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"Modelling Accumulation of Organic Chemicals in Aquatic Food Webs"

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These are preliminary lecture notes, intended only for distribution to participants.

Chemical Dynamics in Fresh Water Ecosystems

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7 MODELING ACCUMULATION OF ORGANIC CHEMICALS IN AQUATIC FOOD WEBS

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INTRODUCTION

The purpose of this paper is to provide an overview of models of organic chemical uptake and transfer in aquatic food webs. The degree to which the aquatic food chain may accumulate chemicals above some equilibrium value associated with uptake from the water has been of concern for a number of years. Models which consider both aqueous and dietary exposure routes can assist in determining the degree of bioaccumulation or the lack thereof. Furthermore, chemical food chain models (food chain and food web are used interchangably throughout this paper) in site-specific cases can provide valuable frameworks for determining the efficacy of environmental control actions in reaching target chemical concentrations in key aquatic organisms, such as fish species used in human diets.

Two general classes of models are described: (1) generic equilibrium models which are useful for screening analyses and provide insight into the principal mechanisms of chemical transport and accumulation, and (2) site-specific models which may be time- and age-dependent. In both cases, the aquatic system is divided into ecological compartments (e.g., phytoplankton, small fish, or a top predator in a specific age class) and abiotic compartments (e.g., water column and sediment). Figure 1 shows a generic compartment model with the notation to be used in this paper. Figure 2 shows a typical site-specific age-dependent food web for the striped bass in the Hudson River.

THEORY

Lipid and Organic Carbon Normalizations

Partitioning of organic chemicals into aquatic organisms is governed to first-order by the lipid pool of the organism (Mackay 1982, Connolly and Pedersen

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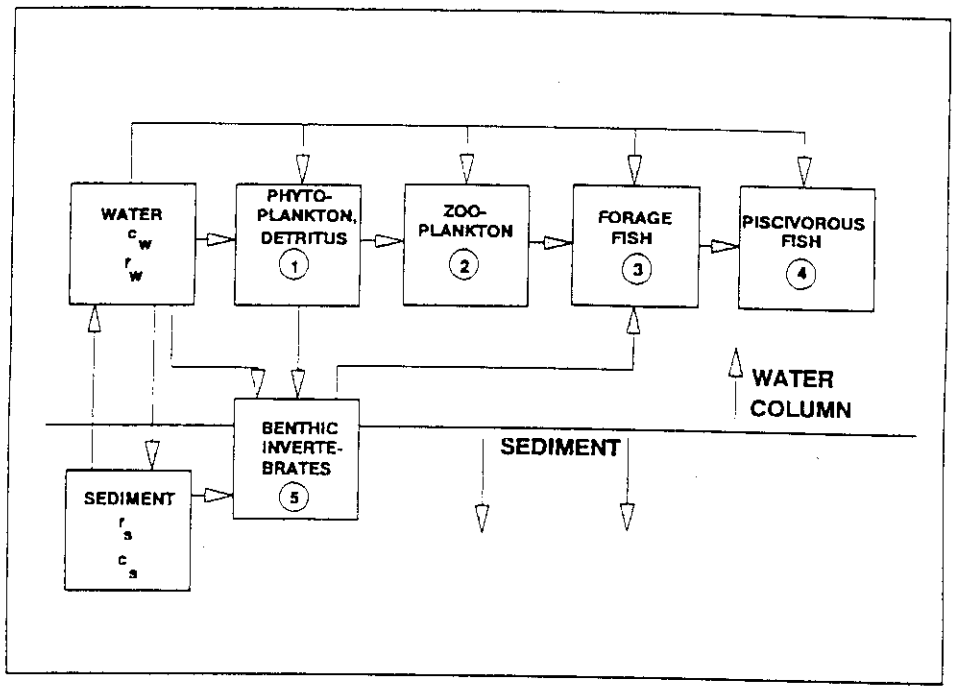

Figure 1. Schematic of a five-compartment generic food web model.

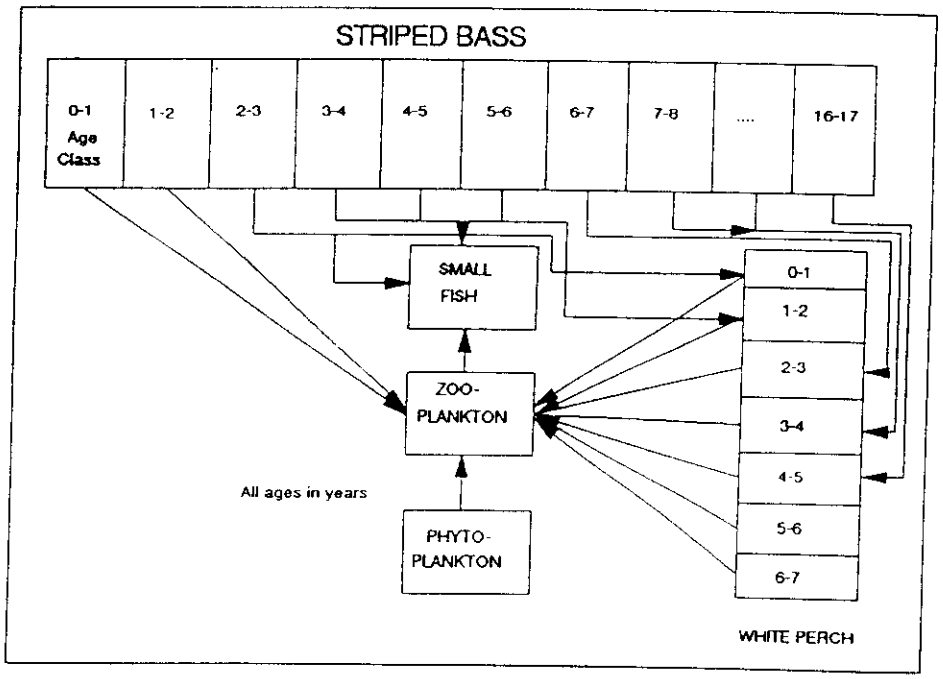

Figure 2. Compartments of age-dependent striped bass model for Hudson River (Thomann et al. 1989).

1988, Thomann 1989). Also, as noted in a review of sediment water quality criteria (USEPA 1989),and as discussed by Bierman (1990), the partitioning of organic chemicals is determined to a large degree by the amount of organic carbon present in the particulate matter. It is recognized that other components (e.g., protein) may influence the distribution of the chemical. Hallam et al. (1989) provide a detailed model of chemical uptake which includes this component. However, it is not expected that the distribution of chemical in these other components will be high due to the relatively low chemical affinity for such phases. The model equations presented herein are therefore written in terms of chemical concentrations in aquatic organisms on a lipid basis and for abiotic particles on an organic carbon basis.

The tendency for organic chemicals to partition into lipid and organic carbon pools is broadly represented by the octanol-water partition coefficient (K_{ow}). In this work, to first approximation, the preference for chemicals to partition to octanol, lipid, and organic carbon is considered identical.

The chemical concentration in an organism on a lipid basis, v[μg chemical/g(lipid)], is related to the wet weight chemical concentration, v_{wt}[μg chemical/g(wet)], and the fraction lipid, f_L[g(lipid)/g(wet)], by

$$v = \frac{v_{wt}}{f_L} \tag{1}$$

A plot of wet weight concentration against lipid fraction should therefore be linearly related. Figure 3 shows the relationship between the wet weight concentration of two PCB mixtures (Aroclors 1016 and 1254) for white perch for the Hudson River in the vicinity of Troy, New York. The correlation of the wet weight concentration to lipid fraction for the 1016 mixture, and to a lesser degree for the 1254 mixture, is apparent and thus the variability is significantly reduced by a normalization to lipid content of the fish. Figure 4 computed from the data in Gruger et al. (1975) shows the effect of lipid normalization to body components of the coho salmon for three PCB congeners. On a wet weight basis, the range across the components is almost an order of magnitude while on a lipid basis, the variability is reduced considerably. It is interesting to note that the brain PCB concentration is consistently lower than the other fish components. Figure 5 illustrates the importance of lipid normalizing in interpreting trophic transfers of chemicals. In the upper panel, the trend of total PCB on a wet weight basis is not clear with increasing trophic level. The lower panel however shows that when the data are lipid normalized, food chain accumulation appears to be occurring up through the striped bass as a top predator with a low lipid fraction.

Normalizations with organic carbon for abiotic compartments show similar reductions in the variability of chemicals sorbed to particulate matter expressed on a dry wet basis (e.g., Karickhoff et al. 1979, Karickhoff 1984, and USEPA 1989.)

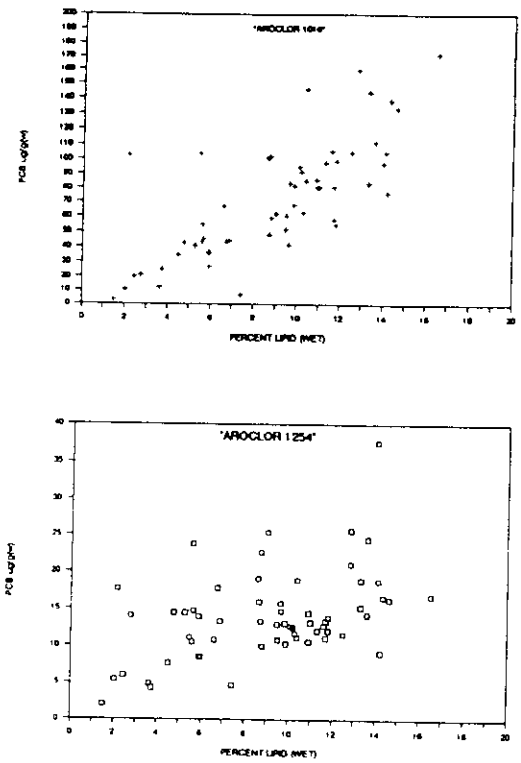

Figure 3. Wet weight PCB concentrations vs percent lipid for two Aroclors, white perch, Hudson River in vicinity of Troy New York. Compiled from data of NYS DEC.

General Equations

For any ecological compartment and/or age class within a compartment (see Figures 1 and 2), the mechanisms included in the general modeling framework are

1. Direct uptake of the dissolved chemical from the water by diffusive exchange across organism membranes
2. Food web accumulation of the chemical resulting from consumption of contaminated prey
3. Depuration of the chemical due to all loss pathways
4. Growth and respiration of the organism and the effect of such physiological factors on chemical concentration and the rates of uptake of chemical
5. Migration of the organism through temporally and spatially varying water concentrations

Uptake from Water Only

The uptake and subsequent internal transport of chemicals from water by aquatic organisms has been the subject of a number of studies. See, for example,

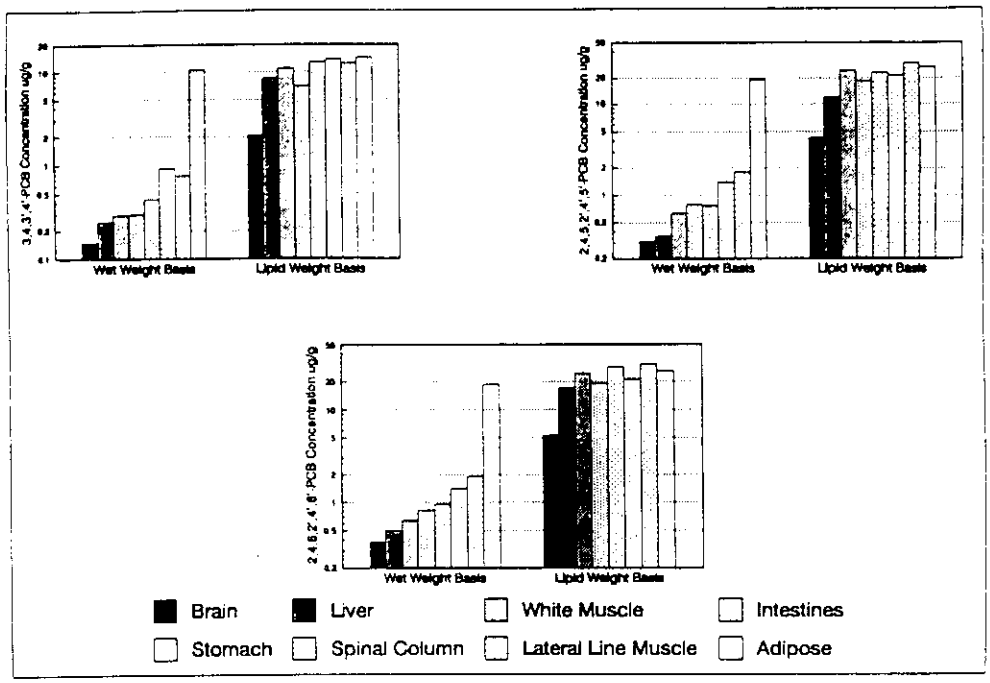

Figure 4. Comparison of PCB concentrations in compartments of juvenile coho salmon on a wet weight and lipid normalized basis. Compiled from data in Gruger et al. 1975.

Norstrom et al. (1976), Gobas et al. (1986), Gobas and Mackay (1987), Barber et al. (1988), and Erickson and McKim (1990).

Assuming an organism is exposed to a chemical in the water phase only, then a mass balance equation around the average organism in a compartment may be written as an exchange process across a lipoprotein membrane as follows:

$$\frac{dv_m}{dt} = k_u w_L \left(c_{w,s} - c_B \right) - K_l v_m \tag{2}$$

where V_m is the chemical whole body burden [μg chemical/organism], k_u is the chemical uptake rate [L/day-kg(lipid)], w_L is the lipid weight, $c_{w,s}$ is the "freely available" dissolved chemical in the water column or in the interstitial water of the sediment (see Figure 1), c_B is the "free" concentration of the chemical in the blood and K_l is the loss rate of chemical due to mechanisms other than reverse transfer across the membrane (e.g., losses from skin surface, fecal losses, and chemical metabolism). If the blood concentration is considered in equilibrium with the tissue concentration v(μg/kg/(lipid)) then

$$\frac{v}{c_B} = N_{wl} \tag{3}$$

where N_{wl} is a lipid concentration to blood concentration partition coefficient. To first approximation,

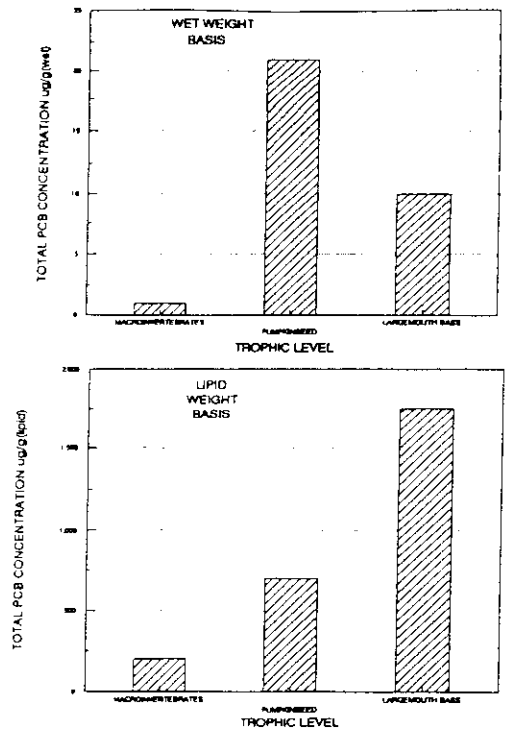

Figure 5. Comparison of PCB concentrations in a Hudson River food chain. Upper: on wet weight basis; lower: on lipid basis. Compiled from data of NYS DEC.

$$N_{wl} \approx K_{ow} \tag{4}$$

and Equation 2 is

$$\frac{dv_m}{dt} = k_u w_L \left(c_{w,s} - \frac{v}{K_{ow}} \right) - K_1 v_m \tag{5}$$

Since the whole body burden is related to the chemical concentration by

$$v_m = v w_L \tag{6}$$

the chemical concentration on a lipid basis is given by

$$\frac{dv}{dt} = k_u c_{w,s} - K' v \tag{7}$$

where

$$K' = \frac{k_u}{K_{ow}} + K_1 + G \tag{8}$$

for G(day^{-1}) as the growth rate of organism lipid.

For zero K_1 and growth, Equation 8 shows that the excretion rate is inversely related to the K_{ow} of the chemical.

At equilibrium, a lipid-based whole body Bioconcentration Factor (BCF) [μg/kg(lipid) ÷ μg/L(water)] can be defined from Equation 7 as

$$N_w = \frac{v}{c_{w,s}} = \frac{k_u}{K'} \tag{9}$$

The BCF is therefore the ratio of the chemical concentration (from water exposure only) to the freely dissolved chemical concentration, either in the water column or in the sediment interstitial water.

Uptake from Water and Food

In addition to the chemical intake from water, the organism also receives chemical input from consumption of contaminated food. This mass input of chemical depends on the rate of feeding, the chemical concentration of the food source and the assimilation efficiency of the chemical.

The general mass balance equation for the whole body burden for a given compartment, i, is then similar to Equation 2 for water uptake but with the additional mass input due to feeding (Norstrom et al. 1976, Thomann 1981, Thomann and Connolly 1984, Connolly and Tonelli 1985, Thomann 1989, Connolly 1991). Therefore,

$$\frac{dv_i}{dt} = k_{ui} c_{w,s} - K_i' v_i + \sum_j \alpha_{ij} p_{ij} I_{L,i} v_j \tag{10}$$

where

$$i = 2 \ldots n$$

for "n" compartments above the phytoplankton and where α_{ij} is the chemical assimilation efficiency (g chemical absorbed/g chemical ingested); p_{ij} is the food preference of i on j; $I_{L,i}$ is the lipid-specific consumption of organism i, (g(lipid) prey/g(lipid) predator-d); and t is real time (days).

For a simple chain where organism i feeds only on i-1,

$$\frac{dv_i}{dt} = k_{ui} c_{w,s} + \alpha I_{L,i,i-1} v_{i-1} - K_i' v_i \tag{11}$$

where

$$I_{L,i,i-1} = p_{i,i-1} I_{L,i} \tag{11a}$$

At equilibrium,

$$v_i = \frac{k_{ui} c_{w,s}}{K_i'} + g_{i,i-1} v_{i-1} \tag{12}$$

for $g_{i,i-1}$ as a food chain multiplier given by

$$g_{i,i-1} = \frac{\alpha I_{L,i,i-1}}{K_i'} \tag{12a}$$

The extent of any food chain magnification above that for exposure to water only is then given by the interaction of net chemical intake ($\alpha \cdot I$) and overall loss rate, K'. Chemicals that are excreted slowly and assimilated strongly then will tend to accumulate more readily in the food chain.

For a pelagic system, the phytoplankton are considered as the base of the food chain (compartment #1, see Figure 1). The relationship between the chemical concentration in the phytoplankton and that in the water over a range of K_{ow} is a subject of some research. Field and laboratory data (e.g., Lederman and Rhee 1982, Oliver and Niimi 1988, see also Connolly 1991 for further review and discussion of data) indicate a phytoplankton BCF approximately equal to log K_{ow} up to about 5–6. Thereafter, the data indicate a constant BCF independent of K_{ow}. Swackhammer (unpublished data) has shown that the BCF for the phytoplankton appears to be related to the growth stage of the phytoplankton biomass.

The mass of chemical in the phytoplankton per volume of water v_1[μg/L] is related to the phytoplankton chemical concentration v_1[μg/kg(lipid)] by

$$v_1 = v_1 w_1 f_{L1} \tag{13}$$

where w_1 [kg(w)/L] is the total phytoplankton biomass and f_{L1} [kg(lipid)/kg(wet)] is the fraction lipid of the phytoplankton.

A mass balance equation for the phytoplankton chemical mass per volume of water using sorption-desorption kinetics is then given as

$$\frac{dv_1}{dt} = k_{u1} w_1 c_w - K_1 v_1 \tag{14}$$

Using Equation 13 gives the equation for the concentration as

$$\frac{dv_1}{dt} = k_{u1} c_w - K_1 v_1 - G_1 v_1 \tag{15}$$

where G_1 is the net growth rate of the total phytoplankton biomass. The phytoplankton BCF, N_1, at equilibrium is then given by

$$N_1 = \frac{v_1}{c_w} = \frac{k_{u1}}{K_1 + G_1} \tag{16}$$

The effect of the phytoplankton biomass growth rate may then influence the phytoplankton BCF at higher K_{ow} levels where the excretion rate is presumably low.

Parameter Estimation

The preceding model framework contains two broad classes of parameters: those associated with organism physiology (e.g., growth and respiration rates) and those associated with the specific chemical (i.e., uptake and depuration rates and chemical assimilation efficiency.)

Chemical Parameters

Uptake Rate

The chemical uptake rate is related to the respiration rate of the organism and the efficiency of transfer of the chemical across the organism membrane. One expression is given by (see e.g., Connolly 1991)

$$k_{ui} = \frac{a_{oc} a_c \rho}{a_{wd} f_L c_{o2}} \beta \tag{17}$$

where a_{oc} is oxygen to carbon ratio, a_c is the carbon to dry weight ratio, a_{wd} as the wet to dry ratio, β is the ratio of chemical transfer efficiency (E_c) to oxygen transfer efficiency (E_o), ρ is the organism oxygen respiration rate [g(w)/g(w)-

day] and Co_2 is the oxygen concentration (mg/l). E_c has been shown to be a function of K_{ow} e.g., McKim (1985) with high K_{ow} (less than six) showing a decline in E_c. Thomann (1989) has expressed $E_c(K_{ow})$ as

$$
\begin{aligned}
&For \log K_{ow} = 2\text{–}3: \quad LogE_c = -1.5 + 0.4 \log K_{ow}; \; for\, w > 10\text{–}100g(w) \\
&For \log K_{ow} = 2\text{–}5: \quad LogE_c = -2.6 + 0.5 \log K_{ow}; \; for\, w < 10\text{–}100g(w) \\
&For \log K_{ow} = 3\text{–}6: \quad E_c = 0.5; \qquad\qquad for\, w > 1\ 0\text{–}100g(w) \\
&For \log K_{ow} = 5\text{–}6: \quad E_c = 0.8; \qquad\qquad for\, w < 10\text{–}100g(w) \\
&For \log K_{ow} = 6\text{–}10: \; LogE_c = 1.2 - 0.25 \log K_{ow}; \; for\, w > 10\text{–}100g(w) \\
&\qquad\qquad\qquad\qquad LogE_c = 2.9 - 0.5 \log K_{ow}; \; for\, w < 10\text{–}100g(w)
\end{aligned}
\tag{18}
$$

Excretion Rate

Equation 8 indicates

$$K = \frac{k_u\left(E_c\left(K_{ow}\right), \rho\right)}{K_{ow}} + K_1 + G \tag{19}$$

Equation 19, for $K_1 << G$, has been shown by Thomann (1989) to be approximately representative of observed excretion data for fish.

Chemical Assimilation Efficiency

The chemical assimilation efficiency is also an apparent function of K_{ow}. A summary of available data for fish (using statistical routines in Wilkinson 1988) is shown in Figure 6 (Parkerton, unpublished data). The scatter in the data is large but there is a clear decline in α for log K_{ow} greater than about 6.5. In the sediment food web model discussed below, α and E_c/E_0 were assigned using Figure 6 as follows: for log K_{ow} = 2–4, Equation 18 (for w < 10–100g(w)) was used, for log K_{ow} = 4.5–6.5, α and E_c/E_0 = 0.7; for log K_{ow} = 7.0, 7.5, 8.0, 8.5, and 9.0, α and E_c/E_0 = 0.5, 0.3, 0.1, 0.05, and 0.01, respectively.

Organism Parameters

The above equations for chemical accumulation are related to the bioenergetics of the organism via growth, feeding and respiration rates. Norstrom et al. (1976), Hallam et al. (1989) and Connolly (1991) discuss organism energetics for use in chemical accumulation models.

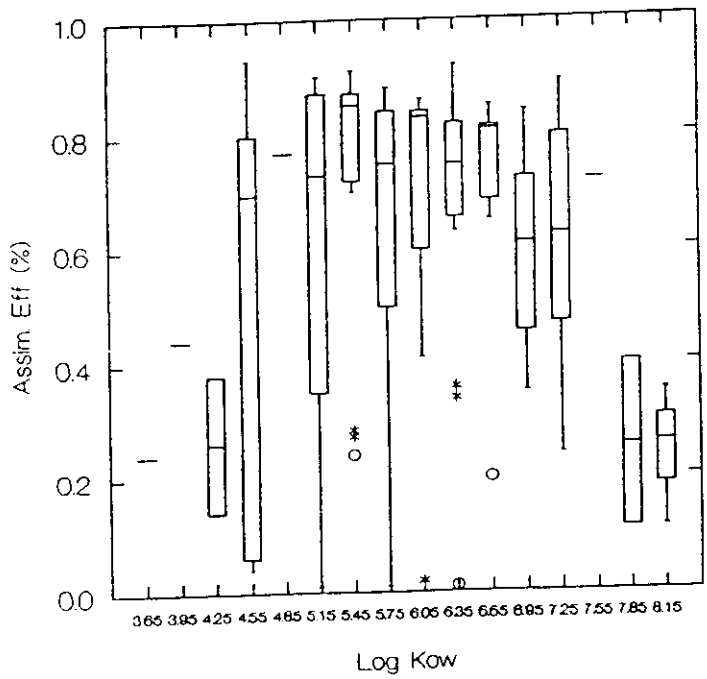

Figure 6. Variation of chemical asimilation efficiency for fish. Legend: centerline of bar = median, upper and lower limits of bar = 25th & 75th percentiles, upper and lower lines of bar = 5th and 95th percentiles, asterisks, circles and dashes = outliers.

The energy usage rate P_i[cal/g(w)–d] as given by Connolly (1991) is

$$P_i = \lambda_i \left(\rho_i + G_i \right) \tag{20}$$

for growth rate, G and respiration rate, ρ in [g(w)/g(w)-d] and λ_i in [cal/g(w)$_i$]. The energy intake rate by the animal is then the energy usage rate divided by the fraction of ingested energy that is assimilated, a. The food consumption rate, C_i in [g(w)$_i$/g(w)$_{i-1}$-d] is then given by

$$I_i = \frac{\lambda_i}{\lambda_{i-1}} \frac{\rho_i + G_i}{a} \tag{21}$$

for λ_{i-1} as the caloric density [cal/g(w)$_{i-1}$] of the food. Connolly (1991) assumes differences in caloric density to be related to the wet weight to dry weight ratio, i.e., the caloric density of dry tissue was assumed to be the same for predator and

prey. Therefore, the lipid-specific consumption rate for use in Equation 10 is given by

$$I_{L,i} = \frac{(G+\rho)}{a}\left(\frac{a_{wd,i-1}}{a_{wd,i}}\right)\left(\frac{f_{L,i}}{f_{L,i-1}}\right) \tag{22}$$

where $a_{wd,i}$ and $a_{wd,i-1}$ are the wet-dry weight ratios for predator and prey, respectively. For organisms feeding on sediment organic carbon,

$$I_{LOC,i} = \frac{G+\rho}{a \cdot a_{wd,i}}\left(\frac{f_{oc,i}}{f_{L,i}}\right) \tag{22a}$$

where $I_{LOC,i}$ is in g(OC)sed/g(lipid)$_i$-day and $f_{oc,i}$ is the fraction organic carbon of the predator.

Growth Rate

The growth rate of an organism may be estimated from the weight-age data according to

$$G = \frac{\left(dw/dt_a\right)}{w} \tag{23}$$

for t_a = age.

A generalized growth rate expression is given by (see summary in Thomann 1981)

$$G(T) \approx 0.00586(1.113)^{T-20} w^{-0.2} \tag{24}$$

for T in °C.

Respiration Rate

The generalized respiration weight relationships for two temperatures as given in Norstrom (1976), (see also Thomann 1981) provide a means for estimating the respiration temperature relationships for organisms in the lower levels of the food chain.These relationships can also be used in generic chemical models.

$$\rho(T) \approx 0.0263(1.065)^{T-20} w^{-0.2} \tag{25}$$

The general form for the respiration rate of fish in site specific dynamic computations follows that used by Thomann and Connolly (1983) and Connolly and Tonelli (1984). Thus, the respiration rate for those conditions is given by

$$\rho = bw^{\gamma} e^{dT} e^{vU} \tag{26}$$

for U, the swimming speed given by

$$U = \omega w^{\delta} e^{\phi T} \tag{27}$$

where T is the water temperature (°C) and b,γ,d,v,ω,δ and ϕ are coefficients set at 0.043, 0.3, 0.03, 0.0176, 1.19, 0.32 and 0.045, respectively, based on the aforementioned previous work.

EQUILIBRIUM GENERIC MODELS

Pelagic Models

A simple four level generic food chain can be used to calculate the expected concentration in a compartment such as a piscivorous fish. The approach follows that of Thomann (1981, 1989). Assume that in Figure 1 there is no interaction with the sediment.

Let N_i be the Bioaccumulation Factor (BAF) for the ith level on a lipid basis (μg/kg(lipid) ÷ μg/L) as

$$N_i = \frac{v_i}{c_w} \tag{28}$$

Then the equilibrium BAF for each level above the phytoplankton is given from Equation 12 as

$$N_2 = N_{2w} + g_{21} N_1 \tag{28a}$$

$$N_3 = N_{3w} + g_{32} N_{2w} + g_{32} g_{31} N_1 \tag{28b}$$

$$N_4 = N_{4w} + g_{43} N_{3w} + g_{43} g_{32} N_{2w} + g_{43} g_{32} g_{21} N_1 \tag{28c}$$

where N_{iw} is the BCF for Equation 9. Neglecting growth and non-excretory loss mechanisms, $N_{iw} \approx K_{ow}$ and then

$$N_2 / K_{ow} = 1 + g_{21} \tag{29a}$$

$$N_3 / K_{ow} = 1 + g_{32} + g_{32}g_{21} \tag{29b}$$

$$N_4 / K_{ow} = 1 + g_{43} + g_{43}g_{32} + g_{43}g_{32}g_{21} \tag{29c}$$

The accumulation of the chemical above an equilibrium with K_{ow} (an increase in the fugacity or chemical potential as discussed by Connolly and Pedersen 1988), is therefore seen to increase with trophic level.

The behavior of $g_{i,j-1}$ can be obtained to first approximation by considering the allometric relations of respiration and growth from Equations 24 and 25. Using Equation 17 with $a_{oc} = 2.67$, $a_{wd} \approx 5$ to 6, $a_c = 0.4$, $E_o = 0.8$, and $c_{02} = 8.5$ mg/l, the uptake rate is given approximately by

$$k_u \approx 1000 \frac{w^{-0.2} E_c}{f_L} \tag{30}$$

Substitution of this equation and Equation 19 into Equation 12a and using Equation 22 with approximately constant lipid and wet-dry weight ratios gives

$$g \approx \frac{0.046\alpha(K_{ow})}{a\left(\frac{1000E_c}{f_L K_{ow}} + 0.01\right)} \tag{31}$$

As seen, g is approximately independent of the weight of the organism. Also, it is interesting to note that for $K_{ow} > 10^6$, $f_L \approx 0.10$ and $E_c = 0.1$ to 1.0,

$$g \approx (2 \rightarrow 5)\frac{\alpha(K_{ow})}{a} \tag{31a}$$

indicating that for this K_{ow} region, the food chain multiplier is proportional to the ratio of the chemical uptake efficiency and the food assimilation efficiency.

If Equation 18 is used for both E_c and for α, then

$$g \cdot a \approx \frac{0.046}{\frac{1000}{f_L K_{ow}} + \frac{0.01}{\alpha(K_{ow})}} \tag{32}$$

Figure 7 shows a plot of (g·a) versus K_{ow} using Equation 18 for α (K_{ow}). As seen in this figure, (g·a) is small for log K_{ow} less than about 4 to 5, increases to

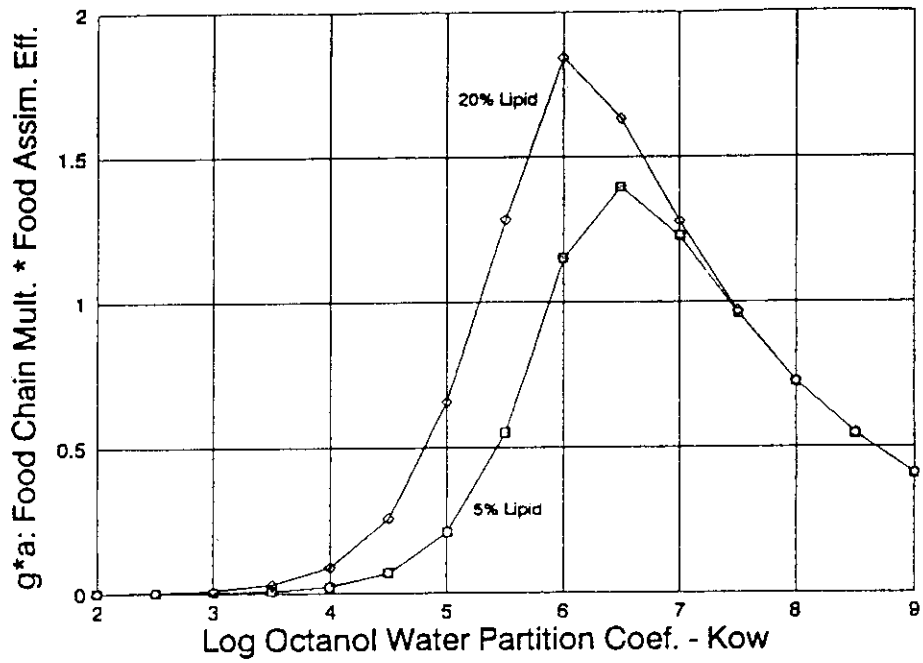

Figure 7. Variation of the product of food chain multiplier and food assimilation efficiency with octanol-water partition coefficient using Equation 32 and Equation 18 for w > 10 to 100 g(w).

a peak at log K_{ow} of about 6 to 6.5 and then declines. Thus, food chain effects are generally not significant for chemicals with log K_{ow} less than about 4 to 5. For more lipophilic chemicals, i.e., log K_{ow} greater than five and less than seven, food chain effects may be significant. For example, for log K_{ow} of six, and a food chain of organisms of about 10% lipid, the (g·a) factor is about 1.2. If the average food assimilation efficiency is 0.8, then g is 1.5. Using Equation 29c, the top predator would then have a BAF/K_{ow} of about eight times that due to uptake from the water only.

Sediment-Pelagic Models

A generic modeling framework for the accumulation of chemicals in aquatic systems which includes interaction with sediment chemical and sediment biota can also be derived from the previous equations (Thomann et al. 1992). Concern has been expressed for sediment-mediated transfer of chemicals in producing fish lesions (e.g., Malins et al. 1984) and in possible trophic transfer (Connor 1984). The bioavailability of chemicals from sediments is also of concern in establishing sediment quality criteria (USEPA 1989). A large number of laboratory experiments of chemical uptake from sediments by benthic invetebrates and to a lesser degree by fish have been conducted (e.g., Fowler et al. 1978, Oliver 1987, Landrum et al. 1989, Rubenstein et al. 1984). Likewise, field

relationships between sediment chemical concentration and aquatic biota have been measured by many investigators (e.g., Oliver 1987, Oliver and Niimi 1988, Nalepa and Landrum 1988, Mudroch et al. 1989, Pereira et al. 1988, Huckins et al. 1988).

Bierman (1990) has summarized a considerable data base relating sediment concentrations to concentrations in benthic invertebrates and fish. In that work, it was concluded that clear relationships were not evident between organic carbon-normalized sediment and lipid-normalized biota. The analysis of Bierman (1990) is, however, based on a simple partioning between sediment and biota.

Model Structure and Equations

The compartmental structure of the food web examined in this model is shown in Figure 1. Five interactive biological compartments are considered together with the particulate and dissolved components in the water column and sediment. Benthic invertebrates obtain chemical via uptake from a combination of interstitial water and overlying water and direct ingestion of chemical on sediment particles and/or from phytoplankton and detrital material at the sediment-water interface. Forage fish accumulate chemical directly from the overlying water and from food in some linear combination from zooplankton and benthic invertebrates. By allowing the benthic community to interact with both the sediment and the overlying water column, the chemical transfer between the sediment and the overlying water must also be included. The equation for each of the biological compartments is developed in turn.

Applying Equation 10, the mass balance equation for the chemical in the benthic compartment (#5) is given at steady-state by

$$\frac{dv_5}{dt} = 0 = \left[k_{u5}\left(b_{5s}c_s + b_{5w}c_w\right)\right] + \left[\left(p_{5s}\alpha_{5s}I_{loc.5}\right)r_s + \left(p_{51}\alpha_{51}I_{L.5}\right)v_1\right] - \left[\left(K_5'\right)v_5\right] \tag{33}$$

The first bracketed term on the right hand side of this equation represents the uptake of available chemical by benthic organisms from the sediment interstitial water and the overlying water column where b_{5s} and b_{5w} are the fraction of uptake from sediment and overlying water, respectively, ($b_{5s} + b_{5w} = 1$). The second bracketed term represents the uptake of chemical from ingestion of sediment (r_s; μg/g (org C)) and phytoplankton (v_1) where p_{5s} and p_{51} are the preference for sediment and phytoplankton, respectively ($p_{5s} + p_{51} = 1$). The third term is the loss of chemical due to excretion (K) and growth (G).

For the third compartment, the forage fish, the model equation is given by

$$\frac{dv_3}{dt} = 0 = k_{u3}c_w + p_{32}\alpha_{32}I_{L.3}v_2 + p_{35}\alpha_{35}I_{L.3}v_5 - \left(K_3 + G_3\right)v_3 \tag{34}$$

In this equation, p_{35} and p_{32} represent the relative feeding preference of forage fish for benthic invertebrates and zoooplankton, respectively, ($p_{35} + p_{32} = 1$). Note that if $p_{35} = 1.0$, then this compartment represents a bottom dwelling fish feeding only on the benthic community.

The phytoplankton, zooplankton and piscivorous fish equations are given by application of Equation 10.

In order to assess relative bioaccumulation of chemical from the sediment or the overlying water column, the following ratios can be defined.

Let v_i/r_s be the ratio of the organism chemical concentration on a lipid basis to the sediment chemical concentration on a carbon basis (with units μg/g(lipid) ÷ μg/g(organic carbon) or g(organic C)/g(lipid)). This ratio has been termed the Biota Sediment Factor (BSF), by Parkerton (1991). Also, let

$$\pi_s = \frac{r_s}{c_s} \tag{35}$$

$$\pi_{ws} = \frac{r_s}{c_w} \tag{36}$$

Equation 35 is the sediment partition coefficient, i.e., the ratio of the sediment chemical concentration (organic carbon basis) to the interstitial freely dissolved chemical concentration. Equation 36 is the partitioning between the sediment chemical concentration and the overlying water freely dissolved concentration.

The BSF is given from Equation 33 as

$$S_5 = \frac{v_5}{r_s} = \frac{N_{5w}}{\pi'} + g_{5s} + g_{51}\frac{N_{1w}}{\pi_{ws}} \tag{37}$$

where

$$\pi' = \frac{\pi_s \pi_{ws}}{b_{5s}\pi_{ws} + b_{5w}\pi_s} \tag{37a}$$

$$g_{5s} = \frac{p_{5s}\alpha_{5s}I_5}{K_5 + G_5} \tag{37b}$$

$$g_{5l} = \frac{p_{5l}\alpha_{5l}I_5}{K_5 + G_5} \tag{37c}$$

The first term of Equation 37 represents the uptake of chemical from the water phase, either sediment interstitial water or overlying water. The second term is

the chemical accumulation due to consumption of sediment organic carbon. The third term represents the accumulation due to consumption of overlying phytoplankton. It can be noted that the BSF in general is a complicated function of sediment and overlying water dissolved and particulate chemical concentration, feeding rates and preferences, and the usual uptake, excretion, and growth rates.

Insight can be gained into the preceding equations by considering the following approximations. Let

$$\pi_s \approx K_{ow} \tag{38a}$$

$$N_{lw} \approx K_{ow} \tag{38b}$$

The first equation assumes that the sediment partition coefficient (on an organic carbon basis) is equivalent to the octanol-water partition coefficient, K_{ow}. The second of these equations assumes that growth effects and metabolism of contaminants are small and that the lipid-normalized BCF is also approximately equal to the octanol-water partitioning coefficient. From Equation 37 with $b_5 = 1.0$ (i.e., exposure to sediment only), the BSF is

$$S_5 \approx 1 + g_{5s} \tag{39}$$

Thus, if the sediment magnification factor, g_{5s} is small, the ratio of organism to sediment chemical concentration will be approximately unity, indicating no significant bioaccumulation from the sediment.

The BSF (S_3) for the forage fish (compartment #3) is given from Equation 10 as

$$S_3 = \frac{v_3}{r_s} = \frac{N_{3w}}{\pi_{ws}} + g_{32}S_2 + g_{35}S_5 \tag{40}$$

where S_2 is the BSF for the zooplankton. Note the inclusion of the sediment to water interaction given by π_{ws}.

The BAF for the forage fish (#3) with consumption of benthic organisms is given by (Thomann et al. 1992)

$$N_3 = \frac{v_3}{c_w} = \left\{N_{3w} + g_{32}\left(N_{2w} + g_{21}N_{1w}\right)\right\} + \left\{g_{35}\left[N_{5w}\left(b_{5s}\frac{\pi_{ws}}{\pi_s} + b_{5w}\right) + g_{5s}\pi_{ws} + g_{51}N_{1w}\right]\right\} \tag{41}$$

As seen, the first group of terms in braces is the BAF from a three-step food chain (see Equation 28b). The second term in braces is the accumulation due to consumption of benthic organisms.

Approximating Equation 41 by using Equation 38 and considering the forage fish to feed only on the benthic invertebrates ($g_{32} = 0$) and the invertebrates to be feeding on and exposed only to the sediment ($b_{5w} = 0$, $g_{51} = 0$) gives

$$N_3 = K_{ow} + (g_{35} + g_{35}g_{5s})\pi_{ws} \tag{42}$$

The effect of the sediment interaction is now clearer. The BAF is elevated above the equilibrium level of K_{ow} by the magnitude of π_{ws} and the food chain effects. Equation 42 can be contrasted to a forage fish feeding exclusively in a pelagic chain. Thus

$$N_3 = K_{ow} + (g_{32} + g_{32}g_{21})K_{ow} \tag{43}$$

Assuming the food chain multipliers are approximately similar, the impact of the sediment is the ratio of π_{ws} to K_{ow}.

Sediment-Water Column Interaction

The preceding equations for the BSF include the interaction between the water column and sediment. The ratio π_{ws} Equation 36 emerges when the benthic invertebrates are feeding on both sediment organic carbon and the carbon phytoplankton. The partitioning between the sediment and water column can be shown (Thomann et al. 1992) to be given at steady-state as

$$\pi_{ws} = \frac{\delta f_{ocw}\pi_w}{f_{ocs}} \tag{44}$$

where f_{ocs} and f_{ocw} are the sediment and water organic carbon fraction, respectively, and δ is a complicated function of settling and resuspension velocities of the particulates, net deposition velocity, sediment decay of chemical, and partitioning of chemical in water column and sediment (see Di Toro et al. 1982) given by

$$\delta = \frac{(v_u + v_d)f_{ps} + (\pi_s / \pi_w)K_f f_{ds} / \phi_s}{(v_u + v_d)f_{ps} + K_f f_{ds} / \phi_s + K_{ds}H_s} \tag{45}$$

where v_u and v_d are the resuspension and net deposition velocities (cm/yr), respectively, f_{ps} and f_{ds} are the fraction of chemical in particulate and dissolved

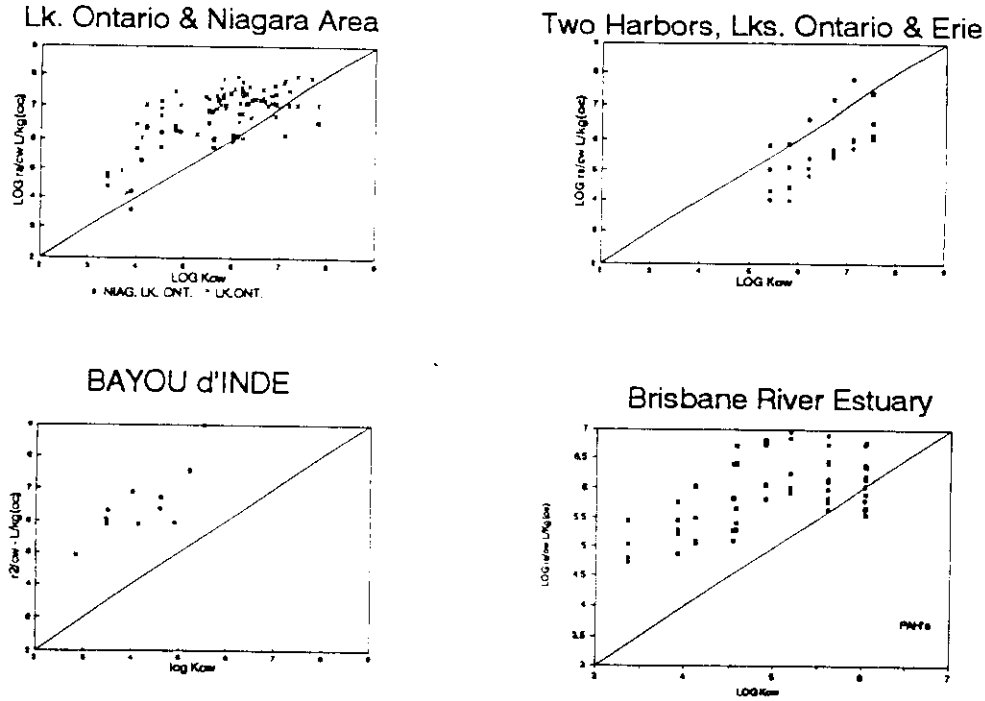

Figure 8. Variation of $r_s/c_{ws} = \pi_w s$ for several water bodies. Lake Ontario and Niagara area (Oliver and Niimi 1988, and Oliver and Charlton 1984), Two Harbors (Mudroch et al. 1989), Bayou d'Inde (Pereira et al. 1988), Brisbane River Estuary (Kayal and Connell 1990).

form, K_f is the interstitial diffusion rate (cm/d), ϕ_s is the sediment porosity and K_{ds} is the sediment decay rate (day^{-1}).

The water column partition coefficient is calculated using the formulation of Di Toro (1985) given by

$$\pi_w = \frac{K_{ow}}{1 + f_{ocw} K_{ow} m_w / 1.4} \tag{46}$$

for π_w in L/kg(oc) and m_w is the suspended solids concentration (kg/l).

Figure 8 shows the relationship of π_{ws} for several different areas and indicates that the partitioning is usually above K_{ow} levels. The preceding equations can be used to represent these data if sufficient information is available for the parameters such as net deposition velocity, suspended solids, etc.

CALIBRATION AND APPLICATION OF GENERIC MODELS

Pelagic Models

Applications of the generic model are given in Thomann (1981), (drawing on earlier work by Norstrom et al. 1976) and Servos (1988). In Connolly and

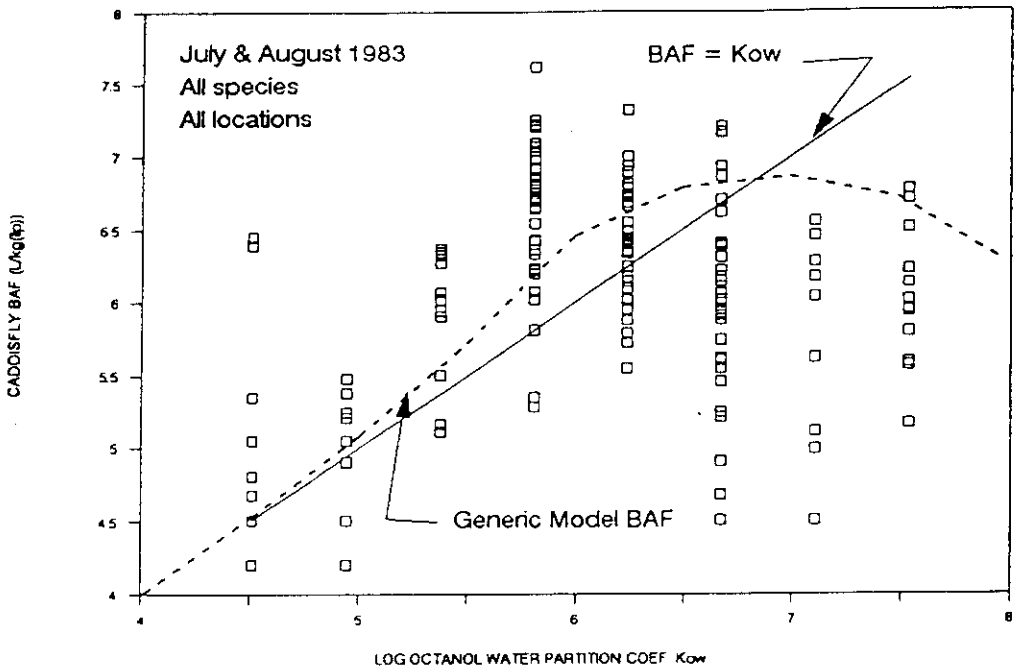

Figure 9. Comparison of generic model BAF to PCB congener data for caddisfly in Upper Hudson River. Data compiled from Bush et al. 1985 using percent lipid of 6.2%.

Pedersen (1988) and Thomann (1989), a four-step food chain with parameters as a function of K_{ow} was used. An additional application of Thomann (1989) is shown in Figure 9 using the data of Bush (1985) on PCB congener accumulation in caddisfly larvae in the upper Hudson River. Equation 28a was used, caddisfly were assumed at 10 mg(w), 2% lipid, weight/dry weight = 5 and a food conversion efficiency of 0.3. The phytoplankton BCF was assumed equal to K_{ow} for log $K_{ow} \leq 6$. Above that level, the phytoplankton BCF was held constant at 10^6. Equation 18 was used to estimate chemical efficiency. The simple model as shown in Figure 8 is a reasonable representation of the general trend of the data. Bioaccumulation above BAF = K_{ow} is noted in the region of $5 \leq \log K_{ow} \leq 7$. The decline above log K_{ow} of 7 is due to an assumed decreased chemical assimilation efficiency.

Food Web Models with Sediment Interaction

The schematic for this model is shown in Figure 1. As noted earlier, an important parameter in such a model is the sediment-water column interaction given by π_{ws}. Data from Oliver and Charlton, (1984) for the Niagara River region of Lake Ontario and Oliver and Niimi (1988) for the open Lake Ontario are used to calibrate the relationship between sediment and overlying water concentrations. The data for Lake Ontario shown in Figure 8 were used for π_{ws}. (See Thomann et al. 1992 for additional details).

The principal parameters that must be determined for the calibration of the food web-sediment model may divided into three groups. The first group of parameters are associated with the organism physiology including weight, food conversion efficiency, growth rate, and specific consumption rate. The second group of parameters reflect the behavior of the chemical and include the uptake and excretion rates and the chemical assimilation efficiency. The third group consists of the feeding preference factors. The parameter specifications for the first group follows that of Thomann (1989) where organism weight is assigned to each compartment, and allometric relationships are used to estimate growth and respiration and subsequent food consumption rates. Table 1 summarizes the parameters for the first group. Chemical uptake is calculated from weight and efficiency of transfer from the waterphase. The efficiency of aqueous uptake as well as the chemical assimilation efficiency of ingested prey is an assumed function of K_{ow} using Equation 18. Excretion is taken as the ratio of uptake to the octanol-water partition coefficient. Feeding preference parameters are determined from a sensitivity of the model using field data. Data from Oliver and Niimi (1988) are used for model calibration.

Figure 10 (top) from Thomann et al. (1992) shows the results of a sensitivity of the amphipod/sediment ratio given two assumptions on feeding behavior. For both A and B, the amphipod are assumed exposed to the overlying water only [i.e. $b_{5w} = 1.0$ in Equation 33]. Curve A indicates results when amphipods are assumed to feed exclusively on the sediment [$p_{5s} = 1.0$ in Equation 33]. Curve B assumes an exclusive phytoplankton diet [$p_{5l} = 1.0$ in Equation 33]. As seen, the data appear to reflect some combination of feeding on sediment and overlying water particulates as well as exposure to interstitial and overlying water. Following analyses of combinations of feeding and water exposure, Figure 10 (bottom) shows the results of a 20% exposure of the benthic invertebrates to the interstitial water, 80% to overlying water chemical concentration and a 20% consumption of sediment particulate organic carbon. These combinations are not necessarily unique and other relationships between exposure and feeding may provide an equally credible representation of the observed data. The log K_{ow} region from about 6 to 8 shows a BSF greater than one indicating some bioaccumulation of chemical above an expected equilibrium value of about one (neglecting effects of organism growth). The values of v_5 of less than one are a result of exposure to overlying water chemical concentration.

Figure 11 from Thomann et al. (1992) shows the computed sculpin/sediment ratio compared to the observed data. The sculpin are considered a forage fish. For this computation, the amphipod parameters are from Figure 10 (bottom) and the sculpin are assumed to consume 80% benthic invertebrates and 20% zooplankton. The sediment/water column interaction is given from Figure 9. The particular shape of the model in Figure 11 is a result of a complicated interaction between contaminant exposure in the sediment and overlying water and chemical assimilation efficiency. The "water only" level is computed from Equation

Table 1. Model Parameters for Food Web Pelagic/Sediment Model (From Thomann et al. 1992)

Component No.	Weight (g(w))	$f_{L,i}$ % Lipid	Net Energy eff a^a	a_{wdi}	G Growth rate $(d^{-1})^b$	r Respiration rate $(d^{-1})^c$	$C_{L,i}$ Specific consumption[d]
1[f]	-	1	-	10	-	-	-
2	0.01	5	0.30	5	0.025	0.090	0.154
3	100	8	0.80	4	0.004	0.014	0.016
4	1000	20	0.80	4	0.0025	0.0090	0.0058
5	0.002	3	0.20	7	0.035	0.125	0.381
							1.52[e]

[a] g(OC) assim/g(OC) ingested (see Equation 22a).
[b] Equation 23.
[c] Equation 24.
[d] Equation 21 - g(1p)/g(1p)-d.
[e] Equation 22 - g(OC)/g(1p)-d.
[f] #1 = Phytoplankton, given by partitioning to water concentration.

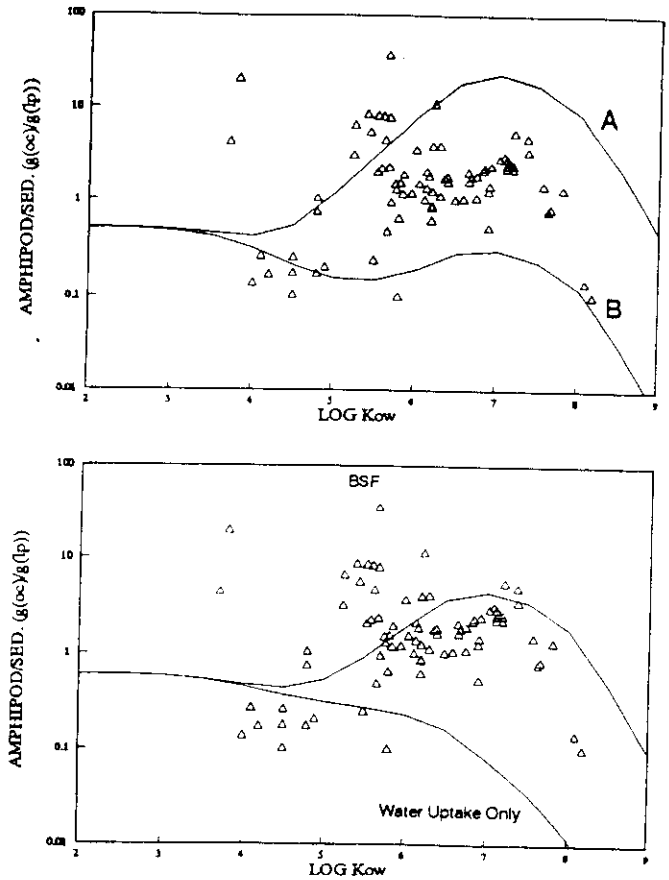

Figure 10. Comparison of observed data of Oliver and Niimi (1988) to benthic invertebrate accumulation model using E(33). See text for discussion.

40 with zero feeding. As seen, above a log K_{ow} of about five, this model indicates that virtually all of the sculpin chemical concentration is due to uptake from the food route.

SITE-SPECIFIC MODEL

Site-specific models incorporate all of the preceding mechanisms with various levels of the food chain as functions of time and age (see e.g., Thomann and Connolly 1984, Connolly and Tonelli 1985, and Connolly 1990). Two additional applications are discussed here.

PCB-Hudson Estuary Striped Bass

The food chain accumulation of PCBs in the striped bass of the Hudson Estuary has been evaluated by Thomann et al. (1989, 1991). An age-dependent

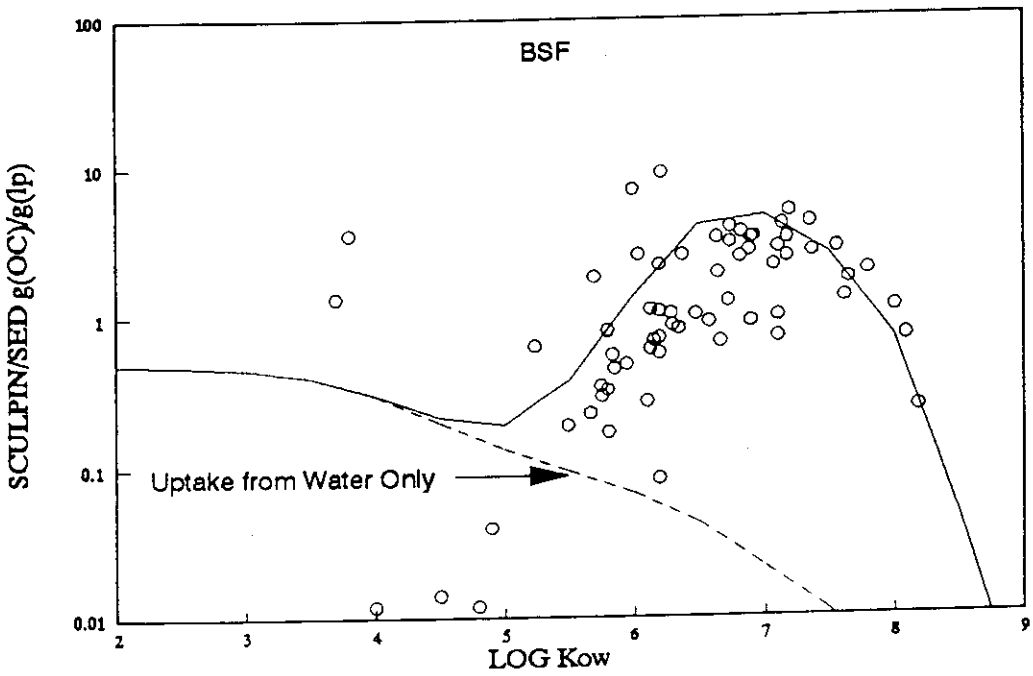

Figure 11. Comparison of observed data of Oliver and Niimi (1988) to sculpin chemical data using Equation 40. Solid line = total accumulation from food and water.

model (see Figure 2) was used and calibrated to the striped bass residue data. An important part of that model is the determination of the food web interactions used to construct model linkages. These interactions are reviewed here as an example of the factors that must be considered in a site-specific model.

Food Web Interactions

The determination of the food web interactions for the striped bass begins with an evaluation of feeding patterns by various age classes. A variety of feeding studies have been conducted where stomach contents of the striped bass are examined, typed, and enumerated. O'Connor (1984), Gardinier and Hoff (1982), and Setzler et al. (1980) provide a basis for estimating the diet of the striped bass. An earlier general survey of striped bass life history is given by Raney (1952).

In general, these studies indicate that the striped bass progress from primarily invertebrate feeders in age classes zero to one to two years to primarily piscivorous feeders in older age classes.

For striped bass in age class zero to one+, collected during 1974 to 1977, Gardinier and Hoff (1982) indicate a diet of primarily invertebrates. Major groups included *Gammarus*, calanoid copepods, and cladocerans. Gardinier and Hoff (1980) indicate that 80 to 100% of the diet of "small striped bass" was *Gammarus fasciatus*. O'Connor (1984) in a survey of striped bass stomach

contents in the New York Harbor region in the winter of 1983 also concluded that for fish, the principal component of the diet was *Gammarus* although other taxa were also present.

For age class zero+ to about two years, Gardinier and Hoff (1980) reported a mixed diet of fish (blueback herring, tomcod, bay anchovy and mummichog) and invertebrates. Seasonal variations were significant. In June, fish made up 67% of the total diet, but by September, invertebrates comprised 83% of the total diet. For Long Island Sound, Setzler et al. (1980) summarizing the work of Schaefer (1970) indicated that 85% of the food volume of striped bass of age less than about three years consisted of invertebrates. *Gammarus* and mysis shrimp *Neomysis americanca* were dominant.

For age classes greater than about two+, the striped bass are almost entirely piscivorous. The percentage of fish remains high with increasing size of the striped bass. For striped bass between 200 to 399 mm, fish made up 31% of the stomach contents. For striped bass greater than 800 mm (> about eight years old), fish made up about 86% of the stomach contents. A similar result is summarized by Seltzer et al. (1980) who indicate that fish make up greater than 65% of the diet of striped bass greater than six years old. The fish consumed include white perch, Atlantic tomcod, blueback herring, and spottail shiner.

The lower levels of the food web are considered to be composed of a "phytoplankton" compartment which is considered to be in a sorption-desorption equilibrium state with the dissolved water concentration of a given PCB homolog. The phytoplankton are then preyed upon by a "zooplankton" compartment, the characteristics of which are considered to be represented by *Gammarus*.

The next level is assigned as a representation of "small fish", a compartment meant to reflect a mixed diet of fish of about 10 g in weight. This compartment would therefore include such fish as zero to one+ tomcod and herring. The white perch are considered to feed exclusively on zooplankton.

The striped bass is divided into seventeen age classes, the characteristics of which are discussed more fully below. For classes zero to two years, the striped bass are assumed to feed on the zooplankton (i.e., *Gammarus*). For age classes from two to six years, the striped bass are assumed to feed on a mixture of small fish and age class yearling white perch. For striped bass older than six years, white perch from two to five years old are assumed to comprise the diet.

The total number of state variables then in the food web model is 29, since each age class of a species represents a separate state variable.

The calibrated striped bass model indicated significant bioaccumulation as shown in Figure 11. The top figure shows the calculated time history of total PCB (μg/g/(lp)) in the striped bass for the mid-Hudson region over a 40-year period. (A physico-chemical model was used to calculate the time variable water column concentrations; see Thomann et al. 1991). As shown, better than 90% of the total PCB residue is calculated to be due to the food chain transfers depicted in Figure 2. Figure 12 (bottom) shows the calculated contribution due to water only

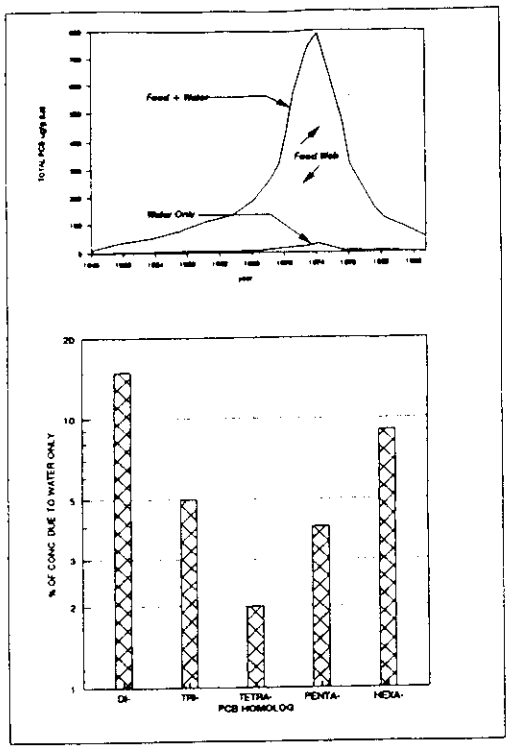

Figure 12. (Top) Contribution to total PCB concentration in Hudson River striped bass age dependent, time dependent model from food web and water only. (Bottom) Variation of uptake due to water only as a function of PCB homolog group. From Thomann et al. (1989).

exposure as a function of PCB homolog. The variation is due largely to the assumed variation in chemical assimilation efficiency which was homolog dependent. For the tetra PCBs, only 2% of the striped bass chemical concentration is considered to be due to aqueous exposure. This percentage rises to about 10% for the less assimilable lower and higher chlorinated PCBs.

An important step in determining the ecosystem response to various load simulations is to analyze the behavior of the mean concentration of a top predator as a function of the percent below a certain target level of, say, 2 μg/g(w) for PCBs. The question addressed for the Hudson striped bass was:

> What is the estimated mean concentration in the striped bass (over the sampled age class of three to six years) so that a given percentile of the fish will be below 2 μg/g(w)?

A log normal distribution of the striped bass PCB concentration is assumed based on the analysis of the existing data (Thomann et al. 1989). The only other

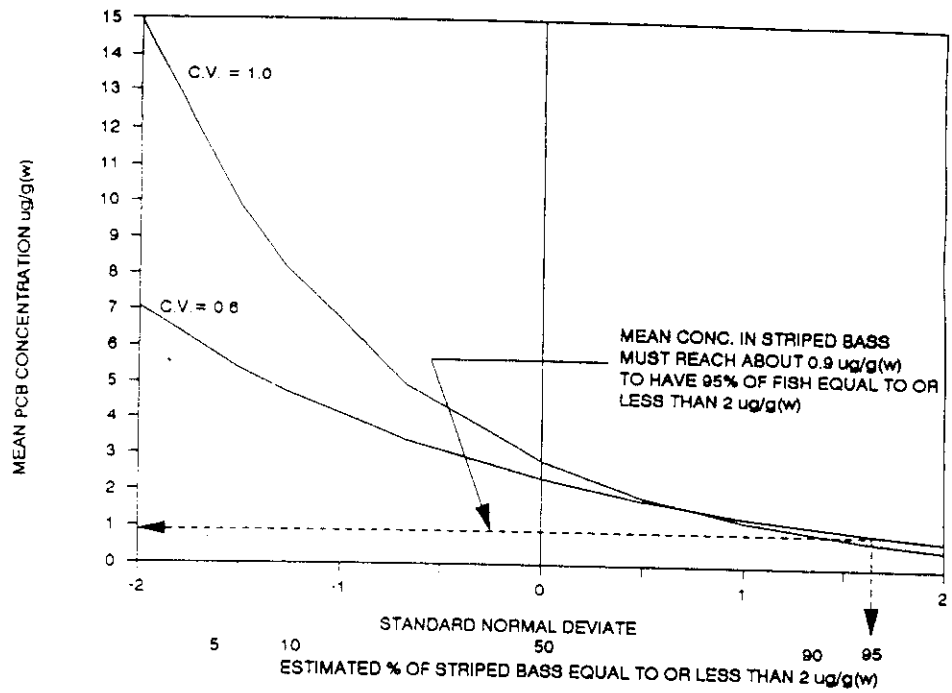

Figure 13. Relationship between mean total PCB concentration in Hudson River striped bass and percentiles equal to or less than 2 μg/g(w) from Equations 47–49.

parameter to be specified is the coefficient of variation of the log normally distributed variable. The equations are as follows:

$$\sigma^2_{\ln x} = \ln\left[1 + \delta_x^2\right] \tag{47}$$

$$\mu_{\ln x} = \ln x - \sigma_{\ln x} \cdot z \tag{48}$$

$$\mu_x = \exp\left[\mu_{\ln x} + \frac{1}{2}\sigma^2_{\ln x}\right] \tag{49}$$

where $\sigma^2_{\ln x}$ is the variance of log transformed fish concentration, δ_x is the coefficient of variation, $\mu_{\ln x}$ is the log transformed mean concentration, ln x is the logarithm of the target concentration (here set equal to 2 μg/g(w)), Z is the standardized normal deviate, and μ_x is the required mean fish PCB concentration.

Figure 13 shows the relationship between the percentile of striped bass concentration and the mean concentration for coefficients of variation of 0.6 and 1.0. These values are approximately the range of coefficients as obtained from the measured data.

As indicated in Figure 13, if a mean concentration of about 0.9 μg/g(w) is reached in the striped bass, 95% of the fish would be expected to have concentrations below 2 μg/g(w). A mean concentration of about 3 μg/g(w) would result in about 50% of the fish below 2 μg/g(w). It can also be noted that the difference between the two coefficients of variation is not significant for percentiles greater than 50%. The results of this analysis as displayed in the figure were used to estimate the time it will take to reach various percentiles of PCB concentration.

LAKE ONTARIO PCB

Modeling the PCB Time History in the Lake Ontario Lake Trout Food Chain

As part of an International Joint Commission (IJC) study to compare various modeling frameworks a model of the fate of PCBs in the water column, sediment, and biota of Lake Ontario was developed (Connolly et al. 1987). The lake was treated as a completely mixed water column overlying a vertically segmented sediment. The model simulated dissolved and particulate PCB concentrations over the period 1943 to 1981. Measured water column total PCB concentrations in 1980 and 1981 and measured surficial sediment PCB concentrations in 1968, 1972, 1979, and 1981 were used in model calibration. The computed water column dissolved PCB and sediment dissolved and particulate PCB defined exposure time histories that were used to compute the PCB time history in the lake trout food chain.

The food chain model used was essentially that previously developed to model PCB in the lake trout food chain of Lake Michigan (Thomann and Connolly 1984, Thomann et al. 1987). The species included, in addition to lake trout, were the alewife, the pelagic invertebrate *Mysis relicta*, the benthic invertebrate *Pontoporeia hoyi* and phytoplankton. *Pontoporeia* are deposit feeders and thus provide a vector for transferring sediment PCB to the upper levels of the food chain.

The Lake Michigan model was modified to make the PCB excretion rate a function of the animal's lipid content. Consistent with laboratory data the excretion rate was assumed to be inversely related to the fraction lipid of the animal (f_L). Specifically, the excretion rate constant was computed as follows:

$$K = \frac{k_u}{f_L K_{ow}} \tag{50}$$

where k_u is the uptake rate constant at the gill and K_{ow} is the octanol-water partition coefficient for PCB (log K_{ow} was assumed to be 6.3).

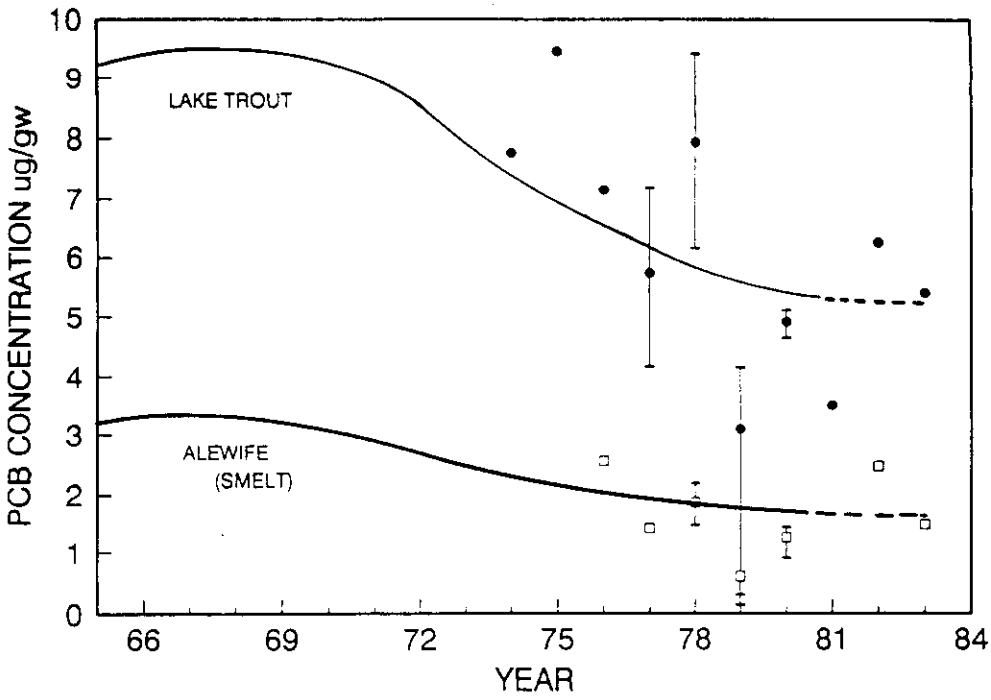

Figure 14. Calculated and observed time history of total PCB in the Lake Ontario lake trout food chain (Connolly et al. 1987).

Using a PCB partition coefficient of 30 L/g(w) for phytoplankton and an alewife PCB assimilation efficiency of 0.6 (rather than the 0.7 value used in the Lake Michigan calibration) the model reproduced the time history of both lake trout and alewife (data for smelt included) PCB concentrations fairly well (Figure 14). As seen in the figure, the computed average lake trout concentration reaches a peak of about 9.5 μg/g(w) in the late 1960s and declines to about 5.5 μg/g(w) in 1980. The maximum PCB concentration occurs in 11-year old trout. Their computed average concentration in 1980 is 9.7 μg/g(w). A similar pattern is seen for alewife. By 1980 their average concentration has declined to about 2 μg/g(w), with an average maximum concentration of 3.3 μg/g(w) occurring in six-year old alewife.

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