PCB Elimination by Yellow Perch (*Perca flavescens*) during an Annual Temperature Cycle

GORDON PATERSON,*
KENNETH G. DROUILLARD, AND
G. DOUGLAS HAFFNER

Great Lakes Institute for Environmental Research and Department of Biological Sciences, University of Windsor, 401 Sunset Avenue, Windsor, Ontario, Canada, N9B 3P4

The significance of temperature on aquatic species ecology and physiology is well recognized yet its effects on chemical bioaccumulation kinetics are less well understood under natural conditions. In this study, yellow perch were dosed with a polychlorinated biphenyl (PCB) mixture and allowed to depurate the chemicals over 1 year under an ambient temperature cycle characteristic of northern temperate latitudes. PCB elimination kinetics during the summer months at optimal water temperature for perch (23 °C) were similar to those observed in lab studies with other species reared at their optimal temperature. During the fall and winter seasons, however, elimination of only 11 PCB congeners of log $K_{ow} \leq 5.7$ was observed and half-lives averaged >1000 d for these PCBs. PCB elimination was again observed with the onset of spring temperatures but elimination rates averaged 2.6 times slower for readily metabolized congeners and 7.5 times slower for more persistent PCBs than observed during the summer. Bioenergetics modeling efforts predicted maximum values for respiration, fecal egestion, and growth rates during summer months but also predicted rapid declines in these chemical dilution processes during the fall and winter concurrent with changes in temperature. As temperature increased into the spring, bioenergetic rates were predicted to increase but only achieved $\sim\!85\%$ of maximum rates predicted for summer peak temperatures. These results indicate that minimal chemical elimination occurs in perch when metabolic functioning falls to low maintenance levels during the fall and winter. These seasons encompass approximately 8 months of the year at northern temperate latitudes and therefore these patterns have significant consequences for understanding mechanisms of foodweb biomagnification of hydrophobic organic chemicals in aquatic systems.

Introduction

Temperature is one of the primary variables regulating aquatic species bioenergetics (1). Physiological processes such as feeding, respiration, and fecal egestion rates, and ultimately growth, are substantially determined by ambient temperatures and these will directly control the kinetics of chemical dynamics in organisms. Experiments designed to calibrate toxicokinetic parameters for freshwater fish often minimize temperature variation and typically employ ex-

perimental systems that closely control temperatures to coincide with the thermal optima of the species in question (2-4). Under natural conditions, however, fish experience a range of temperatures within a daily period due to behavioral activities including feeding and predator avoidance (5). In addition, at north temperate latitudes, thermal optima exist for limited periods during the year, especially for species considered to occupy cool—warm water, littoral habitats. Thus, for species whose preferred water temperatures are near or above 20 °C, key bioenergetic parameters controlling chemical dynamics may only be maximized for a short time frame during an annual cycle.

The limited number of studies which have documented temperature relationships for hydrophobic organic contaminant toxicokinetics in fish indicate that elimination kinetics are positively correlated with temperature (3, 6-9). However, it has also been suggested that toxicokinetic relationships developed under constant temperature conditions may differ from those determined under fluctuating temperatures such as those experienced or selected by fish in nature (10). These discrepancies occur because the bioenergetic response to temperature change can differ depending on whether such changes are abrupt or allow for an acclimatized response (11). Since most aquatic species experience a range of temperatures on a daily basis, there is a need to develop toxicokinetic datasets which have been measured under thermal conditions representative of those experienced by a species in their natural environment. Little or no information currently exists on chemical dynamics for fish experiencing the daily, seasonal, and annual temperature cycles characteristic of north temperate latitude lakes and rivers. Growth potentials for fish are predicted to be maximized when prey densities and thermal optima overlap, an event that occurs only briefly throughout the annual cycle in such systems (12). This suggests that maximum bioenergetic potentials are also only reached during a limited period of the year, primarily in the summer and fall when optimal environmental conditions for growth exist (1, 12-14). Bioenergetic models predict limited feeding and fecal egestion for cool-warm water fish during winter months suggesting that chemical kinetics are also minimized during this time (1, 13, 14). Hibernation and migration by bears and salmon are known to deplete lipid reserves thereby increasing chemical fugacity (15, 16). Thus, changes in proximate composition, as related to losses or gains in whole body lipid content, can influence chemical partitioning between central and storage compartments of the animal and further modify chemical kinetics (17).

Yellow perch have been relatively well studied for both bioenergetic modeling purposes $(1,\ 5)$ and in chemical accumulation and depuration experiments $(4,\ 13)$. Additionally, this species inhabits cool to warm water environments with a preferred temperature of approximately 23 °C (1) and is widely distributed throughout northern temperate latitude systems (18). In this study, juvenile yellow perch were dosed with a PCB mixture and allowed to depurate the chemicals over a 1 year period while held under ambient temperature and photoperiod conditions. The purpose of this research was to investigate the effects of an annual temperature cycle on PCB elimination kinetics in yellow perch. It is hypothesized that chemical elimination rates will be maximized during periods when bioenergetic processes are optimized, and

^{*} Corresponding author e-mail: patersj@uwindsor.ca.

TABLE 1. Wet Weight, Sum PCB Concentrations, and Hepatosomatic Index (HSI) Data (mean \pm 1 SE) of Juvenile Yellow Perch Dosed with Aroclor Technical Mixture

treatment	weight (g)		sum PCB (ng·g ⁻¹ wet wt)		HSI (%)	
	0 d	365 d	0 d	365 d	0 d	365 d
control dosed	$\begin{array}{c} 8.7 \pm 1.7 \\ 10.1 \pm 2.2 \end{array}$	$\begin{array}{c} 24.8 \pm 1.4 \\ 27.4 \pm 3.2 \end{array}$	$\begin{array}{c} 40.6 \pm 1.9 \\ 1743.4 \pm 126.8 \end{array}$	$\begin{array}{c} 36.6 \pm 1.8 \\ 546.2 \pm 42.1 \end{array}$	$\begin{array}{c} 2.4 \pm 0.1 \\ 2.1 \pm 0.3 \end{array}$	$\begin{array}{c} \textbf{1.4} \pm \textbf{0.1} \\ \textbf{1.6} \pm \textbf{0.2} \end{array}$

therefore chemical toxicokinetics in freshwater fish can be used as tracers of metabolic rate in calibrated species.

Methods

Fish Husbandry. Juvenile yellow perch (Table 1) averaging 8.3 ± 0.4 g (mean \pm SE) were obtained from an aquaculture facility (Leadley Environmental Inc., Essex, ON, Canada) and acclimated in a 5000 L recirculation system holding tank prior to the initiation of the experiment. The experimental tank was located in an outdoor greenhouse facility maintained under ambient environmental temperature and photoperiod conditions. Water condition was maintained with a biological filtration system exchanging the tank volume four times daily with an ultraviolet light source placed on the tank inflow to minimize bacterial contamination. Filtration tanks were backwashed weekly with approximately 35% of the tank volume replaced with aquaculture pond water at a temperature within 2 °C of the experimental tank temperature. Daily water temperature readings were recorded with individual temperature loggers (Hoskin Scientific, Burlington, ON, Canada) placed in the experimental tank, with water quality parameters (pH, dissolved oxygen, oxidation/reduction potential, conductivity) measured weekly (Hydrolab, Campbell Scientific Corp., Edmonton, AB, Canada).

Fish were measured for total length and weight and were dosed by intraperitoneal injection with a 1:1:1 mixture of Aroclors 1248/1254/1260 dissolved in safflower oil (19). Dosing occurred 14 days prior to the initiation of experimental sampling. An oil dosing volume of 1.25 μ L·g⁻¹ was used to achieve nominal day 0 concentrations of approximately 2000 $ng \cdot g^{-1}$ wet wt $\Sigma PCBs$ (Table 1). Control fish were injected with an equal volume of clean safflower oil containing no PCB solution and the soft ray portion of the dorsal fin was clipped on these individuals. To account for potential external PCB sources, chemical recycling, and background food concentrations, control fish were maintained in the experimental tank with dosed individuals. Fish were fed a daily maintenance ration (1.5% wet weight) of commercial fish food (Martin Mills Inc., Elmira, ON, Canada) throughout the course of the study.

Control and dosed fish were collected at days 0, 10, 30, 60, 120, 180, 240, 300, 330, and 365 of the experiment with day (d) 0 of the study occurring June 21, 2003. Five control and experimental fish were collected at each sampling date. Total and fork lengths, sex, gonad, liver, and body weights were measured at sampling and fish were processed immediately following collection. From the five fish collected for each treatment group, the largest individuals were processed alone, with the remaining four fish separated into two samples of similar size and sex generating three replicates for each sampling date. Samples were ground into a whole body homogenate using a stainless steel blender. Animals were maintained and handled following the Canadian Council for Animal Care Guidelines.

PCB Analysis. Analytical methods are described in detail in ref 20. Briefly, sample homogenates (\sim 2.5 g) were ground with Na₂SO₄ and spiked with three 13 C-PCB recovery standards (IUPAC 37, 52, and 153). The homogenates were packed in glass columns containing 50 mL of 1:1 hexane/

dicholormethane, allowed to stand for 1 h, followed by elution with another 250 mL of extraction solvent. Extracts were concentrated to approximately 10 mL. A 1 mL portion of the sample was removed for gravimetric lipid determination, with the remaining extract cleaned up by gel permeation chromatography followed by florisil chromatography (21). Extracts were concentrated to 1 mL, capped in 2 mL gas chromatograph (GC) vials, and stored at 4 °C until instrumental analysis. Method blanks and an in-house reference homogenate (Detroit River carp) were co-extracted for every batch of five samples. Recoveries for the three internal standards averaged $102\,\pm\,0.9\%$ and samples were not corrected for recovery.

PCB analyses were completed on a Hewlett-Packard 5890 GC equipped with a 5972 mass selective detector (MSD) and a HP-7673 autosampler. Detection limits for PCB congeners ranged from 0.1 to 0.3 ng·g $^{-1}$ wet wt. PCB concentrations in blanks were near or below detection limits and sample correction was not necessary. Σ PCB concentrations for the in-house reference homogenate averaged 3517 ± 107 ng·g $^{-1}$ wet wt (mean \pm SE) and were in compliance with the Great Lakes Institute for Environmental Research analytical laboratory's quality assurance guidelines (mean \pm 2 SD).

Data Analysis. The polynomial function describing the temperature profile throughout the duration of the experiment was determined using the nonlinear regression module in SYSTAT (22). The regression analysis was run through multiple iterations to achieve optimal fit to the data. All statistical analyses were completed using SYSTAT version 8.0 for windows with a criterion for significance of P < 0.05.

Water temperature averaged $23.2\pm0.5\,^{\circ}\mathrm{C}$ for the first 60 d of the experiment and did not exhibit any significant decline over this period (P=0.719). During the fall season between days 60 and 180, water temperature decreased significantly (P<0.001) from 24.4 ± 0.9 to $2.7\pm0.1\,^{\circ}\mathrm{C}$ and increased significantly from days 180 to 300 (P<0.001). From 300 to 365 d, water temperature increased from 13.0 ± 0.7 to $21.2\pm0.8\,^{\circ}\mathrm{C}$ with an average temperature of $19.1\pm0.5\,^{\circ}\mathrm{C}$ recorded for this period. From this annual temperature profile, elimination rate constants (k_2) for each congener were determined for the periods including experimental days 0-60, 60-180, 180-300, and 300-365. These time frames are herein defined as the summer (0-60 d), fall (60-180 d), winter (180-300 d), and spring (300-365 d) elimination periods, respectively.

Elimination rate constants for individual PCB congeners were derived from the slopes of the least-squares regression of the PCB concentration data across each of the seasonal elimination periods defined above. Each elimination rate constant was determined on a mass balance basis calculated using PCB congener mass values (ng) derived from multiplying the wet weight PCB congener concentration (ng·g⁻¹ wet wt) by the mass (g) of the fish at the time of sampling. An elimination rate constant was also calculated for the entire experimental duration (0–365 d). Any detectable PCB concentrations measured in control fish were averaged and subtracted from those measured in the dosed individuals at each sampling date. The general elimination rate constant

calculations can be expressed as follows:

$$ln[PCB] = a(t) + b$$
(1)

$$k_2 = |a| \tag{2}$$

Where [PCB] is the PCB congener mass with a and b representing the regression slope coefficient and constants, respectively. The PCB congener elimination rate constant is reported in units per day. PCB congener half-lives $(t_{1/2})$ and times to 95% of steady state $(t_{0.95})$, measured in days, were calculated per eqs 3 and 4, respectively, following first-order rate kinetics.

$$t_{1/2} = \ln(2)/k_2 \tag{3}$$

$$t_{0.95} = \ln\left(\frac{1}{1 - 0.95}\right) / k_2 \tag{4}$$

Average concentrations measured at each sampling event were used to determine elimination rate constants. Congeners were also categorized into metabolized or persistent groups based on their pattern and degree of chlorination. Metabolized PCBs are typified by the absence of chlorine substitution at the meta-para site on at least one of phenyls rings of the congener (23). For persistent PCBs, chlorine substitution is present at either of the 4,4′, 3,4′,5, 3′,4,5′ or 3,3′,5,5′ sites on the phenyl rings. Log K_{ow} values reported for all congeners were from Hawker and Connell (24).

Bioenergetics Model. The yellow perch bioenergetics model developed by Kitchell et al. (1) was used to predict changes in bioenergetic processes including consumption, specific dynamic action, fecal egestion, excretion, respiration, and growth rates $(g \cdot g^{-1} \cdot d^{-1})$ as influenced by the water temperature that yellow perch experienced throughout the course of the experiment. Winberg (25) described the fate of consumed energy into three basic pathways as outlined in eq 5:

$$C = G + R + W \tag{5}$$

where the sum total of consumed energy (C) is allocated toward growth (G), respiration (R), and that lost in waste products (W), specifically fecal (F) and excretory (E) losses. Consumption was modeled as a function of the maximum weight specific consumption rate (C_{\max}) as influenced by water temperature (r_c) and ration (P) (I).

$$C = C_{\text{max}} \times P \times r_c \tag{6}$$

with maximum weight specific consumption rate described by the allometric relation in eq 7.

$$C_{\text{max}} = a_1 B W^{b_1} \tag{7}$$

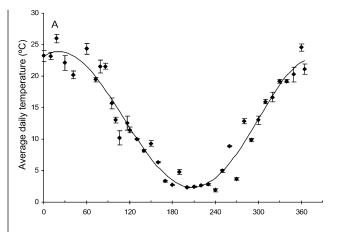
where a_n and b_n represent the intercept and slope, respectively, for maximum consumption or respiration with body weight represented by BW. Respiration rate was modeled similarly as a function of body weight ($R_{\text{max}} = a_2 BW^{b_2}$), activity (A), water temperature (r_R), and specific dynamic action (SDA).

$$R = R_{\text{max}} \cdot A \cdot r_R + SDA \tag{8}$$

An activity multiplier of 1 was used to simulate laboratory determined activity respiration (1) and specific dynamic action was modeled as a constant proportion (0.15) of consumption less energy lost via fecal egestion (26).

Fecal egestion (*F*) and excretory (*E*) losses were modeled as proportions of consumption (*C*) and water temperature (*T*) as described below;

$$F.E = C \cdot \alpha T^{\beta} \cdot e^{\gamma} P \tag{9}$$



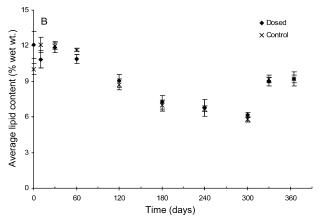


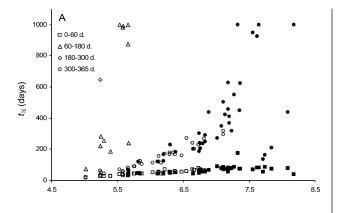
FIGURE 1. (A) Average daily water temperature profile recorded across duration of experiment. Values are arithmetic means of 4 daily readings. Curve represents the best fit polynomial (R^2 = 0.942) for average daily water temperature. (B) Average lipid content of control and dosed fish at time of sampling. Values represent arithmetic means of 5 fish. Error bars in both panels represent \pm 1 SE.

with α , β , and γ representing a separate set of regression constants for the temperature dependence of fecal egestion and excretion and P as outlined above. Growth rates from the bioenergetics calculations were determined by solving eq 5 for growth (G). The maximum and optimum temperatures used for the temperature dependence of each bioenergetic parameter were those described by Kitchell et al. (I) for juvenile yellow perch.

Results and Discussion

Under an annual temperature cycle typical of northern temperature latitudes (Figure 1A), PCB elimination by yellow perch occurred only during the spring and summer months when average daily water temperatures were near or above 20 °C. Elimination rate constants (k_2) calculated for all 72 PCB congeners were highest during the summer elimination period with the corresponding half-lives for both metabolized ($R^2 = 0.887$) and persistent congeners ($R^2 = 0.200$) being positively correlated with chemical log $K_{\rm ow}$ (Figure 2A). Half-lives for persistent PCBs averaged 67 d during this period and were significantly higher than the average half-life of 49 d determined for metabolized congeners after adjustment for the log $K_{\rm ow}$ covariate (P < 0.001). Daily water temperatures averaged 23.2 \pm 0.5 °C and did not change significantly (P = 0.719) across this time period.

During the fall elimination period, water temperature declined significantly ($P \le 0.001$) from 24.4 ± 0.9 to 2.7 ± 0.1 °C. Water temperature averaged 9.5 ± 0.6 °C during the fall and elimination was observed for 11 PCB congeners (PCBs



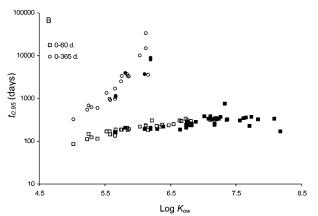


FIGURE 2. (A) PCB congener half-lives $(t_{1/2})$ during the summer (0-60 d), fall (60-180 d), winter (180-300 d), and spring (300-365 d) experimental periods. Half-life values were calculated using the elimination rate constants derived from PCB congener mass data. (B) Times to 95% steady-state concentration values $(t_{0.95})$ for PCB congener mass data. The $t_{0.95}$ values were calculated using the elimination rate constants derived across the summer elimination period (0-60 d) and across the entire study duration (0-365 d) using the PCB congener mass data. Solid and open symbols in both panels represent persistent and metabolized PCB congeners, respectively.

19, 18, 17, 16/32, 24/27, 45, 22, 33/20, 26, 40, 25). PCB halflives during this period ranged from 72 to >1000 d with no elimination of congeners of $\log K_{\text{ow}} > 5.7$ observed. Excluding congeners with half-lives > 1000 d, the average congener halflife during this period was 456 \pm 125 d. No elimination of persistent congeners was observed during the fall period. The coldest water temperature was recorded on day 216 (<0.1 °C) with an average of 5.2 ± 0.4 °C recorded between 180 and 300 d. During the winter period, elimination was observed for PCB 18 only (log $K_{ow} = 5.2$) with a half-life of 645 d. From 300–365 d, water temperatures increased from 13.0 \pm 0.7 to 21.2 ± 0.8 °C and averaged 19.1 ± 0.5 °C across this period. Elimination was observed for 71 of the detectable congeners during the spring and, for metabolized congeners, half-lives were within a factor of 3 for those calculated during the initial 60 d, regardless of chemical log K_{ow} . Half-lives for persistent congeners of log $K_{ow} \le 6.5$ during the spring averaged 3.2 times those calculated for these congeners during the summer period of the study. However, for persistent congeners of log $K_{\text{ow}} > 6.5$, half-lives were on average 9 times longer than the half-life values calculated from summer elimination rates.

When elimination rate constants were calculated across the entire duration of this study, only PCB 19 had a half-life $<100\,$ d (74 d) and the shortest half-life calculated for any persistent PCB congener was $>200\,$ d. A total of 25 congeners displayed elimination over the entire study duration with an average half-life of $>1000\,$ d. Such long half-lives have

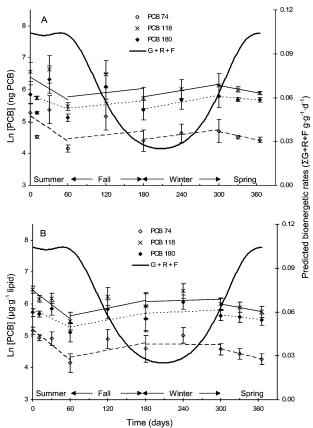


FIGURE 3. (A) Congener mass (mean \pm SE) profiles for PCBs 74 (\diamond), 118 (\times), and 180 (\spadesuit) across summer (0–60 d), fall (60–180 d), winter (180–300 d), and spring (300–365 d) elimination periods. (B) Lipid-normalized PCB concentration (mean \pm SE) profiles for congeners 74 (\diamond), 118 (\times), and 180 (\spadesuit) across summer (0–60 d), fall (60–180 d), winter (180–300 d), and spring (300–365 d) elimination periods. In both panels, dashed, solid, and dotted lines represent best fit linear regressions for PCB congeners 74, 118, and 180, respectively, during each elimination period with the thick curve describing the predicted cumulative sum of the bioenergetic processes of growth (G), respiration (R), and fecal egestion (F).

important considerations for steady-state kinetics. Time frames for 95% steady-state concentrations from elimination rates constants determined for perch at 23 °C during the summer correspond to periods <1 year for these small individuals to achieve 95% steady-state concentrations for all PCBs in this study (Figure 2B). Using the elimination rate constants determined over the entire duration of the study, however, yields 95% times to steady state averaging >12 years, regardless of congener chlorination pattern. These predictions confirm prior observations that the assumption of steady state is often inaccurate of the actual condition with respect to dietary and environmental PCB concentrations (2, 27, 28).

PCB congeners 74, 118, and 180 were chosen to illustrate these changes in elimination patterns and compared to the predicted trend for the combined energetic expenditures of growth, respiration, and fecal egestion across an annual temperature cycle. Half-lives for PCBs 74, 118, and 180 ranged from 44 to 72 d during the first 60 d of the experiment, while (Figure 3A) each of the bioenergetic processes were also predicted to average 99% of their optimum rates during the summer. All of the bioenergetic functions were predicted to decline substantially co-incident with the decrease in water temperature observed after 60 d and each of these processes averaged <55% of their maximum rates during the fall/winter. All of the modeled bioenergetic processes were predicted to reach their lowest rates during the winter with no elimination

of PCBs 74, 118, and 180 observed in this period. As water temperature rose during the final 65 d, all bioenergetic rates were predicted to increase to 99% of maximum by study termination but averaged <90% of optimum during these days with excretion and respiration averaging only 74% and 73% of their respective maximum rates. Elimination of PCBs 74, 118, and 180 was observed during this early spring period but half-lives were higher, at 165, 186, and 448 d, respectively, than calculated during the first 60 d of the experiment in the summer.

Examining the lipid-normalized concentration profiles for these three congeners further demonstrated the significance of the overwinter period on PCB toxicokinetics (Figure 3B). Perch lipid reserves decreased from 10.9% to 7.2% (wet wt) between 60 and 180 d with a further decline to 6.2% observed by 300 d (Figure 1A). Such depletion of lipid reserves is known to increase PCB fugacity in animals (15-17) that result in chemical redistribution within the organism to potentially more sensitive tissues (29, 30). The fugacities of PCBs 74, 118, and 180 were observed to increase during the fall and winter seasons primarily due to lipid loss. However, no loss of chemical mass occurred through this time frame. These results demonstrate that the overwinter period is significant for understanding potential increases in chemical toxicity due to the redistribution of the body burden associated with lipid mobilization.

The PCB elimination rates observed for perch during the summer period were similar to those observed for these chemicals by Fisk et al. (3) in rainbow trout held at 12 °C. However, when reared at 8 °C, PCB half-lives for rainbow trout have been found to be approximately double those reported for the fish held at the higher temperature (9). A half-life range of 79-95 d has been reported for PCB 153 by perch held at 20 °C (4) which compares well with a half-life of 64 d for PCB 153/132 during the initial 60 d of the current study. Rainbow trout are considered a cold water species typically occupying 12-20 °C waters with a preferred temperature of 11 °C (31). Perch, however, are a cool—warm water species inhabiting 20–28 °C waters with a bioenergetic optimum temperature of 23 °C (1, 31, 32). These results not only indicate that different species held close to their respective thermal optima can eliminate PCBs at similar rates, but also that minor changes in these respective preferred temperatures may be sufficient to change chemical elimination rates. Beyond the initial 60 d of this study, however, PCB elimination patterns differed substantially from those expected under controlled laboratory conditions.

The primary mechanisms of chemical elimination include fecal egestion, growth dilution, and loss across respiratory surfaces (33). These elimination routes are all driven by species bioenergetics which, in perch, are closely linked to seasonal temperature cycles (1, 13, 14). The seasonal periods when PCB elimination was observed in this study coincided with the annual period from mid-April to late August, a time frame when fecal egestion, respiration, and growth rates were predicted to be within 15% of their respective maxima. Norstrom et al. (13) predicted similarly that the majority of annual respiration and, consequently, chemical accumulation by Ottawa River yellow perch occurred during the 4-month period from May to September, co-incident with summer maximum temperatures. Lake Erie perch consumption, respiration, and growth rates are also predicted to be maximized during the late spring and summer months (1). Such model predictions suggest that much of chemical bioaccumulation kinetics should occur during this limited annual period when rate processes are maximized. Additionally, although offered a low maintenance ration, minimal feeding by perch was observed at water temperatures ≤10 °C and this species does not typically exhibit growth below this range (34). The lack of PCB elimination during

this period suggests that the bioenergetic processes which are directly related to consumption including growth dilution, fecal egestion, and respiration effectively cease to facilitate chemical elimination at cold temperatures. The elimination observed for the 11 congeners during the fall and winter was likely a combination of metabolism and to a lesser extent some elimination to water via respiration due to low $K_{\rm ow}$. More significantly, the results of the full annual temperature cycle in this study indicate that chemical kinetics track these predicted bioenergetic changes, and that the extrapolation of laboratory-determined rate constants determined in the fall/winter temperature range may vastly underestimate the processes occurring under natural conditions.

Additional factors potentially contributing to PCB elimination include losses due to maternal depuration to eggs (35) and metabolic transformation (9, 33). Spawning and egg release were observed by perch between 300 and 330 d, however, lipid content of egg masses was <1.3% with congener concentrations near detection limits and no corrections were made for egg concentrations. The experimental design did not separate control from dosed fish thus the collected eggs likely represented a composite from both treatment groups. Further, juvenile perch were used in this study and may not have fully sexually matured by study termination. The release of the appropriate hormones during spawning has been demonstrated to deplete adipose triglyceride stores presumably for egg development (36) and, if not sexually mature, this biochemical control may not have occurred. Such physiology may account for the low lipid and PCB content of eggs collected from perch in this study. Halflives for meta-para unsubstituted PCBs were lower than those calculated for persistent type congeners during the summer period indicating potential biotransformation occurred for these more readily cleared congeners. However, over an annual cycle, this difference was minimal in comparison to such seasonal variability and additional research is required to determine the capacity of juvenile perch to metabolize PCBs.

The results of this study demonstrate that the annual cycles and variability in water temperature at northern temperate latitudes have substantial impact on chemical dynamics in aquatic biota, especially so for chemicals of log $K_{\text{ow}} > 6.5$. More importantly, under an annual temperature cycle, chemical half-lives typically exceeded 1000 d and such slow kinetics dictate that extended time frames are expected for organisms to reach steady-state levels with environmental and dietary concentrations of these chemicals, even in young, rapidly growing individuals. Such temperature effects are even more important for persistent type PCBs which tend to have higher potential for biomagnification (3, 9). This also supports the conclusion of Coristine et al. (37) that congener profiles of aquatic biota will change over time with persistent and potentially more toxic congeners, such as coplanar PCBs, becoming an increasing proportion of the body burden over successive cold water periods. For northern temperate latitudes, the fall and winter seasons encompass up to 8 months of the year and much of species metabolism is predicted to occur in the remaining 4 months (1, 13, 14). This study demonstrates that understanding the overwintering kinetics of hydrophobic chemicals will be crucial for determining the processes affecting their food-web biomagnification.

Acknowledgments

We thank Mr. Todd Leadley for use of the facilities at Leadley Environmental Inc. and assistance with fish husbandry and the design, construction, and maintenance of the experimental facilities. Thanks also to Karen Balkwill for completing much of the chemical extraction procedures and to Sarah O'Rourke, Denis Roy, Jocelyn Leney, and J. Mark Cook for

their assistance with the dosing and sampling of animals during the course of the study. Funding for this project was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) and Canada Research Chair awards to G.D.H. Additional funding was also received from NSERC post graduate and University of Windsor tuition scholarships awarded to G.P.

Supporting Information Available

Table of elimination rate constants and half-lives for 72 PCB congeners in yellow perch during temperature cycles; dissolved oxygen profiles measured across duration of PCB elimination experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

- (1) Kitchell, J. F.; Stewart, D. J.; Weininger, D. Applications of a bioenergetics model to yellow perch (*Perca flavescens*) and walleye (*Stizostedion vitreum vitreum*). *J. Fish. Res. Bd. Can.* **1977**, *34*, 1922–1935.
- (2) Niimi, A. J.; Oliver, B. G. Biological half-lives of polychlorinated biphenyl (PCB) congeners in whole fish and muscle of rainbow trout (*Salmo gairdneri*). Can. J. Fish. Aquat. Sci. 1983, 40, 1388– 1394.
- (3) Fisk, A. T.; Norstrom, R. J.; Cymbalisty, C. D.; Muir, D. C. G. Dietary accumulation of hydrophobic organochlorines: bio-accumulation parameters and their relationship with the octanol/water partition coefficient. *Environ. Toxicol. Chem.* 1998, 17, 951–961.
- (4) Dabrowska, H.; Fisher, S. W.; Dabrowski, K.; Staubus, A. E. Dietary uptake efficiency of 2,2',4,4',5,5'-hexachlorobiphenyl in yellow perch and rainbow trout: role of dietary and body lipids. *Environ. Toxicol. Chem.* 1999, 18, 938–945.
- (5) Schaeffer, J. S.; Haas, R. C.; Diana, J. S.; Breck, J. E. Field test of two energetic models for yellow perch. *Trans. Am. Fish. Soc.* 1999, 128, 414–435.
- (6) Niimi, A. J. Biological half-lives of chemicals in fishes. Rev. Environ. Contam. Toxicol. 1987, 99, 1–46.
- (7) Niimi, A. J.; Palazzo, V. Temperature effect on the elimination of pentachlorobiphenyl, hexachlorobenzene, and mirex by rainbow trout (Salmo gairdneri). Water Res. 1985, 19, 205–207.
- (8) Jimenez, B. D., Cirmo, C. P.; McCarthy, J. F. Effects of feeding and temperature on uptake, elimination and metabolism of benzo(a)pyrene in the bluegill sunfish (*Lepomis macrochirus*). *Aquat. Toxicol.* **1987**, *10*, 41–57.
- (9) Buckman, A. H.; Brown, S. B.; Hoekstra, P. F.; Solomon, K. R.; Fisk, A. T. Toxicokinetics of three polychlorinated biphenyl technical mixtures in rainbow trout (*Oncorynchus mykiss*). *Environ. Toxicol. Chem.* 2004, 23, 1725–1736.
- (10) Spigarelli, S. A.; Thommes, M. M.; Prepejchal, W. Thermal and metabolic factors affecting PCB uptake by adult brown trout. *Environ. Sci. Technol.* **1983**, *17*, 88–94.
- (11) Griffiths, J. S. Effects of acclimation and abrupt temperature changes on the sustained swimming capacity and metabolism of brown trout *Salmo trutta* (Linneaus) and bluegill, *Lepomis macrochirus* (Rafinesque). Ph.D. Thesis, University of Toronto, Toronto, ON, 1977.
- (12) Roy, D.; Haffner, G. D.; Brandt, S. B. Estimating fish production potentials using a temporally explicit model. *Ecol. Model.* 2004, 173, 241–257.
- (13) Norstrom, R. J.; McKinnon, A. E.; De, Freitas, A. S. W. A bioenergetics based model for pollutant accumulation by fish. Simulation of PCB and methylmercury residue levels in Ottawa River yellow perch (*Perca flavescens*). J. Fish. Res. Bd. Can. 1976, 33, 248–267.
- (14) Henderson, B. A.; Trivedi, T.; Collins, N. Annual cycle of energy allocation to growth and reproduction of yellow perch. J. Fish. Biol. 2000, 57, 122–133.
- (15) Polischuk, S. C.; Letcher, R. J.; Norstrom, R. J.; Ramsay, M. A. Preliminary results of fasting on the kinetics of organochlorines in polar bears. Sci. Tot. Environ. 1995, 160/161, 465–472.
- (16) DeBruyn, A. M. H.; Ikonomou, M. G.; Gobas, F. A. P. C. Magnification and toxicity of PCBs, PCDDs, and PCDFs in upriver-migrating Pacific salmon. *Environ. Sci. Technol.* 2004, 38, 6217–6224.
- (17) Leney, J. L.; Drouillard, K. G.; Haffner, G. D. Does metamorphosis increase the susceptibility of frogs to highly hydrophobic contaminants? *Environ. Sci. Technol.* 2006, 40, 1491–1496.

- (18) Scott, W. B., Crossman, E. J. Freshwater Fishes of Canada; Bulletin No. 184; Fisheries Research Board of Canada: Ottawa, ON, 1973.
- (19) Drouillard, K. G.; Fernie, K. J.; Smits, J. E.; Bortolotti, G. R.; Bird, D. M.; Norstrom, R. J. Bioaccumulation and toxicokinetics of 42 polychlorinated biphenyl congeners in American kestrels (Falco sparverius). Environ. Toxicol. Chem. 2001, 20, 2514–2522
- (20) Lazar, R.; Edwards, R. C.; Metcalfe, C. D.; Gobas, F. A. P. C.; Haffner, G. D. A simple, novel method for the quantitative analysis of coplanar (non-ortho substituted) polychlorinated biphenyls in environmental samples. *Chemosphere* 1992, 25, 493–504.
- (21) O'Rourke, S.; Drouillard, K. G.; Haffner, G. D. Determination of laboratory and field elimination rates of polychlorinated biphenyls (PCBs) in the freshwater mussel, *Elliptio complanata*. *Arch. Environ. Contam. Toxicol.* **2004**, *47*, 74–83.
- (22) Wilkinson, L. SYSTAT for windows: Statistics, v. 8.0; SPSS Inc.: Chicago, IL, 1998.
- (23) Boon, J. P.; Eijgenraam, F.; Everaarts, J. M.; Duinker, J. C. A structure-activity relationship (SAR) approach towards metabolism of PCBs in marine animals from different trophic levels. *Mar. Environ. Res.* **1989**, *27*, 159–176.
- (24) Hawker, D. W.; Connell, D. W. Octanol—water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* **1988**, *22*, 382–387.
- (25) Winberg, G. G. Rate of metabolism and food requirements of fishes; Fisheries Research Board of Canada Translation Series No. 194; Ottawa, ON, 1954.
- (26) Hewett, S. W.; Johnson, B. L. *A generalized bioenergetics model offish growth for microcomputers*, v 2.0; University of Wisconsin Sea Grant Institute: Madison, WI, 1992.
- (27) DeLorme, P. D.; Muir, D. C. G.; Lockhart, W. L.; Mills, K. H.; Ward, F. J. Depuration of toxaphene in lake trout and white suckers in a natural ecosystem following a single I.P. dose. *Chemosphere* **1994**, *27*, 1965–1973.
- (28) de Boer, J.; van de Valk, F.; Kerkhoff, M. A. F.; Hagel, P. 8-year study on the elimination of PCBs and other organochlorines in eel (*Anguilla anguilla*) under natural conditions. *Environ. Sci. Technol.* **1994**, *28*, 2242–2248.
- (29) de Freitas, A. S.; Norstrom, R. J. Turnover and metabolism of polychlorinated biphenyls in relation to their chemical structure and the movement of lipids in the pigeon. *Can. J. Physiol. Pharmacol.* **1974**, *52*, 1081–1094.
- (30) Jorgensen, E. H.; Vijayan, M. M.; Killie, J. E. A.; Aluru, N.; Aas-Hansen, O.; Maule, A. Toxicokinetics and effects of PCBs in Arctic fish: a review of studies on Arctic charr. *J. Toxicol. Env. Health Part A* **2006**, 69, 37–52.
- (31) Coker, G. A.; Portt, C. B.; Minns, C. K. *Morphological and ecological characteristics of Canadian freshwater fishes*; Canadian manuscript report of fisheries and aquatic sciences 2554; Ottawa, ON, 2001.
- (32) Hokanson, K. E. F. Temperature requirements of some percids and adaptations to the seasonal temperature cycle. *J. Fish. Res. Bd. Can.* **1977**, *34*, 1524–1550.
- (33) Clark, K. E.; Gobas, F. A. P. C.; Mackay, D. Model of organic chemical uptake and clearance by fish from food and water. *Environ. Sci. Technol.* **1990**, *24*, 1203–1213.
- (34) Malison, J. A. A white paper on the status and needs of yellow perch aquaculture in the north central region; University of Wisconsin: Madison, WI, 2000.
- (35) Russell, R. W.; Gobas, F. A. P. C.; Haffner, G. D. Maternal transfer and in ovo exposure of organochlorines: a model and field verification. *Environ. Sci. Technol.* 1999, 33, 416-420.
- (36) Takashima, F.; Hibiya, T.; Ngan, P.; Aida, K. Endocrinological studies on lipid metabolism in rainbow trout: II, effects of sex steroids, thyroid powder and adrenocorticotropin on plasma lipid content. *Bull. Japan Soc. Sci. Fish.* 1972, 38, 43–49.
- (37) Coristine, S.; Haffner, G. D.; Ciborowski, J. J. H., Lazar, R.; Nanni, M. E.; Metcalfe, C. D. Elimination rates of selected di-ortho, mono-ortho, and non-ortho substituted polychlorinated biphenyls in rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* 1996, 15, 1382–1387.

Received for review February 7, 2006. Revised manuscript received October 30, 2006. Accepted November 3, 2006.

ES060266R