Time Response of the Lake Ontario Ecosystem to Virtual Elimination of PCBs

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This study presents the development, application, and partial validation of an integrated time-dependent whole ecosystem environmental fate and food-chain bioaccumulation model of the time response of PCB concentrations in various media and organisms of Lake Ontario to changes in external PCB loadings to the lake. The model and observed PCB concentration time trends in herring gull eggs, lake trout, sculpins, smelt, water, and sediment data are used to reconstruct the time response and PCB loading history for Lake Ontario and to assess the past and future time response of PCB concentrations in the Lake Ontario food web to PCB inputs. Estimates of loadings, concentrations, half-lifetimes, and changes in PCB composition over time are discussed.

Introduction

During the last 20 years, a considerable amount of effort and resources have been allocated to monitor the elimination of PCB emissions into Lake Ontario. However, there is still uncertainty regarding the extent of the reductions in PCB loadings to the lake that have actually been achieved and, hence, the success of the "virtual elimination" initiative of the 1978 U.S.–Canada Water Quality Agreement. For example, from 1978 to 1992, PCB concentrations in herring gull eggs dropped by approximately 5-fold (1), whereas over the same time period, PCB concentrations in 4-year-old lake trout dropped by only 2-fold (2), and PCB concentrations in smelt and slimy sculpins showed no statistically significant decline (3). In addition, it has been suggested that reductions in PCB loadings may have slowed down or come to a complete halt (4, 5). A possible explanation for these observations is that biological species respond to changes in PCB loadings at different or "species-specific" rates, causing PCB concentrations in certain species to fall over the same time period by a greater amount than those in other organisms. There may also be lag times between the times of loading and concentration reductions, and the rate of concentration decline as well as the composition of PCB mixtures may not be constant over time. If some of

these explanations are correct, then knowledge of the time response of PCB concentrations in various organisms and media of Lake Ontario to changes in total PCB loadings is important for (i) the interpretation of biomonitoring time-trend data in terms of changes in loadings that have occurred, (ii) the prediction of the past and future response of PCB concentrations to PCB loadings, and (iii) the design of monitoring programs that are most effective in detecting reductions or increases in PCB loadings. It is the purpose of this study to explore the fundamental mechanisms underlying the time-dependent relationship between PCB loadings and concentrations in various organisms and media in Lake Ontario. Our methodology is based on the development and partial validation of a time-dependent whole Lake ecosystem simulation model of the transport and food-chain bioaccumulation of PCBs. Since there are no reliable PCB loading data for Lake Ontario to evaluate the success of PCB loading reductions and to construct empirical time-dependent relationships between loadings and concentrations, modeling studies have been used before to characterize the response of Lake Ontario to PCB loadings. Most notably is the modeling work by Mackay (6), Mackay et al. (7). and Endicott et al. (8), who combined steady-state and pseudo-steady-state environmental fate and a food-chain model to relate inputs of PCBs to concentrations in Lake Ontario water, sediments, and biota. Although these and other modelling studies have advanced the understanding of chemical dynamics in aquatic eco-system considerably and form much of the basis of this study, certain limitations for describing the time response of PCB concentration in Lake Ontario have remained. For example, the existing whole-lake models assume equilibrium, steady-state, or pseudo-steady-state conditions and are not truly temporally dynamic. Also, some models ignore the effect of changes in the composition of PCB mixtures, and existing models have been sparingly tested and calibrated against observed time-trend data.

This study attempts to address these limitations by developing a truly time-dependent "ecosystem" model, combining an environmental fate and food-chain bioaccumulation model to predict concentrations of PCB homologs and total PCBs in water, sediments, phyto- and zooplankton, four fish species, and herring gulls from chemical inputs over time and visa versa to interpret time trends of contaminant concentrations in Lake Ontario in terms of changes in contaminant inputs over time. The model is applied to PCBs in Lake Ontario, but when parameterized accordingly, it may be applicable to other organic chemicals and possibly to other lake ecosystems.

Lake Ontario Ecosystem Model

The Lake Ontario ecosystem model is a combination of (i) a time-dependent environmental fate model, which relates total external PCB loadings, including inputs from the atmosphere and river discharges but excluding internal PCB recycling between the water and the sediments, which is addressed within the model, to concentrations in water and sediments and (ii) a food-chain bioaccumulation model, which relates concentrations in water and sediments to those in various organisms over time.

Environmental Fate Model. The environmental fate model for Lake Ontario used in this study is a modification

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TABLE 1

Mass Balance Equations and Methods for Assessment of Rate Constants Used in Environmental Fate Model

Mass Balance Equations and Concentrations

total mass of PCB in water M_W (g)	$dM_W/dt = L + k_{SW}M_S - (k_V + k_O + k_{WR} + k_{WS})M_W$
total mass of PCB in sediments M_S (g)	$dM_S/dt = k_{WS}M_W - (k_{SW} + k_B + k_{SR})M_S$
concentration of PCB in water (g/L)	$C_W = X_W/V_W$
concentration of PCB in sediments (g/kg dry)	$C_S = X_S/(V_S C_{SS})$
freely dissolved concentration of PCB in water (g/L)	$C_{WD} = \phi_{DW}C_W$
sediment solids mass balance & resuspension flux (kg/d)	ResFlux = SetFlux − BurFlux

Rate Constants

outflow (d^{-1})	$k_O = F/(1000 V_W)$
volatilization (d^{-1})	$k_V = S_{AW}\phi_{DW}v_E/V_W$
overall water-to-sediment transport (d^{-1})	$k_{WS} = k_{WS1} + k_{WS2}$
overall sediment-to-water transport (d^{-1})	$k_{SW} = k_{SW1} + k_{SW2}$
solids settling (d^{-1})	$k_{WS1} = S_{AW}v_S(1 - \phi_{DW})/V_W$
water-to-sediment diffusion (d^{-1})	$k_{WS2} = S_{AS}v_D\phi_{DW}/V_W$
solids resuspension (d^{-1})	$k_{SW1} = (\text{ResFlux}/C_{SS})(1 - \phi_{DS})/(1000 V_S)$
sediment-to-water diffusion (d^{-1})	$k_{SW2} = S_{AS}v_D\phi_{DS}/V_S$
burial (d^{-1})	$k_B = S_{AS}v_B(1 - \phi_{DS})/V_S$
degradation in water (d^{-1})	$k_{WR} = 3.4 \times 10^{-5}$
degradation in sediment (d^{-1})	$k_{SR} = 3.4 \times 10^{-5}$

Other Equations

volatilization mass transfer coefficient (m d^{-1})	$v_E = 1/(1/v_{EW} + 1/(K_{AW}v_{EA}))$
air−water partition coefficient (unitless)	$K_{AW} = H/(8.314 \times (273 + T_W))$
temperature dependence of Henry law constant (H)	$\ln H(T_W) = \ln H(298) + 20.18 - 6013.6/T_W$
fraction of freely dissolved PCB in water (unitless)	$\phi_{DW} = 1/(1 + (C_{PW}OC_{PW}K_{OW}/d_{PW})$
fraction of freely dissolved PCB in sediments (unitless)	$\phi_{DS} = 1/(1 + (C_{SS}OC_{SS}K_{OW}/d_{SS})$
settling of sediment solids flux (kg/d)	$\text{SetFlux} = 1000 C_{PW}v_S S_{AW}$
burial flux of sediment solids (kg/d)	$\text{BurFlux} = 1000 C_{SS}v_B S_{AS}$

Lake and Chemical-Specific Properties

lake surface area (m^2)	$S_{AW} = 1.95 \times 10^{10}$
sediment surface area (m^2)	$S_{AS} = 1.17 \times 10^{10}$
average water depth (m)	$D_W = 85.6$
depth of active sediment layer (m)	$D_S = 0.025$
water volume of lake (m^3)	$V_W = 1.67 \times 10^{12}$
sediment volume (m^3)	$V_S = 2.93 \times 10^8$
water temperature (°C)	T_W
water in- and out-flow (L d^{-1})	$F = 7.04 \times 10^{11}$
concentration of particles in water (kg L^{-1})	$C_{PW} = 1.0 \times 10^{-6}$
concentration of solids in sediment (kg L^{-1})	$C_{SS} = 0.16$
density of suspended solids (kg L^{-1})	$d_{PW} = 1.5$
density of sediment solids (kg L^{-1})	$d_{SS} = 2.0$
organic carbon content of suspended solids (unitless)	$OC_{PW} = 0.05$
organic carbon content of bottom sediment (unitless)	$OC_{SS} = 0.027$
density of organic carbon (kg L^{-1})	$d_{OC} = 1.0$
water-side evaporation mass transfer coefficient (m d^{-1})	$v_{EW} = 24.0$
air-side evaporation mass transfer coefficient (m d^{-1})	$v_{EA} = 0.24$
solids settling rate (m d^{-1})	$v_S = 1.0$
water-to-sediment diffusion mass transfer coefficient (m d^{-1})	$v_D = 2.4 \times 10^{-3}$
sediment burial mass transfer coefficient (m d^{-1})	$v_B = 6.2 \times 10^{-6}$
total external loading (g/d)	L
pH of water	$pH = 7$

of the one developed by Mackay et al. (7) with the help of the participants of the Lake Ontario Mass Balance Workshop, organized by the International Joint Commission in Niagara on the Lake, from May 31 to June 2, 1991. The model is based on two mass balance equations describing the net movement of individual PCB homologs in and out of the water and sediment (Table 1). Rate constants are used to represent the key processes controlling the fate of PCB homologs in Lake Ontario, i.e., direct chemical inputs to the water (k_I), volatilization to the atmosphere (k_V), outflow to the St. Lawrence River (k_O), chemical degradation in water and sediments (k_{WR}, k_{SR}), sediment burial (k_B), settling of suspended solids (k_{WS1}), sediment resuspension (k_{SW1}), and chemical diffusion between the water and sediments (k_{WS2}, k_{SW2}). A conceptual diagram of the model is presented in Figure 1. The recipes and data used for deriving and parameterizing the rate constants are presented in Table 1. Octanol−water partition coefficients

(K_{OW}) and Henry law constants (H) for individual PCB homologs were taken from ref 9. The Henry law constant was corrected for temperature according to ref 10 to represent seasonal variations in volatilization rates. The water and sediment degradation rate constants were assumed to correspond to a half-lifetime of 56 years (7). Although their true value is unknown, it is generally recognized to be small compared to other processes in the lake, and hence it has no significant effect on the model calculations. The mass balance equations were solved numerically for each PCB homolog through an Euler-type numerical integration, and total PCB (t-PCB) concentrations were derived by adding the concentrations of the individual homologs. By treating the water and sediments as single homogeneous compartments, the model ignores spatial differences in PCB concentrations to gain a whole-ecosystem understanding of PCB dynamics in the lake. This assumption may be reasonable for PCBs in Lake Ontario
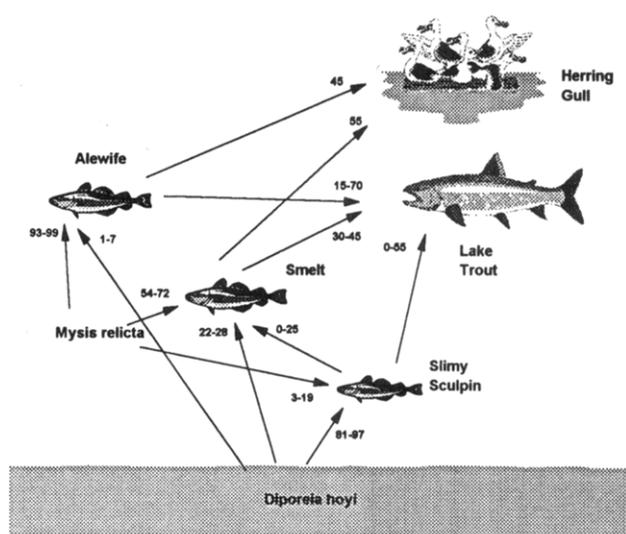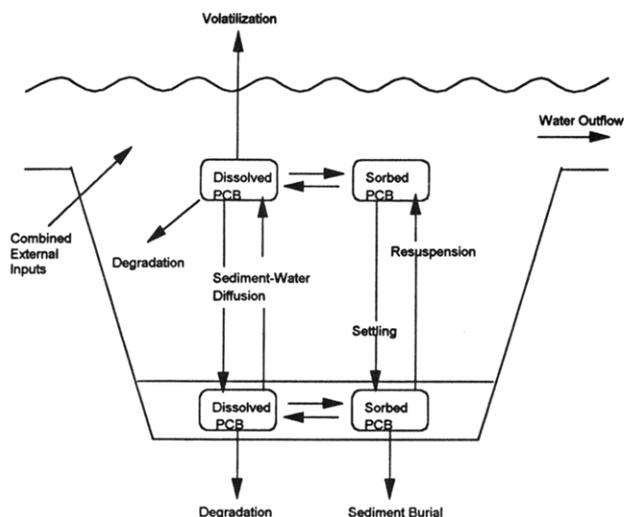
FIGURE 1. Conceptual diagram of the Lake Ontario environmental fate and food-chain bioaccumulation model.

considering that PCB concentrations in surficial sediments show a reasonably uniform distribution among the three main sedimentation basins in the lake (*4*). The mass balance for sediments solids in the lake is based on a settling flux of 1.67 g (m² of sediment)$^{-1}$ day^{-1}, a burial flux of 1 g (m² of sediment)$^{-1}$ day^{-1} and a resuspension rate calculated as the difference between the settling and burial fluxes of 0.67 g (m² of sediment)$^{-1}$ day^{-1}, ignoring the role of mineralization of organic carbon.

Food-Chain Bioaccumulation Model. The food-chain bioaccumulation model consists of several submodels characterizing chemical bioaccumulation in net plankton; zooplankton (*Mysis relicta*); the dominant benthic invertebrate *Diporeia hoyi*; four fish species, i.e., alewife (*Alosa pseudoharengus*), slimy sculpin (*Cottus cognatus*), rainbow smelt (*Osmerus mordax*), lake trout (*Salvelinus namaycush*), and their eggs; and herring gull (*Larus argentatus*) and their eggs. These species were chosen because (i) they include the species that have traditionally been used as biomonitors of PCBs in Lake Ontario and (ii) contaminant time-trend data for these species are available on a whole-lake basis to test or validate the model. The individual submodels are linked together through feeding interactions to represent the Lake Ontario food web (Figure 1). The food-chain bioaccumulation model is a dynamic interpretation of the steady-state bioaccumulation model developed by Gobas (*11*) and a dynamic toxicokinetic model for herring gulls modified after the pharmocokinetic model by Clark et al. (*12*). The models were modified by incorporating changes in organism weight, lipid content, and diet composition over the life span of the organism and by simulating multiple generations or age classes of organisms. These modifications make it possible to (i) simulate changes in chemical concentrations that occur seasonally and throughout the life span of the organisms, (ii) to compare contaminant levels between age classes since several generations coexist at one time, and (iii) to represent intergenerational transfer of contaminants between adults and their respective offspring. In addition, an equation for simulating chemical magnification in the gastrointestinal tract of fish (*13*) was included. Methods and data used for the simulation of chemical bioaccumulation in the Lake Ontario food chain are summarized in Table 2. Additions and modifications made to the earlier models are discussed below.

Plankton and Benthic Invertebrates. Bioaccumulation of PCB in phytoplankton, zooplankton, and benthic invertebrates is represented by an equilibrium partitioning of PCB with respectively the freely dissolved chemical in the overlying water for plankton and the sediment pore water for the benthos. This assumption is reasonable for *Diporeia* since observed concentrations of a variety of PCB congeners in the lipids of Lake Ontario *Diporeia* (*14*) were found not to be significantly ($P < 0.05$) different from those in the sediment when expressed on an organic carbon basis (*15*). There are empirical evidence (*16*) and theoretical grounds to indicate that biomagnification of PCBs beyond the thermodynamically controlled partition coefficient can occur in benthic invertebrate species. However, we have applied the simpler equilibrium model because (i) the equilibrium condition between overlying water and sediments, which needs to be met to achieve biomagnification, does not apply in Lake Ontario for the period of time that PCB concentration measurements were made and (ii) data for a more sophisticated kinetic model for PCB bioaccumulation are not available. The equilibrium assumption is also reasonable for phytoplankton and zooplankton with the possible exceptions of periods when rapid increases in phytoplankton biomass occur (*17, 18*). Our model takes into account that zooplankton absorb chemicals from their diet, but it assumes that biomagnification beyond its partition coefficient with the water and sediments, respectively, is insignificant due to its small size. Since, the half-lifetime of PCBs in the water and sediment compartments rate exceed the half-lifetimes of PCBs in plankton and benthic invertebrates, it is assumed that changes in concentrations in the plankton and benthos mirror those occurring in the water and the sediments, respectively. Lipid levels for net phytoplankton, *M. relicta* and *D. hoyi*, were obtained from ref 14.

Fish. The model for PCB bioaccumulation in fish consists of a whole-fish mass balance equation for each generation, which includes uptake via the gills and through the ingestion of food and elimination via the gill, through fecal excretion, and by metabolic transformation. The rate of each of these processes is represented by a first-order rate constant, and the mass balance equation is solved numerically, applying a condition of "no dietary intake" for newborn fish to initialize the model. The methods for

TABLE 2

Equations and Methods For Assessment of Concentrations of PCB in Time-Dependent Lake Ontario Food-Chain Bioaccumulation Model

(a) Plankton and Benthic Invertebrates

chemical concentration in phytoplankton (g kg^{-1} ww)	$C_P = C_{WD}L_PK_{OW}$
concentration in *Mysis relicta* (g kg^{-1} ww)	$C_Z = C_{WD}L_ZK_{OW}$
concentration in *Diporeia hoyi* (g kg^{-1} ww)	$C_B = (L_Bd_LC_S)/(d_{OC}OC_{SS})$
density of lipids (kg L^{-1})	$d_L = 1.0$
lipid content of phytoplankton (kg of lipid kg^{-1} wwt)	$L_P = 0.005$
lipid content of *Mysis relicta* (kg of lipid kg^{-1} ww)	$L_Z = 0.03$
lipid content of *Diporeia hoyi* (kg of lipid kg^{-1} ww)	$L_B = 0.03$

(b) Fish

mass of chemical in fish (g) (M_F)	$dM_F/dt = (k_1C_{WD} + k_D\Sigma P_iC_{D,i})V_F - (k_2 + k_E + k_M)C_FV_F$
concentration in fish (g kg^{-1} ww)	$C_F = X_F/V_F$
concentration in the diet (g kg prey^{-1})	$\Sigma P_iC_{D,i}$
gill uptake rate constant (L kg^{-1} d^{-1})	$k_1 = 1/((V_F/Q_W) + (V_F/Q_L)/K_{OW})$
gill elimination rate constant (d^{-1})	$k_2 = 1/((V_L/Q_W)K_{OW} + (V_L/Q_L))$
metabolic transformation rate constant (d^{-1})	$k_M = 0$
dietary uptake rate constant (kg kg^{-1} d^{-1})	$k_D = E_DF_D/V_F$
fecal egestion rate constant (kg kg^{-1} d^{-1})	$k_E = 0.4F_DE_DK_{GF}/V_F$
aqueous phase gill uptake transport rate (L d^{-1})	$Q_W = 88.3V_F^{0.6}$
lipid phase gill uptake transport rate (L d^{-1})	$Q_L = Q_W/100$
dietary uptake efficiency in fish (unitless)	$E_D = ((5.3 \times 10^{-8}K_{OW}) + 2.3)^{-1}$
food ingestion rate for fish (kg of food d^{-1})	$F_D = 0.022V_F^{0.85}e^{0.06T_w}$
lipid content of fish (kg of lipid kg^{-1})	L_F
fish weights (kg)	V_F
gut-to fish partition coefficient (unitless)	$K_{GF} = 0.5L_D/L_F$

(c) Herring Gull

mass of PCB in lipids of herring gull (g) (M_{GL})	$dM_{GL}/dt = (k_D\Sigma P_iC_{D,i})L_GV_G - k_EM_{GL}$
concentration in gull (g kg^{-1})	$C_G = L_GC_{GL} = M_{GL}/V_G$
concentration in diet (g kg^{-1})	$\Sigma P_iC_{D,i}$
concentration in egg lipids (g kg of lipid^{-1})	$C_{EL} = 0.47C_{GL}$
concentration in whole egg (g kg^{-1})	$C_E = L_EC_{EL}$
initial concentration in newborn (g kg^{-1})	$C_N = L_GC_{EL}$
whole body clearance rate constant (d^{-1})	$k_E = 0.0024$
dietary uptake rate constant (kg d^{-1} kg^{-1})	$k_D = E_DF_D/V_G$
dietary uptake efficiency (unitless)	$E_D = 0.8$
food ingestion rate (kg d^{-1})	$F_D = 0.210$
lipid fraction of herring gull (kg of lipid kg^{-1})	$L_G = 0.274 - 0.0086T_A$ (juvenile)
as a function of air temperature T_A (°C)	$L_G = 0.136 - 0.0027T_A$ (adult)
lipid fraction of herring gull egg (kg of lipid kg^{-1})	$L_E = 0.077$
herring gull weight (kg) as a function of time t (days)	$V_G = 0.997 \exp[-\exp(-0.088(t - 14.8))]$
monthly mean air temperature (°C)	T_A (from Toronto weather station)

parameterizing the rate constants are given in Table 2 and are essentially those used in ref 11 with the exception of the equation for k_E. Growth dilution is not represented by a rate constant as in other bioaccumulation models, but it is taken into account by solving the mass balance equation for the total mass of chemical in the fish rather than the chemical concentration. Data regarding the weight–age relationship for each of the fish species were obtained from refs 2, 3, 19, and 20. Age-dependent data for the lipid content of lake trout, which increases from 2.15 to 24.5% over the life span of this species, were obtained from refs 2 and 3. Lipid contents for sculpins, alewife, and smelt (2, 3) were not available on an age-dependent basis and were assumed to be constant. The metabolic transformation rate constant k_M is assumed to be zero because, although its true value is unknown, it is generally recognized to be small compared to other elimination rates in fish, and hence it can be ignored.

Herring Gulls. The model for herring gull was modified from that in Clark et al. (12) by simplifying the plasma and lipid storage compartments into a single "whole-organism" compartment with an age-dependent weight and lipid content. Dietary uptake in the gulls is simulated as the product of the feeding rate, the dietary uptake efficiency, the concentration in the diet, and dietary feeding prefer-

ences used to determine the proportion of each prey species in the diet. The feeding rate is estimated from the metabolic energy requirement of 9.3×10^4 kcal/year (21) of a herring gull and the approximate energy density of 1280 kcal/kg (22) of the herring gull's most important prey species, i.e. alewife and smelt. PCB elimination is through fecal egestion, metabolic transformation, and egg laying, in female birds, and is represented by a first-order elimination rate constant k_E. In the absence of an elimination rate constant for PCB homologs, we used the elimination rate constant for photomirex (12) to approximate that of PCBs because the two substances share similar physical–chemical properties and biomagnification factors in herring gulls (23). Herring gulls in Lake Ontario reach adulthood and begin laying eggs in their fourth year. To represent PCB transfer to eggs, we used the egg/gull PCB concentration ratio for PCBs of 0.47 (23). The mean PCB concentrations deposited in the eggs are used to estimate the initial PCB concentration in newborn gulls; hence, the internal concentration of adults influences the concentration in their young. Juvenile gulls (i.e., less than 1 year old) have higher lipid levels than adults, and the size of their fat pools are simulated by an inverse relationship with the air temperature given in ref 22 (Table 2). Average monthly temperatures were taken from the Toronto Island weather station to simulate the seasonal

predator	age	zooplankton	prey species			
			benthos	alewife	sculpin	smelt
alewife	1–2	99	1			
	2–8	93	7			
sculpin	1–2	3	97			
	2–5	19	81			
smelt	1–2	72	28			
	2–5	54	21		25 (0–1)	
trout	1–2			15 (0–1)	55 (1–2)	30 (2–3)
	2–3			15 (1–2)	40 (2–3)	45 (3–4)
	3–4			35 (1–2)	25 (2–3)	40 (3–4)
	4–5			45 (2–3)	25 (2–3)	30 (4–5)
	5–6			50 (2–3)	20 (3–4)	30 (4–5)
	6–7			70 (2–3)		30 (4–5)
	7–8			70 (3–4)		30 (4–5)
herring gull	0–25			45 (2–3)		55 (2–3)

[a] The values in parentheses indicate the age class of prey organism consumed.

fluctuations in lipid content. The lipid contents of herring gull eggs were taken from ref 23. Changes in the gull's body weight over its entire life span were simulated using an equation (22), which relates the gull's body weight to its age in days (Table 2). Herring gulls are assumed to live for 25 years; hence, model calculations are carried out for 25 generations or age classes of gulls. Concentrations in gull eggs are calculated as the average of the concentrations in eggs of the entire population taken into account the population age structure.

Food Chain. A conceptual diagram of the feeding interactions in the Lake Ontario food chain is shown in Figure 1. Diet composition of individual species is summarized in Table 3 and is based on various sources. In recent years, there have been significant changes in the diet composition of some of the organisms in Lake Ontario due to reductions in the alewife and smelt stocks. Gut content studies (24) show that the diet composition of 4+ lake trout has shifted from an 80–81% alewife diet in 1983–1985/1986 to a 84% and 64% smelt diet in 1991 and 1992, with the benthic sculpin becoming a more important diet item over time by increasing from 1% in 1983 to 13% in 1991 and to 31% in 1992.

Application of the Model

To interpret observed t-PCB concentration time trends in various media of Lake Ontario in terms of changes in the total external PCB loadings to the lake over time, model simulations were conducted by selecting loading scenarios for each PCB homolog for the period of 1929–2000. Each loading scenario consisted of a period where the loading of a specific PCB homolog increased at a constant rate per year up to a maximum value, followed by a period where loading declined at a constant annual rate. Although this may be a simplified representation of the actual unknown loading scenario, it provides a systematic approach for estimating historical PCB loadings as rates of increase and decline can be systematically changed and tested for their ability to fit observed data by the sum of the squared relative differences, i.e., $\Sigma((C_{obs,i} - C_{pred,i})^2/C_{pred,i})$, between all observed $(C_{obs,i})$ and predicted $(C_{pred,i})$ concentrations. The loading scenario that resulted in the best agreement between observed and predicted concentration data over time was considered to be the best available estimate of the changes in loadings that have actually occurred. The

quality of agreement between observed and predicted concentrations was first derived for each individual PCB homolog based on homolog-specific concentrations in sediment core profiles (4). However, since the resulting loading scenarios are based on a small set of homolog-specific PCB concentration data, we also derived estimates of the concentrations of t-PCBs by adding the concentrations of the homologs in each of the media and organisms of Lake Ontario, which were then compared to the large data set of observed t-PCB concentrations from refs 2–5, 14, and 25–29. Observed t-PCBs concentrations are based on a summation of individual PCB congeners as reported by the original authors. This may introduce a small error in the comparison between observed and predicted concentrations since different authors base their t-PCB concentrations on a summation of a different number of PCB congeners, although the most abundant PCB congeners are accounted for.

The best overall agreement between observed and predicted PCB homolog and t-PCB concentrations in water, sediments, and biota between 1930 and 1993 was achieved when the model was executed with a loading scenario consisting of an annual increase in loading of 25% up to a maximum loading of 23 200 kg/year in 1961, followed by an annual decline in loading of approximately 15%/year, resulting in a 1991 loading of 619 kg/year, close to Thompson's 1991 estimate of 553 kg/year (30). Figure 2 depicts the agreement between t-PCB concentrations in sediments, water, and Lake Ontario biota that were observed and predicted by our model using this single loading scenario. The majority of the predicted t-PCB concentrations in herring gull eggs, lake trout, and smelt are within a single standard deviation of the mean of the observed data, and in all cases are within the 95% confidence limits associated with the measurements, suggesting that the data sets could be explained by the model's time response to this loading scenario. Observed and predicted t-PCB concentrations in *Diporeia* are in good agreement. t-PCB concentrations, in Lake Ontario water from 1983 to 1990 of 0.44–1.2 ng/L are in good agreement with observed concentrations of 0.95–1.41 ng/L (14, 31–33), although the predicted drop in concentration is not apparent in the observed concentrations possibly due to experimental errors, variability, and small sample size associated with these difficult measurements. Agreement between ob-
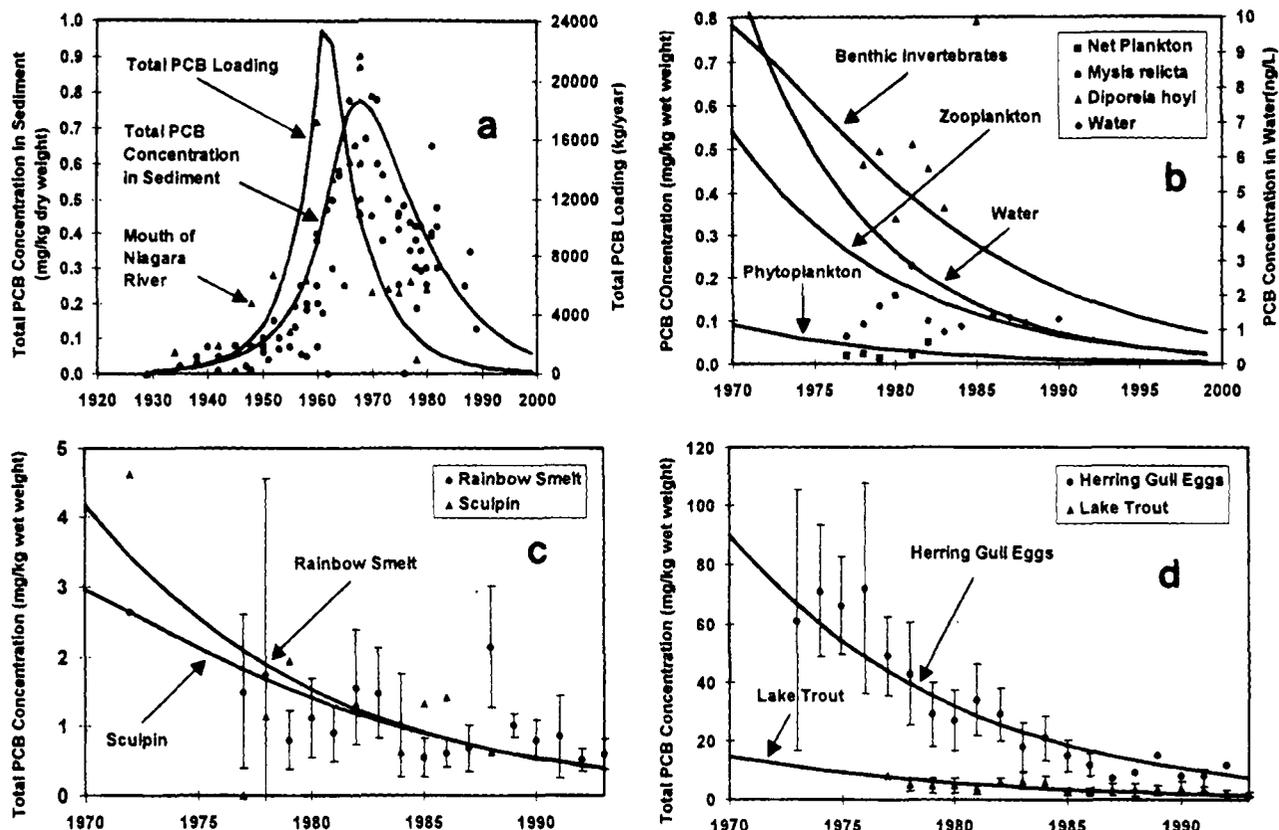
FIGURE 2. : Predicted (solid lines) and observed t-PCB concentrations in Lake Ontario sediments (a); water, benthic invertebrates (*Diporeia hoyi*), zooplankton (*Mysis relicta*), net plankton (b); slimy sculpins, rainbow smelt (c); and 4+ lake trout and herring gulls (d) in Lake Ontario as a function of time (years). Concentrations in sediments from the mouth of the Niagara River are presented at 20% of their actual levels. Estimated total PCB loadings are presented as the solid line in panel a.

served and predicted concentrations in net phytoplankton and *Mysis* is poor but within a factor of 3, which may be due to the inability of lipids to correctly describe PCB partitioning in phytoplankton or experimental error and small sample size (e.g., $n = 3$ for phytoplankton and $n = 2$ for zooplankton (14)). Apart from experimental error in observed plankton data, the apparent contradiction between the satisfactory concentration predictions for the upper trophic fish species while concentration predictions for the lower trophic phyto- and zooplankton levels are relatively poor can be explained by the large fraction of the total PCB intake in fish through the consumption of benthic invertebrates instead of pelagic plankton. For example, in 1990, approximately 92% of the total t-PCB intake in 2-year-old sculpins, 65% in 4-year-old smelt, and 53% in 4+ lake trout are from the consumption of benthic invertebrates.

It should be stressed that the temporal response of the model is sensitive to the selection of the value for the depth of the sediment layer that can be accessed by PCB, which is unfortunately a model input parameter that currently cannot be conclusively measured. It may thus be argued that the predicted rate of decline in PCB loadings reflects the sediment depth chosen. This appeared not to be the case. In model simulations, the value for the sediment depth controlled the relative (i.e., differences) in the rates of decline in PCB concentration over time between the various media, and an active sediment layer of 2.5 cm was selected because it produced the best agreement with the observed data. The rate of decline of PCB loading controlled the absolute rates of decline in the PCB concentrations. A sensitivity analysis revealed that the magnitude of the maximum loading is sensitive to the selection of the value

for the Henry law constant. An overestimation of H results in an overestimation of the maximum loading.

Temporal Response of the Lake Ontario Ecosystem

If the agreement between observed and predicted concentration vs time curves is an indication of the model's ability to describe the dynamics of PCBs in the Lake Ontario ecosystem, then it is interesting to analyze the model's behavior and results in an effort to further improve insights into the interplay of processes controlling the dynamics of PCBs in the Lake Ontario ecosystem. This is a useful endeavor considering that the interpretation of concentration–time curves in terms of historic loadings as well as the prediction of the future response of PCB concentrations in biota to further changes in PCB loadings ultimately requires an understanding of the processes and mechanisms controlling the ecosystem dynamics of PCBs.

One of the interesting results of the time-dependent model is that t-PCB loadings may have peaked around 1961, which is 4–7 years before t-PCB concentrations in sediments of the lake's sedimentation basins reached their maximum levels of approximately 0.74 mg/kg in 1965–1968 (Figure 2). The model's estimate of the time of maximum loadings is in agreement with sediment core data collected from the mouth of the Niagara River, which show peak t-PCB concentrations of 3.6 mg/kg in 1959–1962 (34), corresponding to a maximum total t-PCB loading of approximately 12 100 kg/year. Since estimates of t-PCB loadings into Lake Ontario (30) suggest that the Niagara River has been the main source of PCBs to Lake Ontario, it is reasonable to assume that the timing of maximum t-PCB concentration in the sediments of the Niagara River

should approximately agree with that of the total combined maximum external t-PCB loadings. Hence, both the model results and the sediment core data suggest that there is a significant lag time between the occurrence of maximum t-PCB loadings and maximum t-PCB concentrations in the lake. One of the implications of this is that significant t-PCB loading reductions to Lake Ontario may have taken place before the implementation of the PCB ban in 1974 and before commercial PCB sales in the United States peaked around 1968–1970 (30).

The lag time is the result of the fact that, during the period of loading increase, the concentration in the water climbs seeking to achieve (but not reach) a steady state with the continually increasing loading. Hence, after the maximum PCB loading has been reached, the PCB concentration in the water has still not achieved its steady-state concentration with the earlier lower loading levels, causing it to keep increasing while the loadings are actually declining. In a similar fashion, the concentration in the sediment increases attempting to achieve (but not reach) a steady state with the concentration in the water. After the maximum concentration in the water has been reached, the concentration in the sediments continues to increase because, due to its slower time response, it has not been able to reach its steady-state concentration with the less-than-maximum concentration in the water before the concentration in the water peaked. This behavior is a reflection of the quicker response time of the PCB concentrations in water compared to that in the sediments. An important effect of the rise and the fall of the external PCB loadings to the lake over time and the difference in response times of the PCB concentrations in the water and sediments is that the PCB concentrations in water and sediments were probably continuously out of equilibrium and steady state for the period from 1929 up to now. Model simulations show that after 1962, when external loadings started to decline, the t-PCB concentration in the water fell quickly compared to that in the sediments, causing a sediment–water disequilibrium where the sediment/water PCB fugacity ratio increased from approximately 0.5 to a value of approximately 2.8 in 1982 and 3.2 in the year 2000, which is in agreement with observed data in 1982 (14), which show that the observed whole-lake sediment/water partition coefficient of, for example, PCB101 of 27 (± 10) μg kg^{-1}/130 (± 36) pg L^{-1} or 2.1 × 10^5 L/kg is higher than its steady-state level of 7.1 × 10^4 L/kg or its chemical equilibrium value (equal fugacities) of approximately 0.027 × 10$^{6.4}$ or 6.8 × 10^4, estimated according to ref 35 based on the freely dissolved water concentration. The significance of this sediment–water disequilibrium for the Lake Ontario food chain is that since 1961 the consumption of sediment-dwelling benthic invertebrates has become increasingly more important as a source of PCBs to fish than the consumption of plankton. For example, the t-PCB intake through the consumption of benthic invertebrates increased from 68 to 92% in sculpins and from 9 to 35% in 4-year-old smelt.

Figure 3 illustrates that after t-PCB loadings fell the rate of t-PCB concentration decline in the water exceeded that in the sediments. The rates of t-PCB concentration decline and hence the actual half-lifetimes of t-PCB in the lake water and sediments are not expected to be constant over time, as steady-state models may suggest, but are expected to increase slowly over time, hence causing the half-lifetime to drop in response to loading reductions. The drop in
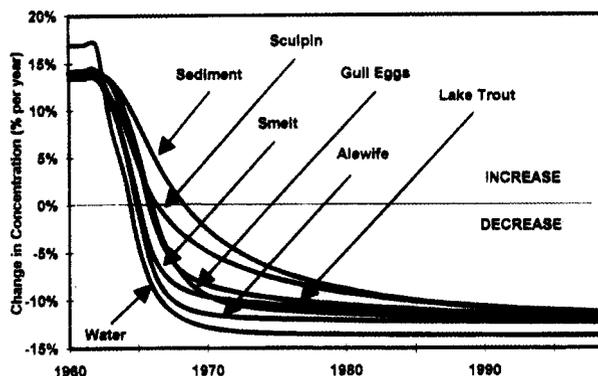
FIGURE 3. Predicted annual changes (in % per year) of the t-PCB concentrations in water, sediments, alewife, rainbow smelt, slimy sculpin, lake trout, and herring gull eggs as a function of time (years) in response to a 15% annual decline in PCB loadings to Lake Ontario after 1961.

half-lifetime is a reflection of the reduction in combined external and internal (i.e., from the sediments) t-PCB loadings into the water, which initially reflects predominantly the rate of reduction in external t-PCB loadings since t-PCB concentrations in the sediments initially do not decline, but later reflects the higher rate of decline in combined external and internal loadings as t-PCB concentrations in the sediments are starting to decline in response to the lower t-PCB concentration in the water. Ultimately, the rates of concentration decline in water, sediments, and biota are expected to converge at a half-lifetime of approximately 5.5 years, corresponding to the maximum rate at which PCBs can be removed from the active sediments layer.

Figure 3 illustrates that significant differences in the time response of PCB concentrations in the various organisms of Lake Ontario can be expected after PCB loading reductions occur but that ultimately PCB concentrations will fall at a similar annual rate of approximately 13% if loadings continue to fall. The time response of the t-PCB concentration to reductions in PCB loadings to Lake Ontario is predicted to be the shortest in alewife and the longest (i.e., slowest) in sculpins and increases in the order of alewife < smelt, herring gull eggs < 4+ lake trout < sculpins. This is generally in agreement with field observations since t-PCB concentrations in herring gulls eggs have fallen over the same time period by a greater amount than concentrations in 4+ lake trout and t-PCB concentrations in sculpins did not show a significant reduction. It should be stressed that the variability in the sculpin data set is large, making it difficult to compare the actual and expected drop in t-PCB concentrations over time. Since the likelihood of detecting large changes in concentrations over time is greater than detecting small changes in concentrations, assuming—for simplicity—a similar variability in concentrations, it follows that the organisms with the faster time response to PCB loadings may be more suitable as biomonitors of changes in loadings than organisms with the slower time response. The most important reason for the difference in time response of the PCB concentrations in the various organisms of the Lake Ontario is diet composition. In essence, the PCB concentration in the sculpin responds slowly to changes in loadings because its diet consists primarily of benthic invertebrates, which in turn receive most of their PCB intake from the sediments, which in comparison to the water respond slowly to changes in PCB loadings. In contrast, the PCB concentration in herring gull eggs
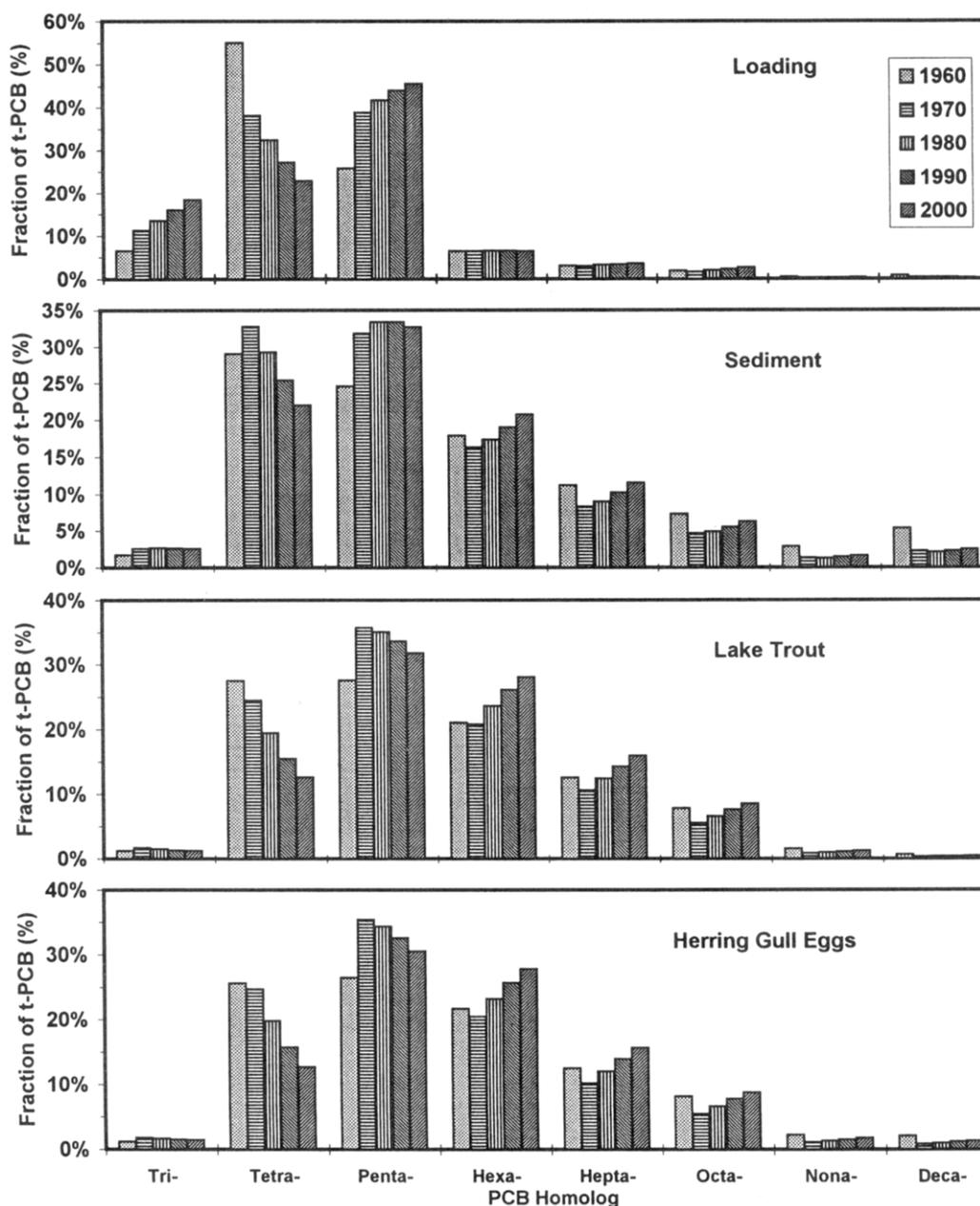
FIGURE 4. Estimated time response of the composition (in %) of the PCB homolog distribution in t-PCB loadings and concentrations in sediment, lake trout, and herring gull eggs of Lake Ontario.

responds more quickly because herring gulls consume predominantly alewife and smelt, which consume primarily pelagic zooplankton, which follow the relatively more rapid changes in the PCB concentration of the water. Growth, weight, and lipid content, which control the rate of PCB elimination from fish, also play a role. A large rate of elimination due to small weight, low lipid content, and high growth rate will result in a faster time response, while a slow rate of elimination will cause a slower time response. However, if the rate of PCB elimination in the organisms exceeds that in the diet of the organisms, then the rate of concentration decline in the diet becomes the rate control-ling step and controls the rate of concentration decline. The relationships between weight, lipid content, growth, sediment−water disequilibria, diet composition, and time response of the PCB concentration are complex and best investigated by conducting model simulations. Simulations of the homolog composition of t-PCB concentrations in fish and herring gulls are presented in Figure 4 and suggest

a gradual shift toward a larger contribution of the more chlorinated homologs, reflecting a similar pattern in the sediments and greater bioaccumulation factors of the more chlorinated congeners.

History and Future of PCBs in Lake Ontario

Assuming that the model provides a realistic description of the time-dependent relationship between the PCB loadings and concentrations in Lake Ontario, it is interesting to investigate what t-PCB concentrations in Lake Ontario biota may have been before the earliest PCB concentration data were recorded. This information may be relevant to studies of the ecotoxicological effects of PCBs in the lake since the reproductive failure of Lake Ontario lake trout stocks since the 1950s is often suggested to be linked to the high PCB concentrations in these fish. It should be stressed that the use of our results for estimating an ecotoxicologically relevant dose of PCBs in Lake Ontario biota may be limited since to evaluate the ecotoxicological significance of PCBs

it is important to know the concentration of individual PCBs congeners rather than PCB homologs or t-PCBs (36, 37). t-PCB concentrations are estimated to have reached maximum levels of 335 mg/kg in herring gulls, 122 mg/kg in gull eggs, 20 mg/kg in 4+ lake trout, 9 mg/kg in 4+ lake trout eggs, 6 mg/kg in smelt and alewife, and 3.4 mg/kg in sculpins.

Several authors have suggested that PCB loadings may have stopped declining since the mid 1980s and have reached a constant value (4–6). There is indeed evidence to support this. A statistical analysis shows a significant change in the rate of decline of the PCB concentrations in herring gull eggs from 14 ± 2 (95% confidence limits) per year before 1987 to 4.4 ± 20%/year (i.e., not significantly different from a zero decline) after 1987. PCB concentrations in 4+ lake trout and smelt also appear to have been constant since 1985. Model simulations, in which PCB loadings dropped annually by 15% from 1961 to 1985 and then remained constant, did not show a significantly better agreement between observed and predicted concentrations partly due to the slow time response of the system and the variability in the data. The hypothesis that atmospheric inputs originating from out of Lake Ontario basin may come to dominate the total loadings into Lake Ontario, and causing a decline in concentration reductions is supported by the marked increase in contribution of trichlorinated PCBs to the estimated t-PCB loadings (Figure 4). If atmospheric t-PCB loadings remain at the estimated levels of 107 kg/year (30), they are expected to dominate total PCB loadings by 1998, and total PCB concentrations will gradually stop declining. In addition to possible reductions in the rate of PCB loading decline, changes in the Lake Ontario food-chain structure may have contributed to a possible reduction in the rate of concentration decline. Model predictions indicate that the large increase in the contribution of sculpins in the lake trout's diet can cause a reduction in the rate of decline of the PCB concentrations over time due to the fact that PCB concentrations in sculpins drop in response to reductions in external PCB loadings at a slower rate than those in smelt and alewife, which were replaced by the sculpins in the lake trout's diet.

Acknowledgments

Literature Cited

(1) Bishop, D.; Weseloh, V.; Burgess, N. M.; Struger, J.; Nortsrom, R. J.; Turle, R.; Logan, K. A. An atlas of contaminants in eggs of fish-eating colonial birds of the Great Lakes (1970–1988) Vol. I; Technical Report Series No. 152; Canadian Wildlife Services: Ontario Region 1992.
(2) Borgmann, U.; Whittle, D. M. Can. J. Fish. Aquat. Sci. 1992, 49, 1086.
(3) Borgmann, U.; Whittle, D. M. J. Great Lakes Res. 1992, 18, 298.
(4) Oliver, B. G.; Charlton, M. N.; Durham, R. W. Environ. Sci. Technol. 1989, 23, 200.
(5) Eisenreich, S. J.; Capel, P. D.; Robbins, J. A.; Bourbonniere, R. Environ. Sci. Technol. 1989, 23, 1116.
(6) Mackay, D. J. Great Lakes Res. 1989, 15, 283.
(7) Mackay, D.; Diamond, M.; Sang, S.; Vlahos, P.; Gobas, F. A. P. C.; Dolan, D. J. Great Lakes Res. 1994, 20, 625.
(8) Endicott, D. D.; Richardson, W. L.; Parkerton, T. F.; DiToro, D. M. A steady-state mass balance and bioaccumulation model for toxic chemicals in Lake Ontario; Technical Report, Lake Ontario Fate of Toxics Committee; U.S. EPA: Duluth, MN, 1991.
(9) Shiu, W. Y.; Mackay, D. J. Phys. Chem. Ref. Data 1986, 15, 911.
(10) Ten Hulscher, T. E. M.; van der Velde, L. E.; Bruggeman, W. A. Environ. Toxicol. Chem. 1992, 11, 1595.
(11) Gobas, F. A. P. C. Ecol. Model. 1993, 69, 1.
(12) Clark, T. P.; Norstrom, R. J.; Fox, G. A.; Won, H. T. Eviron. Toxicol. Chem. 1987, 6, 547.
(13) Gobas, F. A. P. C.; Zhang, X.; Wells, R. Environ. Sci. Technol. 1993, 27, 2855.
(14) Oliver, B. G.; Niimi, A. J. Environ. Sci. Technol. 1988, 22, 388.
(15) Gobas, F. A. P. C. In Chemical Dynamics in Freshwater Ecosystems; Gobas, F. A. P. C., McCorquodale, J. A., Eds.; Lewis Publishers: Chelsea MI, 1992; Chapter 6.
(16) Parkerton, T. F. Ph.D. Dissertation, Manhattan College, New York, 1993.
(17) Skoglund, R. S.; Swackhammer, D. L. Presented at the 34th Conference on Great Lakes Research, Buffalo, NY, June 2, 1991.
(18) Clayton, J. R.; Pavlou, S. P.; Breitner, N. F. Environ. Sci. Technol. 1977, 24, 1203.
(19) Casselman, J. M. Ontario Ministry of Natural Resources, Research, Science, and Technology Branch, Aquatic Ecosystems Section, Glenora Fisheries Station, Picton, Ontario, personal communication, 1994.
(20) Selgeby, J. H. J. Great Lakes Res. 1988, 14, 44.
(21) Norstrom, R. J.; Clark, T. P.; Kearney, J. P.; Gilman, A. P. Ardea 1986, 74, 1.
(22) Rand, P. S.; Lantry, B. F.; O'Gorman, R.; Owens, R. W.; Stewart, D. J. Trans. Am. Fish. Soc. 1994, 123, 519.
(23) Braune, B. M.; Norstrom, R. J. Environ. Toxicol. Chem. 1989, 8, 957.
(24) Whittle, D. M. Windsor, personal communication, 1994.
(25) Murdoch, A.; Murdoch, P. J. Great Lakes Res. 1992, 18, 132.
(26) Bishop, C. A.; Brown, G. P.; Brooks, R. J.; Lean, D. R. S.; Carey, J. H. Arch. Environ. Contam. Toxicol. 1994, 27, 82.
(27) Haile, D. L.; Veith, G. D.; Lee, G. F.; Boyle W. C. U.S. Environmental Protection Agency Report 1975; EPA-660/3-75.
(28) Stevens, R. J. J. Report to the Surveillance subcommittee of the Great Lakes Water Quality Board, 1988.
(29) Whittle, D. M.; Fitzsimons, J. D. J. Great Lakes Res. 1983, 9, 295.
(30) Thompson, S. Estimating the loadings of priority pollutants; Conservation & Protection Branch, Environment Canada: Montreal, 1992.
(31) Biberhofer, J.; Stevens, R. J. Organochlorine contaminants in ambient waters of Lake Ontario; Scientific Series No. 159; 1987.
(32) Environment Canada. Toxic chemicals in the Great Lakes and associated effects: Vol. I. 1991. Contaminant levels and trends; Ministry of Supply and Services Canada.
(33) Halfon, E.; Shito, N. Donald W. Rennie Memorial Series. Great Lakes Mono. No. 4, 1992.
(34) Durham, R. W.; Oliver, B. G. J. Great Lakes Res. 1993, 9, 160.
(35) DiToro, D. M. Chemosphere 1985, 15, 1503.
(36) Peakall, D. B. CRC Crit. Rev. Environ. Control 1975, 5, 469.
(37) Giesy, J. P.; Ludwig, J. P.; Tillit, D. E. Environ. Sci. Technol. 1994, 28, 128A.