THE BIOACCUMULATION OF METHYLMERCURY IN AN AQUATIC ECOSYSTEM

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A model for the bioaccumulation of methyl-mercury in an aquatic ecosystem is described. This model combines predator-prey equations for interactions across three trophic levels with pharmacokinetic equations for toxin elimination at each level. The model considers the inflow and outflow of mercury via tributaries, precipitation, deposition and bacterial methylation to determine the concentration of toxin in the aquatic system. A sensitivity analysis shows that the model is most sensitive to the rate of energy transfer from the first trophic level to the second. Using known elimination constants for methyl mercury in various fish species and known sources of input of methyl mercury for Lake Erie, the model predicts toxin levels at the three trophic levels that are reasonably close to those measured in the lake. The model predicts that eliminating methyl mercury input to the Lake from two of its tributary rivers would result in a 44 percent decrease in toxin at each trophic level.

1. Introduction

Toxins that enter an ecosystem are generally observed to be more concentrated per unit of biomass at higher trophic levels. This phenomenon is known as “bioaccumulation”. Organisms can take up a toxic substance through lungs, gills, skin or other direct points of transfer to the environment. Predators, however, have a major source of toxin in their prey. The mechanism by which predators gain toxin (catching prey) is offset somewhat by mechanism of elimination (toxicokinetics). In this paper we model these two processes to see how they, together, produce the phenomenon of bioaccumulation. The model we develop is a simplified food web with

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three trophic levels interacting with damped Lotka-Volterra dynamics. The model developed here could represent any toxin passed through food. As an application we consider the case of methylmercury in Lake Erie.

Section 2 gives some background information on methylmercury. Section 3 presents the basic model, analyzed in section 4. Numerical results are given for the basic model in section 5. Section 6 refines the portion of the model concerned with elimination of methylmercury from a trophic level through first order toxicokinetics. Section 7 refines the model describing input of methylmercury to the lake and the resulting ambient concentration in Lake Erie water. Section 8 describes the results of the refined model. In section 9 we investigate the sensitivity of the model to changes in parameters, varying each parameter 20% from its default value. Section 10 describes the effect of reducing methylmercury concentrations in the water on toxin concentrations in the trophic levels, using the elimination of toxin sources from the Detroit River and smaller tributaries as an example. Section 11 summarizes all results in a short discussion.

2. Background

Mercury poisoning is a significant health risk for people of all ages and is particularly severe for fetuses, infants and young children. While mercury exposure can occur in a number of ways, people in the United States are most commonly exposed to mercury through the consumption of fish or shellfish containing methylmercury.

Mercury can be emitted into the air as a byproduct of manufacturing or coal burning activities, and is released from volcanoes. Once in the atmosphere, this mercury falls in the form of precipitation and can pollute water sources. Bacteria living in the soils and sediments in and around these water sources convert the mercury into its toxic form, methylmercury (MeHg). In this paper we will ignore sediment exchange processes, and look only at toxins entering from tributaries and air, and toxins leaving via photodemethylation. In the case of Lake Erie, polluted tributaries are a significant source of methylmercury. These sources are included in the system.

Methylmercury makes its way up the aquatic food chain, becoming more concentrated with each trophic level. The model for bioaccumulation of toxin presented here is based on organisms in three trophic levels. The system of trophic levels describes the position that a species occupies in the food chain- essentially what that species eats and what eats them. In-
herent in this system is a transfer of energy, nutrients and toxins embedded in tissues between organisms. The concentrations of such toxins, including methylmercury, can be modeled using a simple pharmacokinetics model, in which a trophic level uptakes a toxin at a some rate and expels the toxin, through excretion, at a second rate of elimination. Since some amount of the toxin remains in the organism tissue thereafter, it is presumably transferred in its entirety to the next trophic level when the organism is eaten. In this sense, a modification of a simple mathematical model for trophic dynamics in combination with a pharmacokinetic model for chemical accumulation in animal tissue provides a theoretical model for bioaccumulation of methylmercury across trophic levels.

3. Basic Model for Bioaccumulation

![Diagram of trophic dynamics and parallel pharmacokinetics]

Figure 1. Box model for trophic dynamics and parallel pharmacokinetics
In any given ecosystem a natural food web exists. The lowest level of the web generally corresponds to the smallest organisms with the largest population, while the highest level is generally occupied by the largest organisms with the smallest population. While most isolated ecosystems can be broken down into hundreds of trophic levels, for the sake of simplicity, this paper will invoke a model for a tripartite trophic system.

3.1. Predator prey

The model defined in this paper defines three trophic levels:

(1) The photosynthetic/asexual producing level, which derives its nutrients from abiotic sources. This population will be defined by the variable $F$, for First trophic level.

(2) The second trophic level, which derives it nutrients for sustenance and growth from population $F$. This population will be defined by the variable $S$, for Second trophic level.

(3) The third trophic level, which derives its nutrients for sustenance and growth from population $S$. This population will be defined by the variable $T$, for Third trophic level.

For the sake of simplicity, implicit in the model are the following assumptions:

(i) There is a natural carrying capacity for the population of $F$.

(ii) The only predator of $F$ is $S$; the only predator of $S$ is $T$.

(iii) $T$ does not have any predators.

(iv) Only a fraction of biomass lost due to predation of populations $F$ and $S$ is transferred to the populations of $S$ and $T$ respectively.

(v) $F$ grows at a relative rate, defined as $g$.

(vi) $S$ dies from natural causes, unrelated to predation by $T$, at a relative rate of $d$.

(vii) $T$ has a relative natural death rate of $q$.

Given these assumptions and variables, we use a standard damped predator prey model to describe the dynamics of the trophic levels. All units are scaled to a total carrying capacity of 1 unit for $F$. The prime notation refers to the derivative with respect to time. As these equations are standard in the literature we omit further description.

$$F' = gF(1 - F) - LFS$$

(1)
3.2. Bioaccumulation

The full bioaccumulation model is an amalgamation of the aforementioned predator-prey model and a pharmacokinetics model. We use a first order pharmacokinetics model which assumes that the organisms of population $F$ have a relative rate of uptake of methylmercury from the environment and a relative rate of elimination of methylmercury from their systems. In this section the rate of elimination is assumed to be the same across trophic levels, an assumption to be refined in Section 6.

$F$, the first trophic level, is the only population with a an uptake rate that depends only on its own biomass. The higher levels of the food chain are assumed to retain all of the toxin that is preserved in the tissues of their prey. Therefore, the bioaccumulation model in some sense parallels the predator-prey model. Thus, for populations $S$ and $T$, the relative rate of methylmercury uptake is equivalent to the relative rate of biomass uptake in the population growth model for each predator group.

The model uses the following assumptions and variables.

(i) Variables $A, B, C$ represent the absolute toxin concentrations in each trophic level $F$, $S$, and $T$, respectively.
(ii) The relative rate of uptake of toxin by $F$ is defined as variable $k$.
(iii) The relative rate of elimination is defined as $j$.
(iv) The rates of toxin uptake are proportional to the predation rates for $T$ and $S$, making them $LAS$ and $nBT$ respectively.
(v) $L$ and $n$ also describe the population lost from each trophic level by predation, and therefore serves as a second means by which methylmercury is eliminated from a trophic level.

With these assumptions the following equations describe the amount of toxin in each trophic level.

$$S' = mFS - dS - nST$$

$$T' = nST - qT$$

Rate of bioaccumulation for population $F$ = uptake due to consumption of $I$- first order pharmacokinetic elimination - loss due to predation by the next trophic level.
\[ A' = kFI - jA - LAS \]  
(4)

Rate of bioaccumulation for population \( S \)
- gain due to predation on \( A \) - first order pharmacokinetic elimination
- loss due to predation by the next trophic level

\[ B' = LAS - jB - nBT \]  
(5)

Rate of bioaccumulation for population \( T \)
- gain due to predation on \( S \) - first order pharmacokinetic elimination

\[ C' = nBT - jC \]  
(6)

Before we describe the basic results of this model it is worth mentioning
the units of measure of various quantities. Biomass of the various levels is
scaled to whatever units describe the lowest level. The carrying capacity
could represent one gram of \( F \) per liter of water, or one total unit of biomass
in the system. Which units are chosen depends on the units in which the
input, \( I \), is described. In this paper we usually use a per volume basis for
all units.

### 4. Analysis of Basic Model

Now that we have determined that our models work separately, we must put
them together in order to really understand the bioaccumulation process.
The graphs of \( A \), \( B \) and \( C \) only tell us the total amount of methylmercury
present in each trophic level. We need to find the amount of methylmercury
per unit biomass to determine whether a certain type of fish is safe to eat
with respect to methylmercury levels. In order to do this, we solve for the
equilibrium values of \( F \), \( S \), \( T \), \( A \), \( B \) and \( C \) by setting the derivative equations
equal to zero:

\[ F_{equil} = 1 - \frac{(Lq)}{(rg)} \]  
(7)

\[ S_{equil} = \frac{q}{r} \]  
(8)

\[ T_{equil} = -\frac{d}{n} + \frac{m}{n}(1 - \frac{Lq}{rg}) \]  
(9)
\[
A_{\text{equil}} = \frac{F_{\text{equil}}kI}{(LS_{\text{equil}} + j)} \tag{10}
\]
\[
B_{\text{equil}} = \frac{LA_{\text{equil}}S_{\text{equil}}}{(j + nT_{\text{equil}})} \tag{11}
\]
\[
C_{\text{equil}} = \frac{nB_{\text{equil}}T_{\text{equil}}}{j} \tag{12}
\]

The Jacobian for this system was computed. For all parameters given in subsequent parts of this paper, the eigenvalues were computed numerically in Matlab and the equilibrium values were found to be stable.

5. Results of Basic Model

Our goal is to combine these two models and apply them using literature values in order to understand the process of bioaccumulation in this ecosystem. Because of the complexity of the population model and limitations in available data, some assumptions were made in this process.

We chose three species as proxies for our three trophic levels as follows, assuming that data found on these species is applicable to the Lake Erie model:

(i) The zooplankton species *Daphnia magna* as species F
(ii) The yellow perch as species S
(iii) The large mouthed bass as species T

Research by Tsui and Wang [1] gives the rate of uptake, \(k\), and the rate of elimination, \(j\), of methylmercury by our proxy species F as \(k = 0.46\) and \(j = 0.056\) per hour which were converted to a per day basis.

We assume that the values of \(k\) and \(j\) are consistent for all species in this basic model. We will see that the model behaves reasonably. In Section 6 we refine the assumptions on excretion parameters, which depend on fish species, size, temperature of water and other factors but certainly differ greatly among trophic levels.

We define the growth rate \(g\) of population \(F\) to be 0.3% per day, based on [2]. The concentration of mercury in the Lake Erie system, \(I\) is taken to be \(1.9010^{-9}\) L/g. Sources vary for this number and we will refine it in Section 6.
As approximately 10% of the biomass lost due to predation is gained by the subsequent trophic level, we define 0.1 as the value of constants $m$ and $r$. These parameters are the most difficult to measure in the field. We will see in Section 8 that the model is sensitive to them. Unfortunately, we have only rule-of-thumb estimates to guide choice of these parameters. We define the values of $L$ and $n$, the constants representing loss in biomass due to predation, to be 0.5. This estimate was based on the assumption that roughly half of the overall mortality rate of each species was due to predation. The mortality rates for species $S$ and $T$ were estimated as well. Because the model is in terms of mortality per day, we took the constants $d$ and $q$ to be 0.035, which implies that each species loses roughly 3.5% of its population daily due to mortality outside of predation.

Initial values of $A$, $B$ and $C$ are all defined as zero, as our model assumes that the concentration of methylmercury in each trophic level is zero at time $t=0$. Determination of initial values for $F$, $S$ and $T$ was more complicated and published values were unavailable. However, literature tells us that population size per trophic levels varies such that $S$ should be roughly 15-20% as large as $F$, and that $T$ should be roughly half as large as $S$, [3]. We therefore set starting populations at $F = 0.95$, $S = 0.14$, $T = 0.075$. Units are in terms of the percent of the total carrying capacity, which is equal to 1, which could be taken as biomass total or per unit of lake volume. Numerical runs used BGODEM software (Reid, 2008), which uses a Runge-Kutta algorithm to numerical integrate systems of ordinary differential equations.

First, we consider our predator-prey model. We see in Figure 2 that our model presents a classic predator-prey relationship. On the left we see the population sizes in each trophic level will change slightly until reaching equilibrium. On the right we can see that the amount of toxin in each trophic level will peak and then reach a point of equilibrium.

Using the equilibrium calculations from Section 4 we find that:

$$F_{equil} = 0.4174$$

$$S_{equil} = 0.3496$$

$$T_{equil} = 0.1347$$

$$A_{equil} = 1.581 \times 10^{-9}$$
Figure 2. Typical output with biomass on the left and toxin on the right.

$$B_{equil} = 4.404 \times 10^{-9}$$  \hspace{1cm} (17)

$$C_{equil} = 5.304 \times 10^{-10}$$ \hspace{1cm} (18)

If the units for $F$, $S$, and $T$ are biomass per gram of carrying capacity of $F$ (either total or per unit lake volume) then the units for $A$, $B$, and $C$ are grams of toxin in respective trophic levels (either total or per unit lake volume). In order to find the concentration of methylmercury per unit biomass, we simply calculate the ratio of bioaccumulation to population size for each trophic level:

$$\frac{A_{equil}}{F_{equil}} = 3.78 \times 10^{-9}$$ \hspace{1cm} (19)

$$\frac{B_{equil}}{S_{equil}} = 1.259 \times 10^{-8}$$ \hspace{1cm} (20)

$$\frac{C_{equil}}{T_{equil}} = 3.9 \times 10^{-8}$$ \hspace{1cm} (21)

So if one unit of lake volume can support one gram of biomass of $F$ in the absence of predators, then the units of $A$, $B$, and $C$ become grams of toxin per gram of biomass in the respective trophic level. These results show that although the actual amount of methylmercury in each trophic level may be low, the ratio of methylmercury concentration to population size is relatively high. Furthermore, there is a significant increase in the
ratio as you move up the food chain; the concentration of methylmercury per unit biomass in the third trophic level is 10.3 times higher than in the first. This is significant because it demonstrates that our model actually does duplicate a system of bioaccumulation.

Equations 10, 11, and 12 show that equilibrium values for toxin levels are all constant multiples of the input level, $I$. Figure 3 illustrates how the concentration of methylmercury per unit biomass in each trophic level increases with the level of contamination of the water.

![Figure 3. Equilibrium toxin concentration rises linearly with input values, with the highest trophic level having the greatest concentration of toxin per unit biomass](image)

Note that higher predators increase toxin per unit biomass much more quickly than the lower levels, in accordance with observation.

6. Refinement of Excretion Parameters for Lake Erie

Although a great deal of ingested MeHg is retained in bodily tissues for a long period of time, organisms do have the ability to remove it from their bodies. The rate at which this occurs is dependent on numerous parameters, especially body mass. The MeHg excreted by the organisms constituting the trophic levels associated with mercury concentrations A, B, and C is reintroduced into the water of the lake. It is assumed that
all such excretions are composed entirely of MeHg. The input from this process is modeled by three different equations since each population has a unique rate of excretion.

\[
I_1 = J_1 A \tag{22}
\]

\[
I_2 = J_2 B \tag{23}
\]

\[
I_3 = J_3 C \tag{24}
\]

\(J_1, J_2, \text{ and } J_3\) are the rates of excretion \((d^{-1})\) for the populations of F, S, and T, respectively. They are multiplied by the total concentration of methylmercury per trophic level, as given by A, B, and C. When the original bioaccumulation model is adjusted for the elimination rate differences among the observed species, the overall behavior of the model is greatly affected.

Figure 4. Typical runs for the system. On the left, \(j_1 = j_2 = j_3\). On the right are the adjusted pharmacokinetic parameters as in Table 1

The graph on the left is computed as in the basic model in section 3, with each species eliminating MeHg at the same rate. The graph on the right assumes that different organisms have different such rates. It is immediately seen that the overall character of the graph is changed. C, which has the lowest levels on the left, now has the highest methylmercury concentration and takes much longer to reach a state of equilibrium. In both studies the toxin per biomass goes up with trophic levels but the effect is much more
pronounced in the refined model. Values used for the elimination rates are given in Table 1 along with sources for these.

7. Refinement of Inputs for Lake Erie

The concentration of mercury in a given lake is subject to a wide variety of processes and ecological events. In the case of Lake Erie, inflow from contributing rivers and streams increases the mercury concentration in the lake at a rate relative to the concentration in the tributaries. Mercury also enters the Lake Erie ecosystem by way of the atmosphere, primarily through wet precipitation and dry deposition. Once in the lake ecosystem, elemental mercury is methylated by bacteria, then absorbed by microorganisms such as plankton, thereby entering the food chain. Thus, this section will examine the concentration of MeHg within the Lake Erie ecosystem and use this information to improve upon the bioaccumulation model put forward in Section 3.

The processes contributing methylmercury to the Lake Erie ecosystem will first be modeled individually and then will be combined into a single differential equation governing $I$, the total concentration of MeHg in the lake. In doing so, we will be able to see how changes in individual components of the equation may influence the overall outcome of the model. Figure 5 summarizes the processes that affect the concentration of mercury in the lake, as well as the bioaccumulation of MeHg among trophic levels.

7.1. Inflow of the Detroit River

The Detroit River is the primary tributary to the lake and its contribution to the total mass of MeHg in the lake is modeled as a first-order differential equation:

$$I_4 = F_D M_D$$

(25)

Where $F_D$ is the flow rate of the river (L/day) and $M_D$ is the concentration of mercury in the river water (g/L).

7.2. Inflow of Subsidiary Tributaries

Tributaries in both the United States and Canada flow into Lake Erie. For simplicity, their input to lake mercury concentration will be analyzed collectively. The structure of the mathematical model is similar to the previous inflow.
Figure 5. Box model for sources of methyl mercury input to Lake Erie

\[
I_5 = F_T M_T
\]

Where \( F_T \) is the flow rate of the tributaries (L/day) and \( M_T \) is the mercury concentration (g/L).

### 7.3. Wet Deposition of Mercury

Mercury can enter an ecosystem through rain and snow. A model for this process is found in the literature [4].

\[
I_6 = C_w P s
\]

Here \( C_w \) is the concentration of mercury in the precipitation (g/L), \( P \) is the depth of precipitation falling on Lake Erie (m), and \( s \) is the surface area of the lake (m²).

### 7.4. Dry Deposition of Mercury

Dry deposition, especially industrial output into the atmosphere, provides another avenue of entry for mercury. The literature, [4], again provides a model.
Here, $C_p$ is the average atmospheric concentration of mercury, $V_d$ is the particle deposition velocity, $s$ is the lake surface area, and the value of .9 is meant to correct for the 10% of the time that it is raining.

### 7.5. Outflow from the Niagara River

The Niagara River is the primary route by which water leaves the Lake Erie ecosystem. It is modeled in a similar fashion as the inputs from the Detroit River and the various tributaries:

$$ I_8 = -F_N I $$

Where $F_N$ is the flow rate constant of the river as a ratio to the overall lake volume. It is essentially what percent of the lakes water leaves through the Niagara River per day and hence and thus has units of d$^{-1}$. $I$ is the concentration of MeHg in the lake (g/L).

### 7.6. Photodemethylation of MeHg

It has been shown that ultraviolet light from the sun can break down MeHg in the lake ecosystem into products that are easily evaporated from the lakes surface. For simplicity, it is assumed that products of MeHg that are evaporated by this process do not return. The model for this process is found in the literature, [5]. As indicated by the authors, UVA and UVB radiation must be considered separately.

$$ I_9 = \int_0^{3.5} .5k_{pA} H e^{xk_A} dx $$

Where $k_{pA}$ is a first-order rate constant ($m^2 E^{-1}$), $I$ is the concentration of mercury in the lake (g/L), $H$ is the average incident light strength ($E = m^{-2} s d^{-1}$), $k_A$ is the attenuation coefficient for UVA radiation in Lake Erie water ($m^{-1}$), and $x$ is the depth. The integral is calculated from 0 to 3.5 meters because at a depth of 3.5 m, the lake water has attenuated 99% of all UVA radiation.

$$ I_{10} = \int_0^1 .8k_{pB} H e^{xk_B} dx $$
All quantities are as above and any change in subscript is simply an indication that UVB radiation is now being considered. As in the previous equation, the integral is calculated from 0 to 1.8 meters because at a depth of 1.8 m, the lake water has attenuated 99% of all UVB radiation.

7.7. Values of Constants

The relevant literature provides values for the constants used in the model. These are described in Table 1 and sources are given.

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7.8. Description of the concentration model for input of methylmercury to Lake Erie

The constants allow an estimate of $I_9$ and $I_{10}$. Calculating the integral over the specified values results in the following:

$$I_9 = 0.0758 \times I$$  \hspace{1cm} (32)

$$I_{10} = 0.0228 \times I$$  \hspace{1cm} (33)

For practical purposes, we will define two new constants: $R_A = 0.0758d^{-1}$ and $R_B = 0.0228d^{-1}$. The differential equation for the concentration of MeHg in Lake Erie can now be combined. Since the input terms of the differential equation describe the mass of mercury entering the lake, the terms $I_1$ through $I_7$ must be divided by the volume, $V$, of the lake (L) in order to determine the total concentration of mercury in the lake. Additionally, since roughly 22% percent of the mercury that enters the lake by way of precipitation, inflow, and deposition is MeHg, we multiply these terms ($I_4$ through $I_7$) by $.22$. We assume that the return of toxin to the water from elimination by organisms is negligible compared to the volume of water, and ignore the contribution of those terms. Our final equation is

$$I' = .22(F_DM_D + F_TM_T + C_wPS + C_pV_dS(9)) - (F_N + R_A + R_B)I \hspace{1cm} (34)$$

The quantity $I$ reaches a stable equilibrium, $I_{equil}$, easily calculated from this equation, which will be incorporated as a constant in the basic model.

8. Analysis and Results of Enhanced Model

We can now refine the parameters of the original model.

$$F' = gF(1 - F) - LFS$$  \hspace{1cm} (35)

$$S' = mFS - dS - nST$$  \hspace{1cm} (36)

$$T' = nST - qT$$  \hspace{1cm} (37)
\[ A' = kF_{equil} - j_1 A - LAS \]  
\[ B' = LAS - j_2 B - nBT \]  
\[ C' = nBT - j_3 C \]  

With these modified equations and a constant input \( I \) calculated as the equilibrium value of equation 34, we have the following equilibrium values for our quantities.

\[ F_{equil} = 1 - \frac{(Lq)}{(rg)} \]  
\[ S_{equil} = \frac{q}{r} \]  
\[ T_{equil} = -\frac{d}{n} + \frac{m}{n}(1 - \frac{Lq}{rg}) \]  
\[ A_{equil} = \frac{F_{equil}kI_{equil}}{(LS_{equil} + j_1)} \]  
\[ B_{equil} = \frac{LA_{equil}S_{equil}}{(j_2 + nT_{equil})} \]  
\[ C_{equil} = \frac{nB_{equil}T_{equil}}{j_3} \]  

It is also worth considering the ratios of toxin concentration at succeeding levels. The ratio of the second to first levels, for example, is given by equation 47.

\[ \frac{B_{equil}}{S_{equil}} \frac{F_{equil}}{A_{equil}} = \frac{LA_{equil}}{(j_2 + nT_{equil})} \frac{(LS_{equil} + j_1)}{kI_{equil}} \]  

This ratio is roughly on the order of \( S/T \), the ratio of biomass from second to third trophic levels, no matter what the various constants are. A similar result holds for the ratio from third to second levels. Also it on the order of \( L^2 \), where \( L \) represents the predation rate, which is another measure of biomass transfer, this time from the first level to the second.
9. Sensitivity of the model to parameter values

Many of the parameters in the model are fairly rough estimates. We tested the sensitivity to model parameters by varying each parameter 20% from the default value given in Table 1. Figure 6 gives a visual key to the sensitivity of the equilibrium values of all quantities to the parameters listed. The horizontal scale is percent change from the default value, denoted by the vertical lines at 100%, 200% etc.

Figure 6. Sensitivity of equilibrium values to parameters of the model
The model was extremely sensitive to constants controlling biomass transfer, exactly those constants most difficult to measure. This suggests two things. First, the process of biomass transfer is the cause of the phenomenon of bioaccumulation. The outputs of the model were far more sensitive to these parameters than to the adjustment of elimination constants $j_1, j_2, j_3$. Bioaccumulation occurs in this model even when all are equal (as in the basic model of section 3). Second, the actual predicted values of toxin per gram cannot possibly be reliable. However we also note that experimentally determined toxin levels also show wide variability, as in [8] for example.

10. The Effect of Reducing River-born Contaminants

The model allows us to estimate changes in toxins at all trophic levels as a result of potential interventions. As an example, we can model what occurs to the observed species should the Detroit River and the lakes various smaller tributaries cease contributing to the influx of mercury. Though cleaning the river and streams of mercury would in reality be an extremely difficult task, it would nevertheless be considerably easier than stopping the atmospheric contributions to the lakes overall MeHg concentration. Additionally, doing so would allow us to gauge the relative importance of atmospheric mercury contribution against direct contribution via adjoined water ways.

If we assume no change in toxin inputs to Lake Erie, parameters in Table 1 lead to an equilibrium methylmercury concentration of $9.0210^{-11}$ g/L. Setting $I_4$ and $I_5$ equal to zero in equation 34 results in a lower equilibrium value for $I$, reducing it by about 44%. In the more toxic environment, the equilibrium value $C$ in the in a value of $1.09210^{-7}$ (g/g), whereas in the environment with reduced toxin it reaches an equilibrium of $6.2610^{-8}$ (g/g). It is easy to see that, at equilibrium, all quotients $A/F$, $B/S$, and $C/T$ are just multiples of the input $I$. Thus any percent reduction in input level will have a corresponding percent reduction in toxin concentration (grams toxin per gram biomass) at all trophic levels.

Although the system is nonlinear, this relationship is linear and independent of any parameters tested in Section 9. As a statement about proportionality, it is also independent of the constants determining $I_{equil}$. The relationship would change, however, if we took into account the return loop of toxins from the trophic levels to $I$, which we assumed was negligible.
11. Discussion

The model constructed in this paper relies on many assumptions, starting with an oversimplification of the food web into three trophic levels related by simple damped Lotka-Volterra dynamics, with elimination through first order kinetics. It uses some estimates for parameters that have been measured carefully and other estimates that are just rough guidelines. It assumes that toxins returned to water via elimination can be ignored. It assumes complete mixing of toxins entering Lake Erie via tributaries, which really should be considered point sources. In order to get actual predicted concentrations out of the model, we must assume that the average biomass of the lowest trophic level is about 1 gram per liter. In spite of all this the model yields some useful results.

11.1. Qualitative results

Standard predator prey relations coupled with first order elimination kinetics are enough to guarantee bioaccumulation will occur as the trophic level rises. Figure 3 shows this relation for one set of parameters. Equation 47 illustrates that the ratio of toxin concentrations from one level to the next rises as the transfer of biomass rises. This relationship holds for all parameters. The predator prey relations are the main “cause” of bioaccumulation in this model, in the sense that the toxin amounts are very sensitive to changes in parameters governing the predator prey relations, as seen in Figure 6.

11.2. Quantitative results

In this model, any percent reduction in ambient toxin levels in the environment \( I_{\text{equil}} \) results in an equal percent reduction in toxin concentration in all trophic levels. That is, the relationship between toxin concentration in any trophic level and toxin concentration in the surrounding water is linear, even though the underlying model is nonlinear. This relationship holds across all choices of constants and is therefore fairly reliable.

We can also use the model to predict actual toxin levels. As discussed in Section 10, the value of \( C \), the predicted amount of methylmercury in the highest trophic level, is \( 1.09210^{-7} \) (g/g). From equation 15 \( T_{\text{equil}} \) is about .135 and so the toxin concentration for that level is about \( 4.610^{-7} \) g/g or .46 mg/kg. Weis [8] estimates tissue concentrations from field data for a variety of species of fish in the Canadian Great Lakes area. The highest
estimated concentrations are for Northern pike and range between .397 and .603 mg/kg. So the toxin levels predicted by this model are actually within known ranges. Because numerical values predicted by this model are reasonably close to reality, the model also provides some weak confirmation that rough estimates of biomass transfer are likely to be close to correct.

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References