VALIDATION OF AQUATOX 1.68 FOR PREDICTING BIOACCUMULATION OF PCBS IN THE LAKE ONTARIO FOOD WEB

Introduction

Certain chemicals are persistent in aquatic systems and tend to accumulate in the tissue of fish and other aquatic organisms, sometimes to levels that make them unsafe for human or wildlife consumption. The "bioaccumulative" compounds, such as polychlorinated biphenyls (PCBs), are the cause of a significant number of advisories against fish consumption throughout the U.S. Exposure to bioaccumulative compounds may be through water, contaminated sediment, or diet.

The extent to which a chemical bioaccumulates depends upon many factors, such as trophic structure (food-chain and food-web relationships), ambient water and sediment characteristics, the chemical characteristics of the pollutant, and the lipid content of the exposed organisms. The bioaccumulation factor (BAF) relates tissue concentration to ambient water concentration of the chemical. BAFs may be useful in setting ambient water quality standards for bioaccumulative chemicals. The various chemical and biological processes that drive bioaccumulation may vary over time. For example, food consumption and therefore dietary exposure will vary with seasonal cycles of prey organisms. However, for purposes of setting water quality standards, regulatory agencies are usually concerned with protection based on lifetime average consumption, and thus with long-term average conditions of the water body and of the fish that are consumed.

Several mechanistic models have been developed to predict BAFs and fish tissue concentrations. For lipophilic compounds, the octanol-water partition coefficient (K_{OW}) is often used as an indication of the compound's bioaccumulative potential. Thomann et al. (1992) and Gobas (1993) developed steady-state models that rely on K_{OW}, organic content of the sediment, lipid content of the organisms, and position in the food web to predict tissue concentrations in the organisms. A recent paper (Burkhard 1998) compared the Thomann and Gobas models against an observed dataset from Lake Ontario (Oliver and Niimi 1988). The two models performed similarly for compounds with log K_{OW}s in the range of three to eight, and they were in good agreement with the observed data. The models were shown to be highly sensitive to several input parameters. Sources of uncertainty also were identified. The purpose of this study is to evaluate the performance of the AQUATOX model using the same assumptions and dataset in so far as possible.

Model Structure

The AQUATOX model is a general ecological risk assessment model that represents the combined environmental fate and effects of conventional pollutants, such as nutrients and sediments, and toxic chemicals in aquatic ecosystems. It considers several trophic levels, including attached and planktonic algae and submerged aquatic vegetation, invertebrates, and forage, bottom-feeding, and game fish; it also represents associated organic toxicants. It can be implemented as a simple model (indeed, it has been used to simulate an abiotic flask) or as a truly complex food-web model. Food-web modeling is now considered necessary for bioaccumulation studies other than screening level (Abbott et al. 1995). "Food web models provide a means for validation because they mechanistically

describe the bioaccumulation process and ascribe causality to observed relationships between biota and sediment or water" (Connolly and Glaser 1998).

The fate portion of the model, which is applicable especially to organic toxicants, includes: partitioning among organisms, suspended and sedimented detritus, suspended and sedimented inorganic sediments, and water; volatilization; hydrolysis; photolysis; ionization; and microbial degradation. Earlier versions of AQUATOX had two modes for representing partitioning of a pollutant, equilibrium fugacity and kinetic partitioning. However, the equilibrium fugacity mode was found to have limited applicability and was discontinued. The effects portion of the model includes: chronic and acute toxicity to the various organisms modeled; and indirect effects such as release of grazing and predation pressure, increase in detritus and recycling of nutrients from killed organisms, dissolved oxygen sag due to increased decomposition, and loss of food base for animals.

Partition Coefficients

Although AQUATOX is a kinetic model, steady-state partition coefficients for organic pollutants are computed in order to place constraints on competitive uptake and loss processes, speeding up computations. They are estimated from empirical regression equations and the pollutant's octanol-water partition coefficient.

Natural organic matter is the primary sorbent for neutral organic pollutants. Hydrophobic chemicals partition primarily in nonpolar organic matter (Abbott et al. 1995). Refractory detritus is relatively nonpolar; its partition coefficient is a function of the octanol-water partition coefficient (N = 34, r^2 = 0.93; Schwarzenbach et al. 1993):

$$KOM_{RefrDetr} = 1.38 \cdot KOW^{0.82} \quad \textbf{(1)}$$

where:

$KOM_{RefrDetr}$	=	suspended refractory detritus-water partition coefficient (L/kg); and
KOW	=	octanol-water partition coefficient (unitless).

This and the following equations are extended to polar compounds, following the work of Smejtek and Wang (1993):

$$KOM_{RefrDetr} = 1.38 \cdot KOW^{0.82} \cdot Nondissoc + (1 - Nondissoc) \cdot IonCorr \cdot 1.38 \cdot KOW^{0.82} \quad \textbf{(2)}$$

where:

Nondissoc	=	un-ionized fraction (unitless); and
IonCorr	=	correction factor for decreased sorption, generally 0.1 (unitless).

Partitioning of bioaccumulative chemicals on organic carbon in sediments in Lake Ontario, as represented by the Oliver and Niimi (1988) data, exhibits a weak relationship with KOW (US EPA 1995, Burkhard 1998):

$$KOC = 25 \cdot KOW \quad \textbf{(3)}$$

where:

KOC = the partition coefficient for particulate organic carbon-water (L/kg).

Converting to organic matter (assuming a conversion factor of 0.526) and generalizing to include polar compounds, this relationship is used in AQUATOX for this project, and only this project, to represent the partitioning of chemicals between water and refractory detritus in sediments:

$$KOM_{RDetrSed} = 13 \cdot KOW + (1 - Nondissoc) \cdot IonCorr \cdot 13 \cdot KOW \quad \textbf{(4)}$$

where:

$KOM_{RDetrSed}$ = sedimented refractory detritus-water partition coefficient (L/kg).

There appears to be a dichotomy in partitioning; data in the literature suggest that labile detritus does not take up hydrophobic compounds as rapidly as refractory detritus. Algal cell membranes contain polar lipids, and it is likely that this polarity is retained in the early stages of decomposition. KOC does not remain the same upon aging, death, and decomposition, probably because of polarity changes. In an experiment using fresh and aged algal detritus, there was a 100% increase in KOC with aging (Koelmans et al. 1995). KOC increased as the C/N ratio increased, indicating that the material was becoming more refractory. In another study, KOC doubled between day 2 and day 34, probably due to deeper penetration into the organic matrix and lower polarity of the partially decomposed material (Cornelissen et al. 1997).

Polar substrates increase the pKa of the compound (Smejtek and Wang 1993). This is represented in the model by lowering the pH of polar particulate material by one pH unit, which changes the dissociation accordingly. The partition equation for labile detritus (N = 3, $r^2 = 1.0$;) is based on a study by Koelmans et al. (1995) using fresh algal detritus:

$$KOC_{LabPart} = 23.44 \cdot KOW^{0.61} \quad \textbf{(5)}$$

where:

$KOC_{Lab\ Part}$ = partition coefficient for suspended labile organic carbon (L/kg).

The equation is generalized to polar compounds and transformed to an organic matter partition coefficient:

$$KOM_{LabDetr} = (23.44 \cdot KOW^{0.61} \cdot Nondissoc + (1 - Nondissoc) \cdot IonCorr \cdot 23.44 \cdot KOW^{0.61}) \cdot 0.526 \quad \textbf{(6)}$$

where:

$KOC_{LabPart}$ = partition coefficient for suspended labile organic carbon (L/kg);
$KOM_{LabDetr}$ = partition coefficient for suspended labile detritus (L/kg); and

0.526 = conversion factor for organic carbon to organic matter.

O'Connor and Connolly (1980; see also Ambrose et al., 1991) found that the sediment partition coefficient is the inverse of the mass of suspended sediment, and DiToro (1985) developed a construct to represent the relationship. However, AQUATOX models partitioning directly to organic detritus and ignores inorganic sediments, which are seldom involved directly in sorption of neutral organic pollutants. Therefore, the partition coefficient is not corrected for mass of sediment.

Association of hydrophobic compounds with colloidal and dissolved organic matter (DOM) reduces bioavailability; such contaminants are unavailable for uptake by organisms (Stange and Swackhamer 1994, Gilek et al. 1996). Therefore, it is imperative that complexation of organic chemicals with DOM be modeled correctly. In particular, contradictory research results can be reconciled by considering that DOM is not homogeneous: refractory humic acids, derived from decomposition of terrestrial and wetland organic material, are quite different from labile exudates from algae and other indigenous organisms.

Humic acids exhibit high polarity and do not readily complex neutral compounds. Natural humic acids from a Finnish lake with extensive marshes were spiked with a PCB, but a PCB-humic acid complex could not be demonstrated (Maaret et al. 1992). In another study, Freidig et al. (1998) used artificially prepared Aldrich humic acid to determine a humic acid-DOC partition coefficient for several dissimilar chemicals (n = 5, r^2, = 0.80), although they cautioned about extrapolation to the field:

$$KOC_{RefrDOM} = 28.84 \cdot KOW^{0.67} \quad \textbf{(7)}$$

where:

$KOC_{RefrDOM}$ = refractory dissolved organic carbon distribution coefficient (L/kg).

Until a better relationship is found, we are using a generalization of their equation to include polar compounds, transformed from organic carbon to organic matter, in AQUATOX:

$$KOM_{RefrDOM} = (28.84 \cdot KOW^{0.67} \cdot Nondissoc + (1 - Nondissoc) \cdot IonCorr \cdot 28.84 \cdot KOW^{0.67}) \cdot 0.526 \quad \textbf{(8)}$$

where:

$KOM_{RefrDOM}$ = refractory dissolved organic matter distribution coefficient (L/kg).

Nonpolar lipids in algae occur in the cell contents, and it is likely that they constitute part of the labile dissolved exudate, which may be both excreted and lysed material. Therefore, the stronger relationship reported by Koelmans and Heugens (1998) for partitioning to algal exudate (n = 6, r^2 = 0.926) is:

$$KOC_{LabDOC} = 0.88 \cdot KOW \quad \textbf{(9)}$$

which was also generalized for polar compounds and transformed for organic matter:

$$KOM_{LabDOM} = (0.88 \cdot KOW \cdot Nondissoc + (1 - Nondissoc) \cdot IonCorr \cdot 0.88 \cdot KOW) \cdot 0.526 \quad \textbf{(10)}$$

where:

KOC_{LabDOC} = partition coefficient for labile dissolved organic carbon (L/kg); and
KOM_{LabDOM} = partition coefficient for labile dissolved organic matter (L/kg).

Unfortunately, older data and modeling efforts failed to distinguish between hydrophobic compounds that were truly dissolved and those that were complexed with DOM. For example, the PCB water concentrations for Lake Ontario, reported by Oliver and Niimi (1988) and used by many subsequent researchers, included both dissolved and DOC-complexed PCBs (a fact which they recognized). AQUATOX distinguishes between truly dissolved and complexed compounds; therefore, the partition coefficients may be larger than those used in older studies.

Bioaccumulation of PCBs in algae depends on solubility, hydrophobicity and molecular configuration of the compound, and growth rate, surface area and type, and content and type of lipid in the alga (Stange and Swackhamer 1994). Phytoplankton may double or triple in one day and periphyton turnover may be so rapid that some PCBs will not reach equilibrium (cf. Hill and Napolitano 1997). Therefore, one should use the term "bioaccumulation factor" (BAF) rather than "bioconcentration factor," which implies equilibrium (Stange and Swackhamer 1994).

Hydrophobic compounds partition to lipids in algae, but the relationship is not a simple one. Phytoplankton lipids can range from 3 to 30% by weight (Swackhamer and Skoglund 1991), and not all lipids are the same. Polar phospholipids occur on the surface. Hydrophobic compounds preferentially partition to internal neutral lipids, but those are usually a minor fraction of the total lipids, and they vary depending on growth conditions and species (Stange and Swackhamer 1994). Algal lipids have a much stronger affinity for hydrophobic compounds than does octanol, so that the algal $BAF_{lipid} > K_{OW}$ (Stange and Swackhamer 1994, Koelmans et al. 1995, Sijm et al. 1998).

For algae, the approximation to estimate the dry-weight bioaccumulation factor ($r^2 = 0.87$), computed from Swackhamer & Skoglund's (1993) study of numerous PCB congeners with a natural phytoplankton assemblage, is:

$$\log(KB_{Alga}) = 0.41 + 0.91 \cdot LogKOW \quad \textbf{(11)}$$

where:

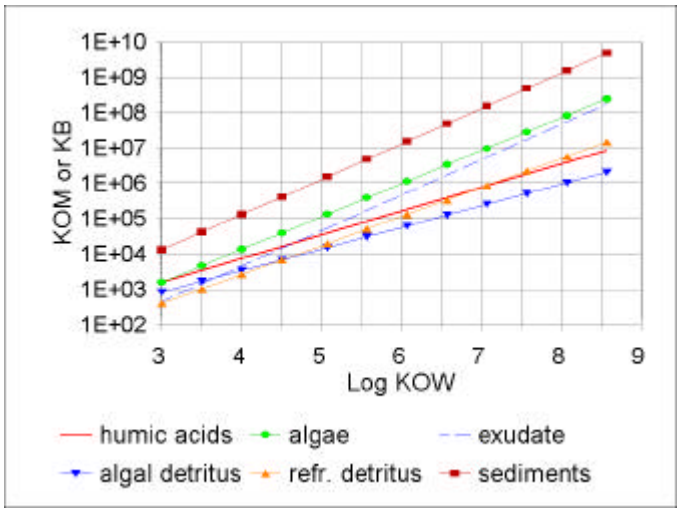
KB_{Alga} = partition coefficient between phytoplankton and water (L/kg).

Rearranging and extending to hydrophilic and ionized compounds:

$$KB_{Alga} = 2.57 \cdot KOW^{0.91} \cdot Nondissoc + (1 - Nondissoc) \cdot IonCorr \cdot 2.57 \cdot KOW^{0.91} \quad \textbf{(12)}$$

Comparing the results of using these coefficients, we see that they are consistent with the relative importance of the various substrates in binding organic chemicals (**Figure 1**). Binding capacity of detritus is greater than dissolved organic matter in Great Lakes waters (Stange and Swackhamer 1994, Gilek et al. 1996). In a study using Baltic Sea water, less than 7% PCBs were associated with dissolved organic matter and most were associated with algae (Björk and Gilek 1999). In contrast, in a study using algal exudate and a PCB, 98% of the dissolved concentration was as a dissolved organic matter complex and only 2% was bioavailable (Koelmans and Heugens 1998).

Figure 1. Partitioning to various types of organic matter as a function of KOW.



For macrophytes, an empirical relationship reported by Gobas et al. (1991) for 9 chemicals with *LogKOW*s of 4 to 8.3 ($r^2 = 0.97$) is used:

$$\log(KB_{Macro}) = 0.98 \cdot LogKOW - 2.24 \quad \textbf{(13)}$$

Again, rearranging and extending to hydrophilic and ionized compounds:

$$KB_{Macro} = 0.00575 \cdot KOW^{0.98} \cdot (Nondissoc + 0.2) \quad \textbf{(14)}$$

For the invertebrate bioconcentration factor, the following empirical equation is used, based on 7 chemicals with *LogKOW*s ranging from 3.3 to 6.2 and bioconcentration factors for *Daphnia pulex* ($r^2 = 0.85$; Southworth et al., 1978; see also Lyman et al., 1982), converted to dry weight :

$$\log(KB_{Invertebrate}) = (0.7520 \cdot LogKOW - 0.4362) \cdot WetToDry \quad \textbf{(15)}$$

where:

$KB_{Invertebrate}$	=	partition coefficient between invertebrates and water (L/kg); and
WetToDry	=	wet to dry conversion factor (unitless, default = 5).

Extending and generalizing to ionized compounds:

$$KB_{Invertebrate} = WetToDry \cdot 0.3663 \cdot KOW^{0.7520} \cdot (Nondissoc + 0.01) \quad \textbf{(16)}$$

Fish take longer to reach equilibrium with the surrounding water; therefore, a nonequilibrium bioconcentration factor is used. For each pollutant, a whole-fish bioconcentration factor is based on the lipid content of the fish extended to hydrophilic chemicals (McCarty et al., 1992), with provision for ionization:

$$KB_{Fish} = Lipid \cdot WetToDry \cdot KOW \cdot (Nondissoc + 0.01) \quad \textbf{(17)}$$

where:

KB_{Fish}	=	partition coefficient between whole fish and water (L/kg);
Lipid	=	fraction of fish that is lipid (g lipid/g fish); and
WetToDry	=	wet to dry conversion factor (unitless, default = 5).

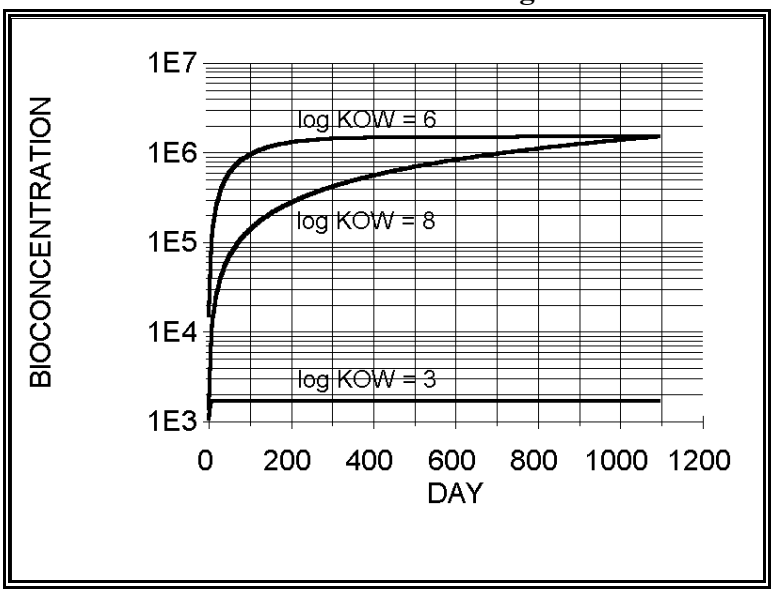
Lipid content of fish is varied depending on the potential for growth as predicted by the bioenergetics equations; the initial lipid values for the species are given. The bioconcentration factor is adjusted for the time to reach equilibrium as a function of the clearance or elimination rate and the time of exposure (Hawker and Connell, 1985; Connell and Hawker, 1988):

$$BCF_{Fish} = KB_{Fish} \cdot \left(1 - e^{(-Elimination \cdot TElapsed)}\right) \quad \textbf{(18)}$$

where:

BCF_{Fish}	=	quasi-equilibrium bioconcentration factor for fish (L/kg);
TElapsed	=	time elapsed since fish was first exposed (d); and
Elimination	=	combined clearance and biotransformation, see **(40)** (1/d).

Figure 2
Bioconcentration factor for fish
as a function of time and log KOW



Nonequilibrium Kinetics

Often there is an absence of equilibrium due to growth or insufficient exposure time, metabolic biotransformation, dietary exposure, and nonlinear relationships for very large and/or superhydrophobic compounds (Bertelsen et al. 1998). Although it is important to have a knowledge of equilibrium partitioning because it is an indication of the condition toward which systems tend (Bertelsen et al. 1998), it is often impossible to determine steady-state potential due to changes in bioavailability and physiology (Landrum 1998). PCBs may not be at steady state even in large systems such as Lake Ontario that have been polluted over a long period of time—the challenge is to obtain sufficient data for a kinetic model (Gobas et al. 1995). In fact, PCBs in Lake Ontario exhibit a 25-fold disequilibrium (Cook and Burkhard 1998).

Sorption and Desorption to Sedimented Detritus

Partitioning to sediments appears to involve rapid sorption to particle surfaces, followed by slow movement into, and out of, organic matter and porous aggregates (Karickhoff and Morris, 1985); therefore, attainment of equilibrium may be slow. This applies to suspended detritus compartments as well. Because of the need to represent sorption and desorption separately in detritus, kinetic formulations are used (Thomann and Mueller, 1987), with provision for ionization:

$$Sorption = k1_{Detr} \cdot Toxicant_{Water} \cdot Diff1_{Carrier} \cdot (Nondissoc + 0.01) \cdot Org2C \cdot Detr \cdot 1e-6 \quad \textbf{(19)}$$

$$Desorption = k2_{Detr} \cdot Diff2_{Carrier} \cdot Toxicant_{Detr} \quad \textbf{(20)}$$

where:

Sorption	=	rate of sorption to given detritus compartment (∶g/L"d);
k1	=	sorption rate constant for given compartment (L/kg"d);
Nondissoc	=	fraction not ionized (unitless);
$Toxicant_{Water}$	=	concentration of toxicant in water (∶g/L);
$Diff1_{Carrier}$	=	factor to normalize rate constant for given carrier (detritus compartment in this case) based on all competing uptake rates (unitless);
$Diff2_{Carrier}$	=	factor to normalize loss rates (unitless);
Org2C	=	conversion factor for organic matter to carbon (= 0.526 g C/g organic matter);
Detr	=	mass of each of the detritus compartments per unit volume (mg/L);
1e -6	=	units conversion (kg/mg);
Desorption	=	rate of desorption from given sediment detritus compartment (∶g/L"d);
k2	=	desorption rate constant for given compartment (1/d); and
$Toxicant_{Detr}$	=	mass of toxicant in each of the detritus compartments (∶g/L).

Because there are several processes competing for the dissolved toxicant, the rate constants for these processes are normalized in order to preserve mass balance. The *Diff1* factor is computed for each direct uptake process by the various carriers, including sorption to detritus and algae, uptake by macrophytes, and uptake across animals' gills:

$$Diff1_{Carrier} = \frac{RateDiff1_{Carrier}}{\sum RateDiff1_{Carrier}} \quad \textbf{(21)}$$

$$RateDiff1_{Carrier} = Gradient1_{Carrier} \cdot k1_{Carrier} \quad \textbf{(22)}$$

$$Gradient1_{Carrier} = \frac{Toxicant_{Water} \cdot kp_{Carrier} - PPB_{Carrier}}{Toxicant_{Water} \cdot kp_{Carrier}} \quad \textbf{(23)}$$

where:

$RateDiff1_{Carrier}$	=	maximum rate constant for uptake given the concentration gradient (L/kg"d);
$Gradient1_{Carrier}$	=	gradient between potential and actual concentrations of toxicant in each carrier (unitless);
$kp_{Carrier}$	=	partition or bioconcentration factor for each carrier (L/kg);
$PPB_{Carrier}$	=	concentration of toxicant in each carrier (∶g/kg).

Likewise, the loss rate constants are normalized; the equations parallel those for uptake, with the gradient being reversed:

$$Diff2_{Carrier} = \frac{RateDiff2_{Carrier}}{\sum RateDiff2_{Carrier}} \quad \textbf{(24)}$$

$$RateDiff2_{Carrier} = Gradient2_{Carrier} \cdot k2_{Carrier} \quad \textbf{(25)}$$

$$Gradient2_{Carrier} = \frac{PPB_{Carrier} - (PPB_{Water} \cdot kp_{Carrier})}{PPB_{Carrier}} \quad \textbf{(26)}$$

where:

$RateDiff2_{Carrier}$ = maximum rate constant for loss given the concentration gradient (L/kg"d); and

$Gradient2_{Carrier}$ = gradient between actual and potential concentrations of toxicant in each carrier (unitless).

Desorption of the slow compartment is the reciprocal of the reaction time, which Karickhoff and Morris (1985) found to be a linear function of the partition coefficient, expressed in hours, over three orders of magnitude ($r^2 = 0.87$):

$$\frac{1}{k2} \approx 0.03 \cdot 24 \cdot KPSed \quad \textbf{(27)}$$

So *k2* is taken to be:

$$k2 = \frac{1.39}{KPSed} \quad \textbf{(28)}$$

where:

KPSed = detritus-water partition coefficient (L/kg, see **Eq. (2)**); and

24 = conversion from hours, as used by Karickhoff and Morris (1985), to days.

The slow compartment may be involved in 40 to 90% of the sorption so, as a simplification, fast desorption of the labile compartment is ignored. This compensates in part for the fact that AQUATOX models the top layer of bottom sediments as if it were in close contact with the overlying water column (interstitial water is not modeled at this time).

The sorption rate constant is set to 1200 L/kg"d in the code, representing the very fast sorption of most chemicals.

Bioconcentration in Macrophytes and Algae

Macrophytes—As Gobas et al. (1991) have shown, submerged aquatic macrophytes take up and release organic chemicals over a measurable period of time at rates related to the octanol-water partition coefficient. Uptake and elimination are modeled assuming that the chemical is transported through both aqueous and lipid phases in the plant, with rate constants using empirical equations fit to observed data (Gobas et al., 1991), modified to account for ionization effects (**Figure 3**, **Figure 4**):

$$Uptake_{Plant} = k1 \cdot Diff1_{Plant} \cdot Toxicant_{Water} \cdot StVar_{Plant} \cdot 1e-6 \quad \textbf{(29)}$$

$$Clear_{Plant} = k2 \cdot Toxicant_{Plant} \cdot Diff2_{Plant} \quad \textbf{(30)}$$

$$k1 = \frac{1}{0.0020 + \frac{500}{KOW \cdot Nondissoc}} \quad \textbf{(31)}$$

$$k2 = \frac{1}{1.58 + 0.000015 \cdot KOW \cdot Nondissoc} \quad \textbf{(32)}$$

where:

$Uptake_{Plant}$	=	uptake of toxicant by plant (∶g/L"d);
$Clear_{Plant}$	=	clearance of toxicant from plant (∶g/L"d);
$StVar_{Plant}$	=	biomass of given plant (mg/L);
1 e -6	=	units conversion (kg/mg);
$Toxicant_{Plant}$	=	mass of toxicant in plant (∶g/L);
k1	=	sorption rate constant (L/kg"d);
k2	=	elimination rate constant (1/d);
$Diff1_{Plant}$	=	factor to normalize rate constant for given plant based on all competing uptake rates (unitless);
KOW	=	octanol-water partition coefficient (unitless); and
Nondissoc	=	fraction of un-ionized toxicant (unitless).

Figure 3. Uptake rate constant for macrophytes (after Gobas et al., 1991)

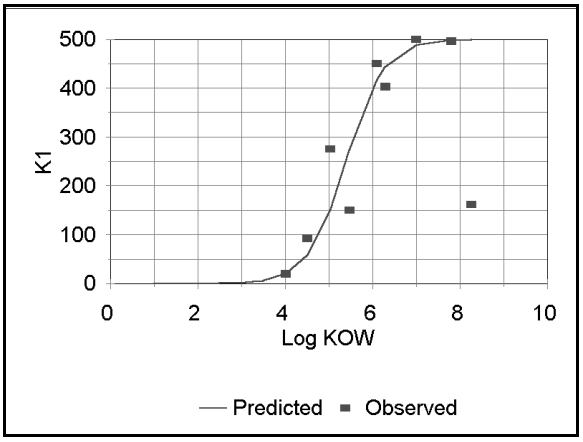
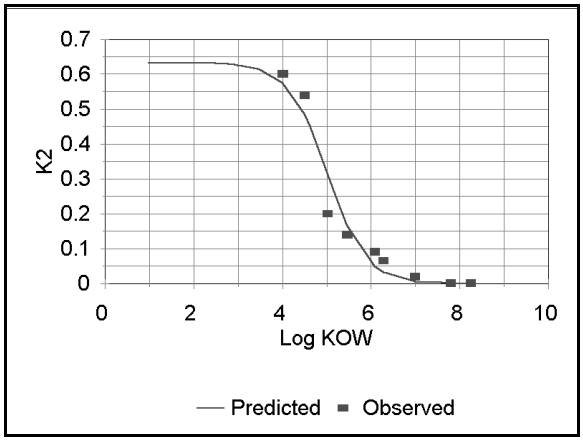


Figure 4. Elimination rate constant for macrophytes (after Gobas et al., 1991)



Algae—There is probably a two-step algal bioaccumulation mechanism for hydrophobic compounds, with rapid surface sorption of 40-90% within 24 hours and then a small, steady increase with transfer to interior lipids for the duration of the exposure (Swackhamer and Skoglund 1991). Uptake increases with increase in the surface area of algae (Wang et al. 1997). Therefore, the smaller the organism the larger the uptake rate constant (Sijm et al. 1998). However, in small phytoplankton, such as the nannoplankton that dominate the Great lakes, a high surface to volume ratio can increase sorption, but high growth rates can limit internal contaminant concentrations (Swackhamer and Skoglund 1991). AQUATOX uses a generalized uptake construct, but explicitly models growth rate and the effect on the BAFs.

The kinetics of partitioning of toxicants to algae is based on studies on PCB congeners showing uptake to be very rapid. Sijm et al. (1998) presented data on several congeners that were used in this study to develop the following relationship for phytoplankton (**Figure 5**):

$$k1 = \frac{1}{1.8\text{E}{-}6 + 1/(KOW \cdot Nondissoc)} \quad \textbf{(33)}$$

Based in part on Skoglund et al. (1996}, but ignoring surface sorption and recognizing that growth dilution is explicit in AQUATOX, the elimination rate constant (**Figure 6**) is computed as:

$$k2 = \frac{k1}{KOW} \quad \textbf{(34)}$$

Figure 5. Algal sorption rate constant.

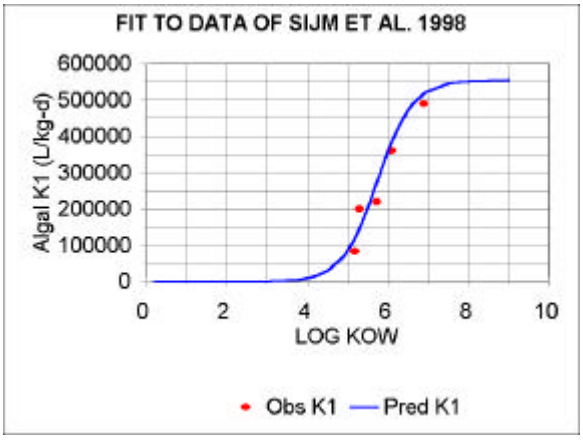
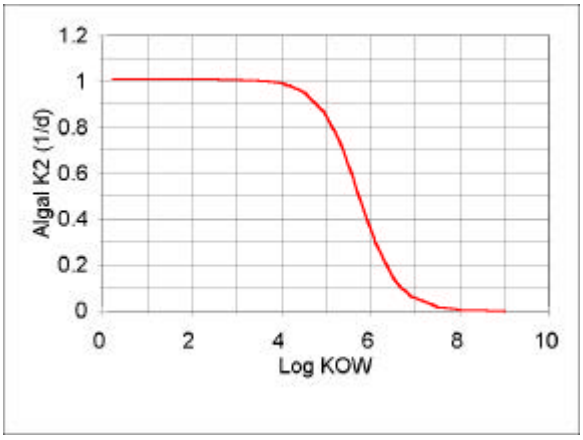


Figure 6. Rate of elimination by algae.



Bioaccumulation in Animals

Animals can absorb toxic organic chemicals directly from the water through their gills and from contaminated food through their guts. Direct sorption onto the body is assumed to be negligible in this version of AQUATOX. Reduction of body burdens of organic chemicals is accomplished through excretion and biotransformation, which are often considered together as empirically determined elimination rates. "Growth dilution" occurs when growth of the organism is faster than accumulation of the toxicant. Fecal loss is important as an input to the detrital toxicant pool. Inclusion of mortality and promotion terms is necessary for mass balance, but emphasizes the fact that average concentrations are being modeled for any particular compartment.

Gill Sorption—An important route of exposure is by active transport through the gills (Macek et al., 1977). This is the route that has been measured so often in bioconcentration experiments with fish. As the organism respires, water is passed over the outer surface of the gill and blood is moved past the inner surface. The exchange of toxicant through the gill membrane is assumed to be facilitated by the same mechanism as the uptake of oxygen, following the approach of Fagerström and Åsell (1973, 1975), Weininger (1978), and Thomann and Mueller (1987; see also Thomann, 1989). Therefore, the uptake rate for each animal can be calculated as a function of respiration (Leung, 1978; Park et al., 1982):

$$GillUptake = KUptake \cdot Toxicant_{Water} \cdot Diff1_{Carrier} \quad \textbf{(35)}$$

$$KUptake = \frac{WEffTox \cdot Respiration \cdot O2Biomass}{Oxygen \cdot WEffO2} \quad \textbf{(36)}$$

where:

$GillUptake$	=	uptake of toxicant by gills (: g/L - d);
$KUptake$	=	uptake rate (1/d);
$Toxicant_{Water}$	=	concentration of toxicant in water (: g/L);
$Diff1_{Carrier}$	=	factor to normalize rate constant for given carrier (animal compartment in this case) based on all competing uptake rates (unitless);
$WEffTox$	=	withdrawal efficiency for toxicant by gills (unitless);

Respiration	=	respiration rate (mg biomass/L"d);
O2Biomass	=	ratio of oxygen to organic matter (mg oxygen/mg biomass; generally 0.575);
Oxygen	=	concentration of dissolved oxygen (mg oxygen/L); and
WEffO2	=	withdrawal efficiency for oxygen (unitless).

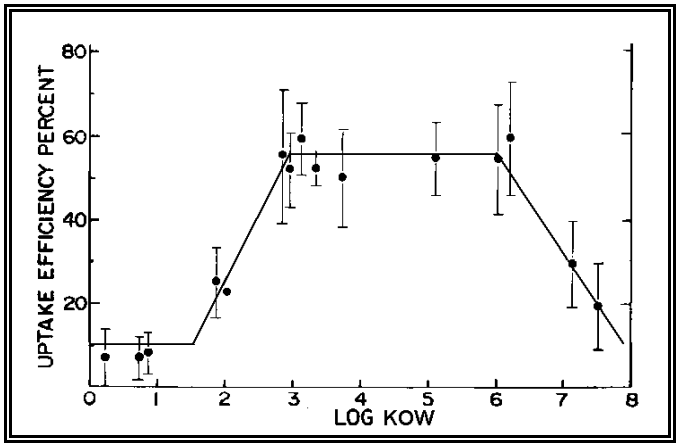
The oxygen uptake efficiency *WEffO2* is assigned a constant value of 0.62 based on observations of McKim et al. (1985). The toxicant uptake efficiency can be expected to have a sigmoidal relationship to the log octanol-water partition coefficient based on aqueous and lipid transport (Spacie and Hamelink, 1982); this is represented by an inelegant but reasonable, piece-wise fit (**Figure 7**) to the data of McKim et al. (1985) using 750-g trout, corrected for ionization:

$$\begin{gathered}
\text{If } LogKOW < 1.5 \text{ then} \\
WEffTox = 0.1 \\
\\
\text{If } 1.5 \le LogKOW > 3.0 \text{ then} \\
WEffTox = 0.1 + Nondissoc \cdot (0.3 \cdot LogKOW - 0.45) \\
\\
\text{If } 3.0 \le LogKOW \le 6.0 \text{ then} \\
WEffTox = 0.1 + Nondissoc \cdot 0.45 \\
\\
\text{If } 6.0 < LogKOW < 8.0 \text{ then} \\
WEffTox = 0.1 + Nondissoc \cdot (0.45 - 0.23 \cdot (LogKOW - 6.0)) \\
\\
\text{If } LogKOW \ge 8.0 \text{ then} \\
WEffTox = 0.1
\end{gathered} \qquad \textbf{(37)}$$

where:

LogKOW	=	log octanol-water partition coefficient (unitless); and
Nondissoc	=	fraction of toxicant that is un-ionized (unitless).

Figure 7. Piece-wise fit to observed toxicant uptake data; modified from McKim et al., 1985.



Ionization decreases the uptake efficiency. This same algorithm is used for invertebrates. Thomann (1989) has proposed a similar construct for these same data and a slightly different construct for small organisms, but the scatter in the data do not seem to justify using two different constructs.

Dietary Uptake—Hydrophobic chemicals usually bioaccumulate primarily through absorption from contaminated food. Persistent, highly hydrophobic chemicals demonstrate biomagnification or increasing concentrations as they are passed up the food chain from one trophic level to another; therefore, dietary exposure can be quite important (Gobas et al., 1993). Uptake from contaminated prey can be computed as (Thomann and Mueller, 1987; Gobas, 1993):

$$DietUptake_{Prey} = KD_{Prey} \cdot PPB_{Prey} \cdot 1e-6 \quad \textbf{(38)}$$

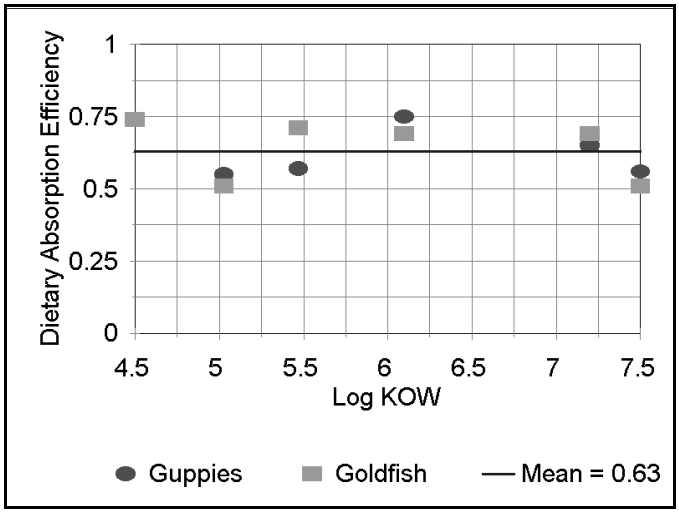
$$KD_{Prey} = GutEffTox \cdot Ingestion_{Prey} \quad \textbf{(39)}$$

where:

$DietUptake_{Prey}$	=	uptake of toxicant from given prey (∶g toxicant/L"d);
KD_{Prey}	=	dietary uptake rate for given prey (mg prey/L"d);
PPB_{Prey}	=	concentration of toxicant in given prey (∶g toxicant/kg prey);
1 e-6	=	units conversion (kg/mg);
GutEffTox	=	efficiency of sorption of toxicant from gut (unitless); and
$Ingestion_{Prey}$	=	ingestion of given prey (mg prey/L"d).

Gobas (1993) presents an empirical equation for estimating *GutEffTox* as a function of the octanol-water partition coefficient. However, data published by Gobas et al. (1993) suggest that there is no trend in efficiency between *LogKOW* 4.5 and 7.5 (**Figure 8**); this is to be expected because the digestive system has evolved to assimilate a wide variety of organic molecules. Therefore, the mean value of 0.63 is used as a constant for small fish. Nichols et al. (1998) demonstrated that uptake is more efficient in larger fish; therefore, a value of 0.90 is used for large game fish. Invertebrates generally exhibit lower efficiencies;

Figure 8. *GutEffTox* constant based on mean value for data from Gobas et al., 1993.



Landrum and Robbins (1990) showed that values ranged from 0.42 to 0.24 for chemicals with log KOWs from 4.4 to 6.7; the mean value of 0.35 is used for invertebrates in AQUATOX.

Elimination—Elimination includes both excretion and biotransformation of a toxicant by organisms. Biotransformation is difficult to model separately and may cause underestimation of elimination (McCarty et al., 1992). Therefore, an overall elimination rate constant is estimated and the derived value is reported in the toxicity record. The user may then modify the value based on observed data.

For purposes of estimating elimination, a modification of **Eq. (35)** is used to compute uptake, assuming a generalized allometric relationship between respiration and the mean weight of the animal (Thomann, 1989):

$$k1 = 1000 \cdot WetWt^{-0.2} \cdot WEffTox \quad \textbf{(40)}$$

where:

k1	=	uptake rate (L/kg"d);
WetWt	=	mean wet weight of organism (g);
1000	=	units conversion (g/kg);
WEffTox	=	withdrawal efficiency for toxicant by gills, see **Eq. (36)** (unitless).

If, as Thomann (1989) assumes, lipid-normalized bioconcentration is equal to the octanol-water partition coefficient at equilibrium and zero growth, then:

$$k2 = \frac{k1}{KOW \cdot LipidFrac \cdot WetToDry \cdot (Nondissoc + 0.1)} \quad \textbf{(41)}$$

where:

k2	=	elimination rate constant (1/d); and
KOW	=	octanol-water partition coefficient (unitless);
LipidFrac	=	fraction of lipid in organism (g lipid/g organism);
Wet2Dry	=	wet to dry weight ratio (5); and
Nondissoc	=	fraction of compound un-ionized (unitless, 1.0 for PCBs).

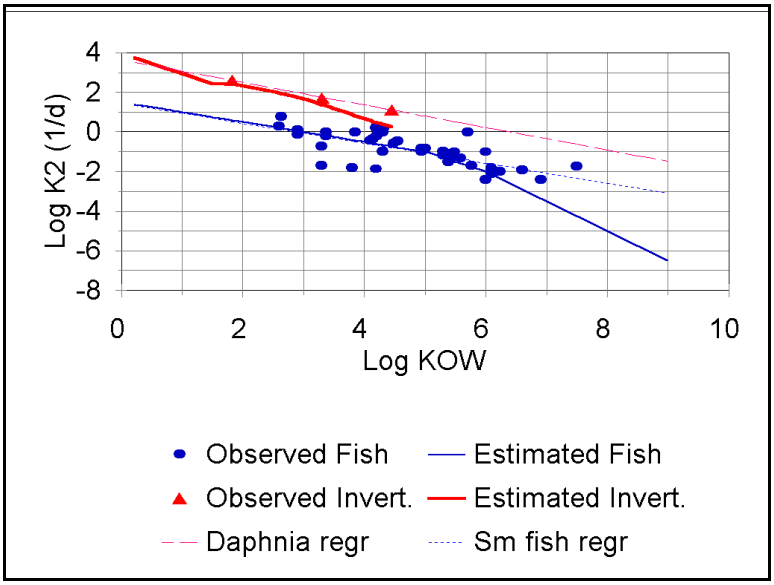
Note that this is the only place where the lipid fraction is used in modeling bioaccumulation in AQUATOX. This simple relationship, although weak, has been used in AQUATOX for both invertebrates and fish (**Figure 9**). However, the fish curve seems to drastically underestimate clearance at higher KOWs. Therefore, as an alternative until the formulation is changed, *k*2 estimates may be entered manually using as guides regression equations for *Daphnia*:

$$\text{Log } k2 = -0.5688 \cdot \text{Log } KOW + 3.6445 \quad \textbf{(42)}$$

and small fish:

$$\text{Log } k2 = -0.503 \cdot \text{Log } KOW + 1.45 \quad \textbf{(43)}$$

Figure 9. Elimination rate constants for *Daphnia* and for 10-g fish; see Thomann, 1989.



For any given time the clearance rate is:

$$Clear_{Animal} = k2 \cdot Toxicant_{Animal} \quad \textbf{(44)}$$

where:

$Clear_{Animal}$ = clearance rate (∶g/L"d); and
$Toxicant_{Animal}$ = mass of toxicant in given animal (∶g/L).

Data Used for Model Evaluation

Data presented by Oliver and Niimi (1988) for various PCB congeners in Lake Ontario sediments, water, and organisms were used to characterize pollutant distributions in that Great Lake food web. Although the data are high quality, they are not synoptic; rather, water samples were taken in April, 1984; sediment samples were taken in May, 1981; suspended sediment samples from November to April for 1982 to 1986; plankton (a mixture of phytoplankton and zooplankton) in July, 1982; mysids in July, 1981 and October, 1984; benthos in June, 1985; sculpin in spring, 1986; alewives and smelt in May, 1982; smaller smelt (not used in the present study) in April, 1986; and salmonids in fall, 1981, and April, 1982. Furthermore, water, sediment, and plankton samples were taken from all three major basins in Lake Ontario; but fish and benthos samples were taken from the western Niagara Basin.

Seventy-two PCB congeners were studied by Oliver and Niimi (1988). Because of computational load, 16 congeners were selected for use in the evaluation of AQUATOX. They were selected to span the range of K_{OW}s and included congeners with higher, and therefore more reliable, concentrations. The freely dissolved concentrations were computed from the reported water concentrations, which included both dissolved PCBs and those associated with dissolved organic matter, using the approach of US EPA (1995).

The feeding relationships of phytoplankton, mysids, the amphipod *Diporeia,* sculpin, alewife, smelt, and salmonids were taken from Burkhard (1998, based on Flint 1986 and Gobas 1993). However, feeding ratios are not constants; what is actually consumed in Nature depends on time-varying prey biomass. Consumption as modeled in AQUATOX treats the preferences as weights for available prey, mimicking the way predation changes in the real world. The assumption made by both Gobas (1993) and Burkhard (1998) is that the plankton analyzed by Oliver and Niimi (1988) were phytoplankton, although Oliver and Niimi state (p. 388) that a plankton sample from a depth of 10 m "would contain a mixture of phytoplankton and zooplankton, phytoplankton should predominate." Furthermore, *Mysis relicta* is treated in the models as if it is the herbivorous or next trophic level, although mysids are opportunistic feeders and prey heavily on zooplankton (www.fw.umn.edu/nresexotics3001/mysisrelicta.html). Therefore, cladocerans were included as the intermediate, herbivorous trophic level, as they are in most implementations of AQUATOX. Feeding preferences for both cladocerans and mysids were based on the literature. The assignment of animals to guilds in AQUATOX is as follows: amphipods, detritivorous invertebrates; cladocerans, herbivorous invertebrates; mysids, predatory invertebrates; sculpin, benthic fishe' alewife, forage fish; smelt, nominally small game fish; trout, large game fish.

Lipid content for the various organisms was based on Oliver and Niimi (1988). Using these as constant lipid fractions is even more misleading; there is ample evidence, presented in Arts and Wainman (1999) and elsewhere, that lipid content is a time-varying function of nutritional state at all trophic levels. Furthermore, many literature values for lipid content (cf. Arts and Wainman 1999), even in Lake Ontario, are two or more times those reported by Oliver and Niimi (1988), allowing for wet and dry weights. Therefore, in this study the lipid values were held constant at the reported values with some misgivings. For comparison purposes, BAFs on a lipid-normalized and freely-dissolved basis were taken from the tables in US EPA (1995) and were checked using the computational procedure presented in that document.

Code and Parameter Changes to Facilitate Analyses

AQUATOX is more mechanistic than the implementations of the Gobas and Thomann models used by Burkhard (1998). Several changes were made to the AQUATOX code, and even more changes were made to the user-supplied parameter values to facilitate the comparison with Burkhard's (1998) results. Because of the requirement that the simulations be run to steady-state with a constant dissolved concentration, the code was changed to disable the differential equation for the dissolved phase. Burkhard (1998) set the dissolved concentration in water to 1 ng/L for all chemicals, primarily because there is no concentration-dependent feedback in the Gobas and Thomann models. However, several of the congeners exhibit dioxin-like toxicity, and the model predicted high bioaccumulation levels that caused chronic toxicity to be manifested over the course of a seven-year simulation period. Therefore, the dissolved concentrations were set to congener-specific levels calculated from the observed concentrations.

The constant dissolved concentration constraint also removed volatilization as a loss term. The model was parameterized so that microbial degradation was not a factor. Version 1.68, which was the version used, does not model biotransformation separately from depuration.

Burkhard (1998) assumed well mixed conditions, but AQUATOX simulates the dynamics of the ecosystem as well as the fate and effects of the pollutant. Stratified conditions characterize Lake

Ontario during most of the growing season. A simulation without stratification showed that the pelagic ecosystem in this deep lake requires a well defined epilimnion in order for phytoplankton dynamics to be represented realistically. Therefore, the simulations were driven by time-varying epilimnetic and hypolimnetic temperatures with mean values (7.4° and 3.6°) and ranges taken from the literature (Canada Centre for Inland Waters, 1979, p 97), and stratification was correctly modeled.

AQUATOX models time-varying lipid fractions. That function was disabled in the code so that lipid fractions were held constant at the initial values. However, in AQUATOX, lipid fractions in animals only affect the estimations of the *k2* (elimination) parameters. Based on initial runs, the estimates of *k2* values were found to be too low at higher K_{OW}s; therefore, they were replaced by estimated values using **(41)** and **(42)**. The result is that the model is insensitive to lipid values in all but algae.

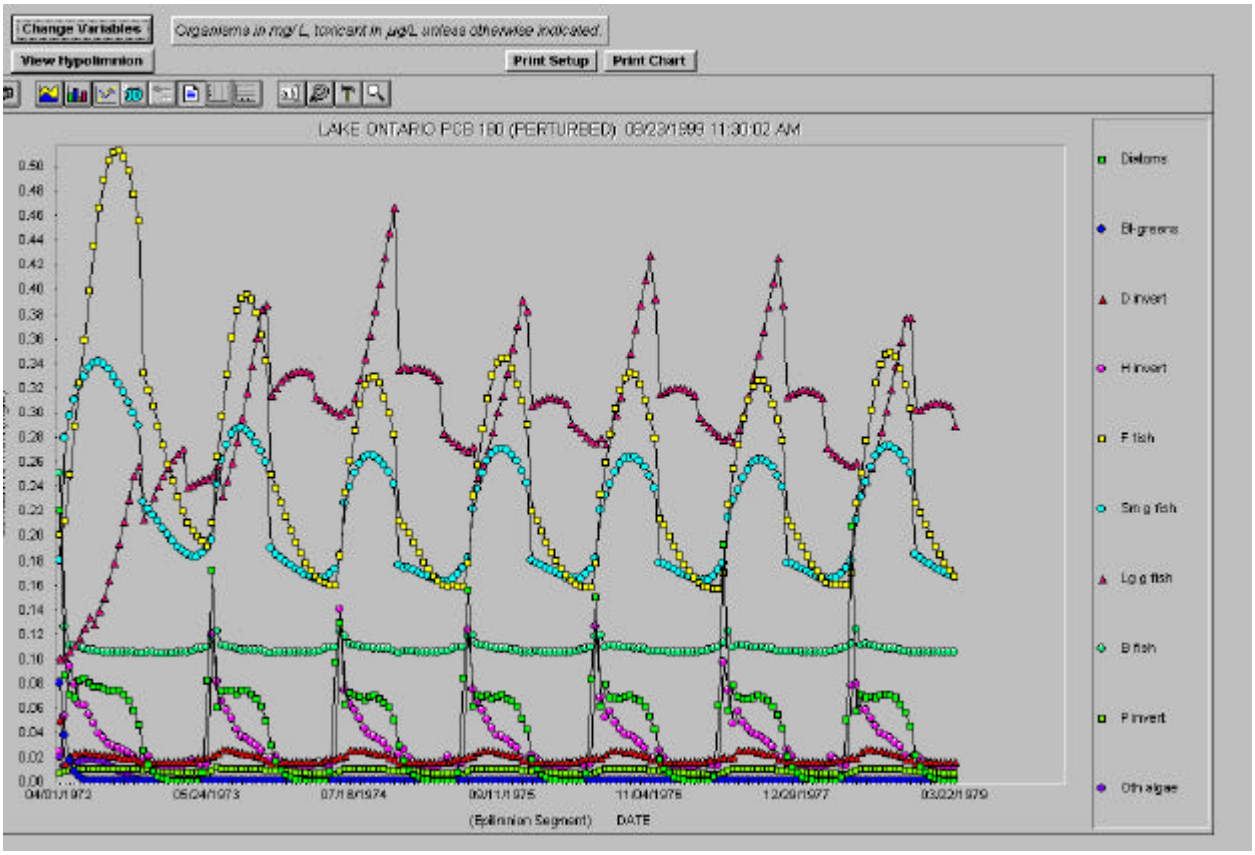
The model was modified so that the partition coefficient for refractory detrital carbon in sediment would be 25 times K_{OW} using **(4)**. This was done only in this application to facilitate the comparison. In the first simulations the only PCBs were those in water; however, steady-state was not reached even after 16 years. Therefore, the initial PCB concentrations in refractory detrital sediments were set to observed values, correcting for organic carbon content in the sediment (2.7%), and greatly shortening the time to steady-state.

In order to accommodate the numerous simulations required for the sensitivity analyses, the code was modified to run in batch mode, and then copy the predicted BAFs at the end of the simulation to a text file suitable for importing directly into an Excel spreadsheet. The initial simulations were run for 16 years to determine time to steady-state. Inspection of the output suggested that seven years was more than sufficient to achieve steady state, even with large perturbations. Therefore, seven years was used for the standard and sensitivity simulations. Because of the time required to run 100 simulations for the uncertainty analysis, a four-year simulation period was used for those simulations. That was determined to be the minimum time required to reach steady state for a chemical with a log K_{OW} of 6.5.

Results and Discussion

AQUATOX simulations were calibrated for the Lake Ontario ecosystem with some difficulty because the model had never before been applied to a Great Lake. In particular, bioenergetic parameters, such as maximum consumption rate (*CMax*), minimum biomass for feeding (*BMin*), and respiration rates were only approximated for sculpin and smelt using other Great Lakes species. The model was run for seven years with 1972-1973 loadings repeated; and, after a transient period, the annual patterns were stable (**Figure 10**). The phytoplankton and zooplankton biomass levels and seasonal trends were similar to those in the literature (Canada Centre for Inland Waters, 1979, Scavia 1980). Unfortunately, no biomass data were found for fish to verify the calibrations, and catch statistics only covered lake trout, cisco and whitefish (Robertson and Scavia 1979).

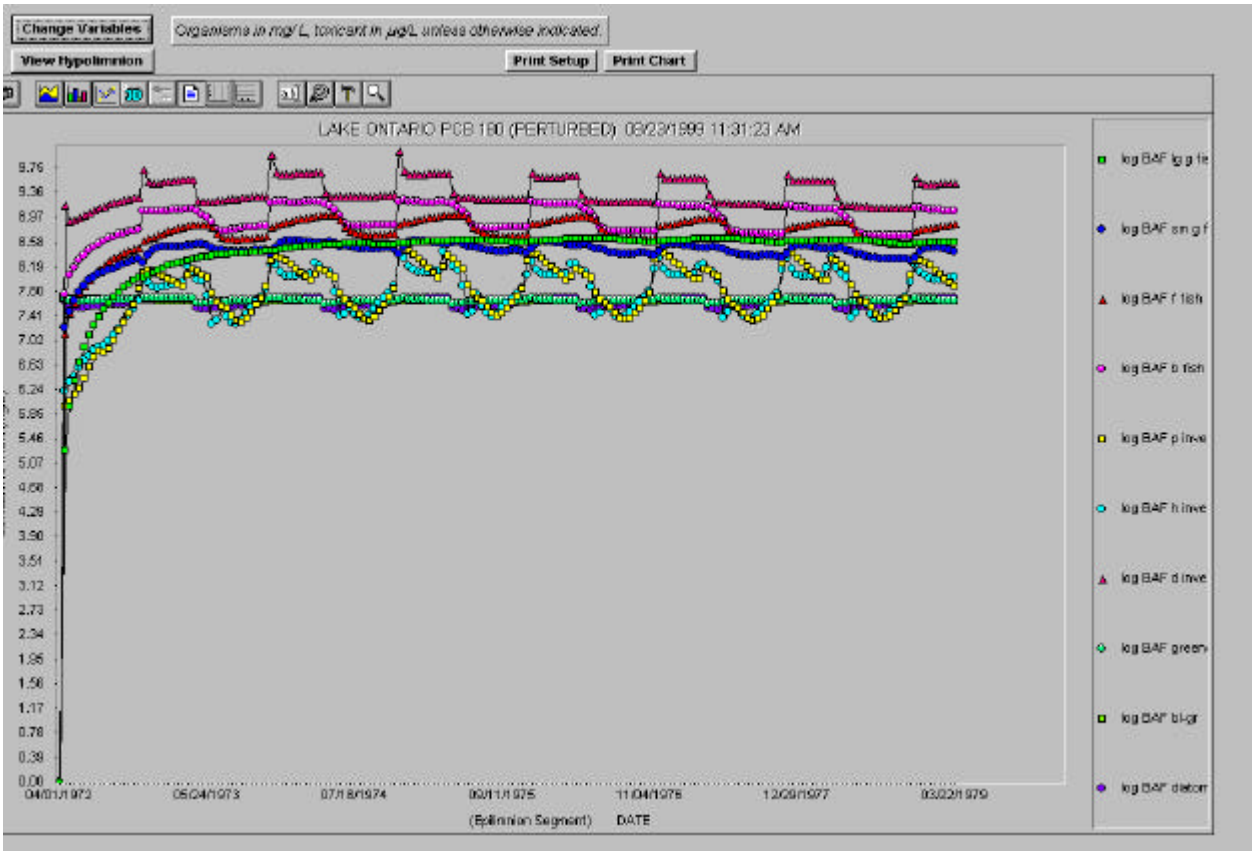
Figure 10. Seven-year simulation of Lake Ontario with predicted epilimnetic biomass patterns.



Comparison of Predicted and Measured BAFs

With the ecosystem model calibrated, AQUATOX was then applied to the 16 PCB congeners, and contaminant concentrations and lipid-normalized BAFs were predicted. The simulations were started with PCBs in the freely dissolved phase in water and in the refractory detrital sediments. In general, the phytoplankton reached steady state quickly and their BAFs varied little over time. Amphipods also attained a dynamic equilibrium quickly with seasonally varying BAFs. Most of the fish exhibited an approach to steady state within a year or two with seasonally varying BAFs. It took about four years for steady-state concentrations to be reached in the lake trout (**Figure 11**), and the BAFs did not exhibit significant seasonal variations. Biomagnification in the higher trophic levels was not well defined.

Figure 11. Seven-year simulation of Lake Ontario with predicted bioaccumulation factors.



The contributions of the various uptake and loss processes differ from one group to another (**Figure 12**,**Figure 13**). Given the dynamics of uptake and loss, especially in the short-lived zooplankton, and the averaging effects of disparate epilimnetic and hypolimnetic sediment concentrations, it is not surprising that there are fluctuations in the BAFs for many compartments. Therefore, the tabulated BAFs were taken at the end of the simulation period, March 31, which corresponded to the time when many of the observed data were collected.

As can be seen from **Figure 14** and **Table 1**, some predictions are remarkably close and others are off by factors of as much as 8.6, as in the case of sculpin. The only predictions that exhibited a noticeably different trend were those for the phytoplankton BAFs, which diverged at lower K_{OW}s (**Figure 14A**). The irregularities in the predictions mirror the fluctuations in the observed data and are related to the varying concentrations of PCBs in the sediments. The best predictions are for lake trout (**Figure 14G**), which are the most important fish in terms of human health hazard. Mysid BAFs are predicted very well (**Figure 14B**), as are smelt BAFs (**Figure 14F**). Phytoplankton BAFs are underestimated (**Figure 14A**); this may reflect the fact that the observations are actually for combined phytoplankton and zooplankton. Amphipods are over-estimated (**Figure 14C**); as will be shown later, the model is sensitive to changes in their bioenergetic parameters, such as maximum consumption rate. The overestimates of sculpin (**Figure 14D**) and alewife (**Figure 14E**) BAFs emphasize the sensitivity of the benthic food web as modeled. The predicted partition coefficients for refractory detrital sediments (**Figure 14H**) are very close to the observed values.

Figure 12. Predicted transfer rates for PCB 180 in Lake Ontario diatoms.

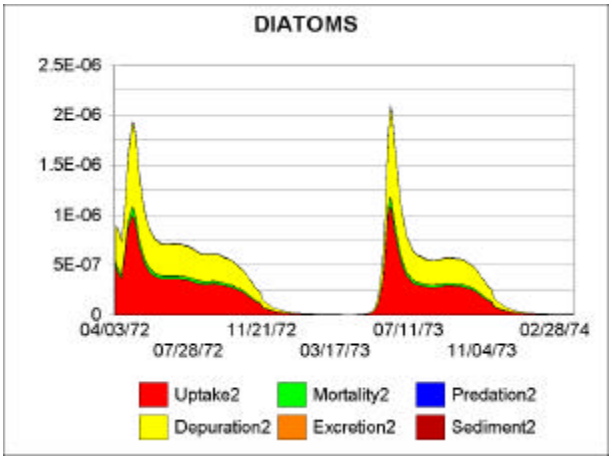


Figure 13. Predicted transfer rates for PCB 180 in Lake Ontario smelt.

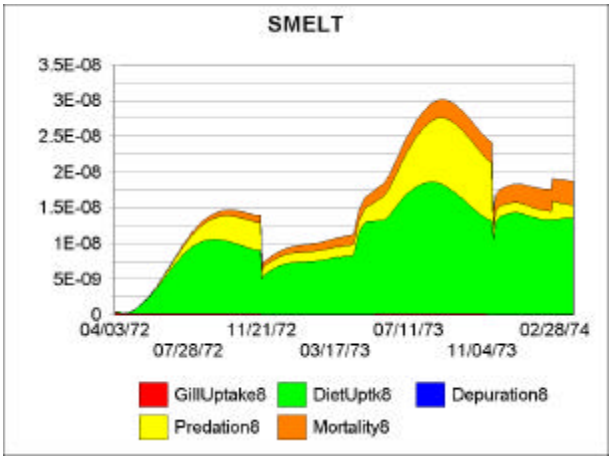
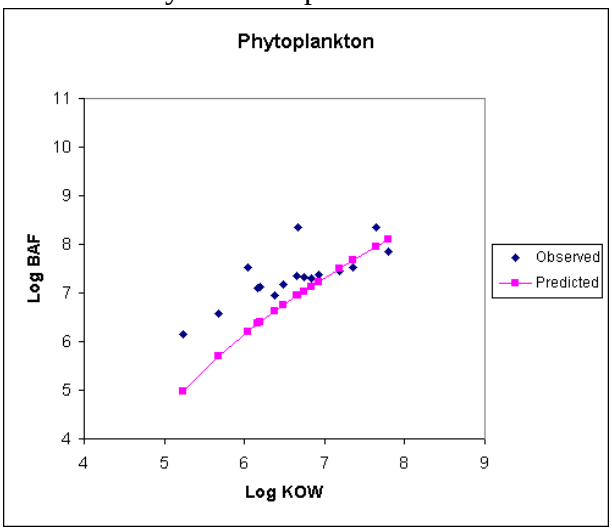
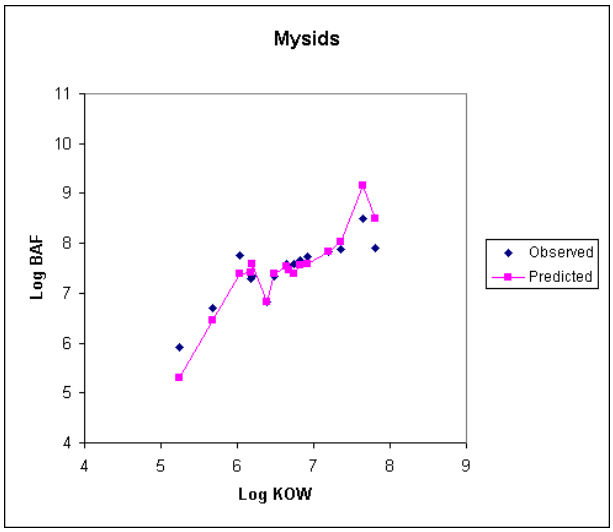


Figure 14. Observed and predicted lipid-normalized and freely dissolved BAFs for PCBs in Lake Ontario ecosystem components.

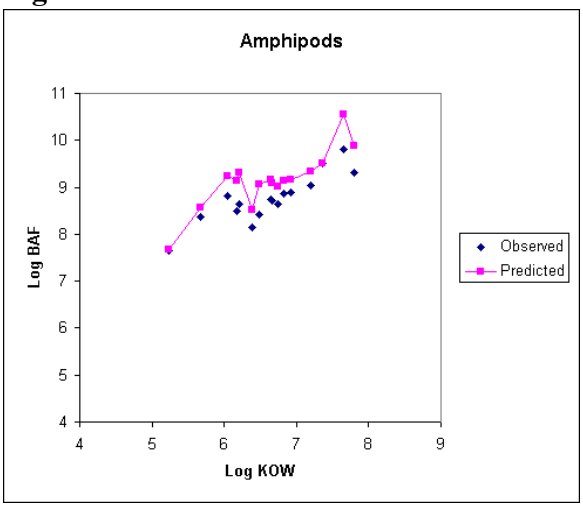


A.

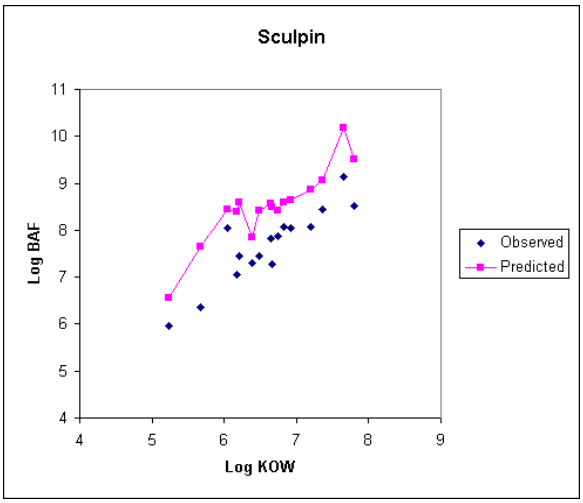


B.

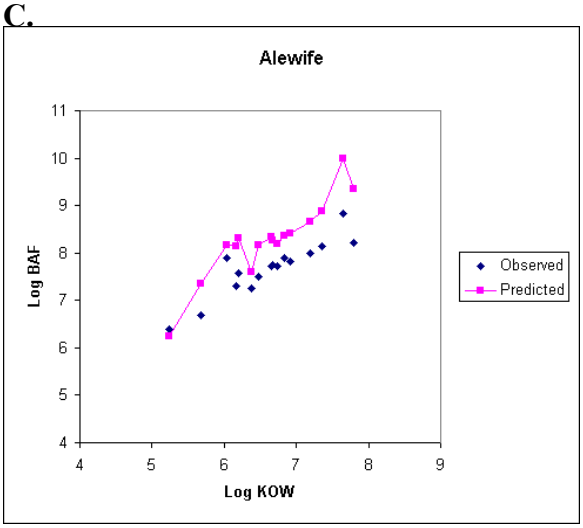
Figure 14. continued



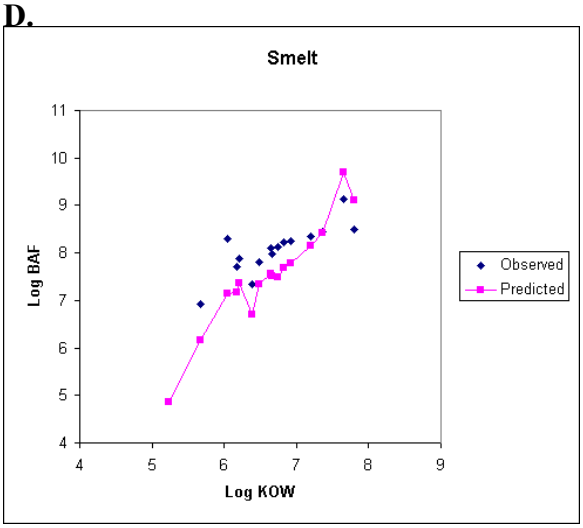
C.



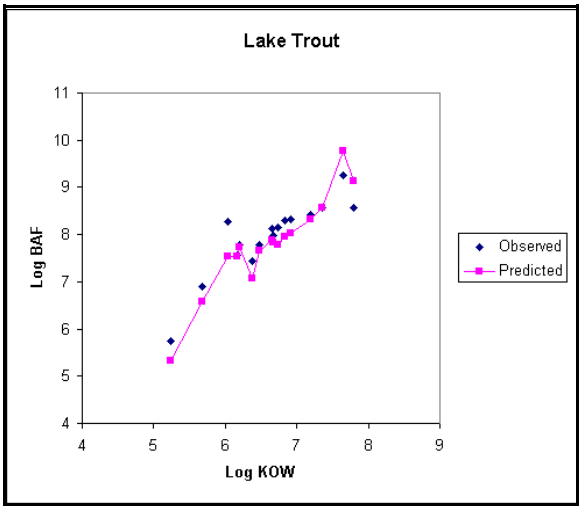
D.



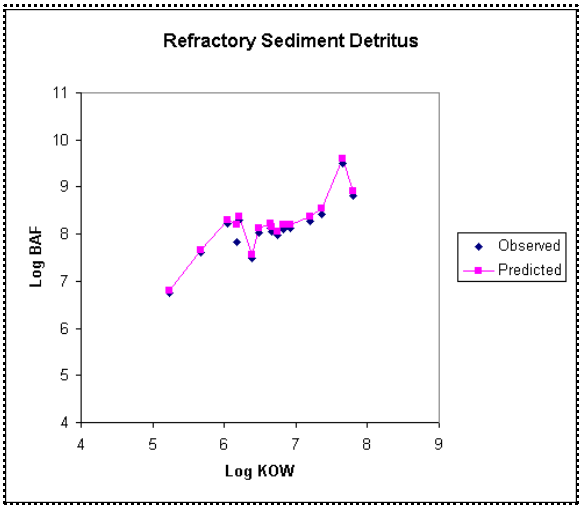
E.



F.



G.



H.

T

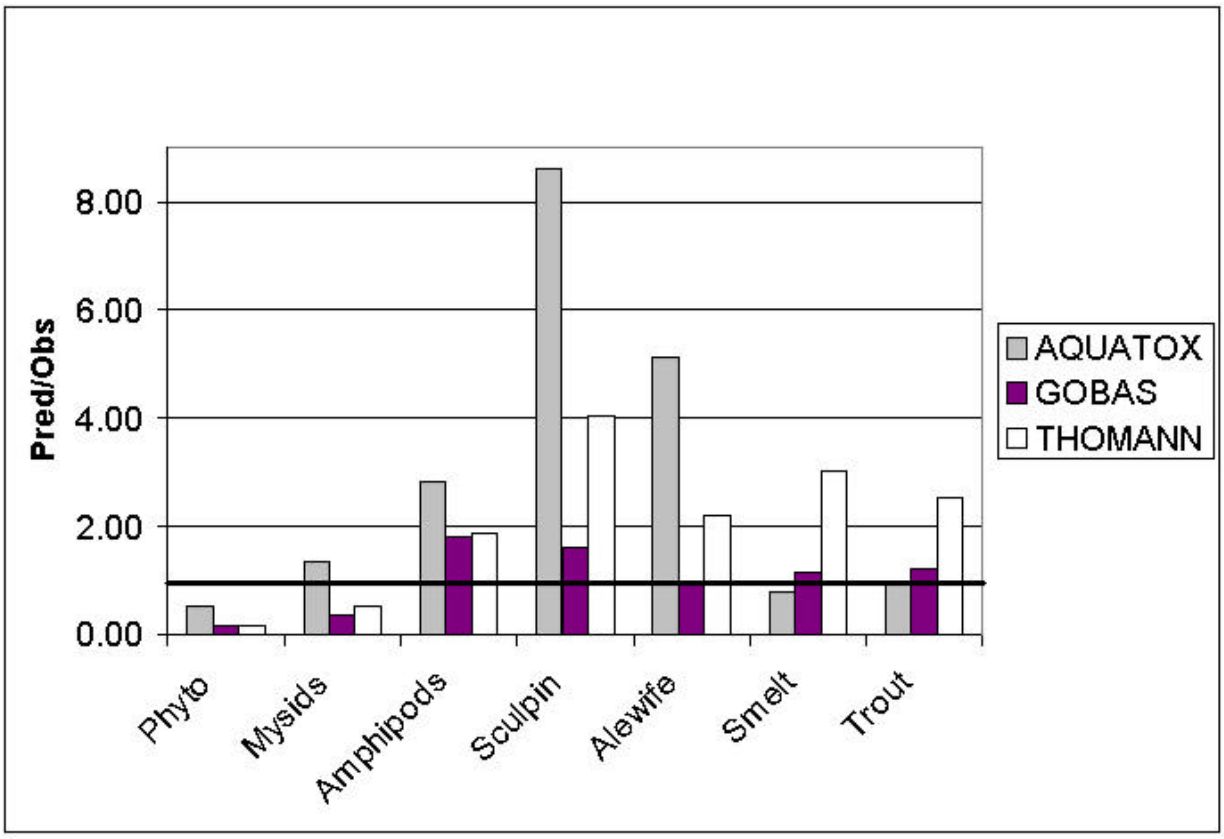
he predicted and observed BAFs can be compared statistically by taking the ratio of the predicted to the observed, as summarized in **Table 1**. A ratio of 1.0 represents perfect correspondence between the predicted and observed BAFs. This is a quantitative summary of the results shown diagrammatically in **Figure 14**, with sculpin and alewife biasing the overall results. The bioenergetics equations for these fish most likely are not parameterized properly; additional literature survey and calibration of the bioenergetic parameters would help correct the discrepancies.

Table 1. Ratio of observed to predicted bioaccumulation factors.

Congener	Log KOW	Phyto-plankton	Mysids	Amphipods	Sculpin	Alewife	Smelt	Trout	Mean for congeners
18	5.24	0.07	0.24	1.02	3.89	0.71		0.38	1.05
28+31	5.67	0.13	0.55	1.55	18.62	4.57	0.17	0.49	3.73
84	6.04	0.05	0.44	2.69	2.51	1.86	0.07	0.18	1.11
70+76	6.17	0.19	1.35	4.57	21.88	6.61	0.28	0.95	5.12
66	6.2	0.19	1.82	4.79	13.49	5.50	0.30	0.87	3.85
101	6.38	0.49	0.98	2.34	3.47	2.19	0.23	0.41	1.44
110	6.48	0.37	1.15	4.37	9.55	4.57	0.33	0.74	3.01
105	6.65	0.40	0.89	2.75	5.62	4.07	0.29	0.55	2.08
149	6.67	0.04	0.87	2.40	16.60	3.24	0.34	0.69	3.45
118	6.74	0.51	0.63	2.34	3.72	3.09	0.22	0.43	1.56
138	6.83	0.68	0.79	1.91	3.39	2.95	0.30	0.46	1.50
153	6.92	0.71	0.72	1.82	3.89	3.89	0.35	0.52	1.70
187+182	7.19	1.15	1.00	2.04	6.31	4.68	0.63	0.79	2.37
180	7.36	1.41	1.38	0.95	4.07	5.25	0.93	1.00	2.14
203+196	7.65	0.39	4.68	5.75	10.96	15.14	3.63	3.24	6.26
194	7.8	1.78	3.89	3.72	10.00	13.80	3.98	3.80	5.85
Grand Mean									2.89
Mean		0.53	1.34	2.81	8.62	5.13	0.80	0.97	
Std Dev		0.51	1.22	1.42	6.14	3.94	1.24	1.03	
Count		16	16	16	16	16	15	16	
Minimum		0.04	0.24	0.95	2.51	0.71	0.07	0.18	
Median		0.39	0.93	2.37	5.97	4.32	0.30	0.62	
Maximum		1.78	4.68	5.75	21.88	15.14	3.98	3.80	
Skewness		1.34	2.11	0.70	0.98	1.85	2.30	2.32	
Kurtosis		1.20	3.89	-0.43	-0.18	3.05	4.06	4.55	

A similar tabular summary was presented by Burkhard (1998) for the Gobas and Thomann models. It is instructive to compare the results of the three models (**Figure 15**). The heavy line indicates unity for the mean and predicted ratios. This is not a rigorous comparison because AQUATOX was only used to simulate 16 PCB congeners, in contrast to the 72 congeners simulated by Burkhard (1998), although there is not any apparent bias in the smaller sample. Burkhard concluded that the Gobas model seems to represent Lake Ontario bioaccumulation better than the Thomann model. However, AQUATOX did equally as well for smelt and lake trout, and the best of the three models for phytoplankton and mysids.

Figure 15. Comparison of predicted/observed BAF ratios for the AQUATOX, Gobas, and Thomann models.



Sensitivity Analysis

Following the approach of Burkhard (1998), sensitivity analyses were run on each key parameter, using the equation:

$$\text{sensitivity} = \frac{P_i \cdot \Delta BAF_i}{BAF_i \cdot \Delta P_i} \quad \textbf{(45)}$$

where:

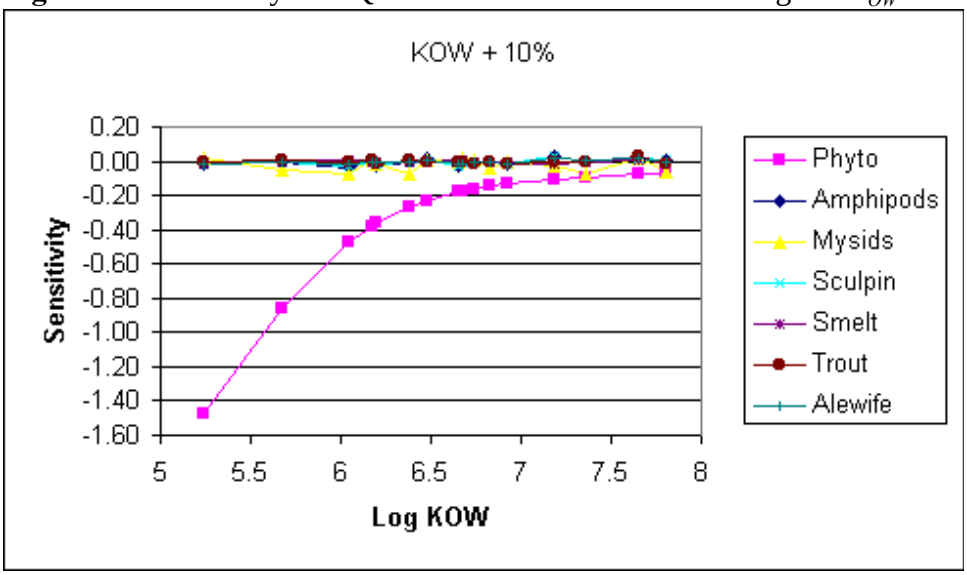
P_i = nominal value of input parameter *i*,
ΔP_i = deviation in the input parameter *i*,
BAF_i = the BAF predicted using the nominal input values, and
ΔBAF_i = the deviation in the predicted BAFs using the nominal and modified input parameter *i*.

A sensitivity of 1.0 means that a change in a parameter results in an equal change in the BAFs predicted by the model. A negative sign indicates that the change is opposite in direction to the parameter change. Because the simulations were run for seven years to ensure steady-state, sensitivity analysis for each parameter for the 16 PCB congeners took eight hours on a Pentium III

500 mHz machine. Therefore, only the following representative parameters were analyzed: K_{OW}, *k2*, preference of amphipods for refractory detritus, $Cmax_{amphipod}$, and $BMin_{sculpin}$.

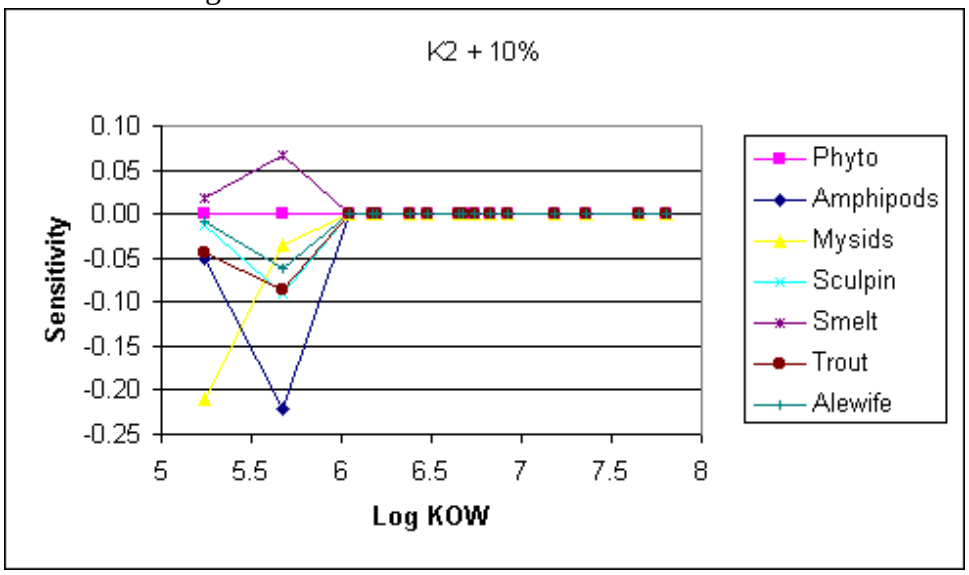
Burkhard (1998) found that Thomann's and Gobas' models were sensitive to variable K_{OW} values within a factor of +/- 2.0. As shown in **Figure 16**, in AQUATOX phytoplankton are highly sensitive to K_{OW}; furthermore, as shown in **Figure 14A,** the predicted algal BAF trend does not parallel the observed trend Both the phytoplankton *k1* uptake and *k2* values are a direct function of the K_{OW} values. In contrast, none of the animals show any sensitivity, reflecting the fact that by manually entering *k2* elimination values the dependence on K_{OW} was overridden.

Figure 16. Sensitivity of AQUATOX BAFs to a +10% change in K_{OW} .



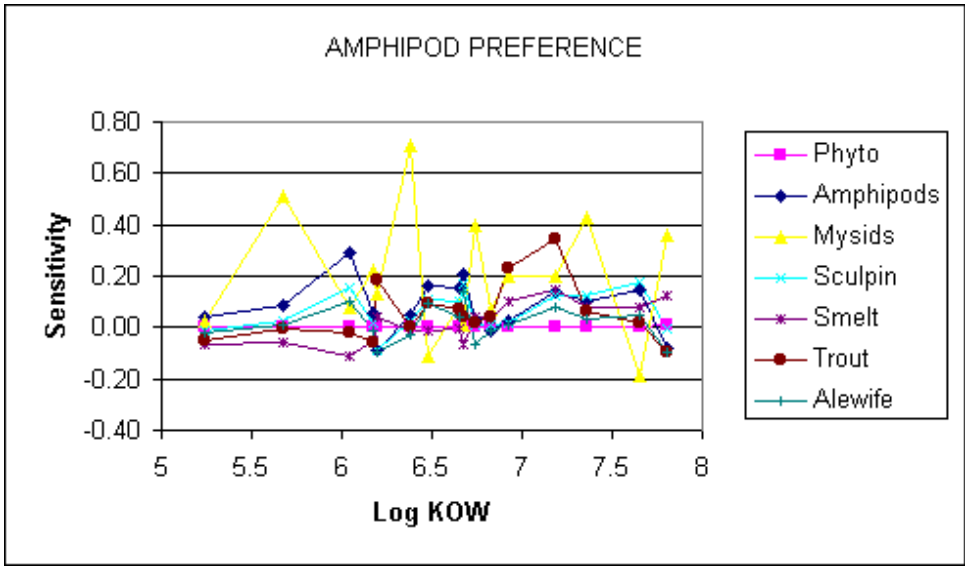
One of the key parameters is the elimination coefficient for each of the organisms. As explained above, the *k2* values can be estimated by the model, see **(40)**. However, those estimates were found to underestimate elimination, so simpler regression equations **(41)** and **(42)** were used to estimate the *k2* values, and those were entered manually in the toxicity parameter screens. In order to test the sensitivity, *k2* +10% values were used in the analyses (**Figure 17**). The sensitivity was small and affected only the lower K_{OW} congeners.

Figure 17. Sensitivity of AQUATOX BAFs to a +10% change in *K2* values for all organisms.



Amphipods provide the primary link between the sediments and the higher trophic levels. They feed on detritus, converting some refractory detritus to labile detritus that can be assimilated or decomposed more rapidly. Therefore, the preference of amphipods for refractory detritus was increased by 10%, from 0.05 to 0.055 and the corresponding preference for labile detritus (primarily freshly sedimented algae) was decreased by 10% in a sensitivity analysis. There were seemingly random fluctuations in the animal BAFs, probably representing differences in the initial PCB concentrations in the sediments (**Figure 18**).

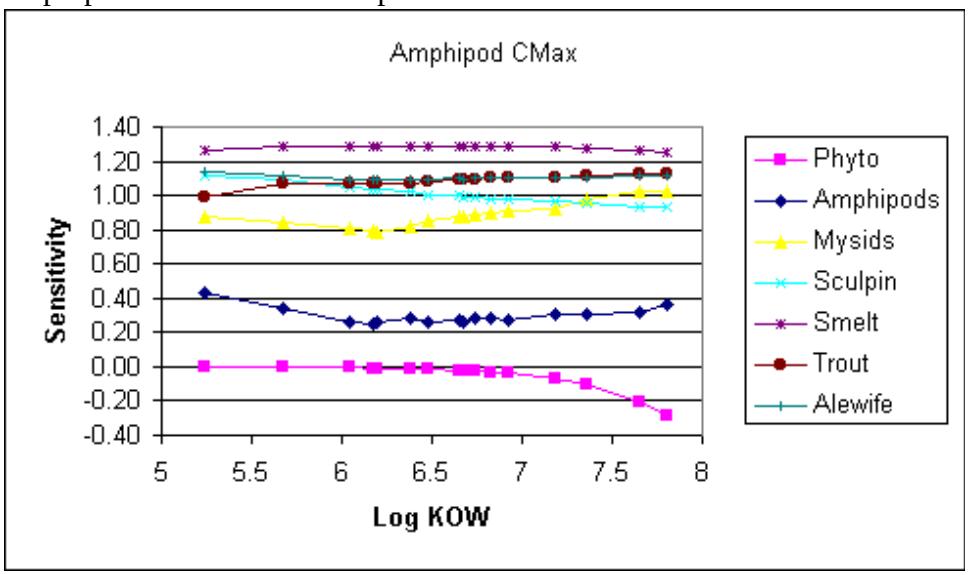
Figure 18. Sensitivity of AQUATOX BAFs to a +10% change in amphipod preference for refractory detrital sediments .



In reviewing the literature on Lake Ontario, the observations of Landrum and Robbins (1990) on the feeding rate of *Diporeia* (the common amphipod in the Great Lakes) were found to be at variance with the maximum consumption rate (*CMax*) used in AQUATOX. Therefore, an analysis was

performed in which *CMax* was changed from 1.3 g/g d to 0.288 g/g d. A systematic response was found from one trophic level to the next (**Figure 19**), suggesting that indeed amphipods are important in the transfer of contaminants, that the effects are magnified at the higher trophic levels and that the *CMax* value should probably be changed in future implementations. Smelt are affected the most, probably due to amphipod biomass dropping below the minimum biomass level (*BMin*) for consumption and uptake of PCBs by smelt. In this and other analyses of sensitivity to bioenergetic parameters, interpretations of the effects on BAFs are difficult because those effects are indirect.

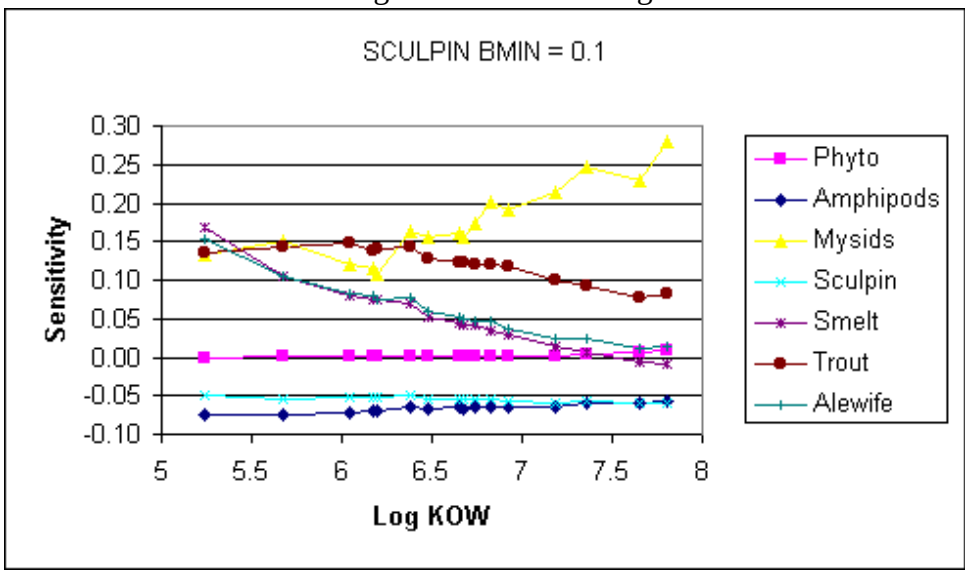
Figure 19. Sensitivity of AQUATOX BAFs to a -77% change in amphipod maximum consumption rate.



Because the trophic feeding relationships seem to be important in the transfer of PCBs in the Lake Ontario food web, the effect of changing the sculpin *BMin* was investigated by changing the value from 0.01 to 0.1 mg/L. This has the effect of providing a refuge from predation for amphipods and, to a lesser extent, zooplankton; mysids were found to respond the opposite to the fish. Because sculpin compete to a certain extent with alewives, and both compete with and are fed on by smelt, changing the feeding dynamics for sculpin affects the other fish species, although the sensitivities are low (**Figure 20**).

In summary, changes in K_{OW} and *k2* values had little effect on the BAFs; and changes in feeding preferences in amphipods had no systematic effect on BAFs, but changes in *CMax* and *BMin* values were important in regulating the transfer of PCBs in the Lake Ontario ecosystem.

Figure 20. Sensitivity of AQUATOX BAFs to a change in sculpin minimum biomass for feeding from 0.01 to 0.1 mg/L.



Uncertainty Analysis

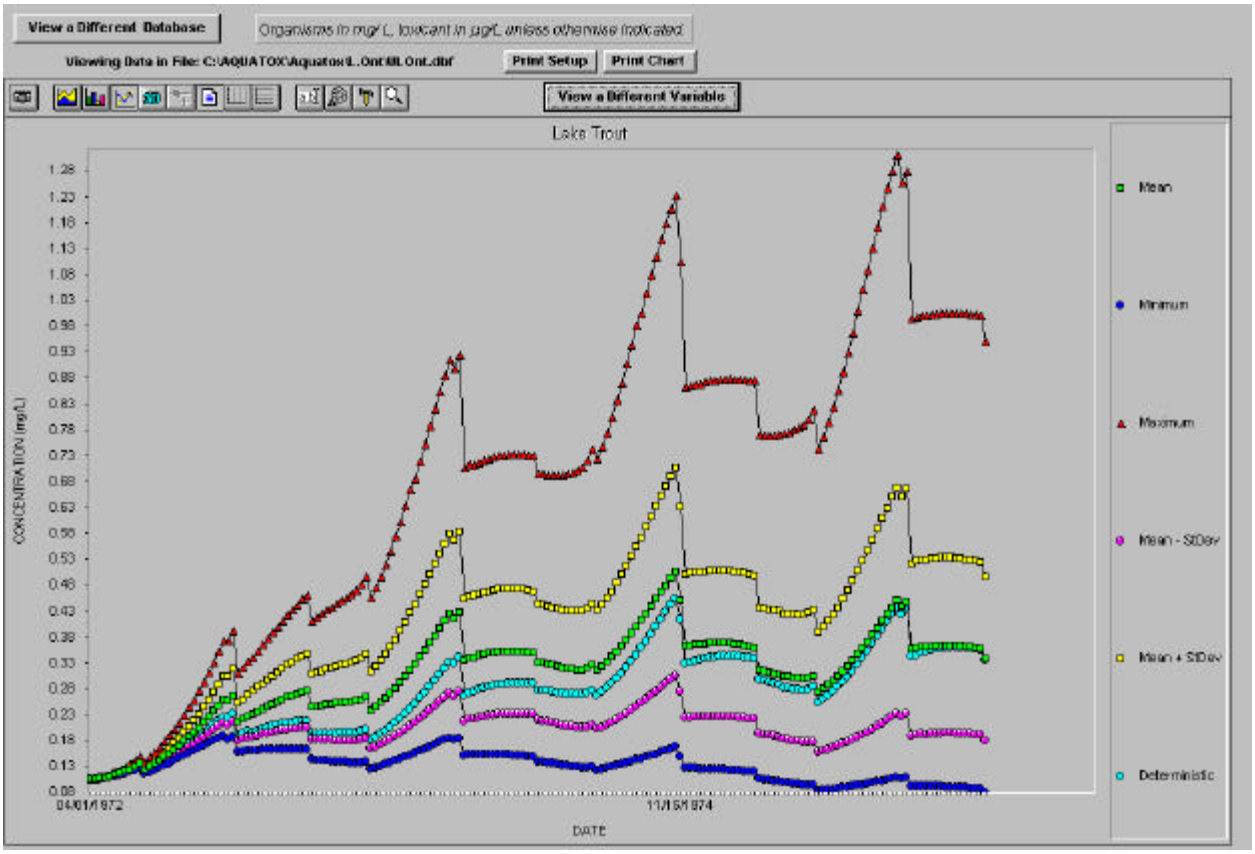
Uncertainty analysis was conducted using the same parameter distributions as were used by Burkhard (1998), in so far as appropriate. However, the contributions of individual parameters were not investigated because of the computational load. Rather, the aggregate uncertainties due to all selected input variables were analyzed simultaneously. Burkhard (1998) used a Monte Carlo procedure with random values taken from normal and lognormal distributions; the simulations were run for 100,000 iterations. Such an approach is neither desirable nor warranted for a complex model such as AQUATOX. Instead, Latin hypercube sampling was performed for 100 iterations; that algorithm took a random sample from each of 100 segments of the normal distributions for each selected input parameter, ensuring that the distributions were well represented. Each of the 100 simulations was run for a four-year period to obtain steady-state. Because of the model complexity and the length of the simulation period, the uncertainty analysis took 40.5 hours to complete on a Pentium III 500 mHz machine. The input parameters are shown in **Table 3**, taken from the AQUATOX Setup. Two parameters, Log K_{OW} and the sediment detritus-water partition coefficient, were converted from lognormal to normal distributions to facilitate the analysis.

Table 3. Parameters used in uncertainty analysis of AQUATOX; Parameter 1 is the mean and Parameter 2 is the standard deviation.

Distribution Name	Type	Param. 1	Param. 2	Param. 3	Param. 4	Used?
Octanol Water Partition Coeff (log)	Normal	6.5	0.2			YES
Sed/Detritus-Water Partition Coeff. (mg/l	Normal	79056941	11900000			YES
D invert: Max Consumption: (g / g d)	Normal	1.3	0.182			YES
P invert: Max Consumption: (g / g d)	Normal	0.085	0.0119			YES
F fish: Max Consumption: (g / g d)	Normal	0.299	0.0343			YES
B fish: Max Consumption: (g / g d)	Normal	0.65	0.1242			YES
Sm g fish: Max Consumption: (g / g d)	Normal	0.3157	0.0311			YES
Lg g fish: Max Consumption: (g / g d)	Normal	0.0188	0.0008			YES
D invert: Respiration Rate: (L / d)	Normal	0.02	0.0012			YES
P invert: Respiration Rate: (L / d)	Normal	0.0023	0.0003			YES
F fish: Respiration Rate: (L / d)	Normal	0.0031	0.000285			YES
B fish: Respiration Rate: (L / d)	Normal	0.0019	3.78E-5			YES
Sm g fish: Respiration Rate: (L / d)	Normal	0.0033	0.000186			YES
Lg g fish: Respiration Rate: (L / d)	Normal	0.001	0.00011			YES
R detr sed(g/m2): Initial Condition (g/sq.(	Normal	600	378			YES
L detr sed(g/m2): Initial Condition (g/sq.(	Normal	160	100.8			YES
Temp: Multiply Loading by	Normal	1	0.1			YES
D invert: Lipid Frac	Normal	0.03	0.0015			YES
P invert: Lipid Frac	Normal	0.05	0.0025			YES
F fish: Lipid Frac	Normal	0.07	0.0035			YES
B fish: Lipid Frac	Normal	0.08	0.004			YES
Sm g fish: Lipid Frac	Normal	0.04	0.002			YES
Lg g fish: Lipid Frac	Normal	0.11	0.0055			YES

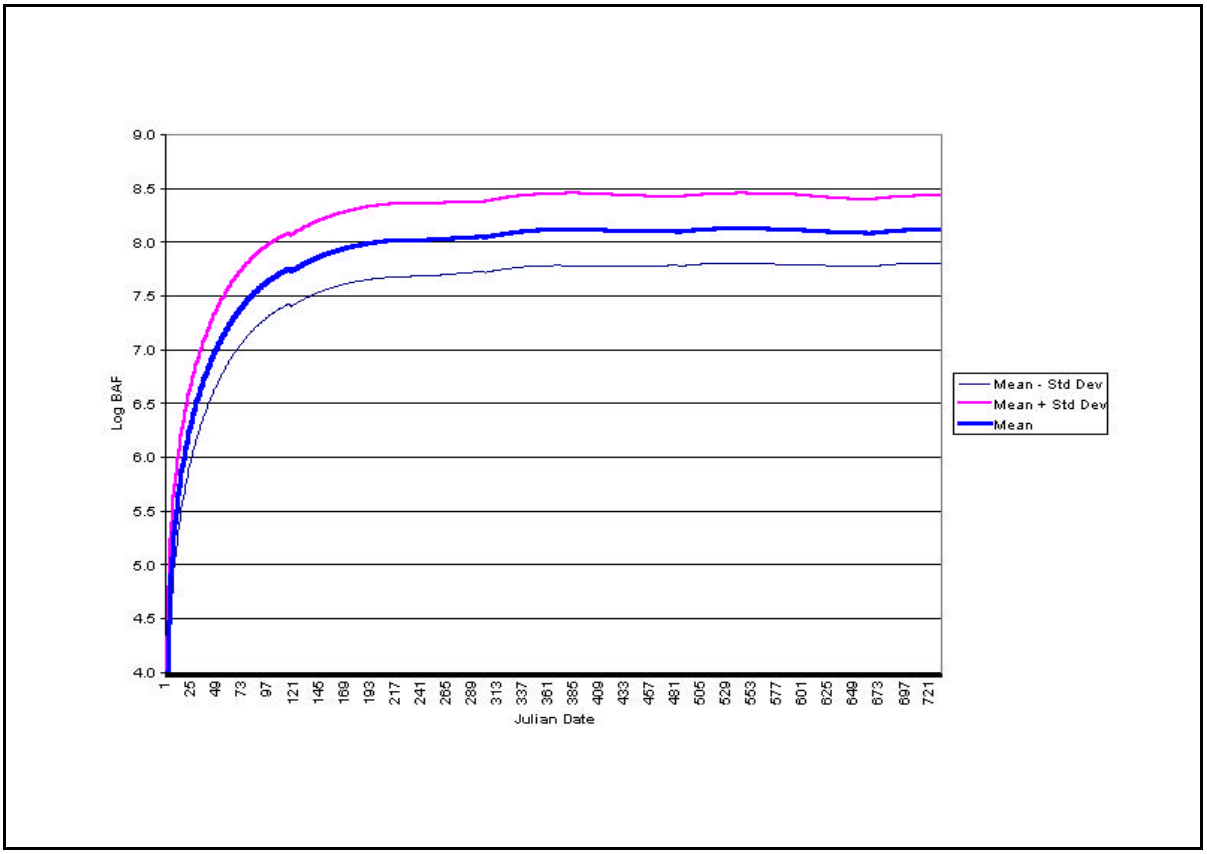
The bioenergetic parameters have a direct effect on the ecosystem components, such as the biomass of lake trout shown in **Figure 22**. Given the number of parameters, the uncertainty exhibited is surprisingly small.

Figure 22. Effect of uncertainty on biomass of lake trout over four years; the mean and deterministic results are very close and are bounded by +/- 1 standard deviation; the top and bottom curves represent the high and low values out of 100 simulations.



The low uncertainty in the trout bioenergetics contributes to the low uncertainty in the trout BAFs (**Figure 23**). Because the trout had no contaminant burden at the beginning of the simulation, it took three or more years for steady state to be reached. The seasonal fluctuations that are evident in the short-lived animals are barely discernible in the large, long-lived trout due to the slow dietary uptake and even slower depuration.

Figure 23. Effect of uncertainty on the log BAFs for lake trout over a four-year period.



The 90th and 10th percentiles, representing the tails of the distributions, were computed from the mean and standard deviations of the BAFs for the various simulated organisms. The ratios of these percentiles were then calculated (**Table 4**).

Table 4. Lipid-normalized, freely dissolved log bioaccumulation factors using uncertainties.

State variable	Mean	Standard Deviation	Ratio 90th:10th
Diatoms	6.77	0.00004	1.00
Mysids	7.84	0.36	1.13
Sculpin	8.88	0.29	1.09
Alewife	8.63	0.31	1.10
Smelt	7.78	0.36	1.12
Lake trout	8.12	0.31	1.10
Refr. sed. detritus	8.63	0.23	1.07
Labile susp. detritus	7.66	0.28	1.10

These low ratios are misleading because manually entered *k2* values desensitize the model to changes in weights and lipid fractions in organisms. Therefore, although the ratio of 1.10 for lake trout is for all selected input parameters, it is not directly comparable with the values of 3.63 and 3.98 for all parameters obtained with the Gobas and Thomann models (Burkhard 1998).

Conclusions

The subset of 16 PCB congeners from the 72 used by Burkhard (1998) provided an adequate basis for evaluating the validity of AQUATOX in predicting bioaccumulation of PCBs in Lake Ontario. Unlike the Gobas and Thoman models, AQUATOX had never been applied to such a large system, but in general, AQUATOX gave acceptable results. It provided better fits to observed data for phytoplankton and mysids than those provided by the Gobas (1993) and Thomann (1989) models as implemented by Burkhard (1998), and equally acceptable results for smelt and lake trout when compared to the Gobas model.

Several modifications to the code were necessary to facilitate direct comparison to the Burkhard (1998) study. Specifically, the freely dissolved contaminant concentration and lipid fractions in organisms were held constant. A procedure for computing the sediment-water partition coefficient was added, and capability for running in batch mode also was provided. All these features were made options in Version 1.68 and subsequent versions.

AQUATOX seems to have been successfully calibrated to represent the Lake Ontario ecosystem. Most predicted bioaccumulation factors were reasonably close to observed values. Phytoplankton BAFs were underestimated according to the observed data, which may be biased by inclusion of zooplankton; predictions were noticeably better than the Gobas and Thomann models as implemented by Burkhard (1998). Mysid BAFs were predicted very well, in contrast to the underestimations in the Gobas and Thomann models, which may reflect the lack of herbivorous zooplankton in those implementations. Amphipods, sculpin, and alewife BAFs were overestimated, suggesting that the bioenergetics parameters may not be well calibrated; indeed, changing the *CMax* for amphipods to a value measured with the Lake Ontario species greatly improved the BAF prediction. The smelt and lake trout BAF predictions were very close to the observed and were better than the predictions of the Thomann model, and equivalent to the Gobas model results.

AQUATOX has many nonlinear relationships in the ecosystem, fate, and effects portions of the model. Therefore, it does not exhibit one-to-one sensitivities to input parameters as do the simpler Gobas and Thomann models. Furthermore, by manually entering estimated *k2* values, the simulations were desensitized to lipid and weight factors. The algal BAFs are relatively sensitive to changing K_{OW} values, although only one congener exceeded a sensitivity of 1.0 (perfect correspondence). BAFs exhibited low sensitivities to benthic feeding relationships. The almost negligible effect of changing preference of amphipods for labile organic matter, which is mostly sedimented phytoplankton, was in sharp contrast to the response of Thomann's model to a similar preference for phytoplankton (Burkhard 1998). This emphasizes the unique capability of AQUATOX in realistically representing ecosystemic relationships affecting contaminant fate. The model properly represented the cascading effect that changing amphipod consumption has on BAFs in the benthic food web. A future task should be to fine-tune the amphipod and fish bioenergetic parameters for Great Lakes species.

AQUATOX exhibited a low degree of uncertainty, especially compared to the Gobas and Thomann models (Burkhard 1998). However, this is probably in part an artifact of the constraints imposed by specifying the *k2* elimination values.

In conclusion, this study has demonstrated the validity and robustness of AQUATOX in estimating bioaccumulation factors for PCBs in Lake Ontario.

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