Environ. Sci. Technol. **1997**, *31*, 3267−3273

Development and Verification of a Benthic/Pelagic Food Web Bioaccumulation Model for PCB Congeners in Western Lake Erie

HEATHER A. MORRISON,*,† FRANK A. P. C. GOBAS,‡ RODICA LAZAR,† D. MICHAEL WHITTLE,§ AND G. DOUGLAS HAFFNER†

Department of Biological Sciences, University of Windsor, Windsor, Ontario, N9B 3P4 Canada, School of Natural Resource and Environmental Management, Simon Fraser University, Burnaby, British Columbia, V5A 1S6 Canada, and Ecotoxicology Division, Great Lakes Laboratory for Fisheries and Aquatic Sciences, Department of Fisheries and Oceans, 867 Lakeshore Road, Burlington, Ontario, L7R 4A6 Canada

A mathematical model is described that estimates chemical concentrations in phytoplankton, zooplankton, filter-feeding and detritovorous benthic invertebrates, and fish. Chemical concentrations are determined at steady-state using conventional chemical, biological, and environmental data. Concentration data for 31 PCB congeners in 14 different fish species, five benthic invertebrate species, water and sediment collected from western Lake Erie, and corresponding feeding preference data were used to verify the model. The results illustrate that 95% of the observed concentrations in filter-feeding benthic invertebrates, detritous feeding benthic invertebrates, and fish were within a factor of 1.8, 1.9, and 2.0 of the model-predicted concentrations, respectively. The ability of this model to predict contaminant transfer in a complex food web and its potential applicability to other food webs indicate that it could be an important tool for managing contaminants on an ecosystem level.

Introduction

Environmental managers have expressed concern about how changes in the ecosystem structure of western Lake Erie are affecting contaminant transfer through the food web. Western Lake Erie has received this attention because it supports an economically important fishery (*1*), it has been heavily impacted by invading species such as zebra mussels (*2*), and it receives a continuous influx of chemical contaminants that have impaired its use by humans and wildlife (*3*). This concern has resulted in the need to be able to predict chemical distributions in this food web and to predict how concentrations will change under different environmental and chemical conditions.

Of all the contaminants entering Lake Erie, polychlorinated biphenyl (PCB) congeners are a particular problem because they are prevalent, persistent, and proven to be harmful to humans and wildlife (*4*). The dynamics of PCBs within the aquatic environment are determined by chemical properties (e.g., hydrophobicity, persistence), biological processes (e.g., food web structure, assimilation efficiencies), and system processes (concentrations, productivity, etc.). Many of these factors vary between aquatic ecosystems; thus, the prediction of bioaccumulation in a particular organism within a given aquatic ecosystem is a difficult challenge for environmental managers.

Food web bioaccumulation models have been developed that account for many of the chemical, biological, and system processes that govern bioaccumulation (e.g., refs 5−7). Although many of these models describe the same processes and are verified for the same ecosystem (usually Lake Ontario), the models differ in the number and types of assumptions that are made and the parameters that are used to quantify chemical uptake and elimination. This study presents a benthic/pelagic food web model that quantifies bioaccumulation using familiar parameters such as chemical concentrations in water and sediment and relationships describing ingestion rates and gill ventilation rates in fish and invertebrates. The model was developed using these data because they tend to be more familiar to environmental managers and are readily available in the literature. The model is unique because it contains steady-state relationships for all biotic compartments except phytoplankton, and it does not use kinetic rate contants. Before the model can be used as a predictive tool, it is necessary to verify its performance in the ecosystem of concern. Model verification requires reliable data describing physical attributes of the environment, chemical concentrations in the food web, and food web structure. The objectives of this study are (a) to develop a user-friendly benthic/pelagic food web bioaccumulation model, (b) to report the distribution of polychlorinated biphenyls (PCBs) in the western Lake Erie food web, and (c) to use this information to verify the food web model.

Model Description

Bioconcentration in Phytoplankton. Bioaccumulation in phytoplankton is assumed to be described by equilibrium partitioning of the chemical between the phytoplankton's organic carbon (OC_{PL}) and water (*8, 9*). The organic carbon−water partition coefficient is used to describe the partitioning of chemical between phytoplankton organic carbon and water; thus, the chemical concentration in phytoplankton (C_{PL}, μg kg^{-1}) is approximately equal to the product of the chemical concentration in water (C_W, μg kg^{-1}), the mass fraction of organic carbon in phytoplankton (OC_{PL}), and the organic carbon−water partition coefficient (K_{OC}) as follows:

$$C_{PL} = C_W OC_{PL} K_{OC} \qquad (1)$$

Bioaccumulation in Zooplankton, Benthic Invertebrates, and Fish. Bioaccumulation of persistent organic chemicals in all species other than phytoplankton is described at steady-state by the same model. This model is based on the premise that predominant routes of chemical uptake are directly from water and through consumption of contaminated food. Chemical elimination includes loss to the water (via the gills), loss by fecal egestion, and loss by metabolic transformation. In addition, the decline in an organism's internal contaminant concentration as its body weight increases over time (i.e., growth dilution) is included in the model.

At steady state, chemical intake from water (U_W, μg d^{-1}) and food (U_D, μg d^{-1}) equals the sum of chemical elimination to the water (D_W, μg d^{-1}), fecal egestion (D_F, μg d^{-1}), metabolic

* Address correspondence to this author at her present address: Ecotoxicology Division, GLLFAS, DFO, 867 Lakeshore Road, P.O. Box 5050, Burlington, ON, L7R 4A6 Canada.

† University of Windsor.

‡ Simon Fraser University.

§ Great Lakes Laboratory for Fisheries and Aquatic Sciences.

S0013-936X(97)00265-4 CCC: $14.00

transformation (D_M, μg d^{-1}), and growth (D_G, μg d^{-1}). Hence

$$U_W + U_D = D_W + D_F + D_M + D_G \quad (2)$$

Uptake of Chemical via the Respiratory Surface (U_W). In aquatic biota, the uptake of chemical from water equals the product of the concentration of chemical dissolved in the water column (C_W, μg L^{-1}), the water ventilation rate across the gill surface (G_W, L d^{-1}), and the efficiency of chemical transfer (E_W):

$$U_W = C_W G_W E_W \quad (3)$$

Uptake of Chemical from Diet (U_D). Net chemical uptake from diet (U_D) can be described as the product of the concentration of chemical in the diet (C_D, μg kg^{-1}), the ingestion rate of food (G_D, kg d^{-1}), and the efficiency of chemical transfer between the gut contents and the organism (E_D):

$$U_D = C_D G_D \mathrm{E}_D \quad (4)$$

Because the diet of most organisms contains a variety of substances, the concentration of chemical in the diet is defined as

$$C_D = \sum P_i C_{D,i} \quad (5)$$

where P_i is the mass fraction of diet containing an item (i), and $C_{D,i}$ is the concentration of chemical in item (i).

For benthic filter-feeders (e.g., mussels, caddisfly larvae), the ingestion rate can be described as the product of the gill ventilation rate (G_W, L d^{-1}), the concentration of suspended solids in the water column (V_{SS}, kg L^{-1}), and the particle scavenging efficiency (σ) describing the fraction of particles that is removed from the water column by the organism and absorbed (*10*):

$$G_D = G_W V_{SS} \sigma \quad (6)$$

In the case of filter-feeders, the concentration of chemical in the diet (C_{SS}) is defined as the product of the mass fraction of diet containing an item (P_i) and the chemical concentration in item (i), i.e., $\Sigma P_i C_{SS,i}$.

Elimination via the Respiratory Surface (D_W). Elimination of chemical to the water can be described as

$$D_W = \frac{C_B G_W E_W}{\varnothing_B K_{LW}} \quad (7)$$

where C_B is the chemical concentration in biota (μg kg^{-1}), K_{LW} is the lipid−water partition coefficient (L kg^{-1}), and $\varnothing_B$ is the fraction of lipid in biota. If the lipid−water partition coefficient is assumed to be approximately equal to K_{OW}, then

$$D_W = \frac{C_B G_W E_W}{\varnothing_B K_{OW}} \quad (8)$$

Elimination of Chemical through Fecal Egestion (D_F). Elimination of chemical by aquatic biota via the feces (D_F) can be described as

$$D_F = \frac{C_B G_F E_D}{K_{BF}} \quad (9)$$

where G_F is the egestion rate (kg d^{-1}) and K_{BF} is the equilibrium biota−feces partition coefficient (kg kg^{-1}). The biota−feces partition coefficient K_{BF} reflects the natural tendency of chemicals to partition between the organism and fecal matter. For hydrophobic substances, the relative solubilities of the substance in the organism and the fecal matter are proportional to the lipid content of the organism ($\varnothing_B$) and fecal matter ($\varnothing_F$). Hence, K_{BF} can be approximated by $\delta_B\varnothing_B/\delta_F\varnothing_F$ where δ_B and δ_F are the densities of the biota and feces, respectively. The lipid or organic carbon content of the fecal matter is related to the lipid or organic carbon content of the diet of the organism since $\delta_F\varnothing_F = (1 - \alpha)\varnothing_D\delta_D$, where α is the fraction of organic carbon or lipid content of the diet (D) that is removed upon digestion. If it is assumed that $\delta_D \approx \delta_B$, then K_{BF} is $\varnothing_B/(1 - \alpha)\varnothing_D$.

Digestion results in the fecal egestion rate (G_F) being less than the dietary ingestion rate (G_D), i.e., G_F is $(1 - \beta)G_D$, where β is the fraction of ingested diet absorbed by the organism. If these substitutions are made into eq 9, chemical elimination via feces can be described as

$$D_F = \frac{C_B(1 - \beta)G_D E_D(1 - \alpha)\varnothing_D}{\varnothing_B} \quad (10)$$

Depuration via Growth (D_G). The dilution of chemical resulting from the growth of new tissue can be described as

$$D_G = C_B G_R \quad (11)$$

where G_R is the growth rate (kg d^{-1}).

Metabolism (D_M). Depuration of chemical via metabolic transformation can be described as

$$D_M = C_B V_B G_M \quad (12)$$

where G_M (d^{-1}) is the metabolic transformation rate constant and V_B (kg) is the mass of biota.

Bioaccumulation in Biota. Combining eqs 2−12 and assuming that steady-state conditions apply, the following expressions for the bioaccumulation of organic contaminants in benthic filter-feeders, benthic detritivores, zooplankton, and fish result;

filter-feeding benthic invertebrates

$$C_{Bff} = \varnothing_B K_{OW} \left[\frac{C_W E_W + C_{SS} V_{SS} E_D \sigma}{E_W + E_D(1 - \alpha)(1 - \beta)V_{SS}\sigma\varnothing_{SS}K_{OC} + V_B G_M \varnothing_B K_{OW}}\right] \quad (13)$$

benthic detritivores, zooplankton, and fish

$$C_B = \varnothing_B K_{OW}[\{C_W G_W E_W + C_D G_D E_D\}/\{E_W G_W + E_D(1 - \alpha)(1 - \beta)G_D\varnothing_D K_{OW} + \varnothing_B G_R K_{OW} + V_B G_M \varnothing_B K_{OW}\}] \quad (14)$$

Definitions and units for each of the parameters are listed in Table 1. These equations can be combined in series to simulate bioaccumulation of organic chemicals in a food web containing any number of zooplankton, benthic invertebrates, and fish species and any number of size classes within a species.

Methodology

General input parameters that were used to characterize the food web were obtained from the literature and are listed in Table 2. Table 3 lists the sample sizes and physical attributes of biota, sediment, and water collected in western Lake Erie during the summers of 1993 and 1994. A detailed description of the field sampling techniques used to collect the sediment and biota is available in Morrison (*11*). Diet compositions for the biota were obtained from the literature and from analyses of fish stomachs collected in this study. These diet compositions are listed in Table 4 and, where necessary, were categorized in terms of sediment, resuspended sediment, phytoplankton, zooplankton, and the 19 benthic invertebrate and fish species included in the western Lake Erie food web.

TABLE 1. Definition of Symbols

parameter	units	definition
C_B, C_W, C_D, C_{SS}	μg kg^{-1}	chemical concn in biota (C_B), water (C_W), diet (C_D), and suspended solids (C_{SS})
G_W	L d^{-1}	rate of water ventilation across respiratory surface
G_D	kg d^{-1}	ingestion rate of food
G_R	kg d^{-1}	growth rate
G_M	d^{-1}	metabolic rate
V_{SS}	kg L^{-1}	concn of suspended solids in water column
E_W, E_D	fraction	efficiency of chemical transfer across respiratory surface and organism (E_W) and between gut contents and organism (E_D)
σ	fraction	particle scavenging efficiency
K_{OW}, K_{OC}		chemical partition coeff between octanol and water (K_{OW}) and organic carbon and water (K_{OC}); $K_{OC} = 0.41K_{OW}$ (*25*)
V_B	kg	vol of organism
α	fraction	fraction of organic carbon or lipid in diet that is removed upon digestion
β	fraction	fraction of ingested diet absorbed by organism
δ	kg L^{-1}	density of a phase
$\varnothing$	fraction	fraction of lipid or organic carbon in a phase
ff		filter-feeder

TABLE 2. Summary of General Input Parameters That Are Used To Characterize Food Web

density of aquatic biota (δ_B)	1.0 kg L^{-1} [a]
density of plankton (δ_{PL})	1.0 kg L^{-1} [a]
density of sediment (δ_S)	1.5 kg L^{-1} [a]
Zooplankton Properties	
ingestion rate (G_D)	1.4×10^{-8} kg d^{-1} [b]
gill ventilation rate (G_W)	3.7×10^{-3} kg d^{-1} [b]
efficiency of PCB transfer via gut (E_D)	68%[c]
efficiency of PCB transfer via gills (E_W)	100%[d]
organic carbon assimilation efficiency (α)	72%[e]
Benthic Invertebrate Properties	
organic carbon assimilation efficiency (α)	70%[f]
efficiency of PCB transfer via gut (E_D)	72%[g]
efficiency of PCB transfer via gills (E_W)	75%[d]
Gammarus	
ingestion rate (G_D)	1.9×10^{-5} kg d^{-1} wwt[h]
gill ventilation rate (G_W)	0.006 L d^{-1} [i]
Hexagenia limbata	
ingestion rate (G_D)	3.4×10^{-4} kg d^{-1} wwt[j]
gill ventilation rate (G_W)	0.016 L d^{-1} [k]
Orconectes propinquus	
ingestion rate (G_D)	0.0009 kg d^{-1} [l]
gill ventilation rate (G_W)	16 L d^{-1} [th]
Zebra Mussels and Caddisfly Larvae	
scavenging efficiency (σ)	100%[m]
Fish	
efficiency of PCB transfer via gills (E_W)	0.75[n]
efficiency of PCB transfer via gut (E_D)	0.75[o]
dietary lipid assimilation efficiency (α)	0.83[p]
ingestion rate (G_D)	($0.022\ M^{0.85} \exp 0.067$) kg d^{-1}, M = kg wwt[q]
efficiency of oxygen uptake (e_{ox})	0.45
O_2 consumption	$\log O_{2\ \mathrm{consumption}} = -0.76 + 0.877 \log M$ mg h^{-1}, M = g wwt[r]
gill ventilation rate (G_W)	($O_{2\ \mathrm{consumption}}/[O_2]e_{ox}$) 24 L d^{-1}
growth rate (G_R)	($0.0005\ M^{0.8}$) kg d^{-1}, M = kg wwt[s]

[a] From ref 26. [b] Estimated from ref 27. [c] Average of refs 28 and 29 for *p,p′*-DDT. [d] Estimated. [e] From ref 30. [f] From ref 31. [g] Average of estimates from refs 32−37. [h] From ref 38. [i] Estimated from *G. pulex*, ref 39. [j] From ref 40. [k] From ref 41. [l] From ref 42. [m] From refs 43 and 44. [n] From ref 45. [o] From ref 46. [p] From ref 47. [q] From ref 48. [r] From ref 49. [s] From ref 5.

Table 5 lists the parameters used to characterize the environment of western Lake Erie.

Water Analysis. Staff of Environment Canada collected three 50.5-L water samples offshore of Middle Sister Island in western Lake Erie and extracted these samples with a Goulden large-volume extractor according to the methods of L'Italien and Fay (*12*). Prior to extraction, water was passed through a Westfalia separator at a continuous flow rate of 4 L/min to remove particulates. This process is capable of removing particles greater than 0.2 μm from the water column (*13*). Dissolved organic carbon is considered to be comprised of particles smaller than 0.45 μm diameter. Because the centrifuging method only removed particles greater than 0.2 μm, it was assumed that approximately half of the dissolved organic carbon (DOC) remained in the water sample after centrifuging. Consequently, to estimate freely dissolved water concentrations, the measured water concentration (C_M) was divided by half the measured DOC concentration (i.e., 0.5DOC) in western Lake Erie and the organic carbon−water partition coefficient (K_{OC}) as follows:

$$C_W = \frac{C_M}{1 + 0.5\mathrm{DOC} \times K_{OC}} \qquad (15)$$

TABLE 3. Sample Sizes and Physical Attributes of Biota, Sediment, and Water Collected in Western Lake Erie during Summers of 1993 and 1994[a]

sample	*n*	mean no. ind./no.	portion	*M* (g, wwt)	SD	% lipid	SD	% lipid whole fish[a]
sediment	12					7.1 (% oc)	1.61	
water	3							
zooplankton	10		whole	11.4 (g dwt)		1.0	0.33	
zebra mussels	20	45	whole	0.011 (dwt)[b]		1.3	0.34	
mayfly larvae	3	25	whole	0.004 (dwt)[c]		2.0	0.25	
caddisfly larvae	1	40	whole	0.008 (dwt)[d]		1.7		
Gammarus	7	80	whole	0.001 (dwt)[e]		2.1	1.04	
crayfish	11	1	whole	1.8[f]		1.9	0.47	
YOY fish	6	13.8	whole	0.4	0.01	2.1	0.10	
emerald shiner	6	2.7	whole	2.5		4.7	1.07	
alewife	3	54	whole	116.0	0.50	7.4	0.43	
trout−perch	6	1	muscle	6.8	2.39	2.9	1.57	10.0
small white sucker	5	1	muscle	29.0	23.30	1.5	1.00	5.0
black crappie	6	1	muscle	69.6	53.03	0.8	0.42	6.0
white perch	6	1	muscle	50.0	28.78	4.7	3.08	8.0
yellow perch	6	1	muscle	36.1	31.16	2.2	1.79	8.0
adult white sucker	5	1	muscle	870.0	243.93	1.2	0.80	8.0
fresh water drum	16	1	muscle	546.5	145.72	1.3	1.61	8.0
gizzard shad	5	1	muscle	585.0	169.75	5.0	4.84	10.0
small mouth bass	12	1	muscle	714.6	216.23	1.1	0.85	12.0
large mouth bass	2	1	muscle	536.0	51.48	3.1	1.20	12.0
walleye	6	1	muscle	1333.0	710.19	0.2	0.01	16.0

[a] wwt, wet weight; dwt, dry weight; SD, standard deviation; *M*, mass. [b] Used shell length−dry weight relationships of Kryger and Riisgard (*50*). [c] Estimated from ref 40. [d] Estimated from ref 51. [e] Used length−weight regressions for *G. fossarum* (*52*). [f] Estimated from carapace length−wet weight relationships (53). [g] Estimated.

TABLE 4. Diet Compositions (% vol) for Western Lake Erie biota[a]

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	ref
zooplankton		100													
zebra mussels	30	40	30												*b*
caddisfly larvae	30	40	30												*b*
Hexagenia	100														
Gammarus	30	30	40												*c*
crayfish	18	25		45	2			10							*d*
YOY fish			100												*e*
emerald shiner			93			1	2	4							*f*
alewife			95		1	1	3								*g*
trout−perch			70		15	5	10								*g*
small white sucker	10		40	15	5	15	15								*h*
black crappie			75				25								*h*
white perch			64	2	3		18		13						*i*
yellow perch			55	35	1		4		5						*i*
adult white sucker	5		50	15	10	5	15								*h*
freshwater drum	5		5	35		9	16		25	5					*k*
gizzard shad	10		50	5		15	20								*l*
small mouth bass			15						55	15	15				*j*
large mouth bass			10					30	45	5	5	5			*m*
walleye		10							60	10	20				*n*

[a] A, sediment/detritus; B, phytoplankton; C, zooplankton; D, zebra mussels; E, caddisfly larvae; F, *Hexagenia limbata*; G, *Gammarus*; H, crayfish; I, YOY fish; J, emerald shiner; K, alewife; L, trout−perch; M, smelt; N, small white sucker. [b] Sediment used as a surrogate for resuspended sediment. [c] Plankton used as a surrogate for zebra mussel pseudofaeces. [d] Estimates from refs 53, 54, and 42. [e] Estimated from ref 55. [f] Estimated from refs 56 and 57. [g] Estimated from ref 56. [h] Personal observation. [i] Estimated from ref 58. [j] Estimated from ref 59. [k] Estimated from ref 60. [l] Estimated from refs 61 and 56. [m] Estimated. [n] Estimated from ref 58.

TABLE 5. Parameters Used to Characterize Western Basin of Lake Erie

mean annual water temp	13 °C
O_2 concn ([O_2])	7.9 mg L^{-1} [a]
particulate organic carbon (POC)	0.54 mg of C L^{-1} [b]
dissolved organic carbon (DOC)	2.2 mg of C L^{-1} [b]
concn of suspended solids (V_{SS})	4.0×10^{-5} L L^{-1} [c]

[a] Assuming that water is 75% saturated (*62*). [b] From ref 63. [c] POC converted to volume of plankton according to ref 64.

Chemical Analysis. With the exception of alewife and plankton, extraction and cleanup of tissue, sediment, and water samples were done by the Great Lakes Institute for Environmental Research (GLIER) according to the methods described in Lazar et al. (*14*). The following PCB congeners listed by IUPAC Number were quantified using gas chromatography/electron capture detection (GC/ECD): 28/31, 52, 49, 44, 42, 64, 74, 70, 66/95, 60, 101, 99, 97, 87, 110, 151, 149, 118, 146, 153, 105, 138, 129, 182/187, 183, 174, 171, 170/190, 203, 195, and 206. The detection level was 0.05 μg kg^{-1}, and recoveries were greater than 90%. The lipid content was determined on subsamples of the extracts and measured gravimetrically using one-tenth of the extract. The lipid content was reported as a percent of organism wet weight. The organic carbon content of plankton and sediment was estimated by loss on ignition according to the methods of Hakanson and Jansson (*15*) and Standard Methods for the Examination of Water and Wastewater (*16*), respectively.

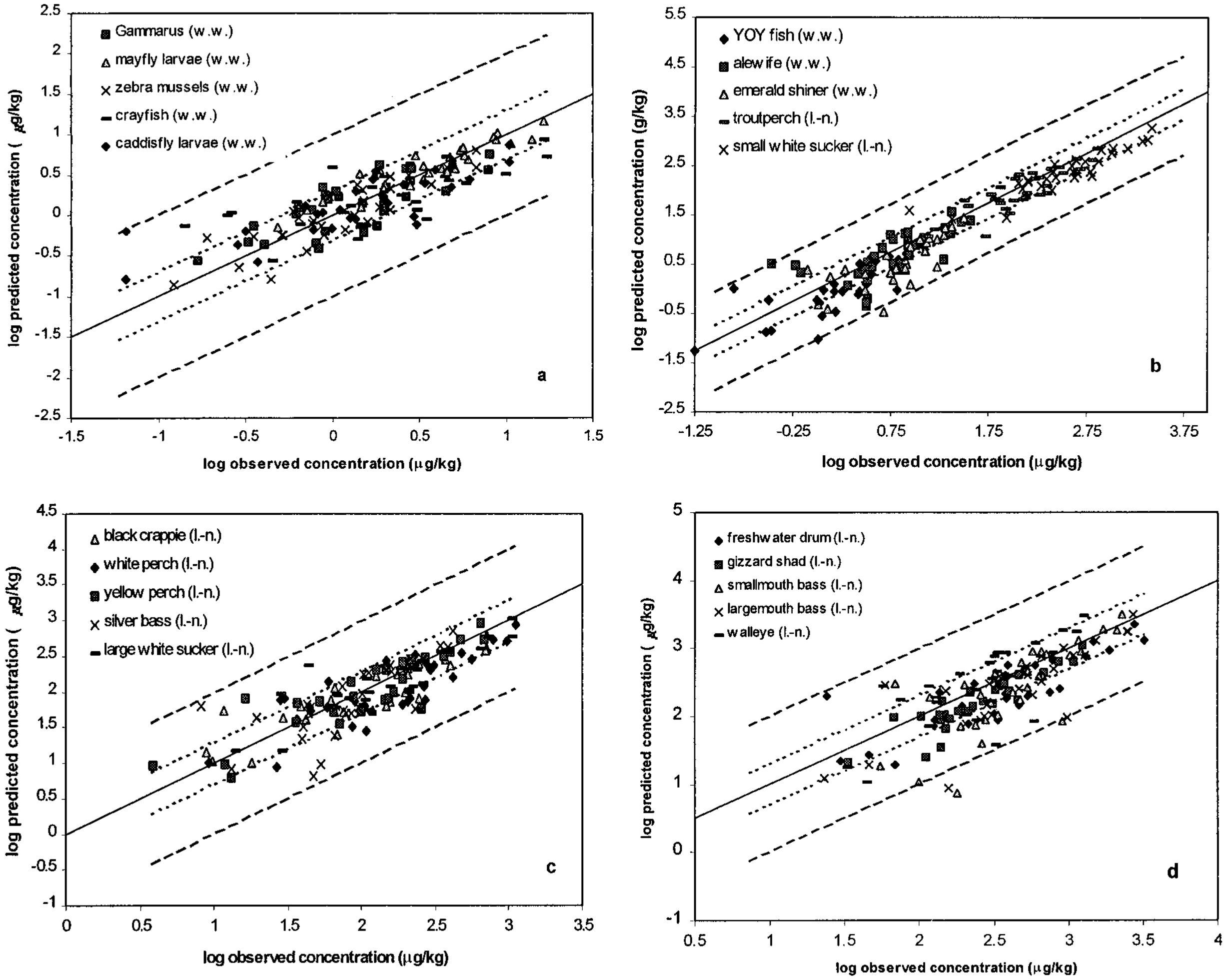

FIGURE 1. Logarithmic plot of predicted versus observed concentrations of 31 PCB congeners in western Lake Erie biota. The solid line represents ideal fit. The dotted line represents 2× the ideal fit, and the dashed line represents 10× the ideal fit. w.w. is wet weight concentration. l.n. is lipid-normalized concentration.

Alewife samples were analyzed for PCB congeners by the Department of Fisheries and Oceans, Great Lakes Laboratory for Fisheries and Aquatic Sciences (GLLFAS). An interlaboratory comparison of PCB congener recoveries determined that there was no significant difference between the results of the GLIER laboratory and the GLLFAS laboratory for the congeners listed in this study (*17*). Preparation and cleanup of samples followed the methods described in Huestis et al. (*18*). Individual PCB congeners were quantified using high-resolution gas chromatography/mass spectometry (GC/HRMS). The dectection limit ranged from 5 to 10 pg g^{-1}, and recoveries were greater than 85%. Lipid was determined gravimetrically on whole sample extracts. Data generated from these analyses are available in tabular form in Morrison (*11*). Water and sediment PCB congener concentrations are available in Morrison et al. (*10*). Octanol–water partition coefficients (K_{OW}) were from Shiu and Mackay (*19*) except for congeners 110, 182/187, 180, and 170/190, which are from Hawker and Connell (*20*).

Assumptions Unique to This Model Validation. Metabolic transformation of the PCB congeners measured in this study was considered to be negligible. Invertebrates and fish have limited metabolic capabilities to biotransform xenobiotics (*21*). When metabolism has been observed in both fish and invertebrates, it has been restricted to the lower chlorinated PCB congeners (*21, 22*). Growth dilution was not considered for zooplankton and benthic invertebrates to simplify the submodels for these organisms.

Results and Discussion

Figure 1a–d illustrates the predicted versus observed concentrations of 31 PCB congeners in benthic invertebrates and fish from western Lake Erie. Overall, predicted PCB congener concentrations in the benthic invertebrates, adult white sucker, silver bass, yellow perch, and walleye were in good agreement with observed concentrations as evidenced by mean predicted versus observed ratios close to 1 (range 0.89–1.11). The model tended to underestimate PCB congener concentrations in other biota, although the majority of model predictions were within a factor of 2 (Figure 1a–d).

Predictions of the zooplankton submodel could not be validated against field data because PCB congener concentrations in zooplankton from western Lake Erie were not available. In order to ensure that model-predicted bioaccumulation in zooplankton was reasonable, PCB congener concentrations were expressed as the logarithms of lipid-normalized bioaccumulation factors (log BAFs) so that they could be compared to field-measured values found in the literature. Field-measured log BAFs for phytoplankton range from 4.8 to 7.8 (*23*) and from 5.0 to 8.0 (*24*). The log BAFs predicted in this study ranged from 5.6 to 8.5 and are higher than the values measured in phytoplankton and above those predicted from equilibrium partitioning of chemical between the zooplankton's lipid and water (5.6–7.4). These predictions seem reasonable because this model assumes that zooplankton biomagnify PCB congeners that they aquire while consuming phytoplankton.

TABLE 6. Relative Contribution of Chemical Uptake from Water and Diet (Expressed as % of Total Uptake) and Chemical Elimination via Gills, Feces, and Growth (Expressed as % of Total Elimination) at Steady State for PCB 42 (log K_{OW} = 5.6) and PCB 153 (log K_{OW} = 6.9) in Aquatic Biota from western Lake Erie

species	PCB 42					PCB 153				
	U_W	U_D	D_W	D_F	D_G	U_W	U_D	D_W	D_F	D_G
Gammarus	0.3	99.7	6.6	93.4		<0.1	>99.9	0.4	99.6	
zebra mussels	16.2	83.8	89.6	10.4		1.2	98.8	30.1	69.9	
zooplankton	86.2	13.8	95.7	4.3		23.9	76.1	52.8	47.2	
walleye	20.1	79.9	85.0	9.7	5.3	0.1	99.9	22.1	50.4	27.5

Overall, the quality of model predictions was evaluated using the 95% probability intervals of the distribution of the ratios of predicted to observed concentrations for each congener measured in each species (C_{pred}/C_{obs}). The geometric means of C_{pred}/C_{obs} for filter-feeding benthic invertebrates, detritivorous benthic invertebrates, and fish were 1.0, 1.0, and 0.8, respectively. These results indicate that overall the model accurately predicted congener concentrations in filter-feeding and detritous feeding benthic invertebrates but tended to underestimate concentrations in fish. The 95% probability intervals reflect the extent of deviation from perfect agreement. For filter-feeders, detritivores, and fish, the 95% probability intervals were 1.8, 1.9, and 2.0, respectively.

Table 6 compares the relative importance of gills, diet, feces and, growth in the exchange of a representative high K_{OW} (PCB 153) and low K_{OW} (PCB 42) congener between western Lake Erie biota and their environment. All aquatic biota exhibited an increase in the relative importance of chemical uptake via diet and elimination via feces as the K_{OW} of the congener increased. Over 99% of PCB 153 accumulated by walleye was through the consumption of contaminated food whereas 79.9% of PCB 42 was accumulated from food. Gills were the predominant route of chemical elimination in zebra mussels, zooplankton, and walleye for the lower K_{OW} PCB. For the high K_{OW} congener, feces were the predominant route of chemical elimination. For detritovorous benthic invertebrates, feces represented the primary route of chemical elimination for all PCBs. The ratio of gill ventilation rate to ingestion rate is much higher for fish (mean, 9700; SD, 600; n, 14) than for these benthic invertebrates (mean, 6000; SD, 10000; n, 3). Consequently, diet and feces are relatively more important than gills as routes of chemical exchange in these species compared to fish.

A sensitivity analysis was performed on the model to identify the most important model inputs affecting the concentration of a representative low and high K_{OW} PCB congener in zooplankton and a representive filter-feeder, detritivore, and fish species (Table 7). In separate simulations, the value of each parameter was lowered 10%, and the effect of this change on model output was evaluated. The representative fish species (walleye) and zooplankton showed a greater sensitivity to changes in model input parameters as the K_{OW} of the congener increased whereas benthic invertebrates exhibited no consistent response in model input sensitivity with increasing K_{OW}. For the representative benthic invertebrate and fish species, the chemical concentration in the diet was the most sensitive parameter for both the lower and higher K_{OW} congener. Consequently, changes in the diets of these organisms are likely to have a profound impact on bioaccumulation.

For zooplankton, the concentration of chemical in water was most sensitive and was equally sensitive for the two PCB congeners. Zooplankton feed by filtering phytoplankton out of the water column. While feeding, zooplankton are consuming chemical from both water and phytoplankton. Because phytoplankton are assumed to be in chemical equilibrium with water, changes in C_W will cause direct and proportional changes in the chemical concentration in phytoplankton. Hence, chemical concentrations in zooplankton are directly affected by changes in C_W.

TABLE 7. Change in Model Output (%) due to a 10% Decrease in Input Parameter Values for a Filter-Feeder (Zebra Mussels), a Detritovore (*Gammarus*), Zooplankton, and, a Fish (Walleye)[a]

	zebra mussels		*Gammarus*		zooplankton		Walleye	
	42[b]	153[b]	42	153	42	153	42	153
C_W	−3.7	−3.1	−2.3	−3.6	−10.0	−10.0	−7.5	−7.8
E_W	7.2	2.7	1.0	0.9	1.5	7.9	7.2	9.8
G_W			1.0	0.9	1.5	7.9	7.2	9.8
C_D	−7.9	−10.2	−10.0	−10.7	−1.4	−7.6	−7.6	−15.5
E_D	−6.7	−2.8	−1.0	−0.8	−1.4	−7.2	−7.2	−14.3
G_D			−1.0	−0.8	−1.4	−7.2	−7.2	−14.3
G_R							0.8	6.2
α	1.3	8.2	9.9	11.1	0.0	0.4	0.5	1.4
β			2.0	4.1	0.0	0.2	0.1	0.9
V_{SS}	−6.7	−2.5						

[a] A sensitivity value of less than 0.05 was reported as zero. [b] PCB number.

Discrepencies between model predicted and observed congener concentrations may be due to a number of factors, but sensitivity analyses performed on the model indicated that changes in input parameters describing chemical accumulation from food (C_D) and water (C_W) had the greatest effect on model outputs. Consequently, it is most likely that the assigned diets and measured water concentrations used as model input parameters represented only approximately the average conditions experienced by all biota captured in this field study.

In conclusion, a mathematical model has been described that estimates chemical concentrations in phytoplankton, zooplankton, filter-feeding and detritovorous benthic invertebrates, and fish at steady state. Model predictions were compared to field-measured concentrations of 31 PCB congeners in western Lake Erie biota. Overall, the predictive capability of the model was good. The ability of this model to accurately predict contaminant transfer in a complex food web indicates that it could be an important tool for predicting the effects ecosystem changes on contaminant concentrations in a wide variety of aquatic species including top predators. Other uses for this model are developing remediation targets, evaluating contaminant-based remediation strategies, and performing biological risk assessments. Although this study has validated the model for PCB congeners in the western basin of Lake Erie, the model is generic and requires only basic data to parameterize it for other organic chemicals and food webs.

Acknowledgments

We thank Katy Haralampides, Geoff Riddle, and the staff of the analytical laboratory of the Great Lakes Institute for Environmental Research, University of Windsor, for their help. We are grateful for the financial support provided by an NSERC-Environment Canada (GLURF) grant to G.D.H. and

F.A.P.C.G. and by the Department of Fisheries and Oceans, Green Plan Toxic Chemical Program to D.M.W.

Literature Cited

(1) *Annual Summary of Commecial Freshwater Fish Harvesting Activities 1992*; DFO, Central and Arctic Region Freshwater Fisheries: Winnipeg, Manitoba, February 1994.
(2) MacIsaac, H. J.; Sprules, W. G.; Johannsson, O. E.; Leach, J. H. *Oecologia* **1992**, *92*, 30−39.
(3) Hartig, J. H.; Thomas, R. L. *Environ. Manage.* **1988**, *12*, 327−347.
(4) Metcalfe, C. D.; Haffner, G. D. *Environ. Rev.* **1995**, *3*, 171−190.
(5) Thomann, R. V.; Connolly, J. P.; Parkerton, T. F. *Environ. Toxicol. Chem.* **1992**, *11*, 615−629.
(6) Gobas, F. A. P. C. *Ecol. Modell.* **1993**, *69*, 1−17.
(7) Campfens, J.; Mackay, D. *Environ. Sci. Technol.* **1997**, *31*, 577−583.
(8) Geyer, H.; Politzki, G.; Freitag, D. *Chemosphere* **1984**, *13*, 269−284.
(9) Mallhot, H. *Environ. Sci. Technol.* **1987**, *21*, 1009−1013.
(10) Morrison, H. A.; Gobas, F. A. P. C.; Lazar, R.; Haffner, G. D. *Environ. Sci. Technol.* **1996**, *30*, 3377−3384.
(11) Morrison, H. A. Ph.D. Dissertation, University of Windsor, Windsor, ON, 1996.
(12) L'Italien, S.; Fay, L. A. *Great Lakes Surveillance Program Field Methods Manual*; WQB/IWD-OR-93-01/I; Water Quality Branch Inland Waters Directorate, Environment Canada: Burlington, ON, 1993.
(13) Allan, R. J. *Sediment-Related Fluvial Transmission of Contaminants Some Advances by 1979*; Scientific Series 107; Inland Waters Directorate Western and Northern Region: Regina, Saskatchewan, 1979.
(14) Lazar, R.; Edwards, R. C.; Metcalfe, C. D.; Metcalfe, T.; Gobas, F. A. P. C.; Haffner, G. D. *Chemosphere* **1992**, *25*, 493−504.
(15) Hakanson, L.; Jansson, M. In *Principles of Lake Sedimentology*; Springer-Verlag: Berlin and Heidelberg, 1983; 316 pp.
(16) *Standard Methods for the Examination of Water and Wastewater*, 16th ed.; APHA, AWWA, and WPCF: Washington, DC, 1985.
(17) Huestis, S. Y. Personal communication, Ecotoxicology Division, Great Lakes Laboratory for Fisheries and Aquatic Sciences.
(18) Huestis, S. Y.; Servos, M. R.; Sergeant, D. B.; Leggett, M.; Dixon, D. G. *Can. Tech. Rep. Fish. Aquat. Sci.* **1995**, *2044*, 30 pp.
(19) Shiu, W. Y.; Mackay, D. *J. Phys. Chem. Ref. Data* **1986**, *15*, 911.
(20) Hawker, D. W.; Connell, D. W. *Environ. Sci. Technol.* **1988**, *22*, 382.
(21) James, M. O. In *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*; Varanasi, U., Ed.; CRC Press Inc.: Boca Raton, FL, 1989; pp 69−91.
(22) Sanborn, J. R.; Childers, W. F.; Metcalfe, R. L. *Bull. Environ. Contam. Toxicol.* **1975**, *13*, 209−217.
(23) Swackhamer, D. L.; Skoglund, R. S. *Environ. Toxicol. Chem.* **1993**, *12*, 831−838.
(24) Thomann, R. V. *Environ. Sci. Technol.* **1989**, *23*, 699−707.
(25) Karickhoff, S. W. *Chemosphere* **1981**, *10*, 833.
(26) Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals*; Lewis Publishers: Ann Arbor, MI, 1992; Vol. 1, p 16.
(27) Peters, R. H.; Downing, J. A. *Limnol. Oceanogr.* **1984**, *29*, 763−784.
(28) Cox, J. L. *Fish. Bull.* (*U.S.*) **1971**, *69*, 443.
(29) Harding, G. C.; Vass, W. P.; Drinkwater, K. F. *Can. J. Fish. Aquat. Sci.* **1981**, *38*, 101−109.
(30) Conover, R. J. *Limnol. Oceanogr.* **1966**, *11*, 346−354.
(31) Lehman, J. T. *Limnol. Oceanogr.* **1993**, *38*, 1550−1554.
(32) Goerke, H.; Ernst, W. *Chemosphere* **1977**, *9*, 551.
(33) Klump, J. V.; Krezoski, J. R.; Smith, M. E.; Kaster, J. L. *Can. J. Fish. Aquat. Sci.* **1987**, *44*, 1574−1583.
(34) Landrum, P. F.; Poore, R. *J. Great Lakes Res.* **1988**, *14*, 427−437.
(35) Jahan-Parwar, B.; Wood, L. W.; Bush, B. *Arch. Environ. Contam. Toxicol.* **1990**, *19*, 944−951.
(36) Klump, J. V.; Kaster, J. L.; Sierszen, M. E. *Can. J. Fish. Aquat. Sci.* **1991**, *48*, 284−289.
(37) Bruner, K. A.; Fisher, S. W.; Landrum, P. F. *J. Great Lakes Res.* **1994**, *20*, 735−750.
(38) Morrison, H. A. Canadian Data Report of Fisheries and Aquatic Sciences 955; Great Lakes Laboratory for Fisheries and Aquatic Sciences: Burlington, ON, 1995.
(39) Rumpus, A. E.; Kennedy, C. R. *Parasitology* **1974**, *68*, 271−284.
(40) Dermott, R. *Hydrobiologia* **1981**, *83*, 499−503.
(41) Stehly, G. R.; Landrum, P. F.; Henry, M. G.; Klemm, C. *Environ. Toxicol. Chem.* **1990**, *9*, 167−174.
(42) Martin, G. W.; Corkum, L. D. *Can. J. Zool.* **1995**, *72*, 1867−1871.
(43) Reeders, H. H.; Bij de Vaate, A.; Slim, F. J. *Freshwater Biol.* **1989**, *22*, 133−141.
(44) Ten Winkel, E. H.; Davids, C. *Freshwater Biol.* **1982**, *12*, 553−558.
(45) Norstrom, R. J.; McKinnon, A. E.; deFreitas, S. W. *J. Fish. Res. Board Can.* **1976**, *33*, 248−267.
(46) Niimi, A. J.; Oliver, B. G. *Can. J. Fish. Aquat. Sci.* **1988**, *45*, 222−227.
(47) Place, A. R. *Am. J. Physiol.* **1992**, *263*, R464−R471.
(48) Weininger, D. Ph.D. Thesis, University of Wisconsin, Madison, WI, 1978.
(49) Thurston, R. V.; Gehrke, P. C. In *Fish Physiology, Toxicology, and Water Quality Management*; Proceedings of an International Symposium, Sacramento, California, Sep. 18−20, 1990; Russo, R. C., Thurston. R. V., Eds.; Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency: Athens, GA, 1993; EP/600/R-93/157; p 95.
(50) Kryger, J.; Riisgard, H. U. *Oecologia* **1988**, *77*, 34−38.
(51) Fox, H. M.; Wingfield, C. A.; Simmonds, B. G. *J. Exp. Biol.* **1937**, *14*, 210−218.
(52) Franke, J. *Arch. Hydrobiol.* **1977**, *48*, 369−411.
(53) Saffran, K. A. M.Sc. Thesis, University of Waterloo, Waterloo, ON, 1993, 102 pp.
(54) MacIsaac, H. J. *J. North Am. Benthol. Soc.* **1994**, *13*, 206−216.
(55) Wu, L.; Culver, D. A. *Can. J. Fish. Aquat. Sci.* **1992**, *49*, 1932−1937.
(56) Muth, K. M.; Busch, W-D. N. *J. Great Lakes Res.* **1989**, *15*, 217−222.
(57) Hartman, K. J.; Vondracek, B.; Parrish, D. L.; Muth, K. M. *J. Great Lakes Res.* **1992**, *18*, 43−50.
(58) Witzel, L.; Bur, M.; Czapla, T.; Einhouse, D.; Haas, B.; Murray, C.; Muth, K.; Nepzy, S.; Sztramko, L.; Thomas, M.; Tyson, J. Report of the Forage Task Group; Report to the Lake Erie Committee and the Great Lakes Fishery Commission; 1995; 38 pp.
(59) Cook, A.; Tulen, L. *Lake Erie Food Web Study 1995: Diet analysis of major predators of Lake Erie*; A program conducted in partnership with Environment Canada, Lake Erie Fish Packers and Processors Association and the Ontario Ministry of Natural Resources; 1995.
(60) French, J. P. R., III; Bur, M. T. In *Zebra mussels: Biology, impacts, and control*; Nalepa, T., Schloesser, D., Eds.; Lewis Publishers: Boca Raton, FL, 1993; pp 453−463.
(61) Bodola, A. *Fish. Bull.* **1966**, *65*, 391−425.
(62) Benson, B. B.; Krause, D., Jr. *Oceanography* **1980**, *25*, 662−671.
(63) Environment Canada STAR Database. Environmental Conservation Branch, Ecosystem Health Division, Canada Centre for Inland Waters, P.O. Box 5050, Burlington, ON, L7R 4A6.
(64) Strathmann, R. R. *Oceanography* **1967**, *12*, 411−418.

Received for review March 24, 1997. Revised manuscript received July 10, 1997. Accepted July 29, 1997.[⊗]

ES970265M

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1997.