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TESTS OF BIOACCUMULATION MODELS FOR POLYCHLORINATED BIPHENYL COMPOUNDS: A STUDY OF YOUNG-OF-THE-YEAR BLUEFISH IN THE HUDSON RIVER ESTUARY, USA

LAWRENCE A. LEBLANC,*† JEFFREY A. BUCKEL,‡ DAVID O. CONOVER,§ and BRUCE J. BROWNAWELL§
†School of Marine Sciences, University of Maine, 5741 Libby Hall, Orono, Maine 04469-5741, USA
‡Center for Marine Science and Technology, Department of Zoology, North Carolina State University, 303 College Circle, Morehead City, North Carolina 28557, USA
§Marine Sciences Research Center, State University of New York at Stony Brook, Stony Brook, New York 11794-5000, USA

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Abstract—A field-based study regarding uptake of polychlorinated biphenyl compounds (PCBs) by young-of-the-year (YOY) bluefish (*Pomatomus saltatrix*) was initiated to test a steady-state model of bioaccumulation and trophic transfer in a rapidly growing fish. Determination of prey composition as well as size-dependent growth and specific consumption rates for YOY bluefish from separate field and laboratory studies enabled the input of these species-specific parameters into the model. Furthermore, the time and duration of the exposure of YOY bluefish to dissolved PCBs from a well-characterized system (Hudson River, USA) was well known. Patterns of accumulation of individual PCB congeners differed relative to the accumulation of total PCBs, with the greatest net accumulation occurring for the higher-molecular-weight congeners. Comparison of lipid-normalized bioaccumulation factors (BAFs) with the octanol–water partition coefficients of individual PCB congeners revealed bluefish to be above the BAFs predicted by lipid-based equilibrium partitioning, suggesting that uptake from food is an important source of PCBs in YOY bluefish. Comparison of measured BAFs with values predicted by a steady-state, food-chain model showed good first-order agreement.

Keywords—Polychlorinated biphenyls Bluefish Hudson River Bioaccumulation modeling Trophic transfer

INTRODUCTION

Much laboratory and field work has been conducted regarding the uptake and depuration of polychlorinated biphenyl compounds (PCBs) and other hydrophobic organic contaminants by a wide variety of species (for review, see Connell [1]). Hydrophobic organic contaminants can be taken up from water as well as from ingested food [2,3]. Various steady-state and kinetic descriptions have been proposed to model organism body burden as a function of exposure regime (i.e., concentrations in water and food) and mechanisms of uptake. A recent article by Arnot and Gobas [4] provides an excellent synopsis of the history and development of bioaccumulation models. For predictive purposes in a nonsteady-state system (e.g., in migratory fish), it becomes essential to understand the mechanisms and routes of PCB uptake. The Hudson River (USA) has received a substantial loading of PCBs in past years, and it continues to receive reduced levels of PCB inputs, which has resulted in the accumulation of PCBs in the aquatic food web [5–8]. A steady-state model developed by Thomann [9,10] and applied to the Hudson River [7] provides a framework with which to evaluate important factors affecting the uptake of hydrophobic organic contaminants from water and trophic transfer of these contaminants in a nonsteady-state or pseudosteady-state system.

A field-based study of PCB uptake in young-of-the-year (YOY) bluefish (*Pomatomus saltatrix*) was initiated as a test of the Thomann steady-state bioaccumulation model with a rapidly growing fish in a well-studied system [11] (http://www.hudsonriver.org/). Exposure concentrations in waters and sediments of the Hudson River estuary, especially for dissolved water concentrations, have been characterized by a number of studies [5]. Unique to the present study was that the time and duration of exposure of these YOY fish to dissolved PCB concentrations was well known, based on published studies of YOY fish of this species in the Hudson River estuary [12–15]. Also, composition of prey species as well as weight-specific growth and consumption rates had been determined for these YOY bluefish [15,16]. Data from the aforementioned study provided more direct measures than typically are available when calibrating bioaccumulation models and useful tests for the effects of growth and consumption rate, both of which are extremely high in YOY bluefish [17–19].

Partitioning models

Models that predict fish body burdens of hydrophobic organic compounds either assume equilibrium partitioning between the water column and the organism or account for uptake and elimination kinetics of exchange between the organism and the external environment.

The simplest models of hydrophobic organic contaminant uptake by organisms are equilibrium partitioning models, which assume that a compound partitions between the environment (water column or sediment) and the lipids of the organism. The partitioning of an organic compound into an organism can be predicted by the degree of lipophilicity of the chemical compound, which often is measured by its octanol–water partition coefficient (K_{ow}) [20–23]. The degree to which the partitioning of an organic chemical approaches an equilibrium condition can be investigated in open systems (i.e., the environment) by calculating bioaccumulation factors (BAFs) and bioconcentration factors (BCFs). The BAF is de-

* To whom correspondence may be addressed (lawrence.leblanc@umit.maine.edu).

fined by several authors (see, e.g., [2,10]) as the ratio of the chemical tissue concentration because of uptake from both water and food routes (μg/kg lipid wt) to the water column concentration (μg/L). When exposure results solely from water, this ratio is called the BCF. These coefficients assume a steady-state, but not necessarily an equilibrium, condition. Normalizing the BAF or BCF to lipid weight assumes that different species of organisms with similar lipid composition in different environments can be compared for their potential to accumulate nonionic hydrophobic organic compounds.

Results from field studies have produced measured BAFs that exceed those predicted by equilibrium partitioning models [2,10]. Those authors have concluded that uptake from food (trophic transfer) accounts for the elevated tissue concentrations. Extensive work by Gobas et al. (see, e.g., [24–26]) and others [27,28] elucidated mechanisms of dietary uptake and elimination and quantified their relative importance in models of laboratory and field-based exposures.

Thomann food-chain model

Models developed by Thomann and Connolly [29] and by Thomann [9,10] account for uptake from water as well as from food. These models take into account the position of an organism in the food chain by allowing a predator at level i to feed on prey, which are at level $i - 1$. Important physiological parameters, such as growth rate (G_i, kg lipid/d), food consumption rate ($C_{i,i-1}$, kg lipid prey/kg lipid predator/d), chemical assimilation efficiency (α, μg chemical absorbed/μg chemical ingested), chemical uptake rate (k_u, L/d/kg wet wt), and chemical excretion rate (K_i, μg/d) are either measured or estimated from literature values. Models with these parameters have been applied in the Great Lakes (USA) [29], New Bedford Harbor (USA) [30], and the Hudson River (USA) [7,31]. The general predictive equation for the model at steady state is

$$\mathrm{BAF} = \frac{k_u}{K_i + G_i} + \frac{\alpha_{i,i-1} \cdot C_{i,i-1}}{K_i + G_i} \cdot \frac{v_{i-1}}{c} \quad (1)$$

where v_{i-1} is the lipid-normalized chemical concentration in the prey species (μg/kg lipid) and c is the chemical concentration in the water to which the prey species is exposed (μg/L). The term v_{i-1}/c is the BCF of the prey (L/kg lipid).

How these terms are estimated is presented in Table 1. The first term on the right side of Equation 1 is the contribution from water to the whole-body concentration, and the second term represents the contribution from the diet. Given the extremely rapid growth rates and consumption rates mentioned previously, YOY bluefish should provide a sensitive test for some of the parameters in the Thomann model.

Table 1. Description of parameters used in the steady-state bioaccumulation model

k_u = uptake rate [(L/d)/kg wet wt]

$k_u = 10^3(w^{-g}/p)E$,

where g is a respiration parameter ($g = 0.2$), p = the % lipid fraction, and w = wet weight (in grams).

E, an estimate of efficiency of transfer across gill surfaces, varies with log K_{ow} and is based on laboratory-based exposure studies as follows:

$\log E = -2.6 + 0.5 \log K_{ow}$, for $\log K_{ow}$ = 2–5
$E = 0.8$, for $\log K_{ow}$ = 5–6
$\log E = 2.9 - 0.5 \log K_{ow}$, for $\log K_{ow}$ = 6–10.

K = chemical excretion rate (d^{-1}), calculated from model $K = k_u/K_{ow}$ (Source: Thomann [10])

α = chemical assimilation efficiency (μg chemical absorbed/μg chemical ingested):

Two estimates:

1) α is fixed at a value of 0.5
2) α varies with log K_{ow}

For Cl-2 homologues: α = 0.71
For Cl-3 homologues: α = 0.8
For Cl-4 homologues: α = 0.8
For Cl-5 homologues: α = 0.63
For Cl-6+ homologues: α = 0.35

(Source: Thomann [10])

$C'_{i,i-1}$ = weight specific consumption rate [kg(w) of prey/kg(w) predator/d]

where w = wet weight (in kg)

(Source: Consumption rates derived from field data [14])

$C_{i,i-1}$ = weight specific consumption rate [kg(lipid) of prey/kg(lipid) predator/d]

$C_{i,i-1} = C'_{i,i-1} \cdot [(p_{i-1}/p_i)]$

G = weight specific growth rate (d^{-1})

(Source: Growth rates derived from field data [14])

G_i is the growth rate of the lipid fraction. Because lipids are reasonably constant during this growing season, growth rates on a wet weight basis were used.

MATERIALS AND METHODS

Acetone, hexane, and methylene chloride were from Burdick and Jackson (pesticide-residue grade; Muskegon, MI, USA). Analytical standards used for surrogate and injection standards, as well as the PCB Aroclor standards, were purchased from Ultra Scientific (North Kingson, RI, USA). Florisil (60/100 mesh) was purchased from Supelco (Bellefonte, PA, USA), and alumina (100–200 mesh) and silica gel (100–200 mesh) were from Bio-Rad Laboratories (Richmond, CA, USA).

Field collection

Collections of YOY bluefish were made with 30- and 60-m beach seine nets at several sites in the Hudson River during the late spring to early fall of 1993 (Fig. 1). Samples were wrapped in solvent-rinsed aluminum foil, placed on dry ice, and transported back to the laboratory, where they were stored frozen at −20°C until analysis.

Water was sampled at several locations on five cruises along the Hudson River estuary from 1991 to 1993 [32]. Four samples collected in Haverstraw Bay from these cruises, along with two samples collected off Croton Point in Haverstraw Bay, during August 1993 were used to calculate mean dissolved PCB concentrations. Whole water was sampled with a solvent-rinsed, 22-L, glass separatory funnel affixed in a weighted aluminum cage or, at Croton Point, with a stainless-steel pressure cylinder. On board the ship, samples were filtered under positive pressure, using high-purity nitrogen, through a glass-fiber filter (14.2 cm, grade GF/F; Whatman International, Maidstone, UK) placed in a stainless-steel filter housing (Millipore, Bedford MA, USA). The filtered water was collected in 4-L, amber-glass bottles, each containing 100 ml of methylene chloride.

Sample preparation

Whole-body samples of bluefish (two to three individuals/sample) were homogenized, after removal of the stomachs, using a Kinematica polytron (Brinkmann Instruments, Westburg, NY, USA) or a Virtis homogenizer (Virtis, Boston, MA,

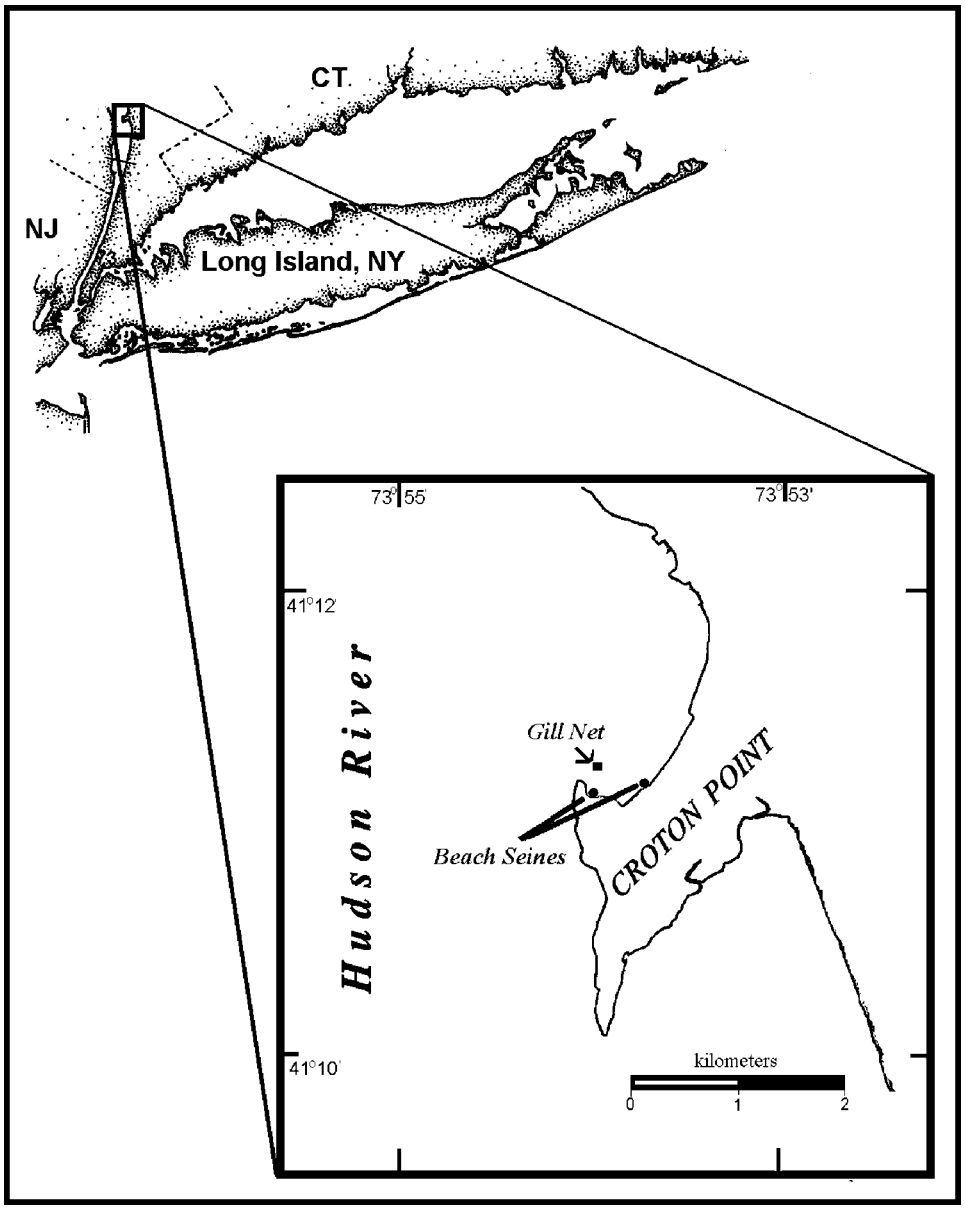

Fig. 1. Location of Croton Point in the Hudson River estuary (USA) along with the position of the gill nets and beach seines used for bluefish and prey collections. NJ = New Jersey; CT = Connecticut; NY = New York. Map reprinted from Buckel and Conover [14].

USA). Prey species also were homogenized in this manner (with stomachs intact). Before homogenization, total length, fork length, and wet weight were measured for each individual.

Polychlorinated biphenyl congeners 29 (2,4,5-trichlorobiphenyl) and 143 (2,2′,3,4,5,6′-hexachlorobiphenyl) were added as surrogate standards at the beginning of the extraction procedures. Approximately 4 g wet weight of homogenate was extracted three times with 25 ml of acetone in 50-ml Corex centrifuge tubes (Fisher Scientific, Pittsburgh, PA, USA). Each sample was homogenized with three 1-min blendings. Extracts were decanted into a 1,000-ml separatory funnel containing 500 ml of NaCl-saturated, pre-extracted, deionized water and then extracted three times with 50 ml of hexane. The hexane extracts were combined and reduced in volume to 10 ml. Two milliliters were removed from each extract for determination of lipid weight, and the rest was reduced in volume to 1 ml for open-column chromatography.

Interfering lipids were removed from tissue extracts by pas-

Table 2. Instrumental conditions for polychlorinated biphenyl analysis

Injection port temperature	375°C
Detector temperature	375°C
Column flow rate	3 ml/min
Carrier gas	Hydrogen
Analytical column	J & W DB-5[a] capillary column (length, 30 m; internal diameter, 37 mm; film thickness, 25 μm)
Temperature program	40°C for 2 min, ramp to 120°C at 30°C/min, then ramp from 120 to 240°C at 2°C/min, and hold for 10 min

[a] J & W DB-5 is a brand name that refers to the column phase; in this instance, it is for a 5% phenyl-methyl polysiloxane.

Table 3. Parameter values used for the Thomann model

Sample date (1993)	Growth rate, G_i (d^{-1})	Excretion rate, K_i (d^{-1})[a]	Consumption rate, $C_{i,i-1}$ (d^{-1})	C:G ratio	Chemical uptake rate, k_u (L/d/kg)	Log prey BCF[b]
June 30	0.032	0.017	0.095	3.0	26570	6.6
August 4	0.045	0.018	0.208	4.6	28324	6.5
Sept 11	0.026	0.006	0.039	1.5	9447	6.4

[a] For congener 70, log K_{ow} = 6.2.
[b] BCF = lipid-normalized bioconcentration factor; for log K_{ow} = 6.2. For bioaccumulation factor calculations plotted in Figure 6, α is fixed at 0.5.

Table 4. Mean dissolved polychlorinated biphenyl congener concentrations from Haverstraw Bay (USA)

Congener no.[a]	Log K_{ow}[b]	Concentration (ng/L)	RSD[c] (%)
10/4[d]	4.84	0.09	89.1
9/7	5.06	0.02	143.0
8/5	5.07	0.04	59.9
19/14	5.02	0.07	57.5
18	5.24	1.10	35.2
15/17	5.30	6.13	42.5
24	5.35	0.11	60.2
16/32	5.16	0.28	117.2
26	5.66	0.11	29.9
28/31	5.67	1.76	39.9
33/21/53	5.60	0.15	64.1
22	5.58	0.30	39.0
52	5.84	0.64	36.7
49	5.85	1.11	28.3
47	5.85	0.31	28.5
44	5.75	0.78	52.8
37/42	5.83	0.24	26.8
64/41	5.95	0.44	26.7
40	5.66	0.20	65.0
70	6.20	0.13	32.4
66/95	6.20	0.34	31.1
92/84	6.35	0.25	39.7
101	6.38	0.66	61.9
99	6.39	0.17	54.4
86/97	6.23	0.22	71.8
87	6.29	0.30	78.5
110/77	6.36	1.32	54.1
151/82	6.64	0.11	81.9
149	6.67	0.17	87.5
118	6.74	0.32	79.2
114	6.65	0.04	123.5
153/132/105	6.92	0.47	79.1
141	6.82	0.08	86.4
138	6.83	0.24	70.5
182/187	7.20	0.07	105.5
174	7.11	0.03	105.0
156	7.18	0.01	165.6
201	7.62	0	0
180	7.36	0.05	102.4
170	7.27	0.12	95.3
199	7.20	0.004	126.0
196/203	7.65	0.004	116.8
208/195	7.71	0.002	139.2
194	7.80	0.001	154.9
206	8.09	0.001	155.4
209	8.18	0.007	134.3

[a] Congener naming convention after Ballschmitter and Zell [37].
[b] Log K_{ow} = log of the octanol–water partition coefficient. Hawker et al. [38].
[c] RSD = relative standard deviation.
[d] Multiple congeners that coelute on the gas chromatography column were summed as one concentration.

sage of the extract through a 10-cm column consisting of 5 g of 5% water-deactivated florisil topped with 2 g of 5% deactivated alumina. The PCB-containing fraction was eluted from the column with 50 ml of hexane and then reduced to from 1 to 2 ml for instrumental analysis. Octachloronaphthalene was added as an internal standard immediately before instrumental analysis.

Water samples were extracted in 4-L separatory funnels using the method described in Achman et al. [32]. Extracts were passed through a column consisting of 7 g of 5% deactivated silica gel (100–200 mesh; Bio-Rad Laboratories). Polychlorinated biphenyl congeners 29 and 143 were added as surrogate standards, and octachloronaphthalene was added as an internal standard, as described above.

Instrumental analysis

Samples were injected onto a Hewlett-Packard 5890A gas chromatograph (Hewlett-Packard now Agilent Technologies, Palo Alto, CA, USA) with a DB-5 fused silica capillary column (length, 30 m; inner diameter, 0.25 mm; film thickness, 0.25 μM; J&W Scientific, Cupertino, CA, USA) and an electron-capture detector (Agilent Technologies). Instrumental conditions and temperature programming are listed in Table 2. Samples were quantified as total PCBs based on a 1:1:1 mixture of three Aroclor standards (Aroclors 1242, 1254, and 1260) as described by Brownawell and Farrington [33] and on a congener-specific basis. Quantitation was based on the surrogate standards, PCB congeners 29 and 143, using peak areas. Recoveries of the surrogate standards were quantified based on the octachloronaphthalene internal standard. Relative response factors of individual congeners were determined using congener mixes obtained from the National Research Council of Canada (Ottawa, ON).

Recoveries of surrogate standards were between 75 and 100%, with a mean recovery (standard deviation) of 84.5% ± 8.3%. Blank concentrations of total PCBs (normalized to mean homogenate wet wt) ranged from 18.3 to 29.9 ng/g and never exceeded 3% of sample values.

Model parameters

Table 1 lists the sources of the parameters used in the Thomann model. The actual values used in the model calculations for these parameters are listed in Table 3. Growth rates and consumption rates were determined from field collections during the spring and summer seasons of 1993 in the Hudson River [14,15] at the same times and from the same population of fish collected for PCB analysis. Mean dissolved concentrations (Table 4), body burden concentrations of PCBs, and lipid weights of predator and prey (Table 5) were determined by the methods described above. The uptake rate, k_u, was estimated according to the method described by Thomann [10],

Table 5. Total polychlorinated biphenyls (PCBs; ng/g wet wt) for young-of-the-year bluefish and prey species homogenates collected at Croton Point (Hudson River, USA)[a]

Young-of-the-year bluefish					
Collection date (1993)	No. of individuals	Mean wet wt. (g)	Lipid wt. (% wet)	PCB concn. (ng/g wet wt)	PCB concn. (ng/g lipid wt)
June 30	4	3.05	1.9	1,160	61,100
July 28	2	30.6	1.5	1,280	85,300
August 4	3	10.2	1.4	1,090	77,900
August 11	3	17.2	1.4	1,870	134,000
August 24	3	29.4	1.3	1,090	83,800
September 11	3	39.6	3.2	1,060	33,100

Prey species						
Collection date/prey species	No. of individuals	Mean wet wt. (g)	Bluefish diet composition (%)	Lipid wt. (% wet)	PCB concn. (ng/g wet wt)	PCB concn (ng/g lipid wt)
June 30						
Morone saxatilis	25	0.13	72	1.8	1,360	75,600
August 4						
Morone saxatilis	4	4	52	2.4	1,530	63,800
Menidia menidia	3	2.36	4	1.2	825	68,800
Anchoa mitchilli	40	0.29	34	1.7	443	26,100
September 11						
Morone saxatilis	2	9.72	21	1.6	796	49,800
Menidia menidia	2	2.55	55	3	1,050	35,000
Anchoa mitchilli	7	0.74	9	1.4	968	69,100

[a] Congener-specific data are available upon request from the corresponding author.

in which uptake was based on body size and uptake efficiencies were a function of log K_{ow} based on experimental data (Table 1). Chemical assimilation efficiencies (α) were based on two estimates. The first was a constant value (0.5), and the second varied with PCB homologue hydrophobicity [7,10]. Model calculations of BAF were made for three dates: June 30, August 4, and September 11, when both bluefish and prey were caught simultaneously. The three prey species analyzed were striped bass (*Morone saxatilis*), bay anchovy (*Anchoa mitchilli*), and Atlantic silverside (*Menidia menidia*). For the August and September dates, weighted mean concentrations of all three species were based on the diet composition determined for each date by stomach content analysis [14]. For the June sample, the PCB concentration in striped bass, which represented 72% of the known diet on this date, was used (Table 5).

RESULTS

Aqueous concentrations of PCB congeners ranged from 0.001 to 6.1 ng/L, with higher concentration and better agreement between replicates for the trichlorobiphenyl (Cl-3) through the hexachlorobiphenyl (Cl-6) compounds (Table 4). Lower concentrations and higher variability was seen for hepta- and octochlorinated biphenyl compounds.

The concentration of total PCBs in the bluefish over the summer was surprisingly constant, despite large differences in body size. Total PCBs in the prey species were more variable (Table 5). Representative whole-body congener concentrations (ng/g lipid) plotted as a function of time and normalized to the first sampling date (time 0) are shown in Figure 2. Because of weekly sampling, the first sampling date represented a residence time of no greater than 7 d for these fish. Differences in the pattern of accumulation between homologue groups can be seen when plotted in this manner, with the greatest net accumulation occurring with the most highly chlorinated congeners. Lower-molecular-weight congeners (e.g., Cl-3) clearly did not accumulate, and higher-molecular-weight congeners (e.g., Cl-6 and Cl-8) went through a maximum before returning to the original concentrations. Total PCBs in the prey species over time were different than those for bluefish. Both striped bass and silversides had net decreases of total PCBs on a lipid-weight basis over time, whereas bay anchovy had a net increase (Table 5).

In Figure 3, log BAF versus log K_{ow} is plotted for 30 PCB congeners for the June 30, August 4, and September 11 collection dates. The solid line in these graphs is the best-fit line through the data, whereas the dashed line is the theoretical prediction based on equilibrium partitioning between a model lipid (triolein) and water derived by Chiou [22], which has the equation log BCF = 0.893(log K_{ow}) + 0.607. Regression parameters of the best-fit lines for bluefish and prey species for all collection dates are listed in Table 6. During June, congeners with a log K_{ow} value of 6.5 or less were above the equilibrium prediction, whereas those congeners with a log K_{ow} value of between 6.5 to 8 fell on or close to the line. During the month of August, PCB levels in YOY bluefish were consistently above the equilibrium predictions. By September, BAFs were very close to the equilibrium predictions (Fig. 3). With the exception of the September date, bluefish were above equilibrium at log K_{ow} = 6 by 0.5 log units. Prey species showed significant variability and generally were above the equilibrium predictions (Table 6).

The ratios of lipid-normalized bluefish concentration to mean weighted lipid-normalized concentration of prey (based on diet composition) reached a maximum at log K_{ow} values of 6 to 6.5 and then decreased for the June and August sampling dates (Fig. 4). For the September date, much variability was

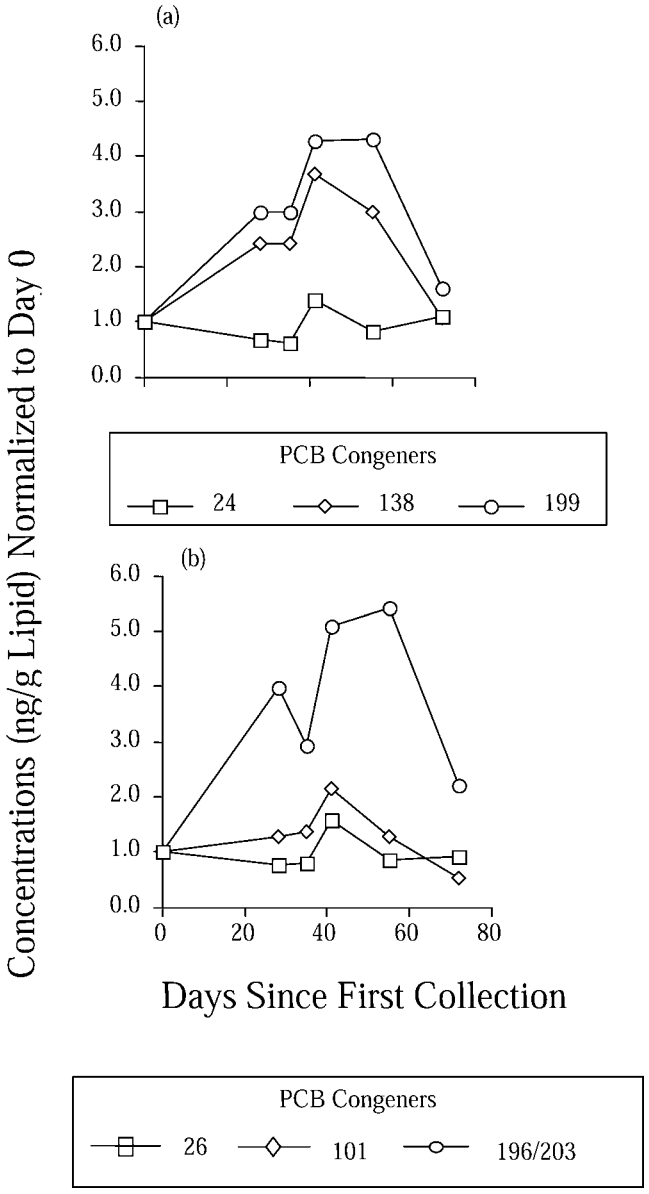

Fig. 2. Accumulation patterns of selected biphenyl congeners in young-of-the-year (YOY) bluefish over time. Concentrations are on a lipid-weight basis (ng/g lipid) and are normalized to the first collection date (June 30, 1993). Polychlorinated biphenyl congeners are identified according to the naming conventions of Ballschmitter and Zell [37] and the International Union of Pure and Applied Chemistry (IUPAC): (**a**) trichloro (24), hexachloro (138), and octachloro (199) biphenyl congeners; (**b**) trichloro (26), pentachloro (101), and octachloro (196/203) biphenyl congeners.

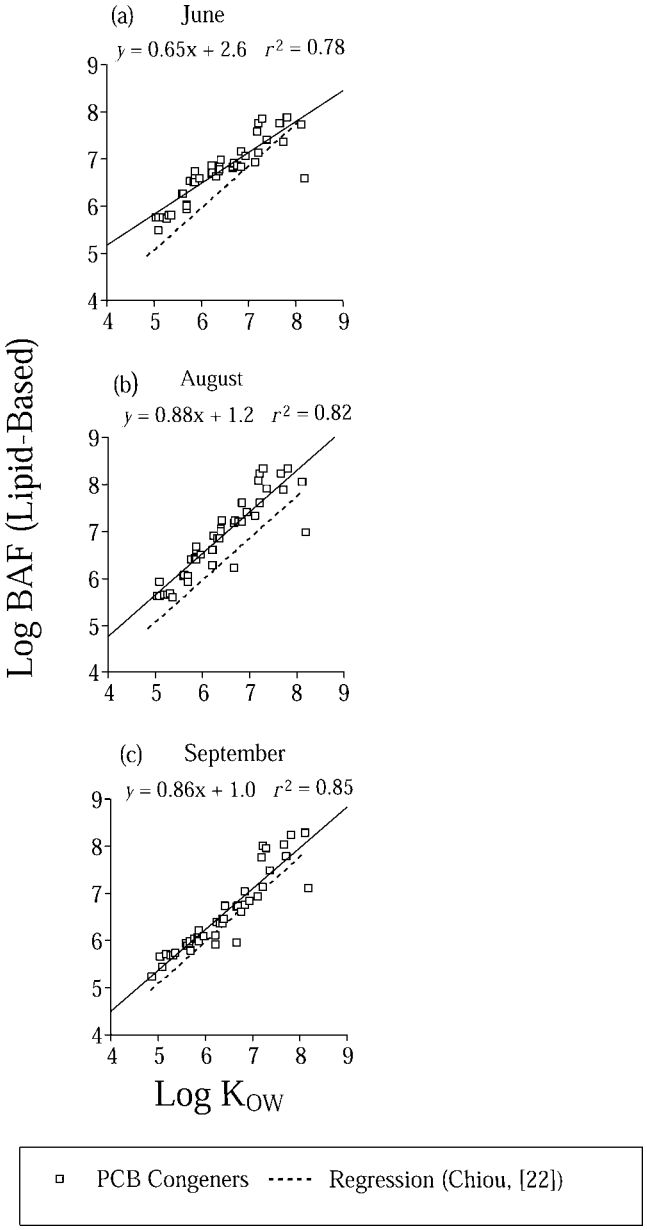

Fig. 3. Plots of the log lipid-based bioaccumulation factor (BAF) versus the log octanol–water partition coefficient (log K_{ow}) for several polychlorinated biphenyl (PCB) congeners: (**a**) June 30 sample; (**b**) August 4 sample; and (**c**) September 11 sample. Superimposed is the best-fit line through all points (solid line), the equation, and the r^2 value of the regression. Also plotted is the theoretical line of Chiou [22] (dashed line; also described in the text). Values of log K_{ow} are from Hawker and Connell [38]. BAF = organism concentration (ng/g lipid wt)/water concentration (ng/L).

found in this ratio, and whereas the ratio values were within the range of the other two graphs, no consistent trend was seen.

In Figure 5, model results are compared with the actual measurements of BAF for the three dates when bluefish and prey were available. Parameters used in the model were as described in Table 1, and a fixed chemical assimilation efficiency (α) of 0.5 was used. Model predictions of BAF matched the measured values fairly well for the June and August sampling dates, as opposed to the equilibrium partitioning predictions (dashed line), which underpredicted the data. The data were above (by at least one log unit) the model predictions of uptake from water only (model BCF). In September, the data were above the model BAF predictions by approximately 0.5 log units.

DISCUSSION

Large differences were seen between accumulation patterns of individual congeners over time compared to the sum of the total PCBs. Although the total PCB concentrations varied by less than a factor of two over the entire study, individual PCB congeners varied by as much as a factor of 12 on a lipid-weight basis (data not shown). These differences were heightened on the last date, when bluefish lipid weight increased. The trichloro (Cl-3) congeners appeared to come into equilib-

Table 6. Regression parameters for log bioaccumulation factors (BAF) for bluefish and prey species

Species	Collection date	Slope	Intercept	r^2	Offset[a] (log K_{ow} = 6)
Pomatomus saltatrix	6/30/93	0.62	2.76	0.76	0.49
	7/28/93	1.02	0.38	0.9	0.54
	8/4/93	0.85	1.42	0.81	0.55
	8/11/93	0.93	1.17	0.88	0.76
	8/24/93	1.08	0.03	0.92	0.56
	9/11/95	0.83	1.25	0.85	0.25
Morone saxatilis	6/30/93	0.55	3.37	0.75	0.71
	8/4/93	0.73	2.17	0.81	0.61
	9/11/93	0.87	1.19	0.84	0.44
Menidia menidia	8/4/93	0.72	2.24	0.82	0.61
	9/11/93	0.77	1.60	0.86	0.28
Anchoa mitchilli	8/4/93	0.73	1.74	0.84	0.17
	9/11/93	0.79	1.78	0.86	0.56

[a] Offset = log BAF measured (linear regression of log BAF vs log K_{ow}) − log BAF regression [22].

rium with this increasing lipid pool, whereas higher-chlorinated congeners (Cl-6 and Cl-8) appeared to decrease, which is consistent with a longer equilibration time for these congeners and an apparent dilution effect as the lipid pool in the fish increased (Fig. 2).

Clear differences were observed between prey species in terms of the accumulation of PCB congeners (Table 5). These differences, which may be caused by differences in physiology and lifestyle, indicate the importance of accurately characterizing the prey composition and PCB concentration in the diet. The availability of diet data based on the analysis of a large number of stomachs gave us robust estimates of diet percentages in bluefish.

Differences in congener accumulation patterns and predator/prey concentration ratios (Fig. 4) reflected differences in the retention of specific congeners by bluefish. Patterns differed markedly between the three sampling dates, with the August date most closely resembling the predictions by Thomann [10] for a top predator. Ratios of greater than one were seen on this date, especially for congeners with log K_{ow} values higher than 6.0, indicating biomagnification. This is consistent with studies reporting greater biomagnification of dietary-derived, higher-molecular-weight PCB congeners relative to lower-molecular-weight congeners in organism tissues [4,24–27]. Lower ratios for congeners with log K_{ow} values higher than 6.5 are attributed to lower assimilation efficiencies for the more highly chlorinated congeners (see, e.g., [24,34]). Lower ratios of predator concentration to prey concentration were observed in June, when the bluefish had just entered the estuary, as well as in September, when considerable variability may have been caused by nonsteady-state conditions in this rapidly growing, juvenile fish.

The data show that measured BAFs for bluefish clearly were above the values predicted via uptake from water alone, and the food-chain model did a remarkable job at fitting the data (at least for the June and August dates), indicating that diet is an important source of PCBs for YOY bluefish. These results agree with those of Oliver and Niimi [2], who found BAF values to be elevated by one or more log units above values predicted by equilibrium partitioning for salmonid fish in Lake Ontario (USA). Those authors ascribed these elevated values to a dietary source. That the model does not fit the data as well on September 11 may reflect the nonsteady-state increase of lipids.

Model sensitivity analysis

For this study, the model parameters that were measured included congener concentrations in bluefish and prey, prey composition in the diet over the season, dissolved water concentrations, and bluefish growth and consumption rates. We believe all these values were robust and likely led to the good correspondence between model and field data. Estimates of growth rates and consumption rates were well constrained because of work by Buckel et al. [16] and by Buckel and Conover [14]. Uptake and excretion rates as well as chemical assimilation efficiencies were estimated as described by Thomann [10]. In the present study, α was estimated two ways, first at a level of 0.5 (i.e., 50% efficiency) and then as a function of K_{ow} (0.3–0.8). The effect of varying α was to decrease BAF predictions at the higher K_{ow} values (Fig. 6a). Uptake rate was estimated as a function of body (lipid) weight and varied with K_{ow} because of the step function E (Table 1). Other estimates of k_u and K from laboratory exposure studies ([35], as described by Connell [1]) also were utilized and took the form of the following regression equation: Log k_u (or log K) = a·log K_{ow} + b (Fig. 6). The net result of using all the combinations of α, k_u, and K on model BAF predictions for August 4 is presented in Figure 6b as a shaded polygon. Variability was greater at lower values of low K_{ow} (±0.5 log units) than at higher values of K_{ow} (±0.2 log units).

The two parameters that affected model predictions to the greatest extent were growth and consumption rates. Recall that in the first term of the BAF equation (Eqn. 1), k_u (uptake from water) is divided by the sum of $K + G$. Because K is a function of k_u ($K = k_u/K_{ow}$), the important variable becomes growth rate (G). The second term in Equation 1 contains chemical assimilation efficiency, consumption rate, excretion and growth rates, and prey BCF. Because the assimilation efficiency was set at 0.5 (i.e., 50%) across all values of log K_{ow}, its effect was neutral. Varying α from 0.3 to 0.8 as a function of K_{ow} had little effect on the model BAF predictions (Fig. 6a). The ratio of consumption rate to growth rate (C/G) therefore was the most important term. Over the three dates, this ratio varied between 4.6 and 1.5, with the lowest value occurring on September 11 (Table 3). Given that prey BCF (i.e., v_{i-1}/c) varied only by 0.2 log units, the ratio of consumption to growth rate drove BAF model prediction and is the reason that BAF predictions were lower on September 11.

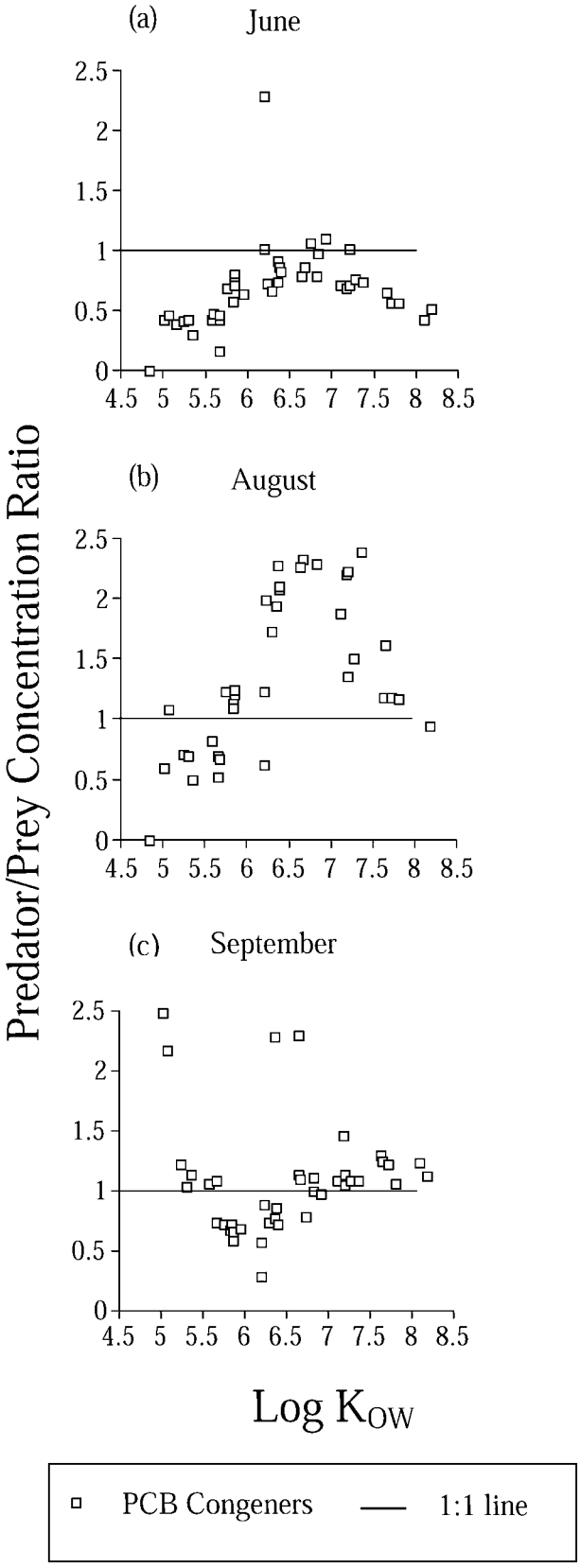

Fig. 4. Plots of the ratio of lipid-based bluefish concentration to the lipid-based concentration of prey species (predator concentration to prey concentration ratio) for the (**a**) June, (**b**) August, and (**c**) September sampling dates. The 1:1 ratio is denoted by the solid line.

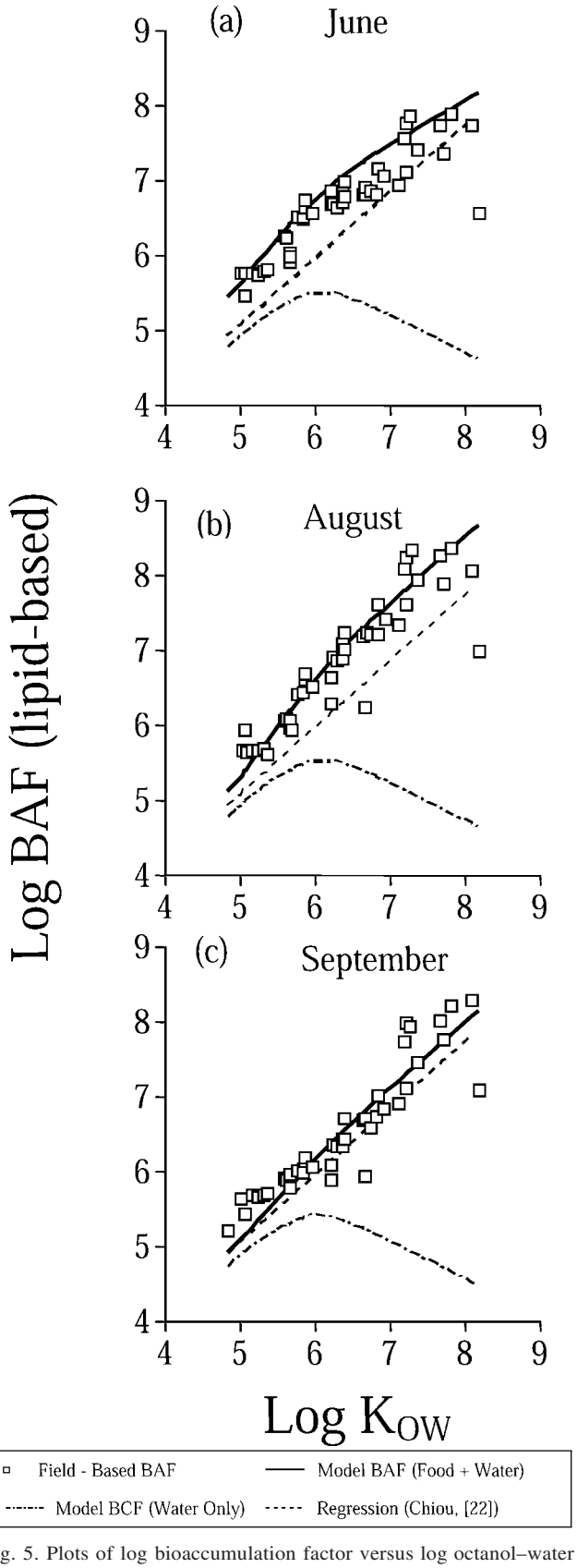

Fig. 5. Plots of log bioaccumulation factor versus log octanol–water partition coefficient (low K_{ow}) for several polychlorinated biphenyl congeners. Superimposed are predictions based on the Thomann model for bioaccumulation factor (BAF; solid line) and bioconcentration factor (BCF; parabola shape) as well as the equilibrium partitioning predictions of Chiou [22] (dashed line). Assimilation efficiency (α) is fixed at a value of 0.5. (**a**) June 30 sample. (**b**) August 4 sample. (**c**) September 11 sample.

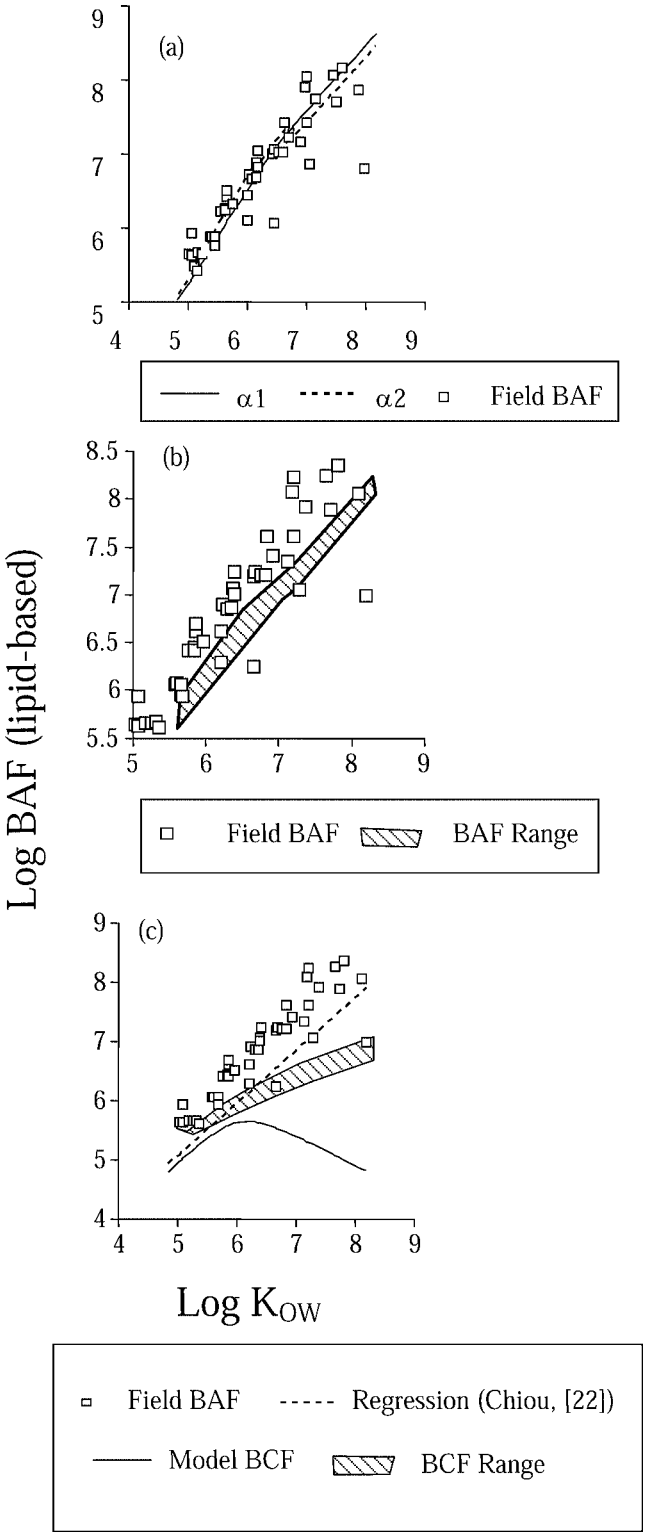

Fig. 6. (**a**) Effect of two different estimates of α (α_1 = 0.5, solid line; α_2 = 0.35–0.8, dashed line) on Thomann model predictions of accumulation factor (BAF) for bluefish collected on August 4 (see Table 1 for further explanation). (**b**) Net effect of all estimates of chemical assimilation efficiency (α), chemical uptake rate (k_u), and chemical excretion rate (K) on Thomann model BAF predictions (striped polygon represents the range of BAF values calculated). In addition to k_u and K estimates described in Table 1, estimates of k_u and K based on laboratory exposures by Konemann and van Leeuwen [35] as described by Connell [1] were included. Regression equations were as follows: Log k_u = 0.18·log K_{ow} + 1.98 and log k_u = 0.34·log K_{ow} − 0.37; log K = −0.41·log K_{ow} + 1.47 and log (1/K) = −0.66·log K_{ow} − 0.95. (**c**) Effect of all estimates of k_u and i (including the regression equations listed above) on Thomann model bioconcentration factor (BCF) calculations. (The BCF is the first term of Eqn. 1 in the text).

Uptake from water alone did not account for a significant fraction of the total uptake, especially for PCB congeners with log K_{ow} values greater than six. The resulting parabolic shape for the graph of uptake rate versus log K_{ow} was described by Könemann and van Leeuwen [35]. A departure from linearity for graphs of log BAF versus log K_{ow} has been described in other laboratory-based exposure studies [1,36]. In our model (i.e., the Thomann model), uptake rate and BCF were nonlinear because of the term E, an estimate of the efficiency of transfer across the gill membranes based, in part, on the previously cited laboratory-based exposure studies. Other estimates of k_u and K were closer to the equilibrium partitioning line at log K_{ow} values greater than six but still departed from the Chiou regression line [22] by more than one log unit (Fig. 6c). What may be needed are species-specific exposure studies to characterize better the uptake and excretion rates of PCBs in YOY bluefish.

CONCLUSION

The major conclusions from the present study are as follows: First, YOY bluefish began rapidly accumulating PCBs on entering the Hudson River estuary. Second, differences over time in the patterns of accumulation of congeners with different amounts of chlorine substitution may have reflected differences in the rates of uptake and excretion between these homologue groups. Third, equilibrium partitioning models underestimated measured BAFs, demonstrating the importance of diet in PCB uptake by bluefish. Fourth, the steady-state, food-chain model predicted measured BAF values well, considering the nonsteady-state nature of a rapidly growing fish species. Part of the reason for the good fit was the very high growth and consumption rates utilized, which were strongly supported by laboratory and field data. Differences between predicted and measured values on September 11 could have been caused by nonsteady-state rapid growth and accompanying lipid production in the juvenile bluefish.

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