parameter model, which like HSPF, process land use data for a delineated watershed to set up the model. Unlike HSPF, SWAT also considers soil data (STATSGO or SSURGO) and accounts for the relationships between soil types and land uses. SWAT is designed to simulate the fate and transport of nutrients and pesticides, particularly export from agricultural land. For pesticides and fertilizers, various management practices can be simulated: different timing and application rates, and tillage operations. SWAT is particularly suited to watersheds that do not have flow gages.

A new version of SWAT has recently been added to BASINS 4; due to changes in the SWAT output format, the link to AQUATOX will require modification .



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

- BASINS GIS to AQUATOX
  - Channel geometry (length, depth, slope)
- WinHSPF to AQUATOX
  - Geometry
  - Time series: flow, water quality (nutrients, BOD, temperature, sand/silt/clay)
- SWAT to AQUATOX *(a new version of SWAT has just been added to BASINS 4; due to changes in the SWAT output format, the link to AQUATOX will require modification)*
  - 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 it correctly for AQUATOX, potentially a huge time savings for the user.

Potential Applications

- Evaluate potential effects of land use changes on aquatic biota
- Evaluate whether BMPs will lead to attainment of water quality standards
- Using new Climate Assessment Tool (CAT) linked to HSPF, evaluate effects of climate change on aquatic ecosystems
- Etc….

Use of AQUATOX in Water Quality Management Decisions

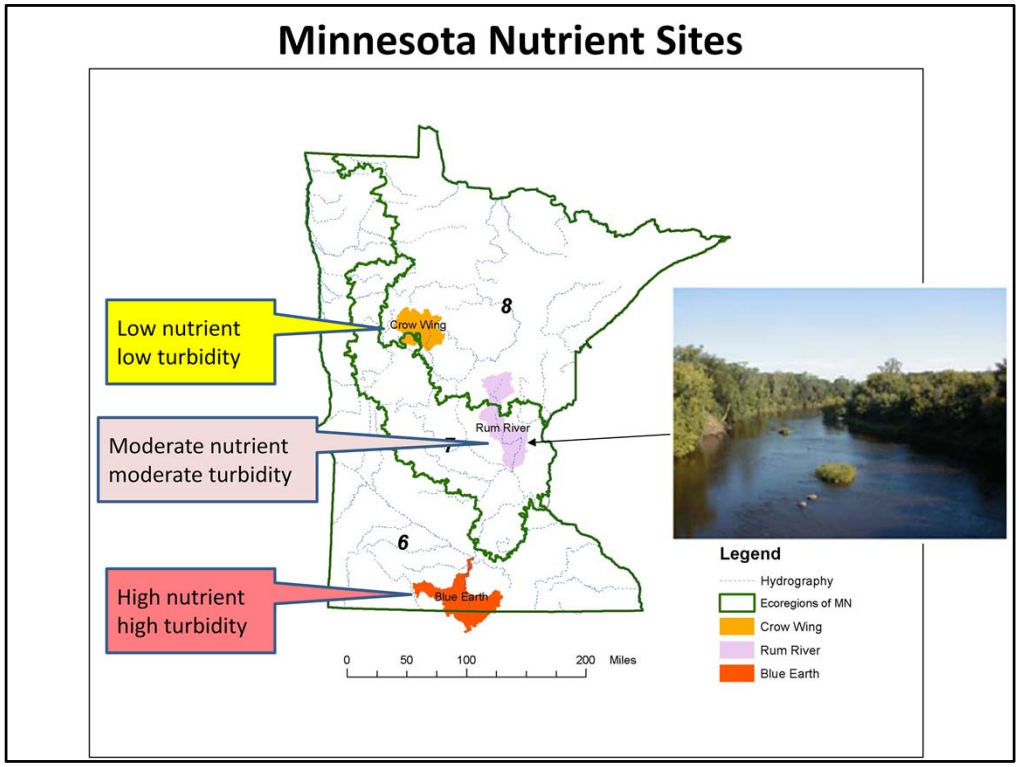
- 2008 peer review suggests AQUATOX is suited to support existing approaches used to develop water quality standards and criteria
  - One tool among many that should be used in a weight- of-evidence approach
- AQUATOX enables the evaluation of multiple stressor scenarios
  - What is the most important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

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

As an example application, we will focus on water quality targets for nutrients, 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
Canopy and light
Nutrients
Organic loads
Flow regime
Herbicides
Combination of factors



We will return to the Minnesota study, but focus on the highly eutrophic Blue Earth River.

Example Nutrient Analyses from Minnesota

- 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
  - Method #1: Accept existing chl *a* target, use AQUATOX to get corresponding TP level
  - Method #2: Use AQUATOX to develop both chl *a* and TP targets 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.

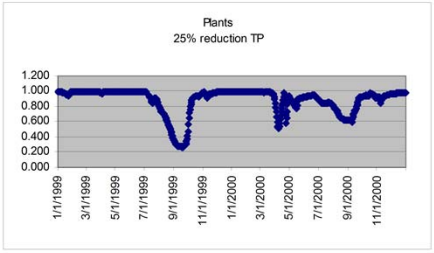
This is a demonstration project designed to investigate how AQUATOX, coupled with the watershed modeling capabilities in BASINS, could be used as a tool in the analysis of potential WQC. The project also looked at whether reasonable management practices and load reductions could be expected to lead to attainment of the criteria.

The illustrations here were developed for the purposes of the workshop and were based on preliminary model simulations, and were not the same as presented in the final paper in Environmental Management. I hope also to provide illustrations of how several of the tools in AQUATOX can be used.

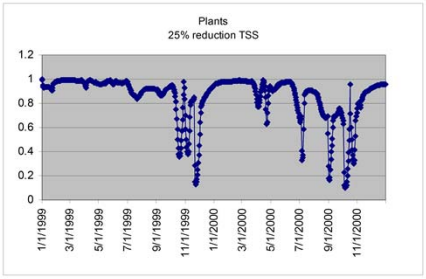
With AQUATOX calibrated across a gradient of nutrient concentrations in similarly sized rivers, we have reasonable confidence in our ability to predict mean responses to hypothetical reductions in nutrient concentrations in the high nutrient system. This exercise focused on the Blue Earth river as an 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.

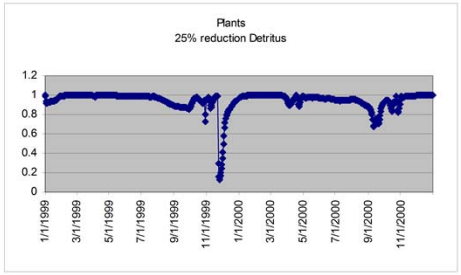
Step 1: Stressor ID using Biotic Index

Algal community response dependent upon stressor



- Reductions in TSS and TP loadings had significant effects on algal community
- BOD reductions had only short-lived effects
- NO3 and NH3 reductions had little effect





First we used one of the biological metrics calculated by 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 4.5 of the Release 3 Technical Documentation for more information.

First I changed the loadings for TSS, TP, BOD, NH3 and NO3 individually to see which made the greatest difference in the plant community (in this instance, the algae). 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 eliminated NH3, NO3 and BOD as significant stressors, and focused on TP and TSS reductions.

Step 2: Run AQUATOX with multiple load reduction scenarios.

Calculate and compare Mean TP and Chl a

TP/TSS multiplier	Mean TP (ug/L)	Mean chl_*a* (ug/L)
1.0 (Baseline condition)	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
Ecoregional criteria	***118.13***	***7.85***

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.

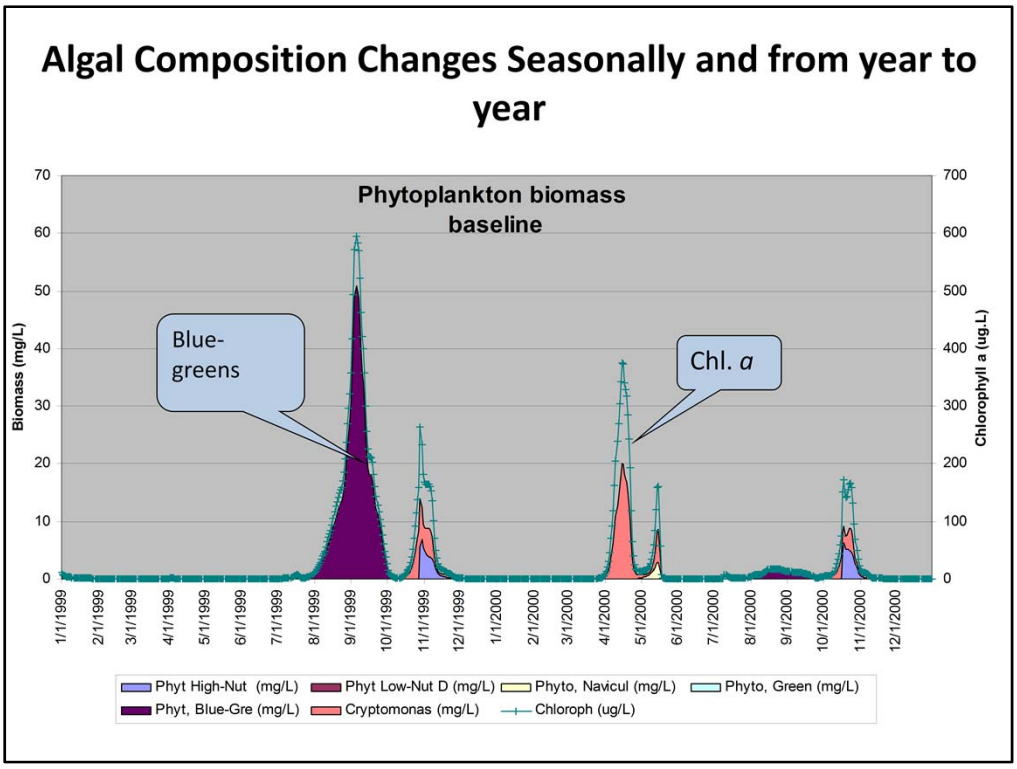
Step 3a: Water Quality Target Development Method #1

- Focus on TP and chl *a* only
- Model results: 80% TP reduction required to meet 7.85 ug/L chl *a*
- Ecoregional WQC: 56% TP reduction required to meet same chl *a* level

Step 3b: Water Quality Target Development
Method #2

- Focus on algal community, not total chl *a*
  - Blue Earth had periodic blooms of blue-green algae (cyanobacteria)
    - Noxious, taste and odor problems
  - At what levels of total chl a do blue-greens reach an "acceptable" proportion of total algae? What is the corresponding TP?
- Where might there 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 into WQS.

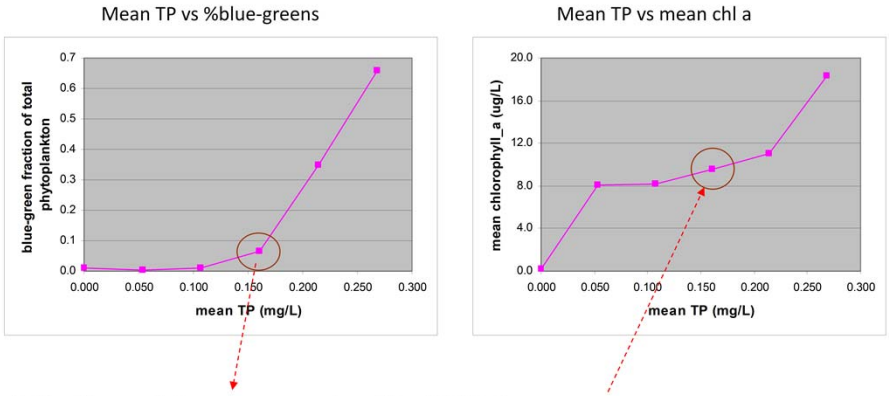


Use the Export function to export results to Excel; and graph them to get visual representation of algal composition changes over time. *(Note: export to Excel is no longer necessary due to the enhanced graphing capabilities of Release 3; however Excel has much more powerful statistics, and exporting results may still be desirable.)*

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 a high-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

- Method 2: Use AQUATOX to estimate chl *a* level associated with a shift in algal community.



Inflection point – corresponds with <10% blue-greens, 0.161 mg/L mean TP, and. 9.5 ug/L mean chl_a.

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.

Summary of Minnesota Analysis

- Stressor-identification: Algal responses linked quantitatively with TP and TSS levels.
- Pollutant reduction scenarios: derived algal response to hypothetical reduction scenarios
- Target development: Derived alternative hypothetical criteria, one based on ecologically meaningful endpoint (%blue-greens).
  - Decision of "acceptable" target is policy question
- Attainability: Link to watershed loading model. Results suggest both 304(a) and hypothetical criteria may be very difficult to achieve in Blue Earth river, 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.

In a next step, though not shown here, 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. These model runs suggested that even extensive use of BMPs might not lead to attainment of the criteria.

Other Possible Analyses

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

Release 3 has additional output and biological metrics that offer additional ways to compare scenarios:

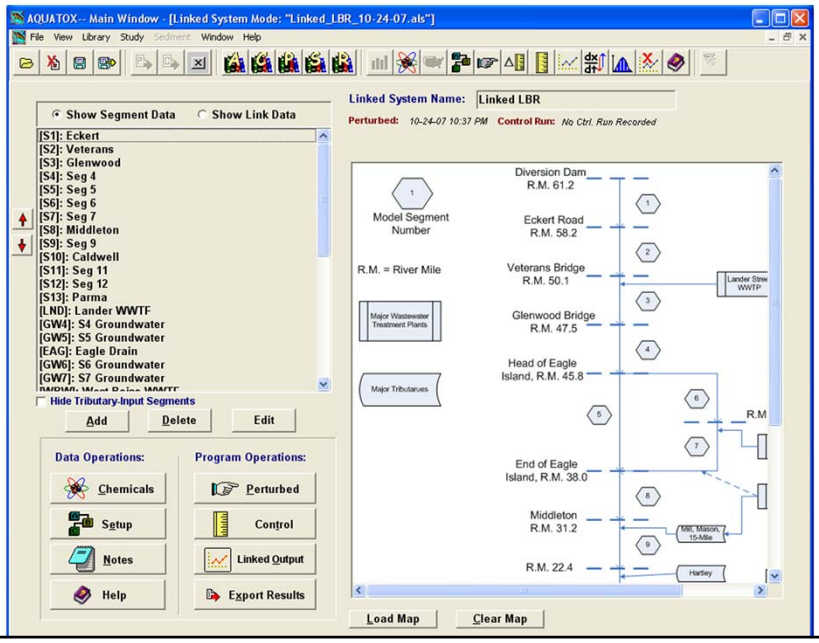
% EPT, % Chironomids, % Amphipods, % Blue-Greens, % Diatoms, % Greens, Gross Primary Production, Turnover, Trophic State Indices

Demonstration: 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.

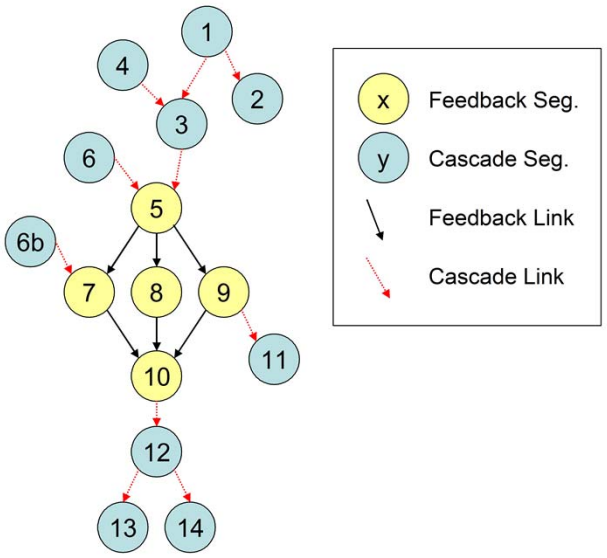
Cascade & Feedback Linkages

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
  - All segments must have the same state variables
- Inflows, point-sources and non-point-source loadings for each segment
- Tributary or groundwater inputs and/or any withdrawals

Interface Demonstration to follow

We will open up **"Tenkiller Ferry Lake OK Results.als"**

This simulation has one river segment linked to the other segments in "**cascade mode.**" This links to eight segments that are linked in "**feedback mode.**" There are also four **"tributary inputs"**

This model takes a while to run so we're opening up a pre-run version with results attached.

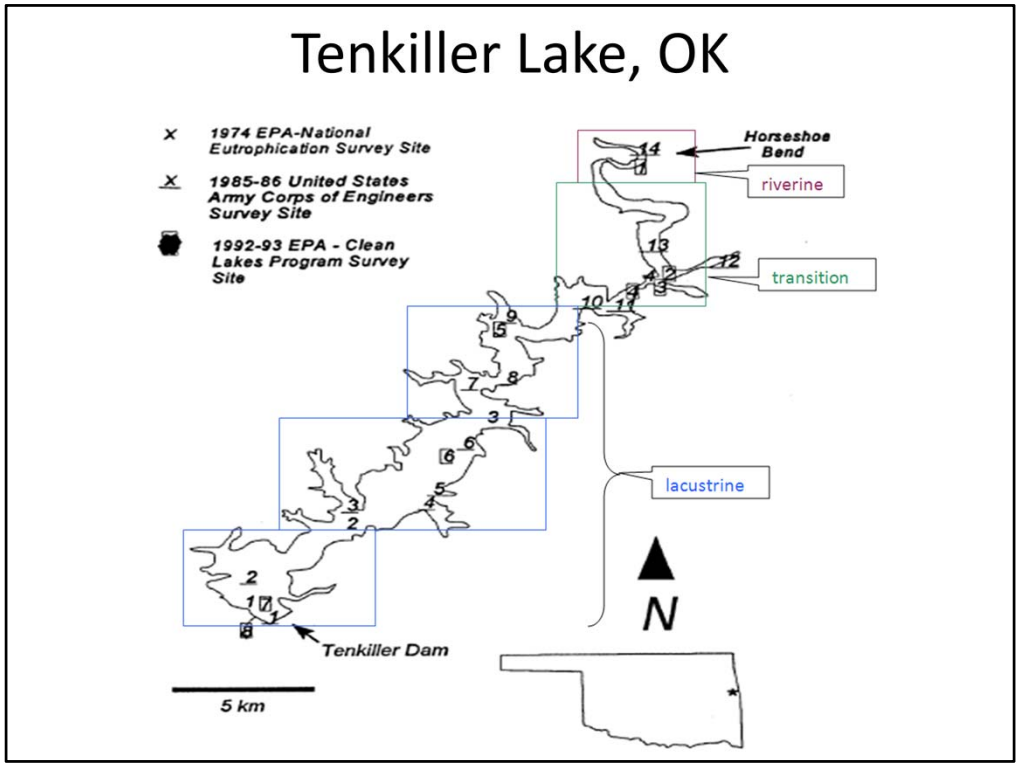
An examination of linked model setup, linked model output examination, water balance considerations and moving through segments will be undertaken.

Modeling Nutrients for Criteria Support in Tenkiller Lake, OK

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 Ferry Lake was selected as the location for a nutrient criteria modeling case study due to its current nutrient problems, and because the State of Oklahoma had expressed interest in a collaborative working relationship with EPA. In addition, some water monitoring data needed to support this modeling project was available.



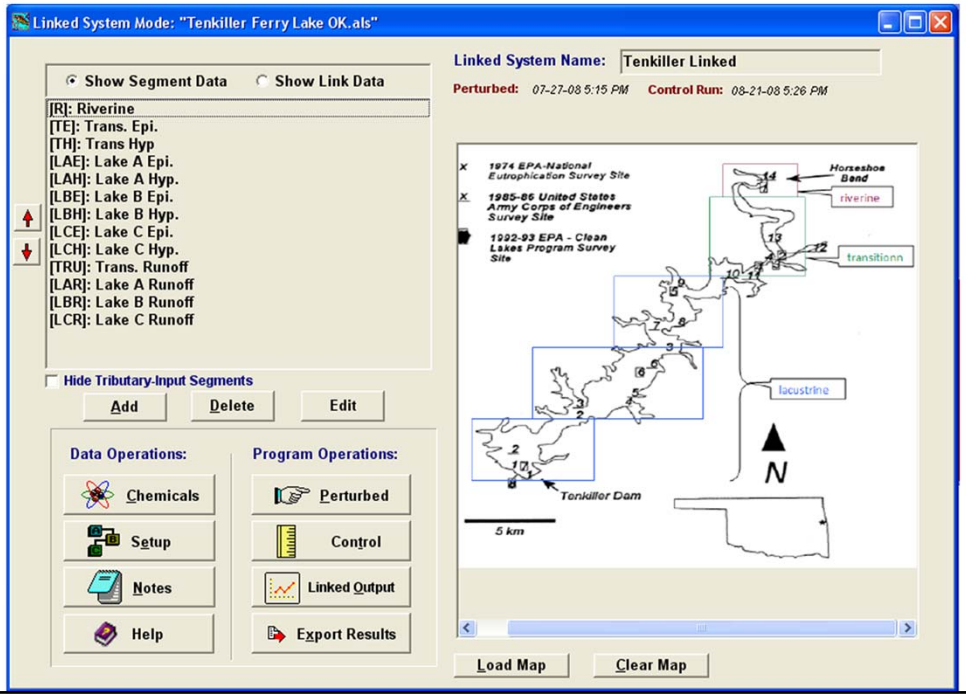
Based on availability of sampling stations, Tenkiller Lake was divided into five horizontal epilimnetic segments and four hypolimnetic segments (the riverine zone was considered to be well mixed).

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)

An existing HSPF watershed model of the Illinois River and its watershed was available, with a recent re-calibration effort for water quantity and quality. Output from this model was linked to AQUATOX simulations of Tenkiller Ferry Lake, and used to provide daily influent hydrologic and nutrient loadings for the simulated time period. Furthermore, the EFDC model had been calibrated for Tenkiller Ferry Lake for 1992-1993, and those simulations provided the flow field for linking segments in AQUATOX.

Tenkiller Lake OK

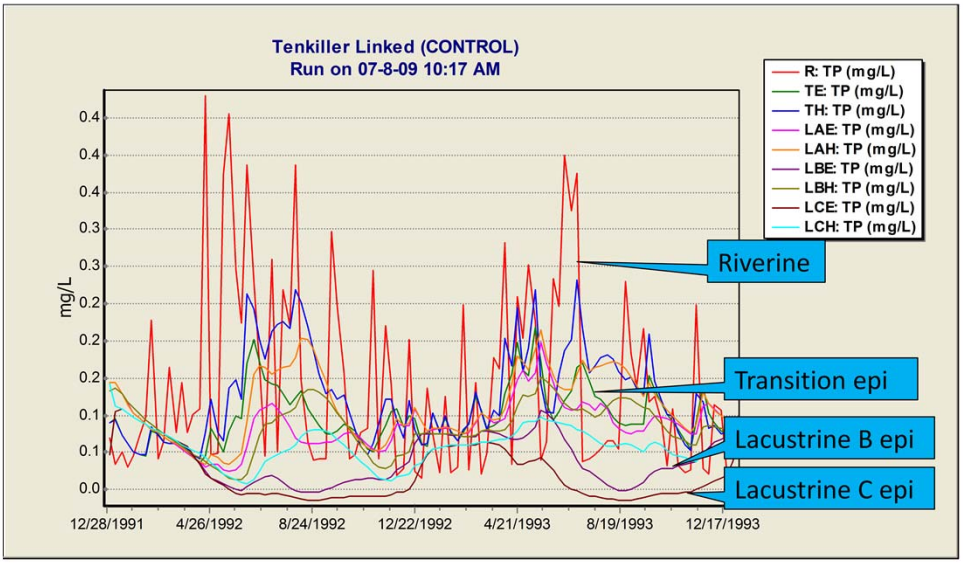


Storm-water plume, algae-rich riverine segment

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

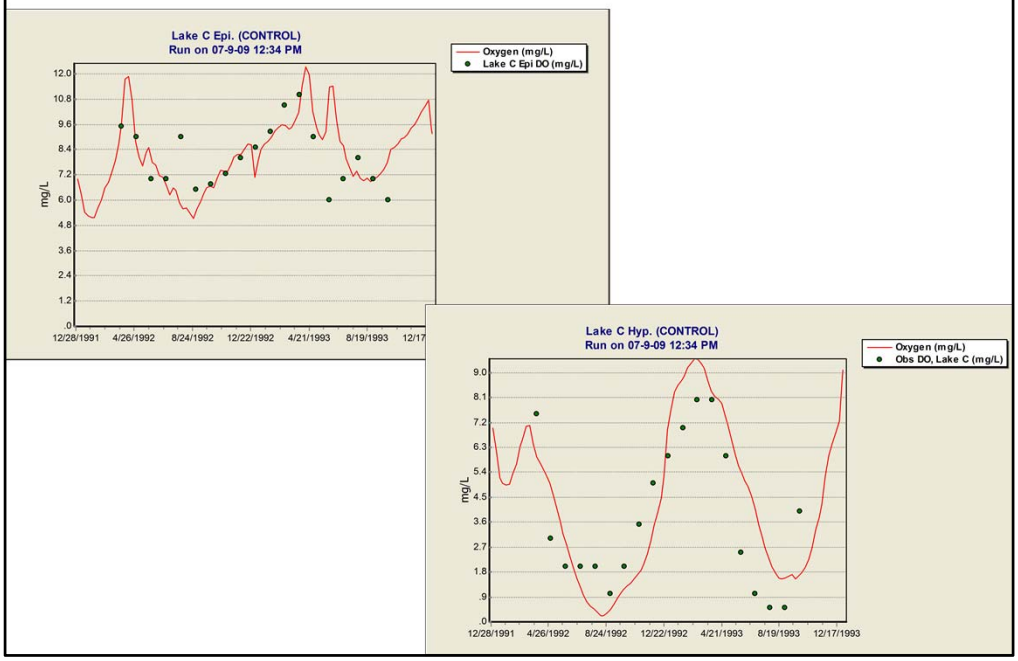
A site visit happened to follow a storm event, and the storm-water plunge zone was an obvious boundary between the riverine and transition zones. Duckweed, a small floating macrophyte, formed a surface concentration in the plunge zone.

Total phosphorus in water column decreases toward dam; loss to sediments is simulated



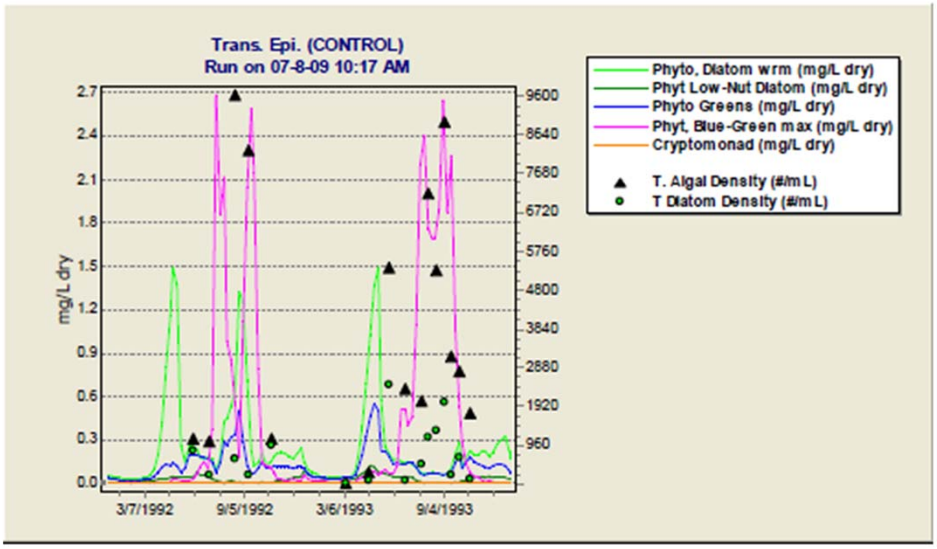
Precipitation of PO4 with CaCO3 was an important loss process.

Simulated and observed dissolved oxygen in Lacustrine C

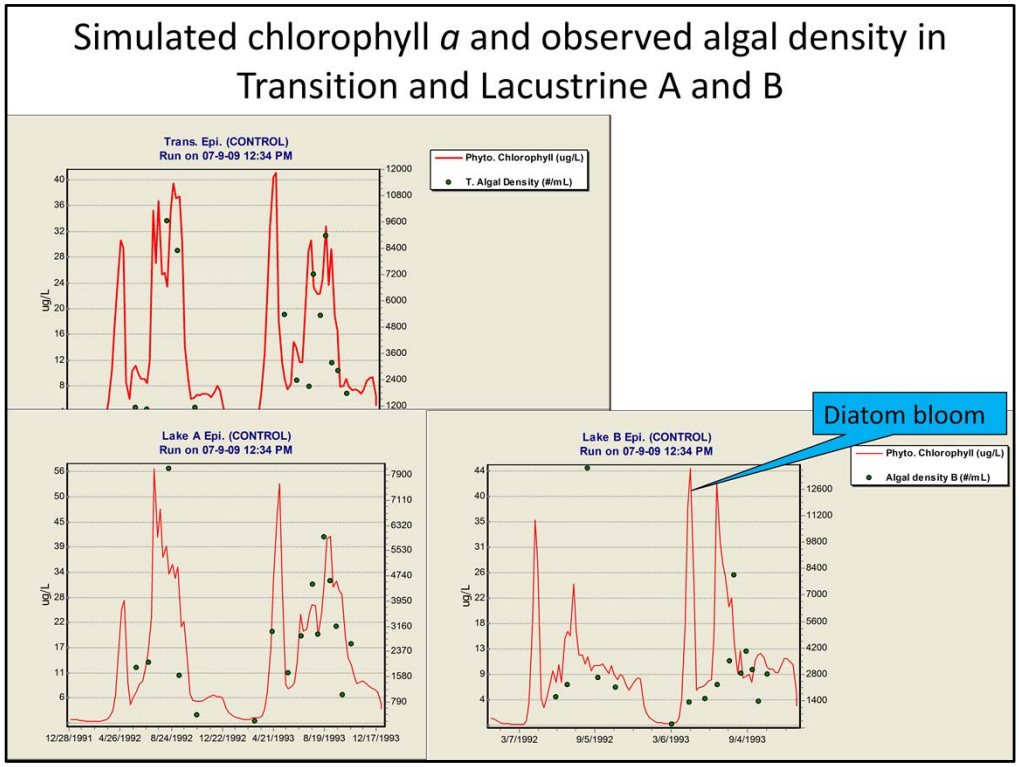


The sediment diagenesis submodel was necessary to represent the influence of bottom sediments on hypoxia.

Simulated & observed algal composition in epilimnetic Transition



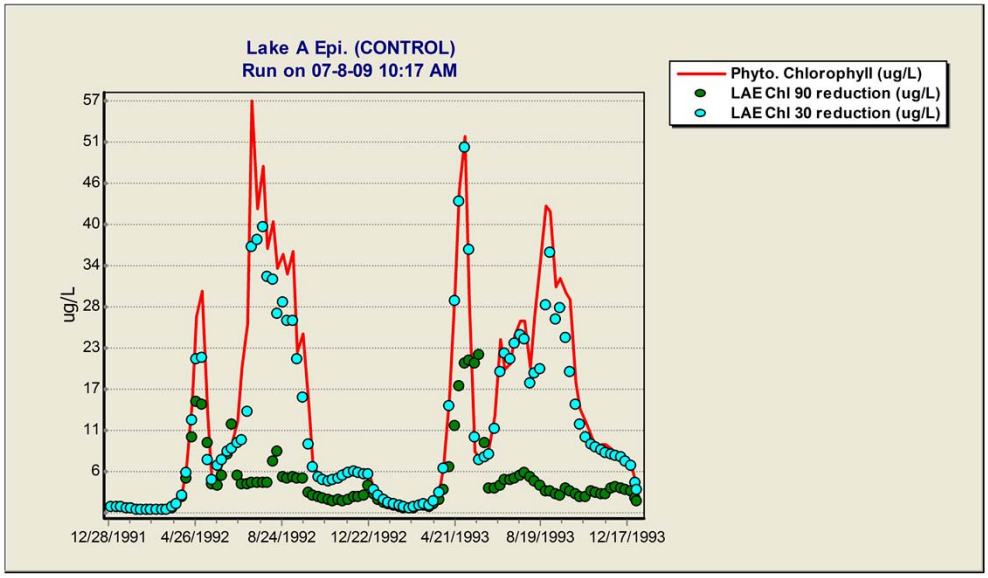
The model fit the available algal data reasonably well based on visual inspection.



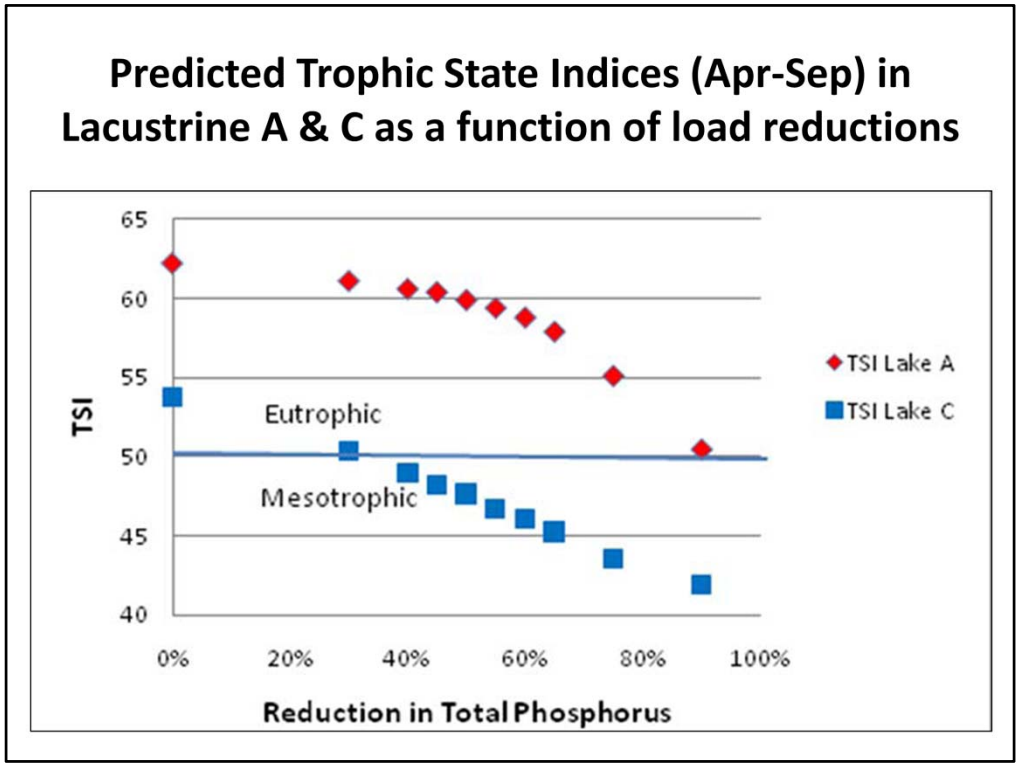
In the absence of good timeseries of observed chlorophyll a, algal density (#/mL) is used to show trends.

A common problem in evaluating goodness of fit is in comparing short-lived phenomena, such as the simulated diatom bloom, with sporadic observed data.

Predicted chlorophyll *a* in Lacustrine A with 30% and 90% load reduction of TP compared to baseline (red)



Load reduction factors were assigned to represent overall load reductions to the lake by a mixture of best management practices (BMP) and point-source reduction scenarios**.** Influent TP, TN, and BOD concentrations were modified concurrently, in a manner representative of their correlated susceptibility to management practices. Any percent TP decrease would be accompanied by percent decreases in the other pollutants**.**



The Trophic State Index, TSI, based on chlorophyll is a useful way of presenting the results in the context of a eutrophication gradient. The simulated TSI values exhibit a gradient toward the dam during the 1992-93 period. This slide shows the predicted responses of both Lacustrine A and C to load reductions. A 30% reduction in TP loads places Lacustrine C on the borderline between eutrophic and mesotrophic, whereas a 90% reduction would be required for Lacustrine A based on the growing season.

Lab 5 – Analysis of the Nutrient Status of DeGray Lake, Arkansas

DeGray Lake is a reservoir on the Caddo River, in the foothills of the Ouachita Mountains of Arkansas. The lake offers a huge span of recreational area and spectacular views. Construction on the dam began in 1962 and was completed in 1972. (*Taken in part from Wikipedia and the US COE*.)

The lake was studied extensively by the Corps of Engineers in the development and verification of the CE-QUAL model. We will model the transient period following impoundment.

Lake Onondaga, NY
Validation and Application

- AQUATOX Validation Site for Release 1
- Was called "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 affects stratification
- *Many problems in lake have been corrected*
  - *recent implementation was recalibrated*

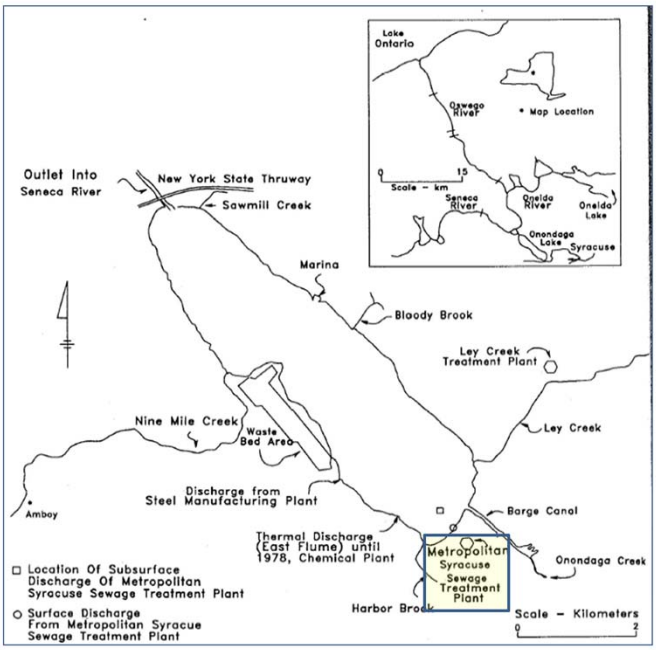
"Lake Onondaga is arguably the most polluted lake in the United States" according to Effler (1996) in the preface to his comprehensive book, which serves as the primary reference for the following information and data on the lake. The shore of this lake in central New York State was industrialized before 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.

Until recently, the lake was 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 was little reduction in ammonia in the sewage effluent. Most troubling were the combined sewer overflows (CSOs) that carried storm water and raw sewage into tributary creeks about 50 times a year. Nearly 20% of the annual inflow into the lake is

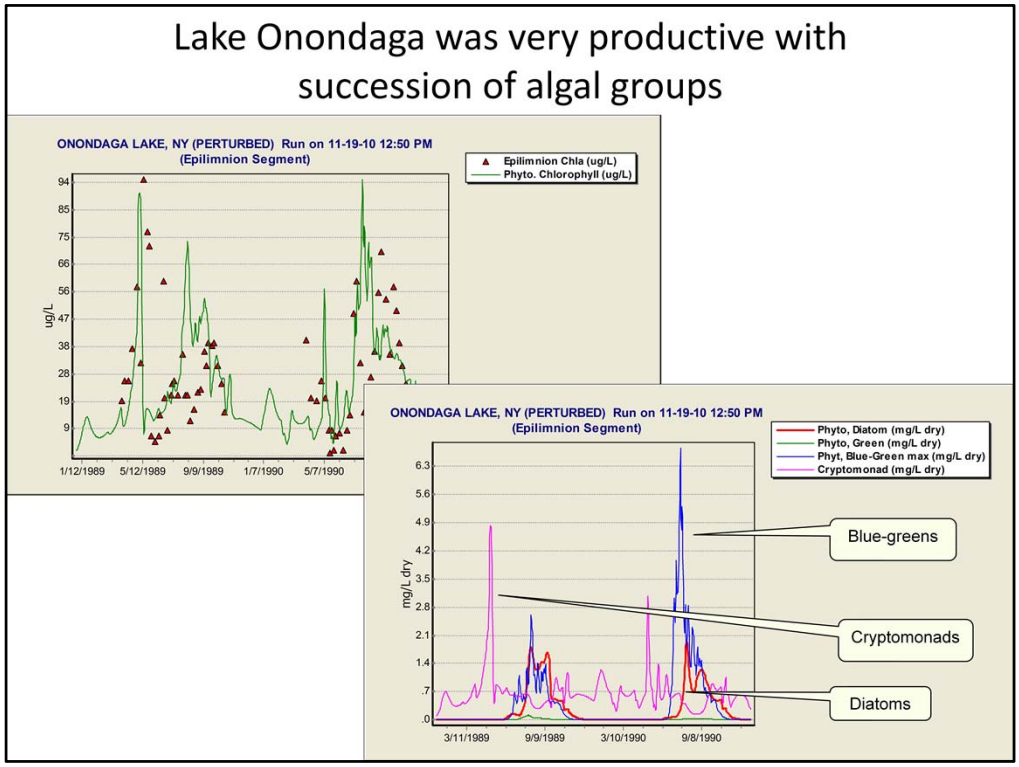
from METRO, which complicates a proposed bypass to the Seneca River below the outlet.

Recently AQUATOX was calibrated to current conditions, including invasive zebra mussels and significantly reduced pollutant loads. The examples given here are based on conditions that prevailed in 1989-1990.

Lake Onondaga NY, heavily polluted

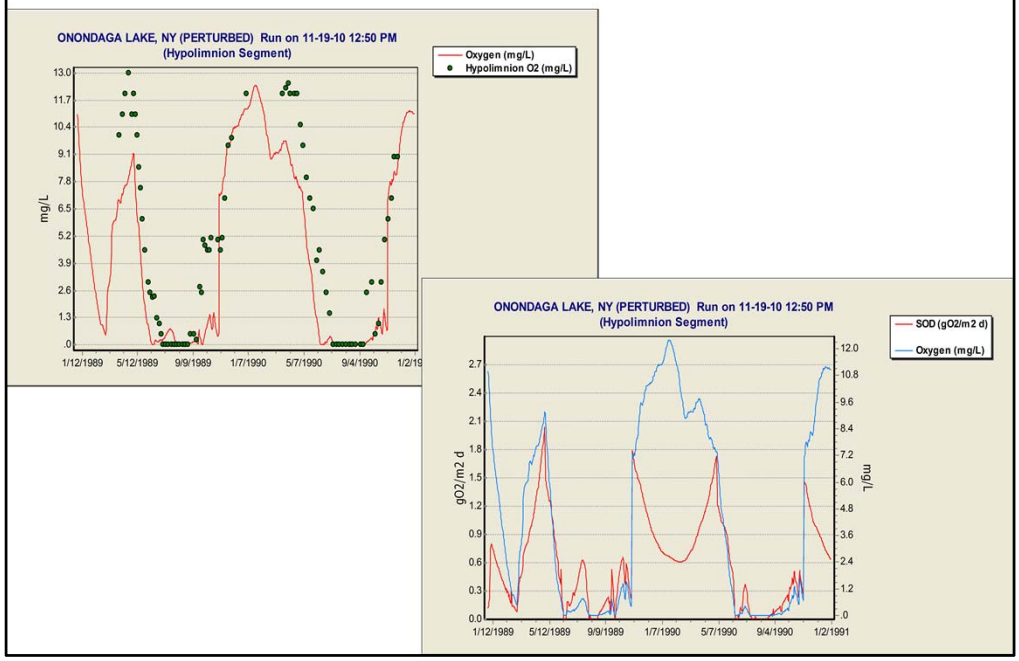


Historically, a number of non-point and point sources contributed to the pollution.

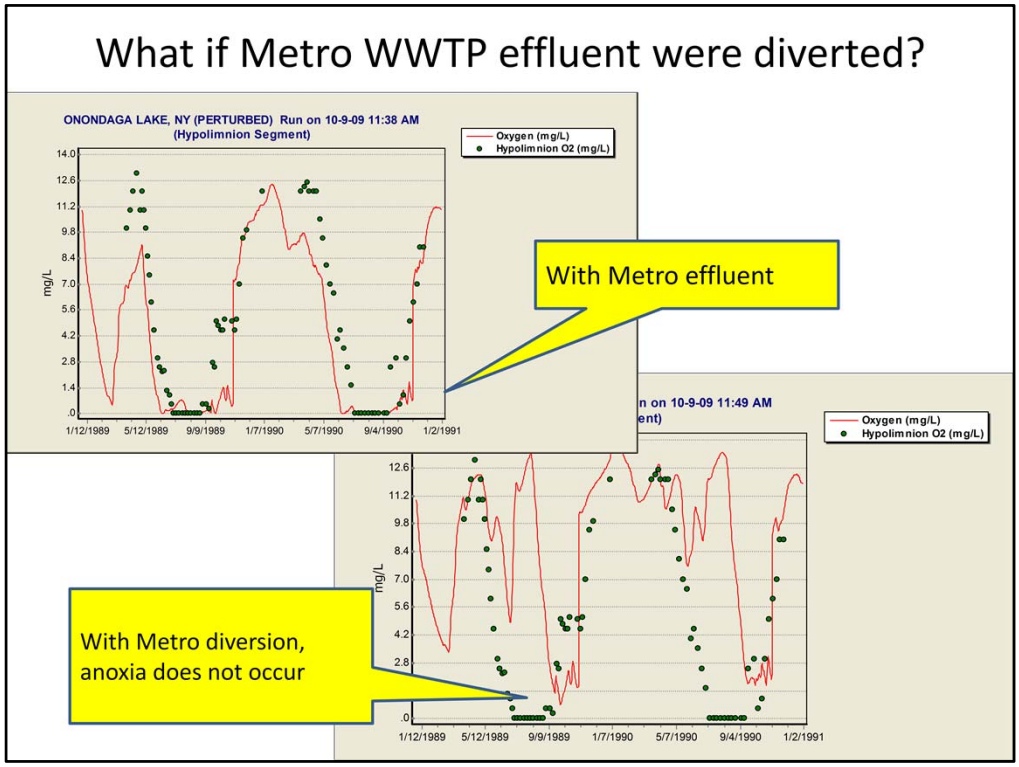


This has now changed with reductions in nutrient loadings and the invasion of zebra mussels.

Hypolimnion goes anoxic with high SOD



Observed data are shown as circles in the above leftmost graph while the AQUATOX simulation is the red line. In the lower graph, Simulated sediment oxygen demand is shown in red.



For example, what might be the effects on dissolved oxygen be if the highly nutrient-enriched (waste water treatment plant) WWTP discharge into Onondaga Lake were eliminated (one possible management option)? AQUATOX predicts a significant decrease in the magnitude and duration of the hypoxia.

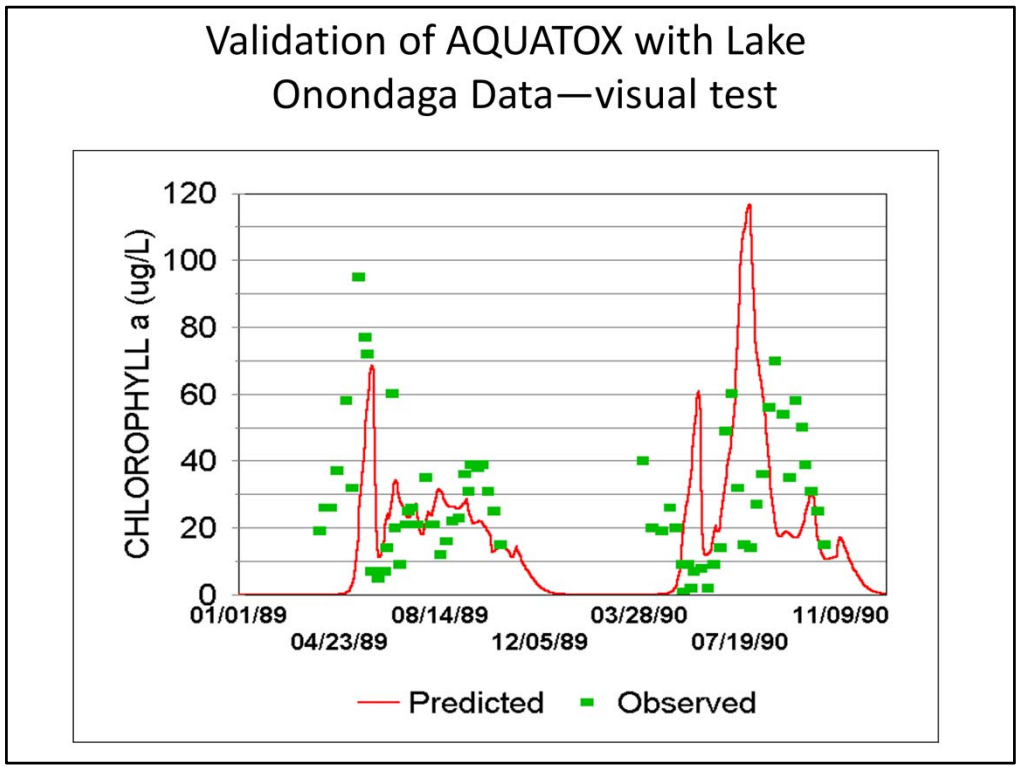
Optional Lab/Demonstration:

If you wish to perform this analysis yourself, here are the required steps:

1. Load **Onondaga Lake NY Sed Diagenesis.aps** from the AQUATOX "Studies" directory.
2. Run the model as "control."
3. Double click on **Total Ammonia as N,** Set loadings from point sources to zero.
4. Double click on **Nitrate as N,** Set loadings from point sources to zero.
5. Double click on **Total Soluble P,** Set loadings from point sources to zero.
6. Double click on **Suspended and Dissolved Detritus.** Click on the "**Point Sources**" button. Set loadings from point sources to zero.
7. Run the model as "perturbed" and examine output.

Other possible perturbations to test are:

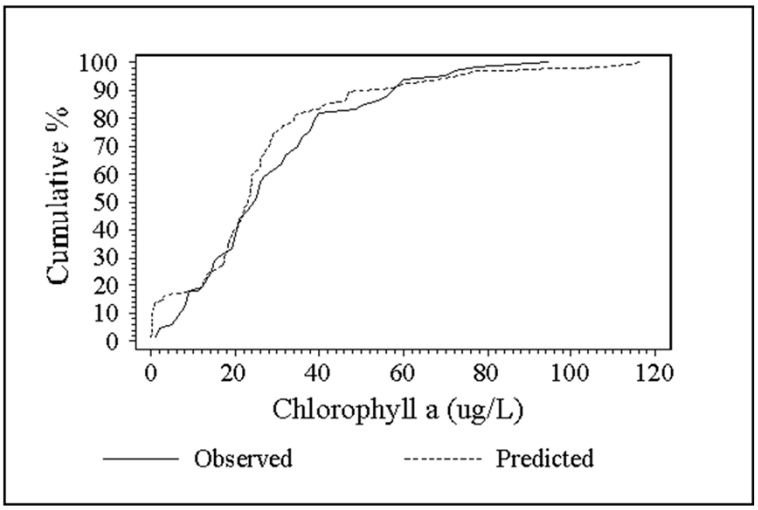
1. Increasing/decreasing nutrient loads from WWTP
2. Adding nutrient loads to inflow water (river)
3. Changing TSS climate



This is from the model validation that was done for AQUATOX Release 1.

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 significantly differ

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.

Miscellaneous Nutrient-related Topics

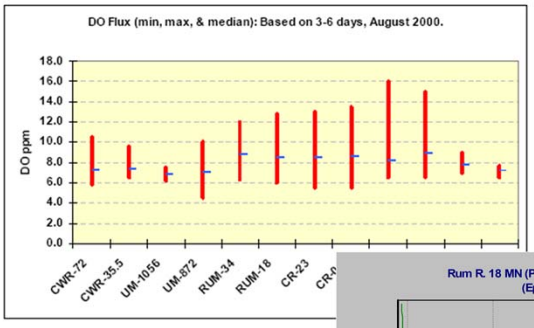
- Diel oxygen
- Effects of low dissolved oxygen
- Ammonia toxicity

Oxygen concentrations can be of critical importance within ecological simulations, as excessively low oxygen makes certain organisms non-viable. Because even short-lived oxygen fluxes can have significant effects, a daily average oxygen simulation is not always sufficient. AQUATOX allows the modeling of oxygen on an hourly basis (Diel oxygen) as we will discuss in these next slides. Following that discussion we will examine how AQUATOX determines the effects that low oxygen may have on different animals within the simulation.

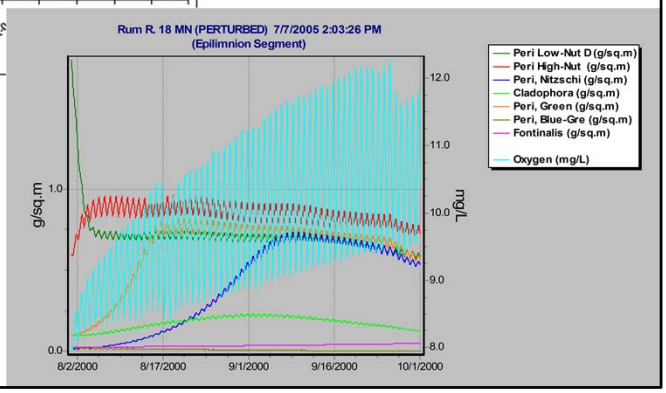
Another potentially toxic setup for organisms involves the effects of ammonia. We will briefly discuss the basis for and construction of the AQUATOX ammonia-toxicity model.

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

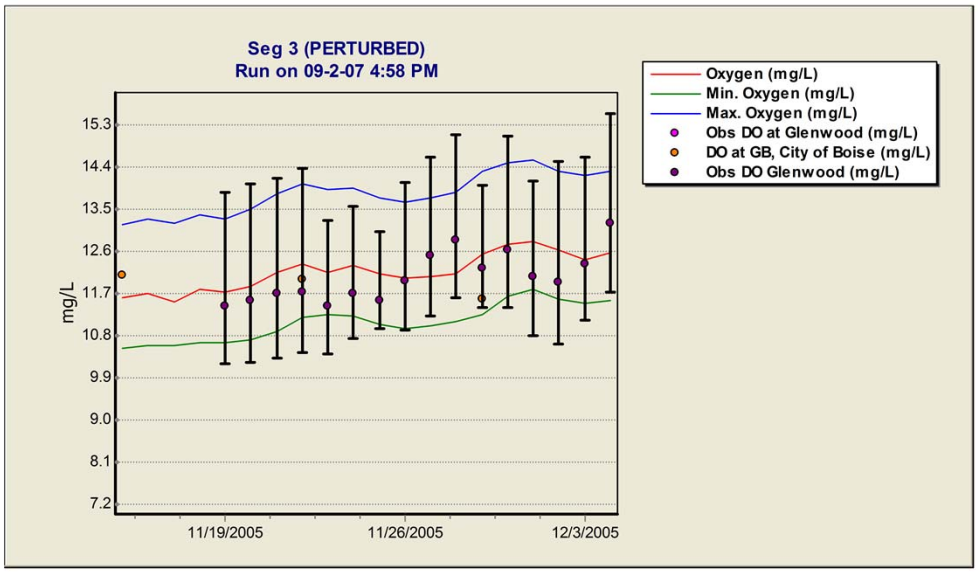


Monitoring data indicate that oxygen levels fluctuate daily

From Technical Documentation (Chapter 5):
Significant fluctuations in oxygen are possible over the course of each day, particularly under eutrophic conditions. This type of fluctuation may now be captured within AQUATOX when the model is run with an hourly time-step. If the model is run with a larger reporting time step (but an hourly integration time-step) the minimum and maximum oxygen concentrations will be output on the basis of the hourly results.

Some important points:
Photosynthesis can be calculated on an hourly basis.
The Light Limitation calculation is modified for hourly simulations to remove the now irrelevant photoperiod.
Stress due to low light-conditions continues to be calculated with an average daily light value.

Diel Oxygen, Hourly Time-step



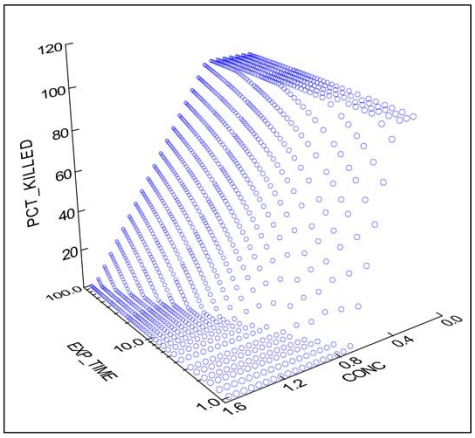
Predicted and observed diel dissolved oxygen at Glenwood Bridge, Lower Boise River, Idaho. This is applicable during low-flow when photosynthesis is dominant within the reach. However, during high flow the DO is completely dominated by loadings from upstream. You should always check the retention times for a particular reach.

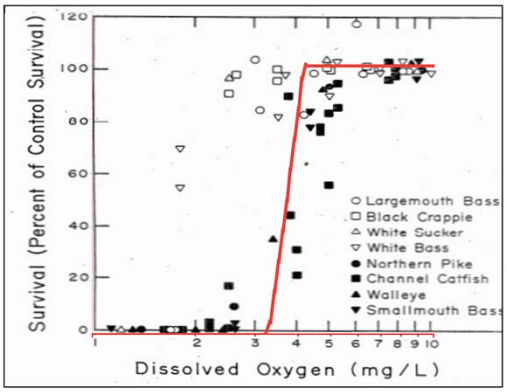
Hourly simulations are accessible through the “setup” menu and converting loadings from daily to hourly is accessible through the oxygen loadings screen (double-clicking on “oxygen” in the state-variables list and selecting the “Hourly Loadings” checkbox).

Low Oxygen Effects

Three dimensional model of effects is a function of exposure time and oxygen concentration.

Species specific $LC50_{24\text{-hour}}$ for O_2 is required





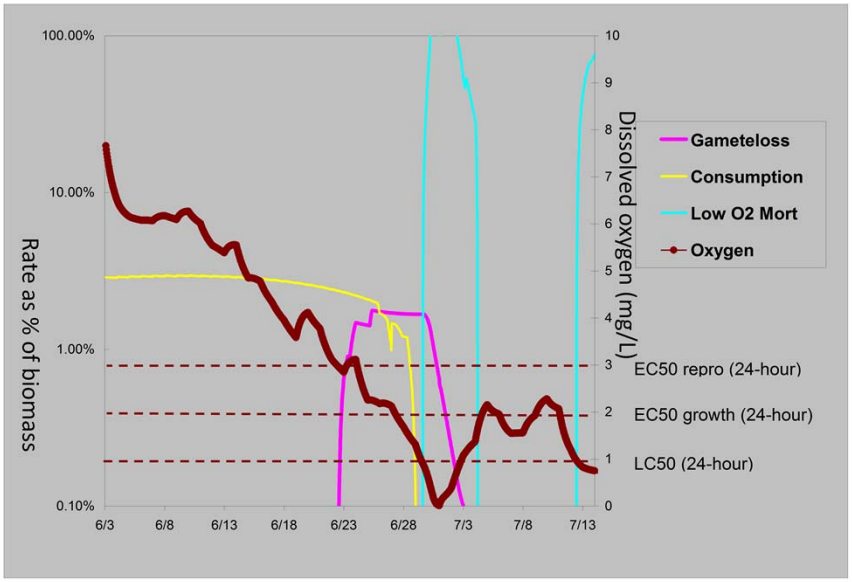
Steep slope for effects matches available data well.
(red line = model predictions with $LC50_{24\text{-hour}}$ of 3.5 mg/L)

AQUATOX represents both lethal and non-lethal effects from low concentrations of dissolved oxygen.
Model is based on the U.S. EPA salt water criteria (U.S. Environmental Protection Agency 2000. *Ambient Aquatic Life Water Quality Criteria for Dissolved Oxygen in Saltwater*).
http://epa.gov/waterscience/criteria/dissolved/docriteria.pdf

Based on these data, for white bass and black crappie a lower LC50 than 3.5 mg/L would be appropriate.

Non-Lethal Low Oxygen Effects

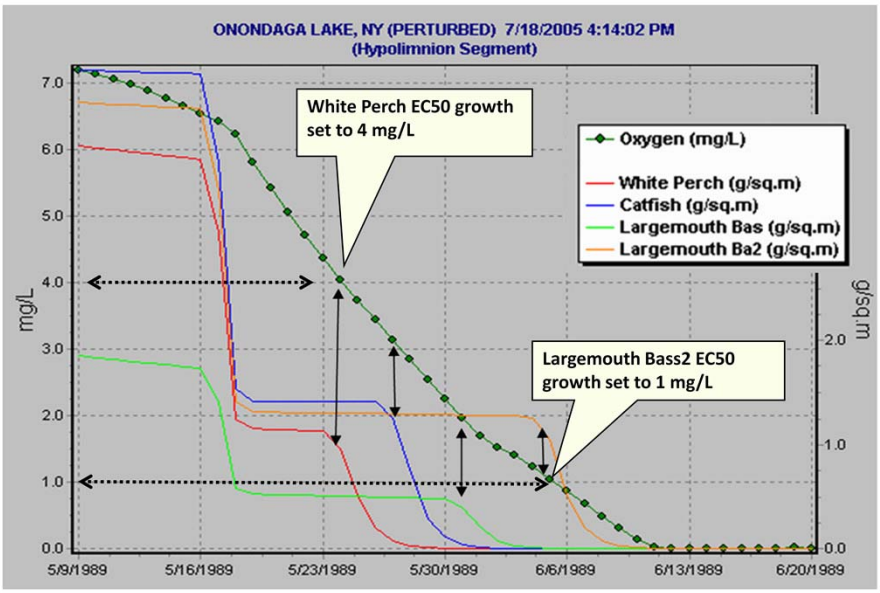
EC50 reproduction and EC50 growth parameters affect timing



The same three dimensional model used for lethal effects is utilized to calculate non-lethal low oxygen effects (functions of exposure level and time.) In this case, EC50 reproduction affects the percent of gametes that are lost and EC50 growth affects consumption rates.

Low O_2 Affects Timing of Migration from Hypolimnion

EC50 growth parameter is key



This is a graph of the Hypolimnion segment. The biomass in the hypolimnion drops to zero when migration takes place due to low oxygen concentrations.

In Release 3, vertical migration occurs when oxygen drops to 0.25 mg/L. Now that lethal and non-lethal oxygen effects are included (and usually at concentrations much higher than that) the 0.25 mg/L trigger doesn't work because all the animals would be dead before they could migrate.

We assume that EC50 growth is the best indicator of when the species has become so intolerant of the oxygen climate that it is going to migrate. This also allows more tolerant species to spend more time in the hypolimnion and less tolerant species to migrate earlier.

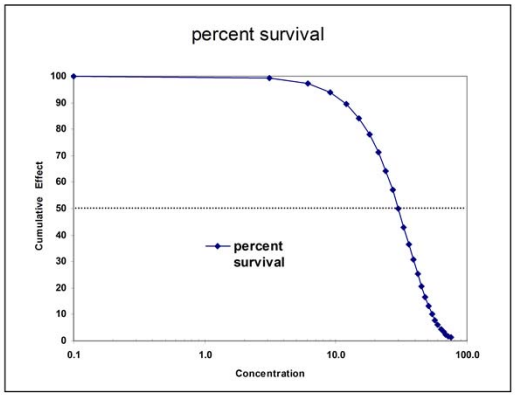
Toxicity Due to Ammonia

Animal Specific Input Parameter Required:

LC50 un-ionized and LC50 ionized calculated from LC50 total as a function of pH

External Toxicity Model Utilized:

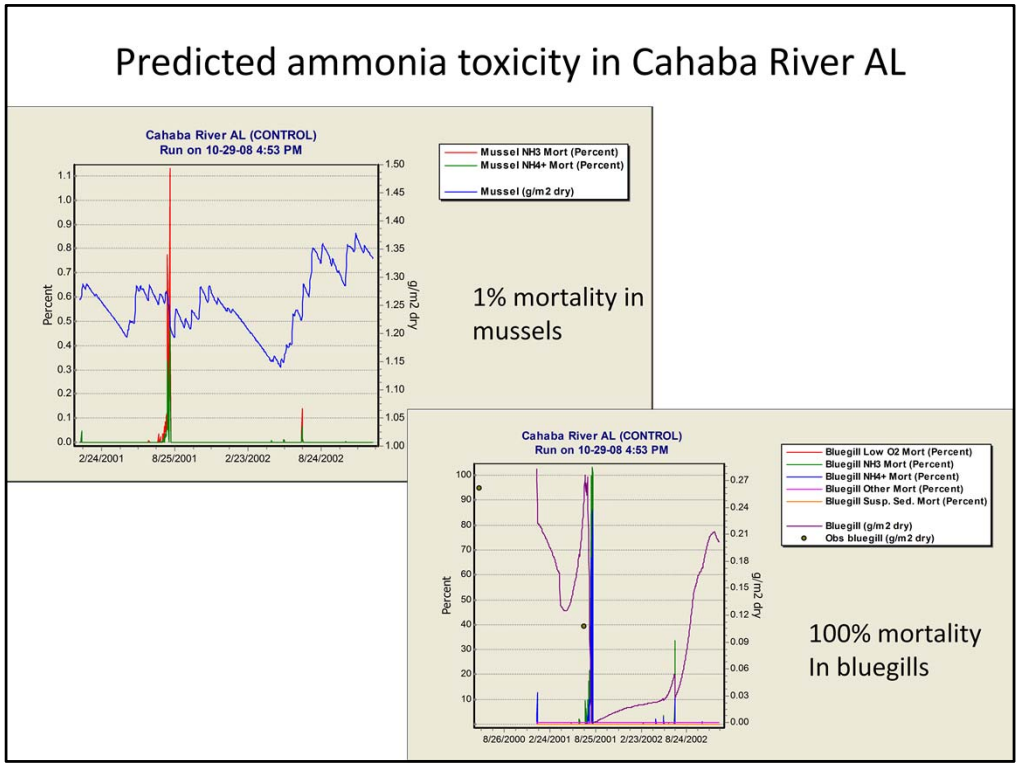
- Effects from un-ionized and ionized ammonia are additive
- Un-ionized ammonia fraction calculated as a function of site pH and temperature



As will be seen later, there are two toxicity submodels in AQUATOX: an internal one (used especially for bioaccumulative compounds) and an external one (used here).

Model data and formulations based on U.S. EPA, 1999, *Update of Ambient Water Quality Criteria for Ammonia,* September 1999, U.S. EPA Office of Water, U.S. EPA Office of Science and Technology Washington, D.C. http://www.epa.gov/waterscience/criteria/ammonia/ Based on this document, it is preferable to base toxicity on total ammonia, taking into account the contributions from the un-ionized and ionized ammonia.

Species specific parameters are also available within this document.



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.

Sediment Effects Overview

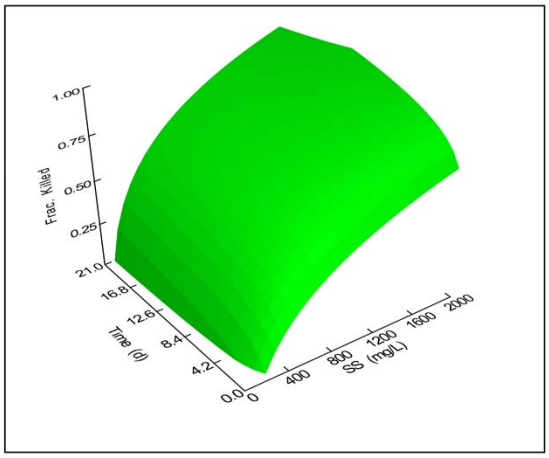
- Mortality
- Reduction in feeding
- Stimulation of invertebrate drift
- Loss of spawning and protective habitat in interstices

AQUATOX can simulate the effects of sediments, either suspended in the water column or deposited on the bottom; it is especially appropriate for streams, although some of the functions are generally applicable.

Effects of suspended and bedded sediments are discussed in Chapter 4 of the *Technical Documentation.*

Suspended and bedded sediment effects

- Mortality
  - Highly Sensitive
  - Sensitive
  - Intolerant
  - Tolerant

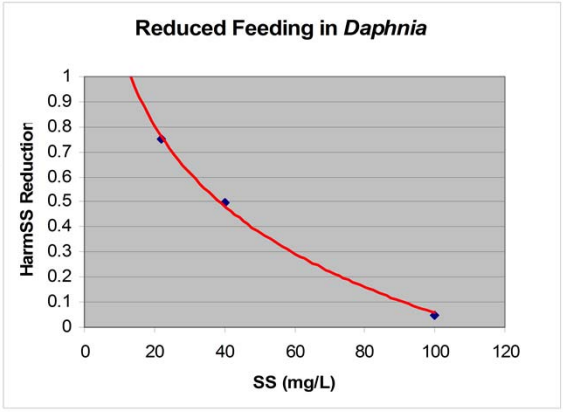


Because of the lack of suitable quantitative data, lethal responses are divided into sensitivity categories specific to this model, with parameters for surrogate species that can be considered representative for groups of organisms.

Suspended and bedded sediment effects

- Reduced Feeding

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



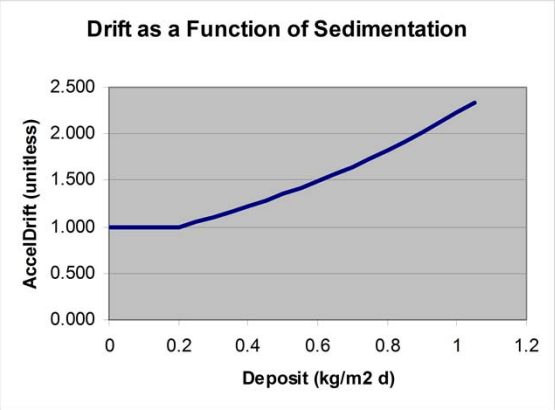
Reduction in feeding occurs in game fish due to visual impairment.
Sediments can also clog filter-feeding apparatuses in invertebrates and some fish.

There may also be dilution of food available to filter feeders and grazers by the inorganic particles, which may be offset by selective sorting of particles and feeding. The dilution of available food decreases as a proportionate function of sediment corrected for the degree to which there is selective feeding

Our initial testing of this construct indicates that *Daphnia* are quite sensitive to this effect.

Suspended and bedded sediment effects

- Increased drift of benthos due to sedimentation



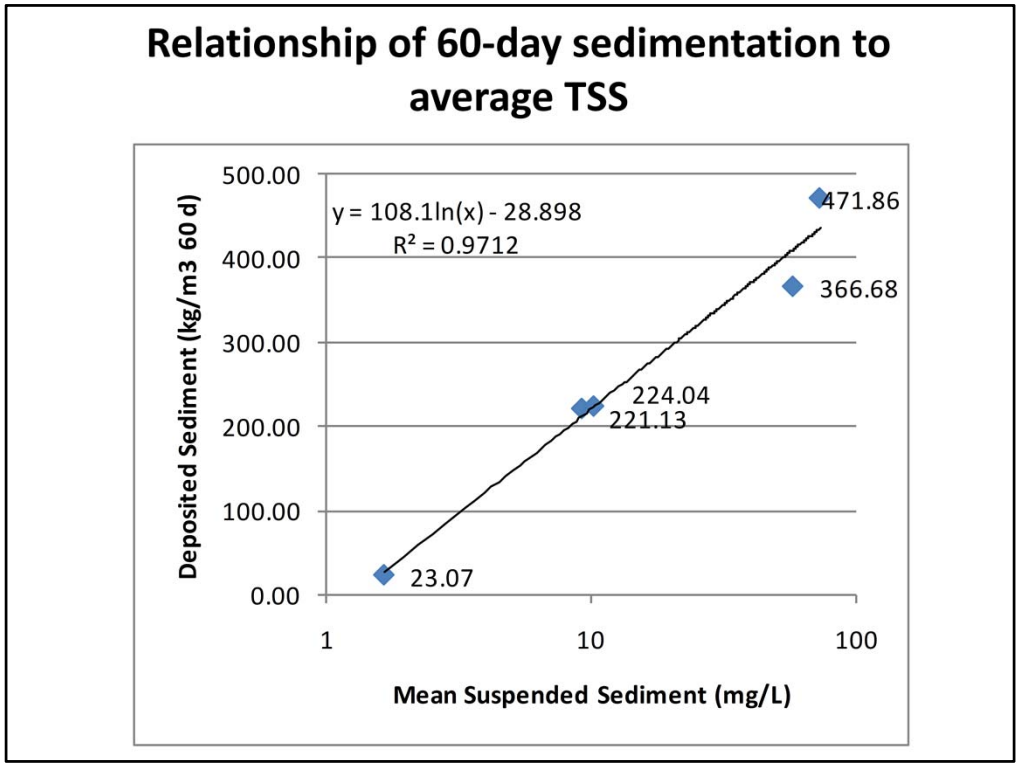
Drift is the loss of zoobenthos due to drift downstream. Units are g/m^3 d.

Increased deposition of sediment may lead to increased drift of benthic organisms. This is represented by a function in which the deposition rate is compared to a trigger value beyond which there is accelerated drift.

Suspended and bedded sediment effects

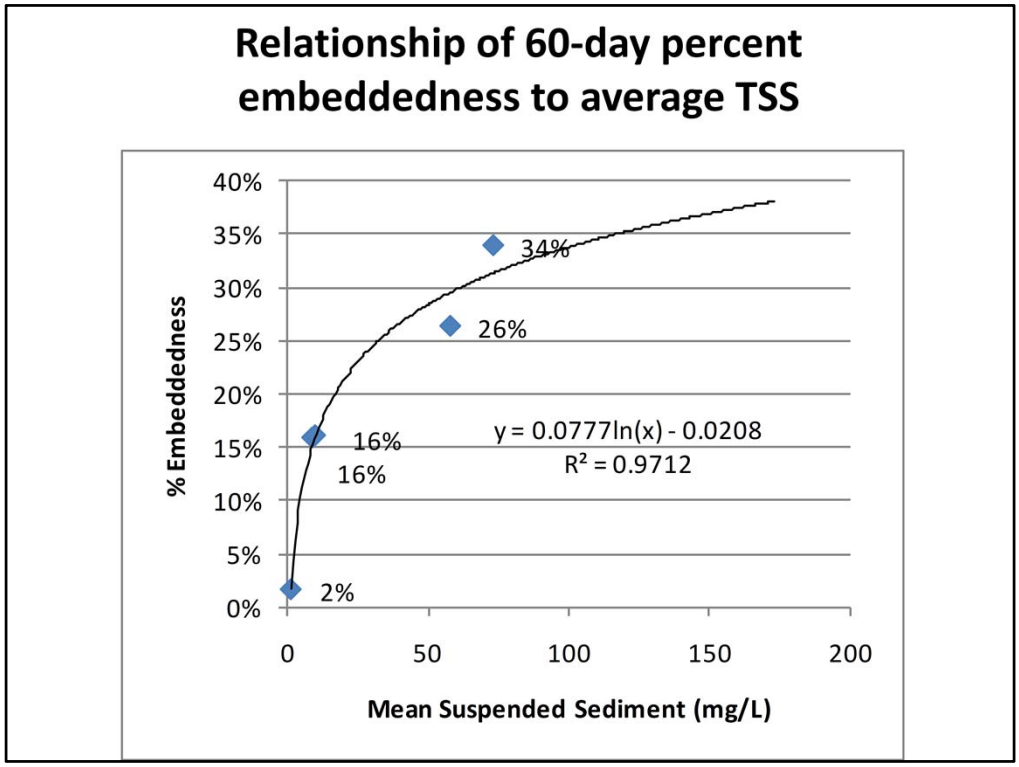
- Deposition of fines and their effect on invertebrates and salmonid reproduction
  - Loss of spawning and protective habitat in interstices
  - Percent Embeddedness calculated as a function of 60-day average TSS

A measure of fines is embeddedness, which is the extent to which sand, silt, and clay fill the interstitial spaces among gravel and cobbles (Osmond et al. 1995). Good spawning substrate is characterized as less than 25% embedded (Flosi et al. 1998). The data that allow us to predict percent fines also yield an estimate of percent embeddedness and that relationship is used in the model.



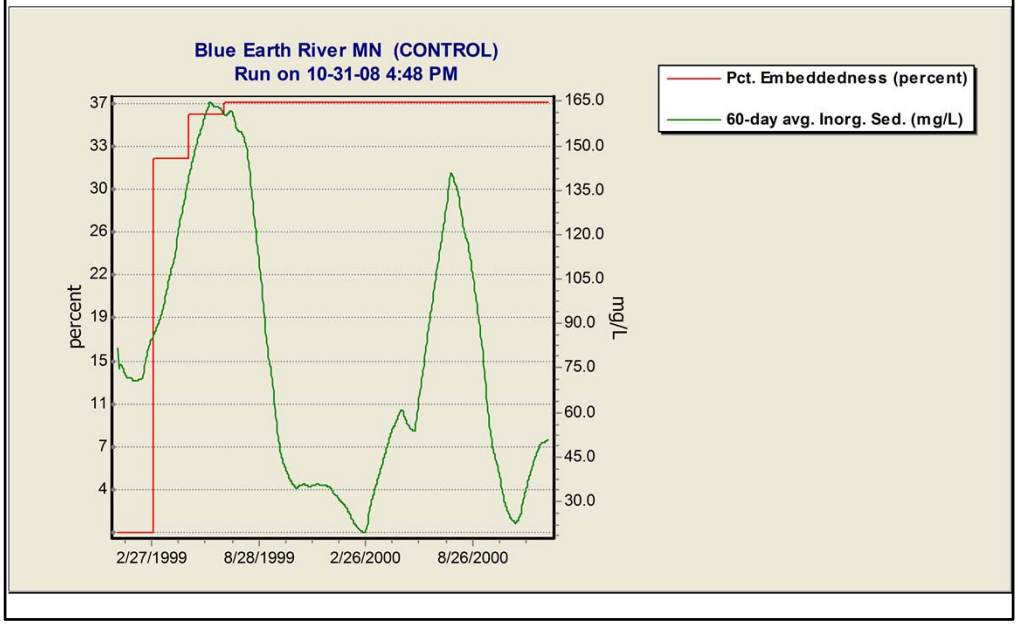
Both salmonid eggs and the yolk-fry or alevins are sensitive to sedimentation of fines, including sand. Sedimentation in spawning gravels can be related to average suspended sediment (TSS) concentrations (Larkin and Slaney 1996). The relationship is logarithmic for average TSS over a 60-day period.

Both sedimentation and percent embeddedness (next slide) are *approximations* based on 5 diverse sites covering a broad range of suspended sediment loadings in a British Columbia watershed.



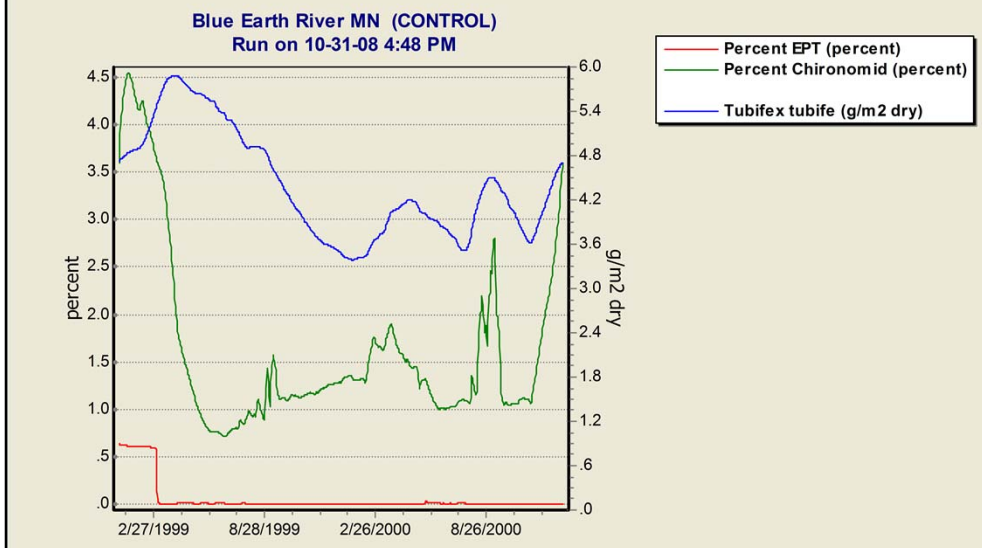
The data that allow us to predict percent fines also yield an estimate of percent embeddedness, and that relationship is used in the model. Although the training data only go to 34% embeddedness, the log relationship using averaged data allows the regression to extend to any reasonable level of suspended sediment. The user can enter an observed "baseline embeddedness" in the site record, and that can be used as an initial condition. A corresponding embeddedness threshold value can be entered in the animal record. If that value is exceeded then exclusion can be assumed (mortality = 100%). Although this functionality is intended for salmonids, it can also apply to other fish such as sculpins and to invertebrates that hide in the interstices. In practice, the maximum 60-day moving average of suspended sediments is used to compute the percent embeddedness; if the initial percent embeddedness is exceeded then the new simulated percent embeddedness is used. The possibility of scour from a high-discharge event resetting the percent embeddedness is ignored.

Computed % embeddedness and sedimentation are quite high in turbid Blue Earth River MN

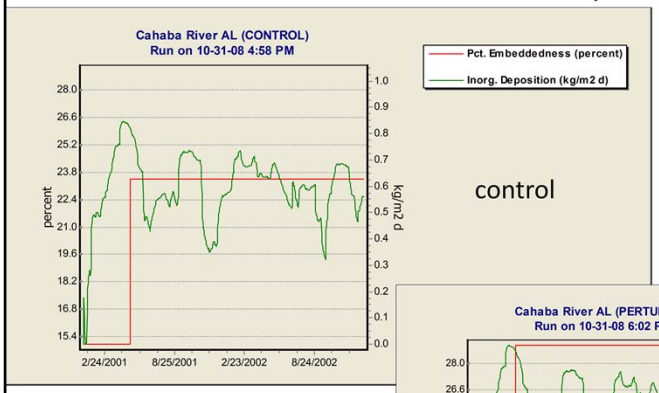


Percent Embeddedness is incremented every 60 days; 37% would exclude many invertebrates and fish.

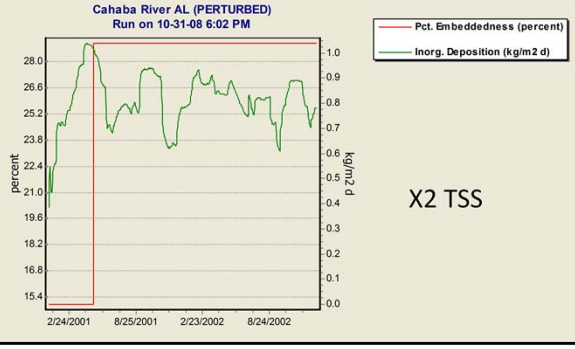
Mayflies, stoneflies, & caddisflies (EPT) are sensitive to embeddedness; chironomids & oligochaetes are not



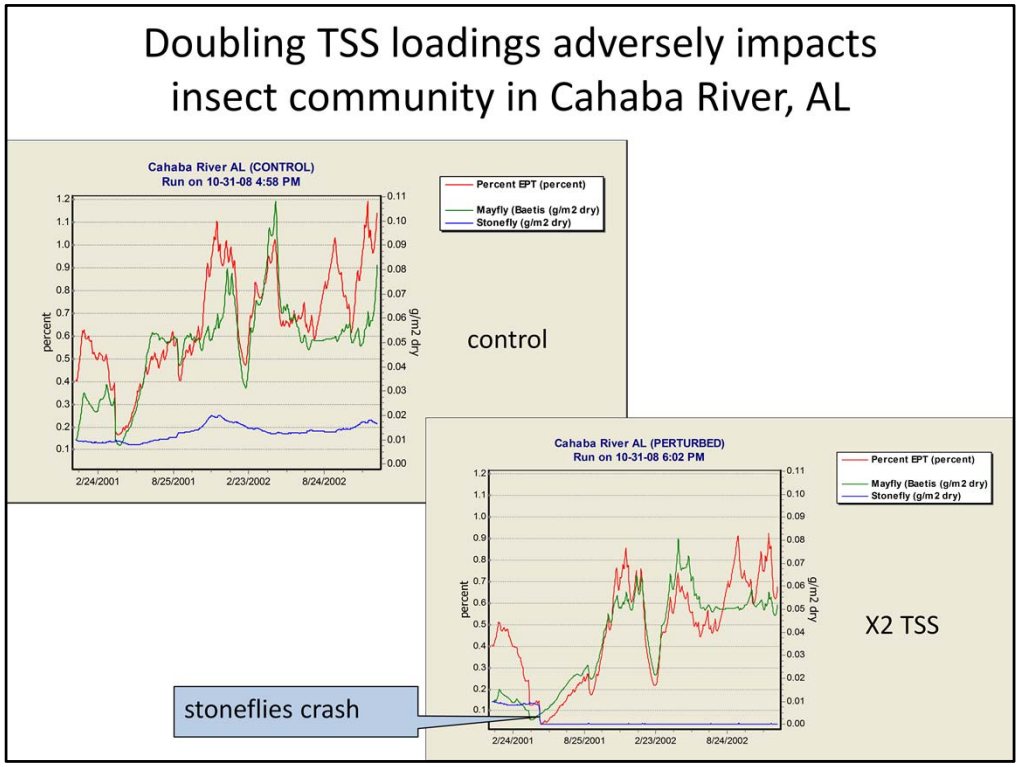
Doubling TSS increases embeddedness in Cahaba River, AL



control

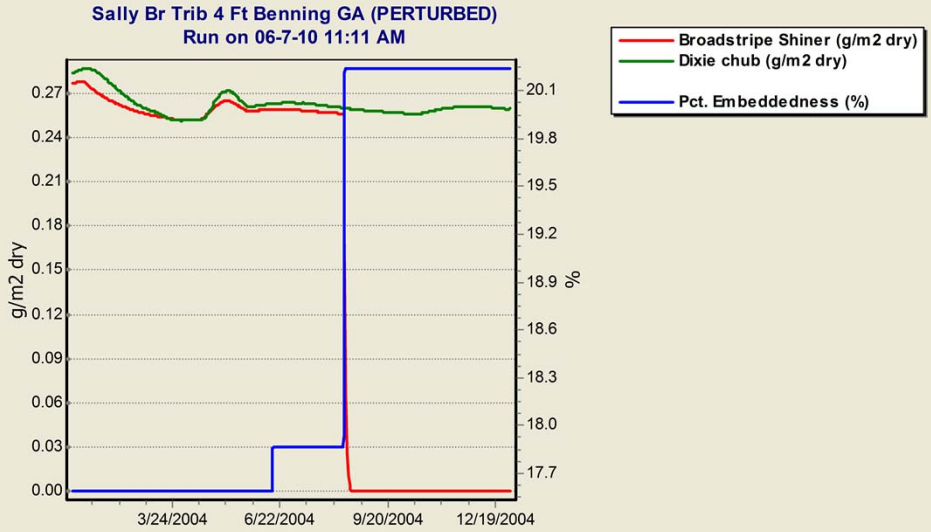


X2 TSS



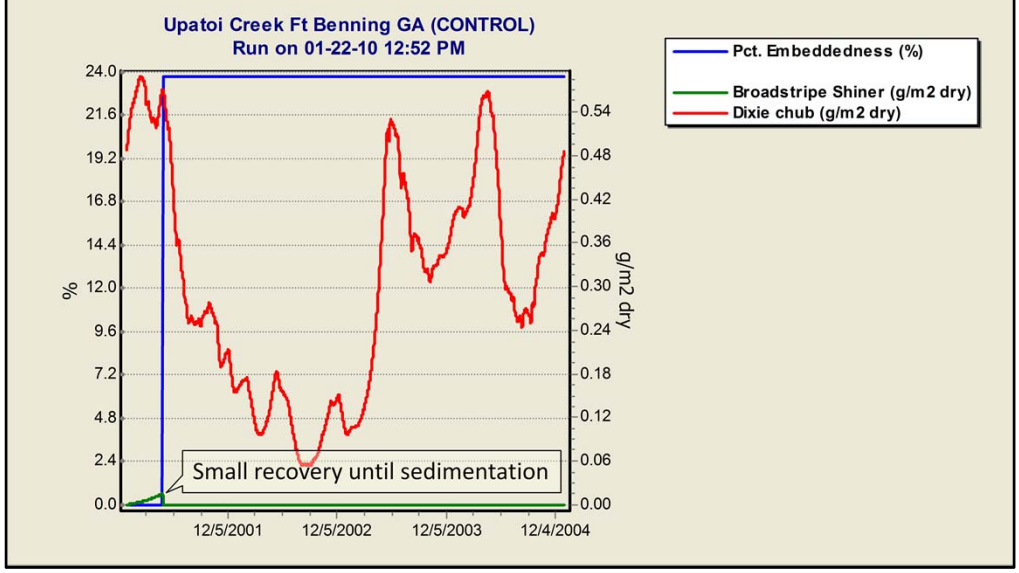
One-year simulation exhibits transient conditions for mayflies. Doubling TSS causes the stoneflies to crash when the embeddedness is updated.

Broadstripe shiner is sensitive to embeddedness; Dixie chub is not; otherwise they are similar



The absence of broadstripe shiner in the streams of Fort Benning Georgia is indicative of disturbed conditions in the watershed. Dixie chub are able to spawn in fine sediments. The fish are very similar except for their spawning demands.

Broadstripe shiner is excluded from another creek due to embeddedness



Here is another example from a larger stream in Fort Benning Georgia.

Lab 6: Analysis of Plant Control in "Clear Lake CA"

- Run control for 3 years
- Add *Hydrilla*
- Run perturbed
- Use difference graph to assess impacts of *Hydrilla*
  - animals
  - nutrients
- Interpret nutrients
  - *Technical Documentation*
  - mass balance plots
- Interpret blue-green algal response

Objective: analyze impacts of invasive plant species

Assuming that we have a calibrated study, we can use it to answer "what if" questions about the site being modeled.

This lab is intended to introduce you to an analysis of the impacts of the invasive aquatic weed *Hydrilla*. Load **Lab6_Clear Lake CA.aps**. This is based on, but not intended to faithfully represent, Clear Lake CA. The macrophyte *Hydrilla* was first found in the lake in 1994 and has been spreading rapidly since then. Eradication efforts have been underway since 1996. The purpose of this exercise is to analyze the impacts of this invasive aquatic weed. If *Hydrilla* were to spread to all of the lake what would be the impacts on the invertebrates, fish, and nutrients? How might it affect the widespread blue-green algal blooms? Why?

Uncertainty and Nominal Range Sensitivity Analysis
Demonstration & Optional Lab

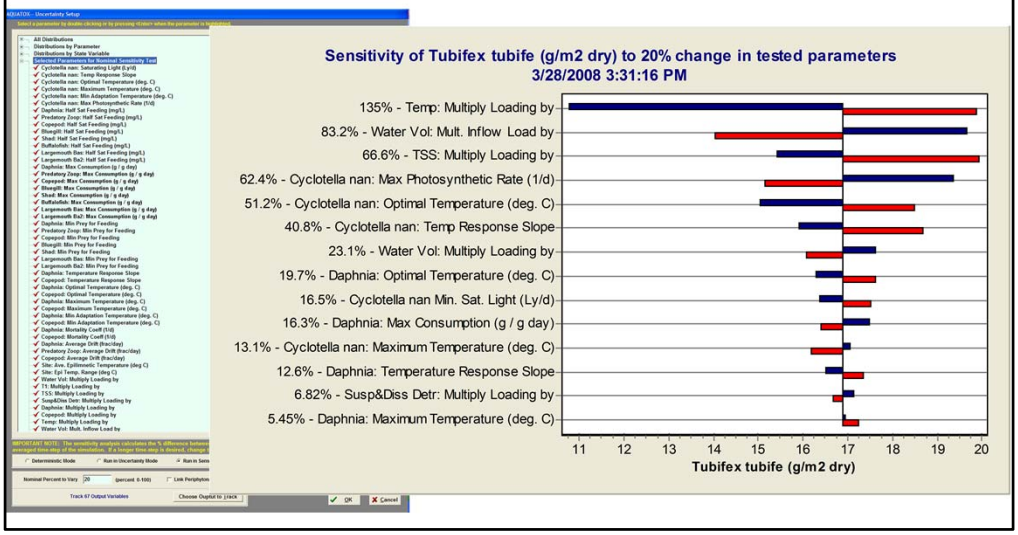
- "Sensitivity" refers to the variation in output of a mathematical model with respect to changes in the values of the model inputs (Saltelli, 2001).
- Sensitivity analysis provides a ranking of the model input assumptions with respect to their relative contribution to model output variability or uncertainty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

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

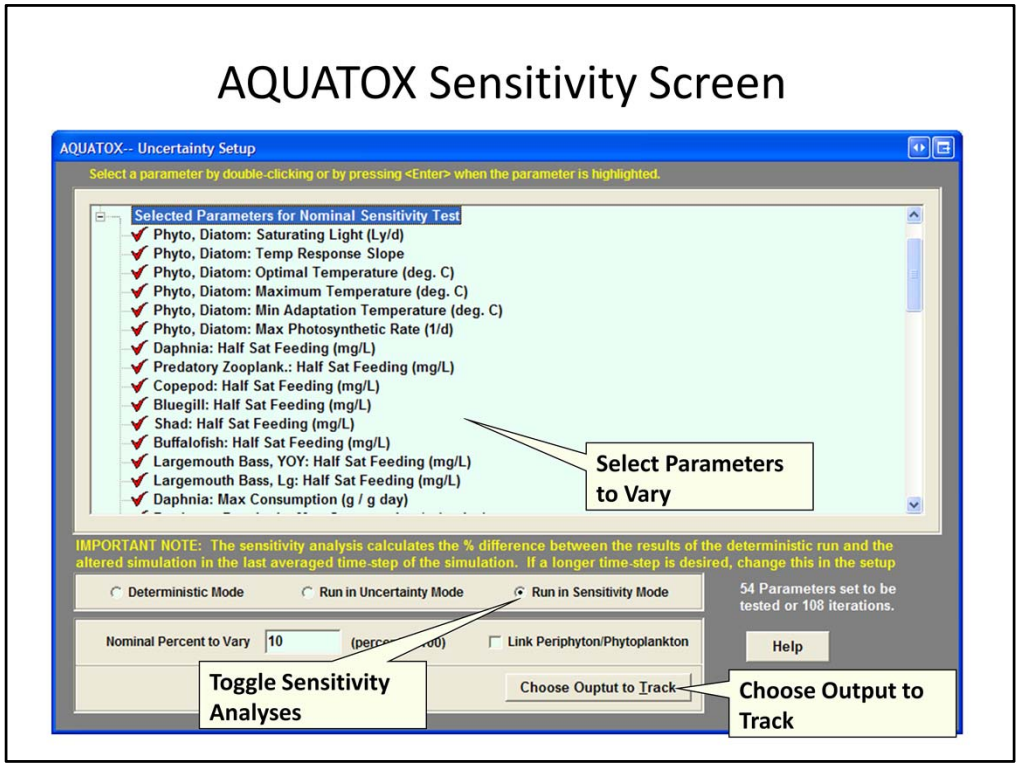
Coralville Sensitivity Analysis Demo

Demonstration of inputs and outputs from Coralville analysis



Using the Coralville study, we will have a quick demonstration of setting up a sensitivity analysis.

The sensitivity statistic is computed for just one reporting time step (which can be any length—often a year). In uncertainty analysis the statistics are computed for each time step, usually a day.



Start by loading **Coralv_ 4yr Sens.aps**

Get to the sensitivity screen by clicking on the “Setup” button and then clicking on the “Uncertainty and Sensitivity” button or by using the uncertainty analysis tool-button.

Keep the parameters selected or select a different set to evaluate.

Note that you can select the percent to vary on this screen and also need to choose which outputs to track.

Sensitivity output is saved in Excel file format.

Finally, you must select the averaging period for your simulation.

For detailed information on how to view and interpret the sensitivity output, review the “Viewing Sensitivity Output” screen in the AQUATOX help file.

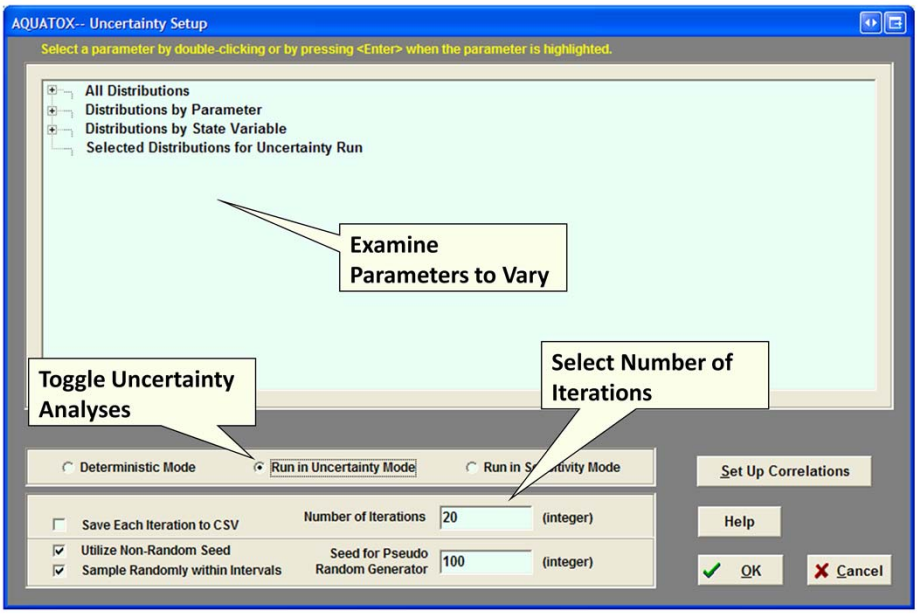
Uncertainty Analysis

- Uncertainty analyses describe sources of incertitude and variability in model simulations
- 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 the number of 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.

AQUATOX Uncertainty Screen

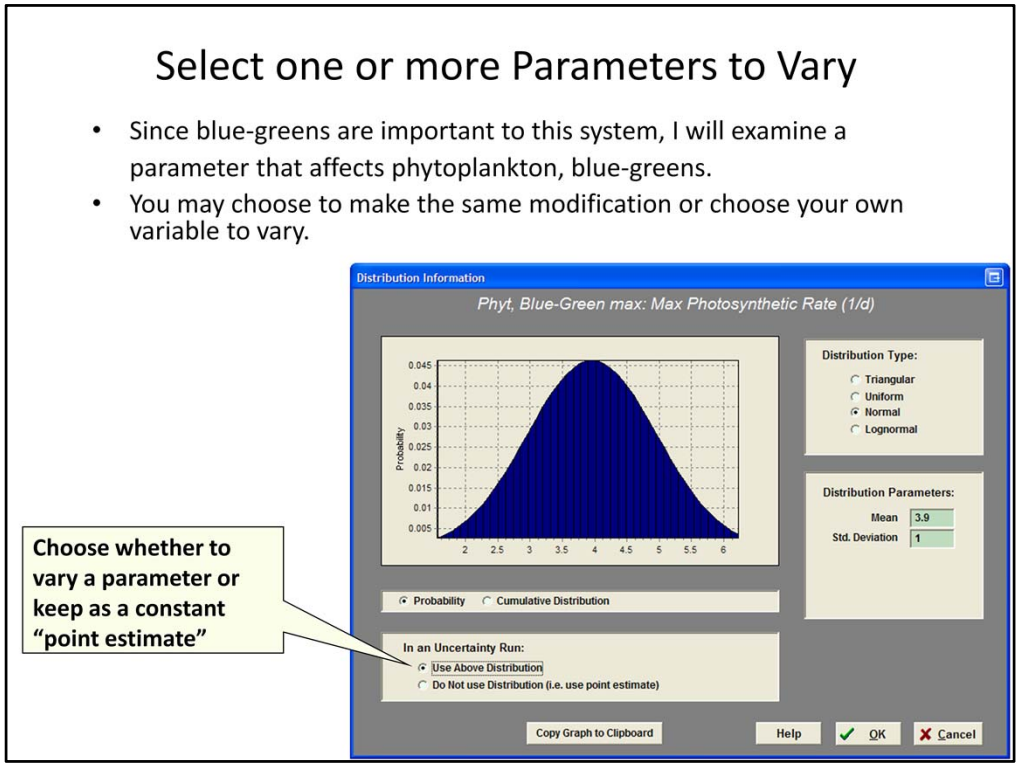


Start by loading **Clear Lake CA.aps**

Get to the uncertainty screen by clicking on the “Setup” button and then clicking on the “Uncertainty and Sensitivity” button or by using the uncertainty analysis tool-button.

Nearly all parameters may be varied within the uncertainty analysis, trophic interactions being the one exception.

Select 20 iterations and to “Run Uncertainty Analysis.” Next we will choose which parameters to vary in this analysis.



Our "sensitivity analysis" indicated that the model is not sensitive to non point-source loadings of phosphate, so we will try a different variable.

To look at the parameters you may modify for the blue greens state variable choose the "+" next to "Distributions by State Variable". Then choose the "+" next to "Bl-green1: [Phyt, Blue-Greens]"

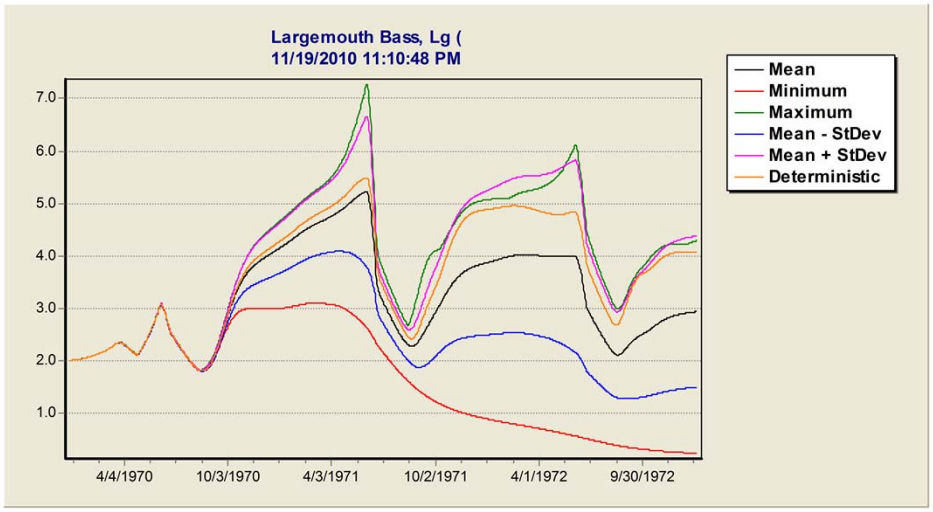
I chose to modify the PMAX (Max Photosynthetic Rate) as there is often some uncertainty surrounding this particular parameter. For my simulation I'm choosing a normal distribution with a **mean of 3.9** (this is the "point estimate" used in the simulation) and a **standard deviation of 1**.

Run the simulation (save the output set as a "db" file when prompted). This set of 20 simulations will probably take about 30 min.

Note, the distributions chosen can reflect variability in various scientific studies that attempt to quantify the given parameter.

You may select as many parameters to vary as you'd like. However, note that the more parameters that you choose to vary, the more iterations are required to produce an output distribution that is stable (i.e. that reflects the true effects of all of the input distributions combined).

Using the Uncertainty Tab on the Output Screen



AQUATOX Uncertainty Output consists of several files:

{filename}.db - A database file with the minimum, maximum, mean, deterministic, and standard deviation for each variable for each day of the simulation.
{filename}2.db – These databases only support so much width so additional variables may need to be saved in additional files.
{filename}.TXT– A text file that indicates what variable draws were chosen for each iteration and the timing of the simulations.
{filename}_decline.CSV – A text file that contains data for the biomass risk graph.
{filename}_{iteration_num}.CSV – the full set of time-series output for every iteration run (optional)

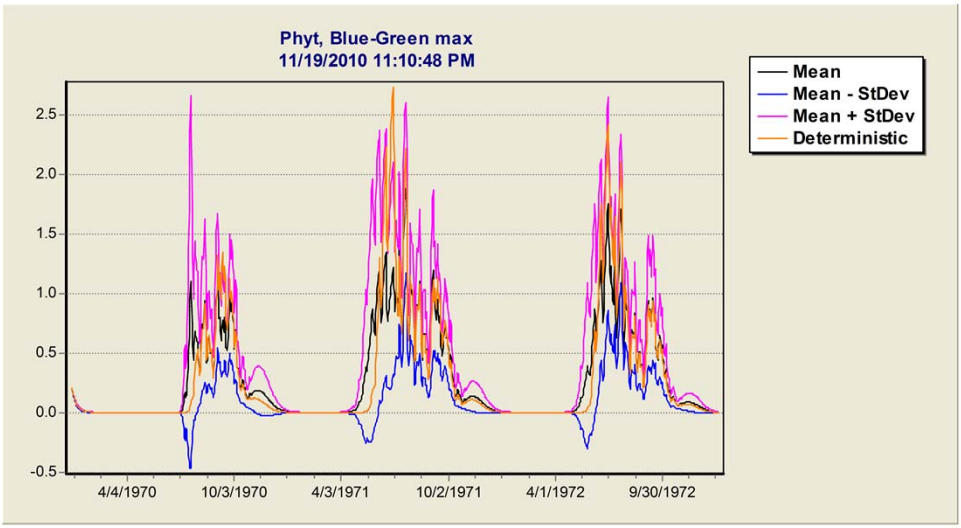
A “deterministic” run is performed without including random draws from the uncertainty analysis, i.e. the deterministic run uses point estimates for all model parameters.

Click on “View a different Variable” to see the other variables within the current db file. Click on “View a different Database” to see if other db files have been created with uncertainty results.

The uncertainty graph gives the user an idea of the spread of the resultant distribution over the entire time-period of the simulation. The results here, for largemouth bass, show strong indirect effects due to the PMAX parameter in Blue-Greens.

NOTE: Apostrophes are not allowed in the file structure for Paradox. If you receive an error, you may circumvent it by placing the db files in a directory that does not have apostrophes in the file path.

Sensitivity of Blue-Greens

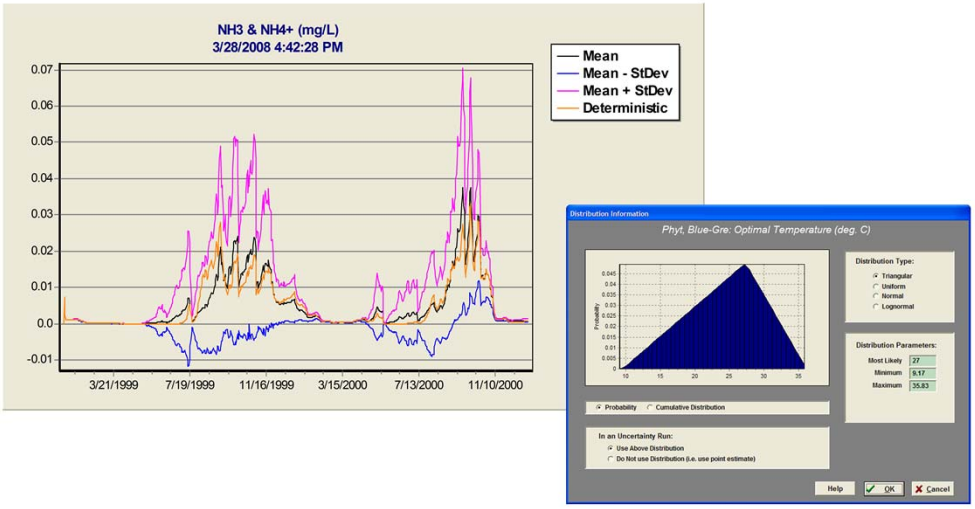


Click on the "View a Different Variable" and select "Phyt, Blue-Greens" The difference in the size of the blue-greens blooms are considerable indicating that blue-greens are indeed quite sensitive to the PMAX parameter.

On your own time, view various different variables and see if you can figure out why or why not the results for these variables are sensitive to the change in the size of the blue-greens bloom.

Blue Earth Uncertainty Analysis Demo

Demonstration of inputs and outputs from Blue Earth River, MN



Input utilizes a graphical interface with several possible distributions for each of the loadings or parameters being tested.
Output includes graphs of the deterministic, mean, +- 1 standard deviation, maximum, and minimum values.
Output can also be shown as a biomass risk graph.
Furthermore, output for each iteration of the analysis can be saved as csv files (in Release 3.1).

AQUATOX– Chemical Fate Overview

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

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, photolysis, hydrolysis, volatilization, and biotransformation 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.
• 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).
• Sorption and desorption are modeled separately as kinetic processes.
• Biotransformation is represented by user-supplied first-order rate constants with the option of also modeling multiple daughter products.
• Bioaccumulation will be discussed later

Chemical Derivatives Tend to be Complex

$$\frac{dToxicant_{Water}}{dt} = Loading + \sum_{LabileDetr}(Decomposition_{LabileDetr} \cdot PPB_{LabileDetr} \cdot 1e-6) + \sum Desorption_{DetrTox} + \sum Depuration_{Org} - \sum Sorption_{DetrTox} - \sum GillUptake - MacroUptake - \sum AlgalUptake_{Alga} - Hydrolysis - Photolysis - MicrobialDegrdn + Volatilization - Discharge + Biotransform_{Microb\ In} \pm TurbDiff$$

$$\frac{dToxicant_{Alga}}{dt} = Loading + AlgalUptake - Depuration \pm TurbDiff - (Excretion + Washout + \sum_{Pred} Predation_{Pred,\ Alga} + Mortality + Sink \pm SinkToHypo) \cdot PPB_{Alga} \cdot 1e-6 \pm Biotransform_{Alga}$$

$$\frac{dToxicant_{Animal}}{dt} = Loading + GillUptake + \sum_{Prey} DietUptake \pm TurbDiff - (Depuration + \sum_{Pred} Predation_{Pred,\ Animal} + Mortality + Recruit \pm Promotion + GameteLoss + Drift + Migration + EmergeInsect) \cdot PPB_{Animal} \cdot 1e-6 \pm Biotransform_{Animal}$$

These are the differential equations for tracking toxicant in water, plants, and animals.

The change in mass of toxicant in the water includes explicit representations of mobilization of the toxicant from sediment to water as a result of decomposition of the labile sediment detritus compartment, sorption to and desorption from the detrital sediment compartments, uptake by algae and macrophytes, uptake across the gills of animals, depuration by organisms, and turbulent diffusion between epilimnion and hypolimnion

Chemical mass is balanced to machine accuracy.

Note that each process within an animal and plant has an effect on the toxicant that is contained within that organism.

Growth dilution is implicitly managed by tracking the mass of each chemical and the biomass of each organism separately.

See Chapter 7 of the Technical Documentation for further details.

HCB in tank

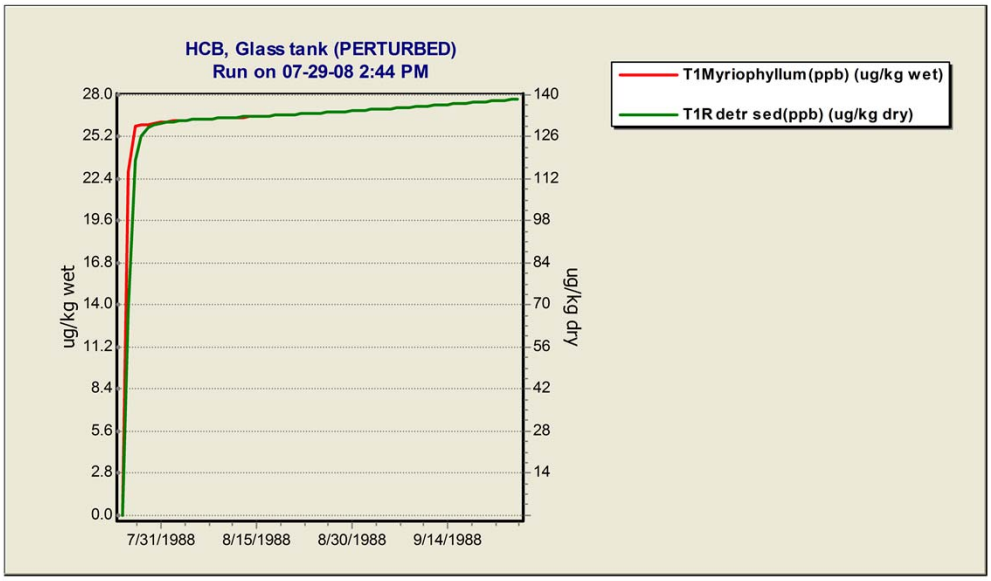
- Reproduces experimental results (Gobas) in which macrophytes are enclosed in an aquarium tank
- A single dose of hexachlorobenzene is applied at the beginning of the simulation
- Simplest type of AQUATOX model setup

From Wikipedia:
"Hexachlorobenzene, or **perchlorobenzene**, is a chlorocarbon with the molecular formula C_6Cl_6. It is a fungicide formerly used as a seed treatment, especially on wheat to control the fungal disease bunt. It has been banned globally under the Stockholm Convention on persistent organic pollutants."

Replication of an experiment conducted by Gobas and others (1991) provides the simplest representation of the model.

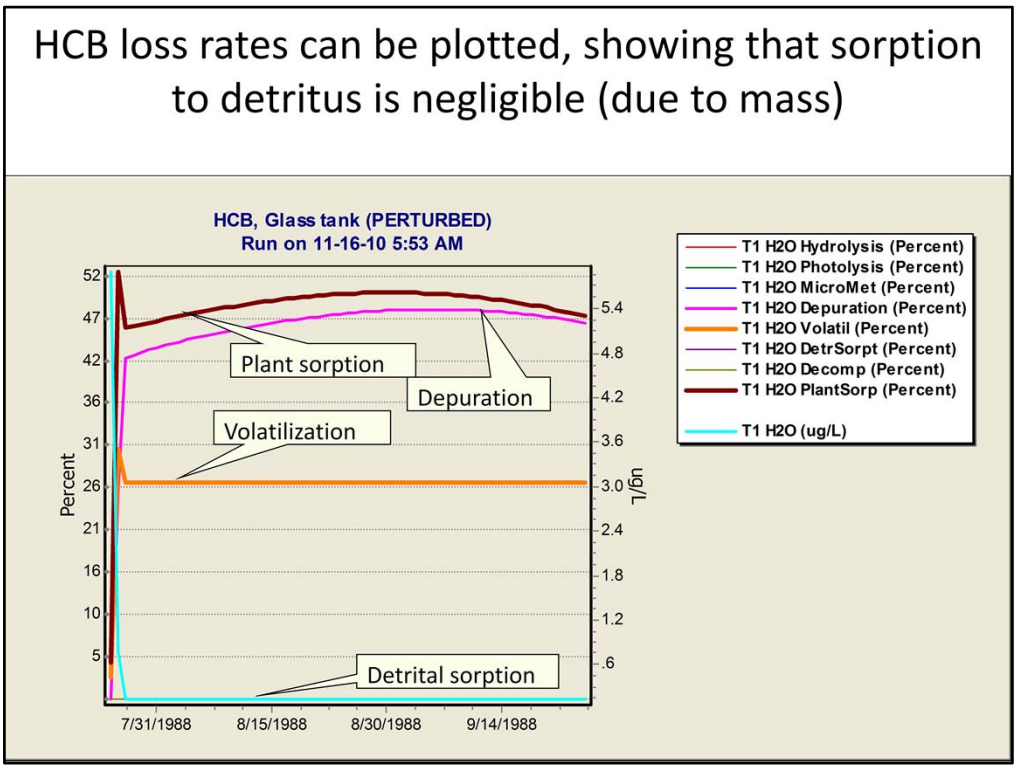
Gobas, F. A. P. C., E. J. McNeil, L. Lovett-Doust, and G. D. Haffner. 1991. Bioconcentration of Chlorinated Aromatic Hydrocarbons in Aquatic Macrophytes (*Myriophyllum spicatum). Environmental Science & Technology 25: 924-929.*

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)



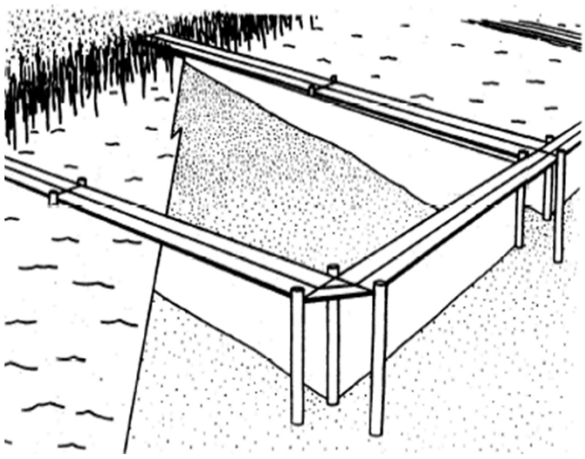
The rates plot indicates that the only significant processes in the tank are sorption by plants and volatilization. As we saw on the previous slide, the rate of sorption by detritus is almost the same as for plants; however the amount of detritus is so small that it accounts for only a fraction of a 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.

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

A series of experiments conducted at the US EPA Laboratory at Duluth MN provided data for testing how well AQUATOX represents chemical fate, bioaccumulation, and toxicity.

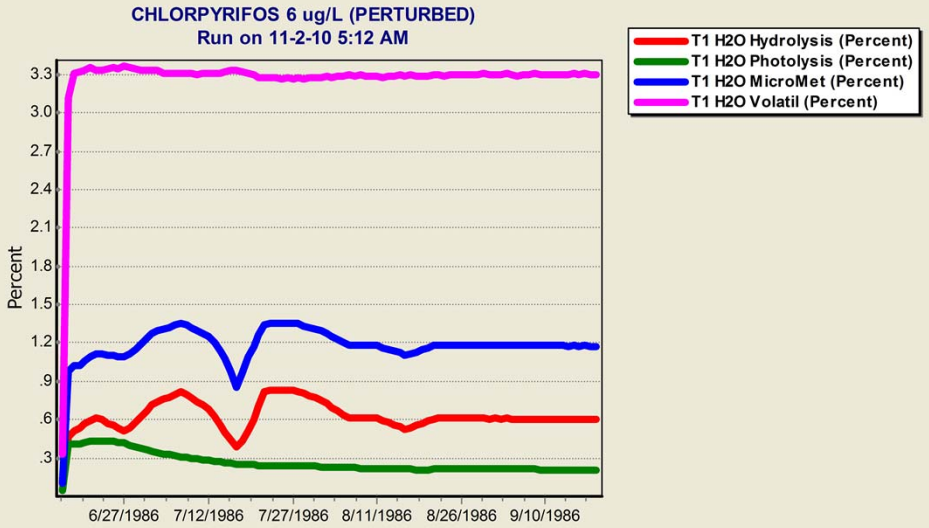
Chlorpyrifos-dosed pond enclosures at Duluth MN
used to validate fate and effects model



AQUATOX has the capability of representing enclosures, including accounting for the extra surface area of the enclosure walls, which is important as substrate for periphyton.

Chemical rates may be tracked

Predicted In-situ Degradation Rates for Chlorpyrifos in Pond

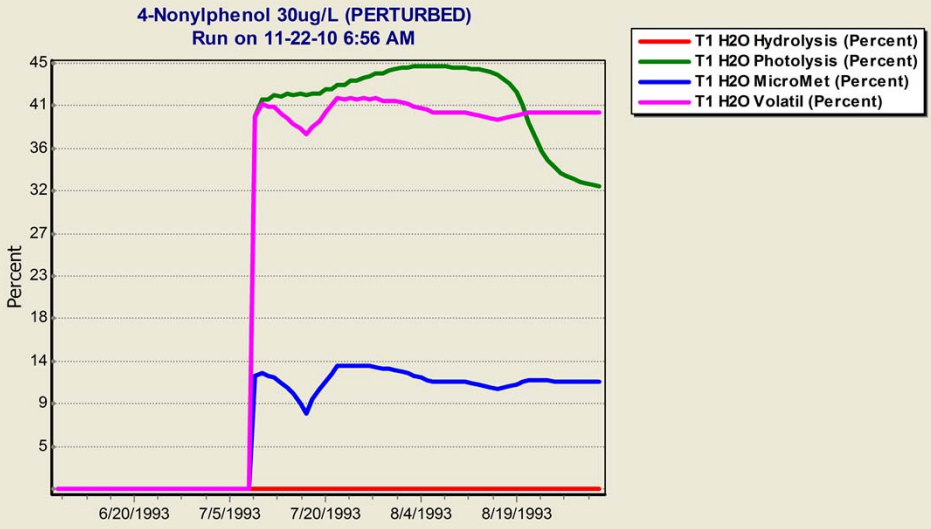


From Wikipedia:
Chlorpyrifos is a crystalline organophosphate insecticide that inhibits acetylcholinesterase and is used to control insect pests. Trade names include Brodan, Detmol UA, Dowco 179, Dursban, Empire, Eradex, Lorsban, Paqeant, Piridane, Scout, and Stipend. Chlorpyrifos is moderately toxic and chronic exposure has been linked to neurological effects, developmental disorders, and autoimmune disorders.

In the US, chlorpyrifos is registered only for agricultural use, where it is "one of the most widely used organophosphate insecticides," according to the United States Environmental Protection Agency (EPA). The crops with the most intense chlorpyrifos use are cotton, corn, almonds, and fruit trees including oranges and apples.

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.

Predicted In-situ Degradation Rates for Nonylphenol
in the Same Pond are Quite Different



From Wikipedia:
"N**onylphenol** is a family of organic compounds, a subset of the alkyphenols. It is a useful precursor to certain detergents. These compounds are classified as a xenobiotic and are controversial pollutants…Millions of kilograms are produced annually…Nonylphenol and nonyphenol ethoxylates have been banned in the European Union as a hazard to human and environmental safety."

Note that, in contrast to chlorpyrifos, nonylphenol disappears rapidly, due in part to high volatilization rates; photolysis is an important degradation pathway and there is no hydrolysis.

Chemical fate clarified using half-Lives and DT95

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

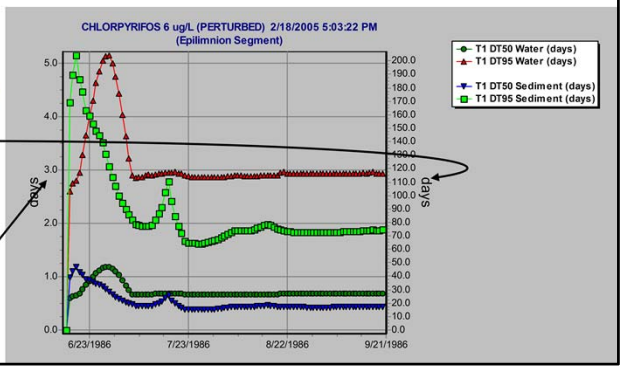
$$Loss_{Water} = \frac{Hydrolysis_{Water} + Photolysis + Microbial_{Water} + Washout + Volat. + Sorption}{Mass_{Water}}$$

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

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.

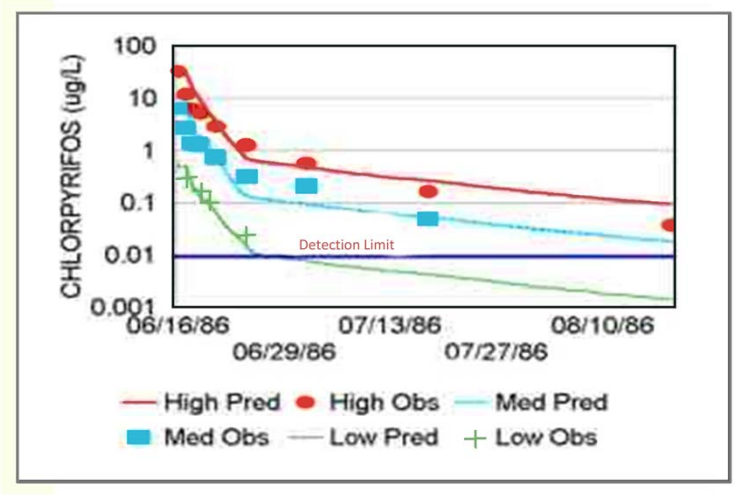
Toxicant mass balance tracking

- 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

Because the model is subject to use in a regulatory context, it is important to have accountability of simulated processes and assurance that mass balance is maintained. This is true for nutrients as well as for organic toxicants.

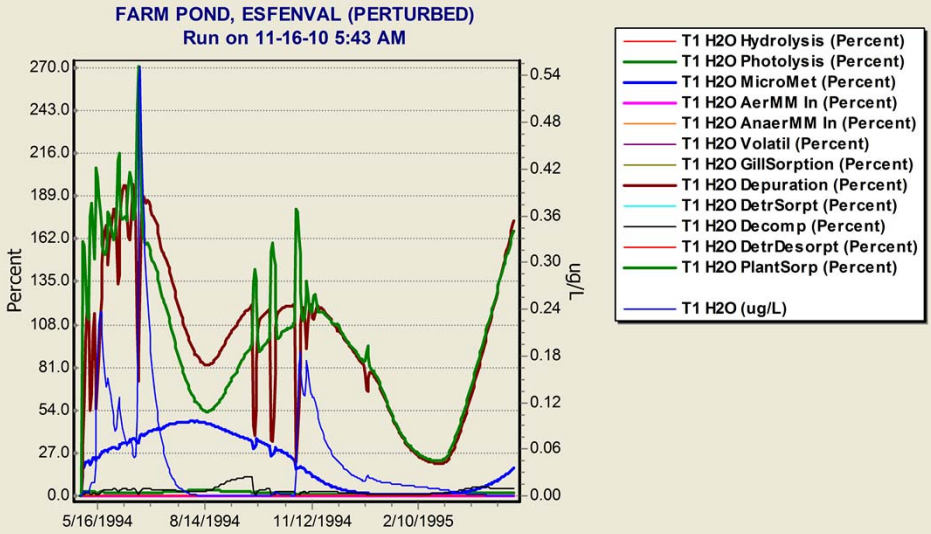
Fate of Chlorpyrifos in the Duluth MN Pond was Predicted Successfully

Multiple Dosing Levels



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

Esfenvalerate in farm pond is taken up and depurated by phytoplankton and lost by microbial degradation

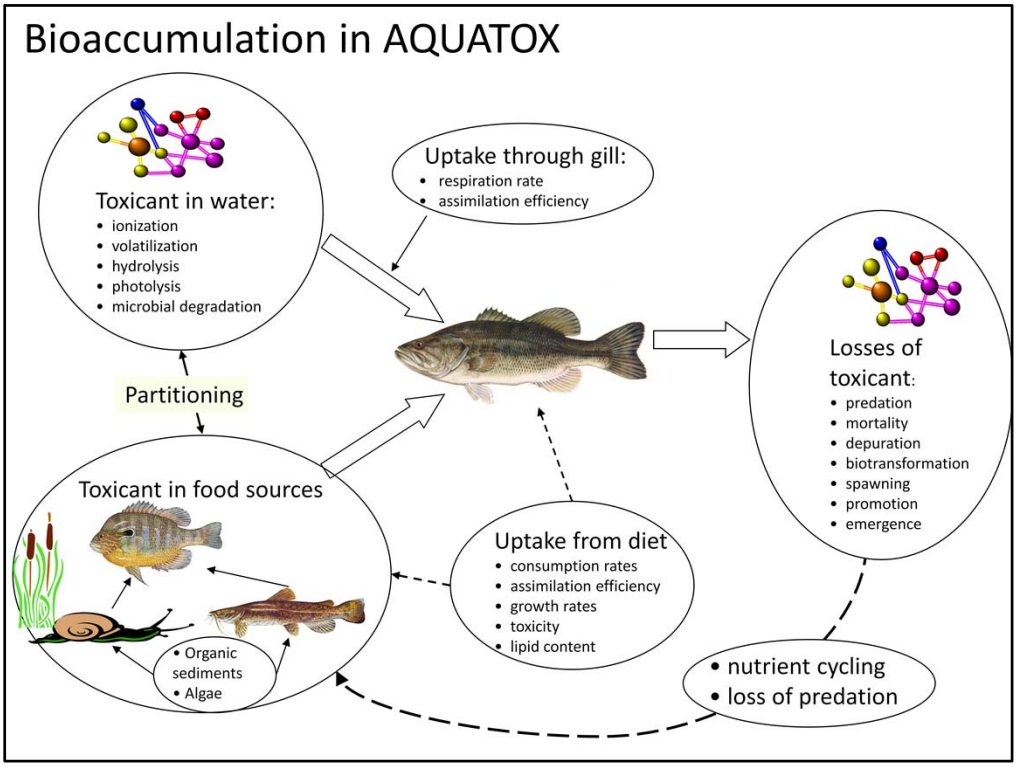


Hypothetical loading of the insecticide esfenvalerate in a farm pond is subject to both uptake and depuration, principally by phytoplankton. Microbial degradation virtually ceases during winter. Sharp spikes reflect instability with small concentrations of pesticide.

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) Bioconcentration Factor (BCF) model available

Having reviewed the chemical fate processes represented by AQUATOX, we will now consider the simulated fate processes involving the biota.

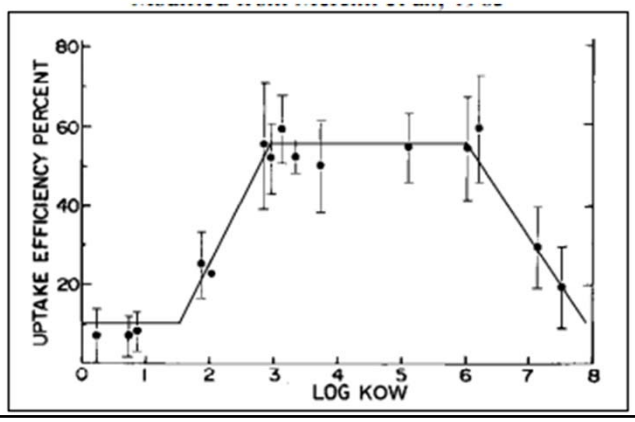


Nonequilibrium concentrations, as represented by kinetic equations, depend on sorption, desorption, and elimination as functions of the chemical and exposure through water and food as a function of bioenergetics of the organism.

Gill Uptake is Function of Respiration and Efficiency of Toxicant Uptake

$$GillUptake = KUptake \cdot Toxicant_{Water} \cdot Frac_{WaterColumn}$$

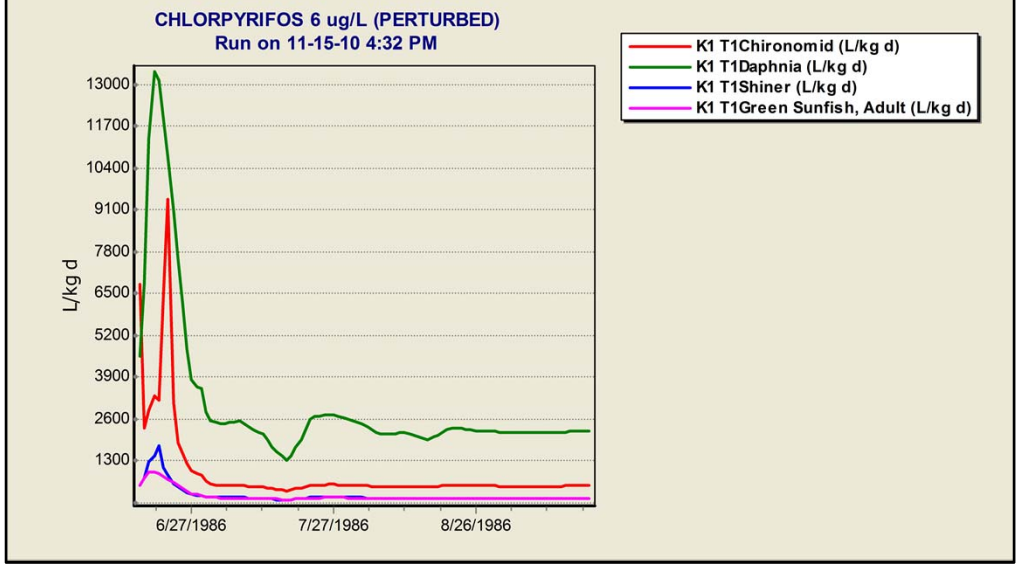
$$KUptake = \frac{WEffTox \cdot Respiration \cdot O2Biomass}{Oxygen \cdot WEffO2}$$



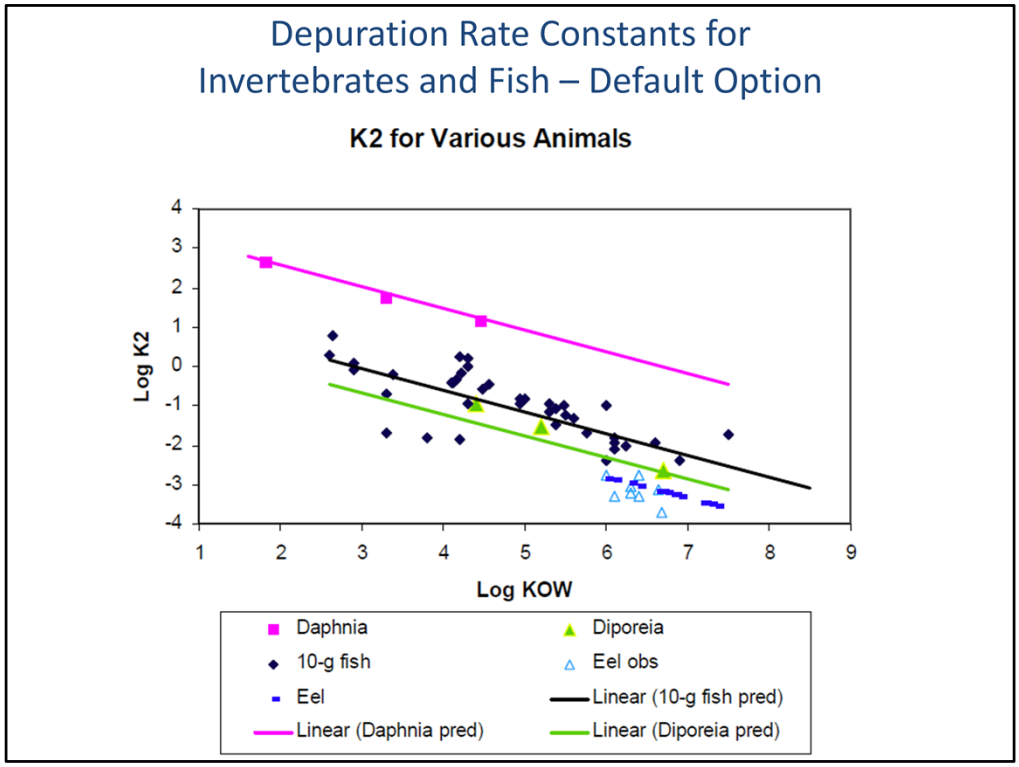
See discussion on pages 248-250 of *Technical Documentation.*

The toxicant uptake efficiency, *WEffTox*, can be expected to have a sigmoidal relationship to the log octanol-water partition coefficient based on aqueous and lipid transport (Spacie and Hamelink, 1982).

Chlorpyrifos Uptake Rates for Invertebrates and Fish in Pond



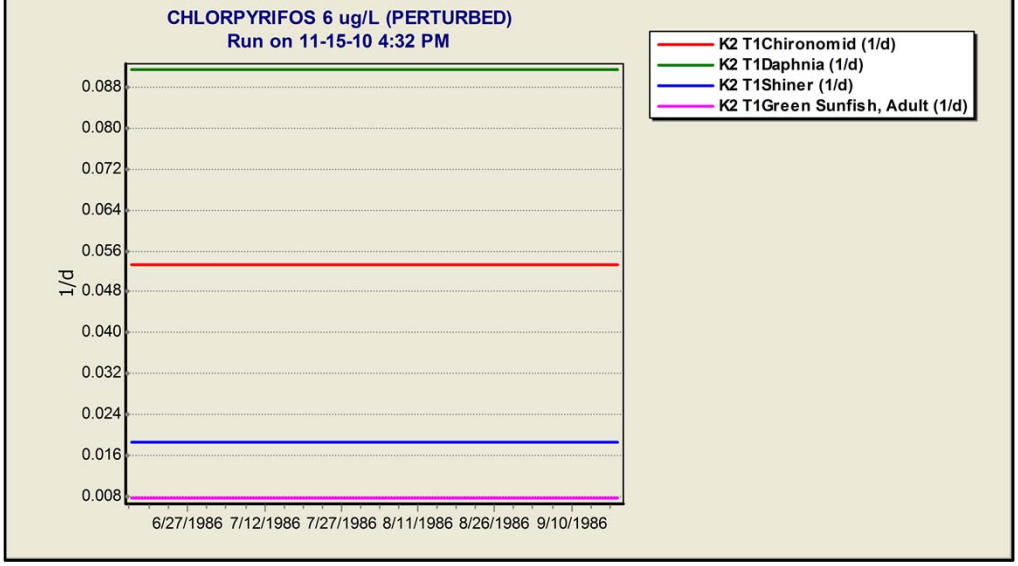
Gill uptake rates are based on time-varying respiration and the Log Kow of the chemical being modeled.



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

In AQUATOX Release 3.1, an alternative k2 estimation procedure is available based on Barber (2003). Barber's (2003) formulation is based on uptake rates divided by LipidFrac×KOW (as a surrogate for BCF). The uptake rate equation utilized is based on an allometric analysis of 517 data points, though there is a high degree of uncertainty in this relationship. Figure 150 in the Technical Documentation shows that the AQUATOX and Barber formulations have different relationships between predicted elimination rates and Kow. Our testing suggests that some studies benefit from one uptake formulation and some benefit from the other; however, at this point there is no general guidance as to which formulation to use in a given application.

Chlorpyrifos Depuration Rate Constants for Invertebrates and Fish in Pond



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:

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

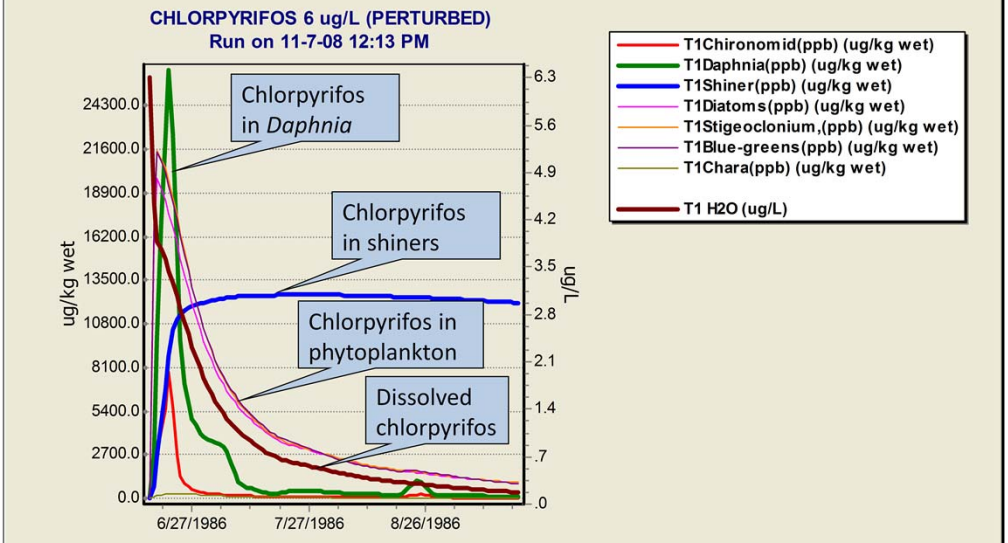
Given these parameters, AQUATOX calculates uptake and depuration in plants and animals as kinetic processes.

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 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 example, chemicals that are taken up very rapidly and those that have an external mode of toxicity, such as affecting the gills directly, are best simulated with an external toxicity construct. For this reason, an alternative uptake model based on equilibrium relationships among K1, K2, and BCF is provided to the user.

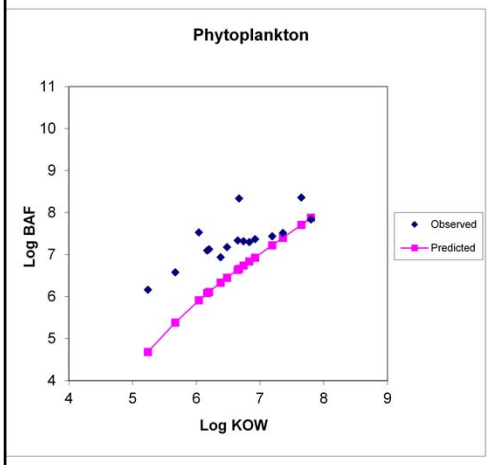
Model can trace how the toxicant is partitioned in the biota

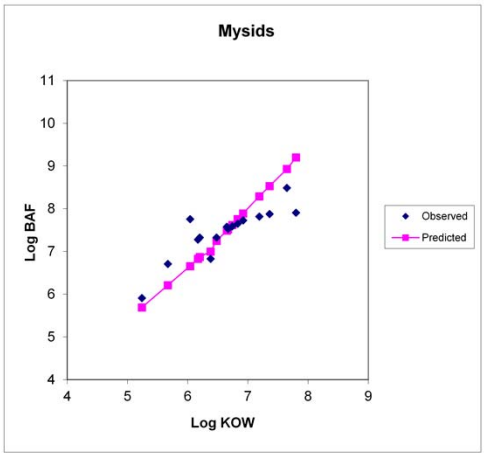


The fate depends in part on the effects: shiners (minnows) are tolerant of chlorpyrifos but *Daphnia* and chironomids aren't.

Lake Ontario Bioaccumulation

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

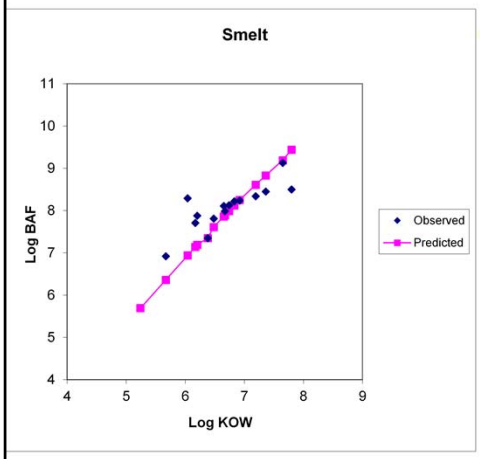


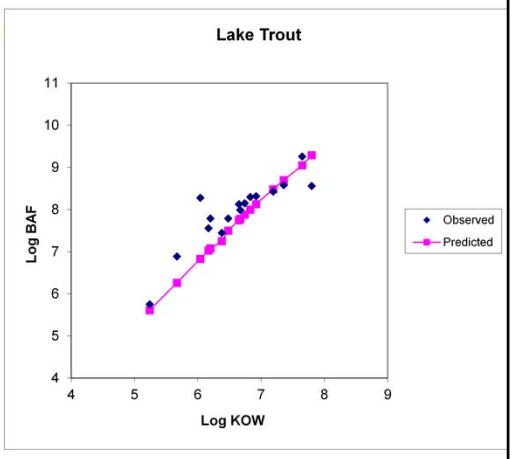


These are graphs from the validation studies done for Release 1.
Phytoplankton BAFs are under-predicted, but observed values include zooplankton.

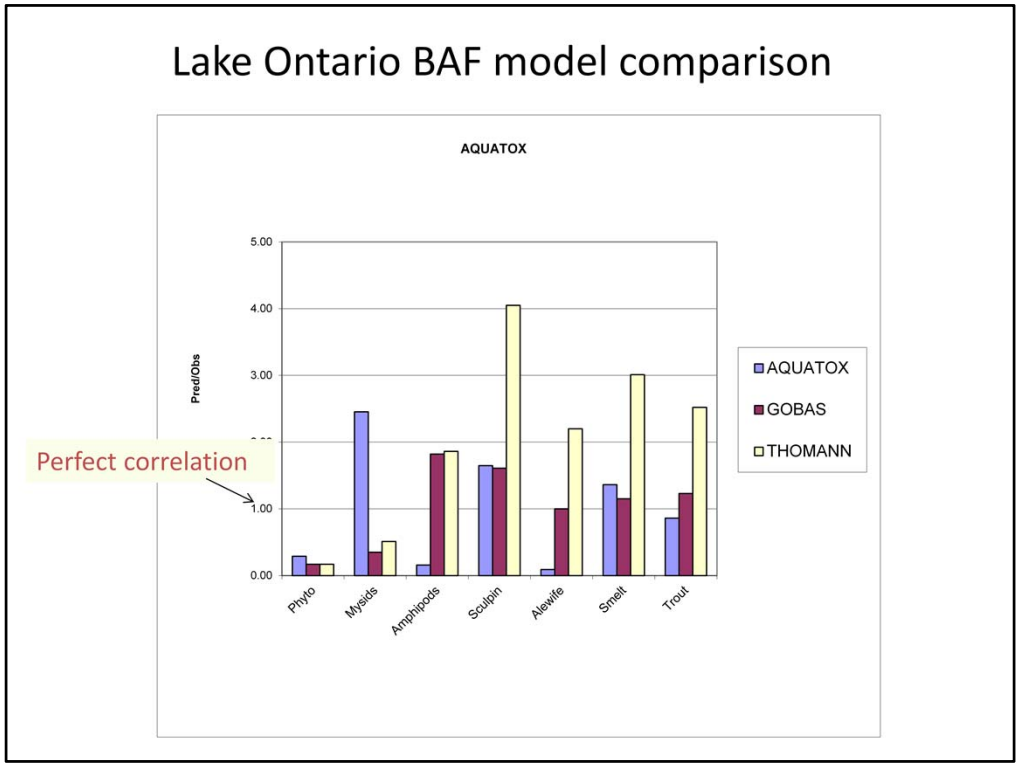
Lake Ontario Bioaccumulation

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



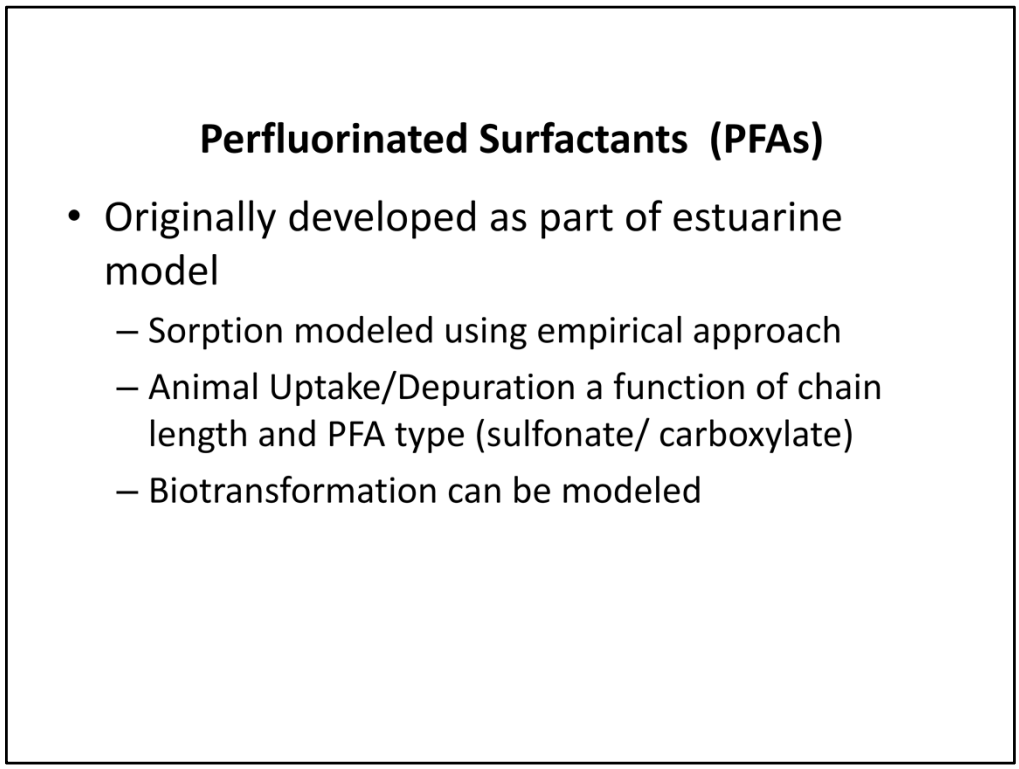


These are the best fits to observed data.



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).

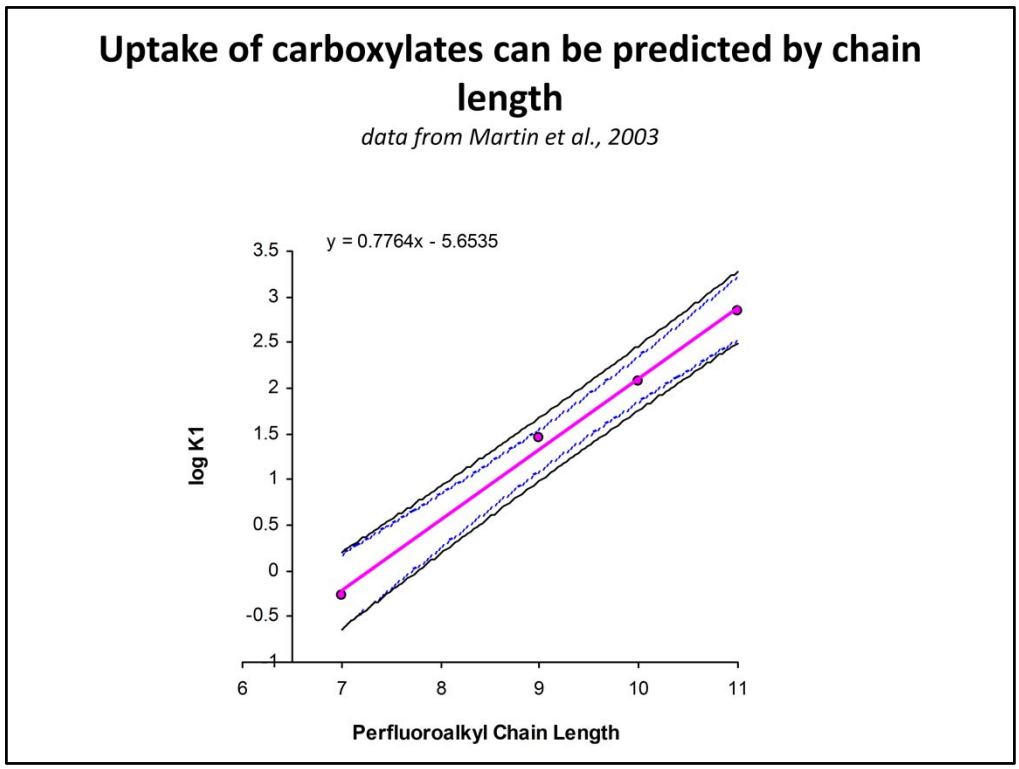
Burkhard, L. P. 1998. Comparison of Two Models for Predicting Bioaccumulation of Hydrophobic Organic Chemicals in a Great Lakes Food Web. Environmental Toxicology and Chemistry **17:383-393.**



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

Several years ago EPA 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.

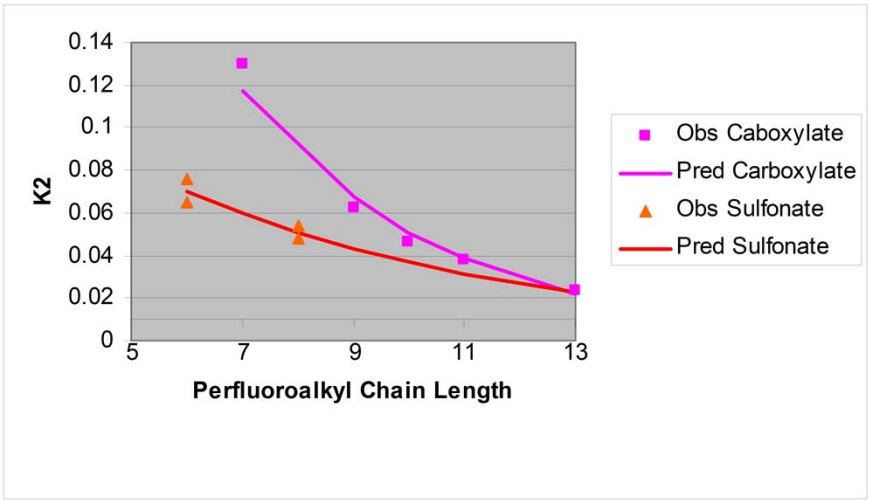


Because PFAs behave differently from most bioaccumulative compounds it was necessary to program estimation procedures for uptake and depuration specific to them. Fortunately, papers documenting such estimation procedures appeared just as we embarked on this project:

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.

PFA Model Data Requirements

- Perflouralkyl Chain Length
- K_{OM} for sediments
- BCF for algae
- BCF for macrophytes
- Toxicity Data (LC50s)

(Parameters provided for PFOS, PFOA)