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Bayesian estimation of kinetic rate constants in a food-web model of polycyclic aromatic hydrocarbon bioaccumulation

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Abstract

Water, sediments, fish and other biota were sampled from fixed stations along bayous in the LaBranche Wetlands of Louisiana as part of an environmental contamination study in 1996 and 1997. In order to understand the biological fate of some of these contaminants, a spotted gar (*Lepisosteus oculatus*) food-web model was developed from site-specific data and established bioaccumulation modeling assumptions. Based on gut contents analysis, the gar were found to feed on terrestrial arthropods, a variety of small fish, aquatic insects, crayfish and grass shrimp. A Bayesian approach (a hierarchical model and Markov Chain Monte Carlo simulation) was used to estimate the kinetic rate constants of uptake from water, dietary uptake and total elimination for the food-web model using site-specific measurements of naphthalene, phenanthrene, and benzanthracene concentrations, reference literature inputs, and a hierarchical statistical model. This iterative simulation method resulted in a distribution of the parameters for each chemical comprised of the last 3000 values from four separate Markov Chains of length 15,000–25,000 iterations. The posterior parameter values were found to be consistent with rate constants published in the literature for various fish species, and were used to determine distributions of predicted gar PAH concentrations.

Keywords: Biomagnification; Bioaccumulation; PAHs; Organics; Hierarchical model

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1. Introduction

In 1996 and 1997, the Center for Bioenvironmental Research at Tulane and Xavier Universities supported environmental studies in the LaBranche Wetlands of southern Louisiana (Lake Ponchartrain Basin, USA). The study area was selected because one of the bayous, Bayou Trepagnier, was the receiving stream for effluents from a petrochemical manufacturing complex for nearly 80 years ending in 1995 (Flowers et al., 1998). In related studies using microcosms Mitra et al. (2000) investigated polycyclic aromatic hydrocarbon (PAH) bioaccumulation from Bayou Trepagnier sediments in grass shrimp (*Paleomonetes pugio*) and clams (*Rangia cuneata*), and Carman et al. (1995) used PAH contaminated sediments from Pass Fourchon, Louisiana, USA to study effects on meiofauna and their trophic interaction with microorganisms. Field investigations include Engelhaupt and Bianchi (2001) who studied the cycling of high molecular weight dissolved organic carbon at the site over 1.5 years, and Oberdorster et al. (1999) who investigated the impact of PAHs on the benthic community structure.

A sign posted at the entry to Bayou Trepganier warns the public of environmental contamination, but the connecting waterways (e.g., Bayou LaBranche and the Engineer's Canal) are used for recreation, fishing and crabbing. The potential for human exposure motivated this research to improve our understanding of the biological fate of these contaminants in this wetlands ecosystem. Thus, we developed a spotted gar (*Lepisosteus oculatus*) food-web model for PAHs in the aquatic ecosystem. The spotted gar occurs in abundance throughout the central United States in lakes, bayous and rivers and feeds on a wide variety of prey. Its tissue accumulates metals and organic compounds typical of environmental mixtures and quantitative neurological and immunological biomarkers of exposure are known (Hartley et al., 1996). Because of toxicant bioaccumulation, gars could pose health risks if consumed by humans.

Many different methods have been used to model chemical bioaccumulation. Previous studies of hydrophobic organic chemical bioaccumulation used modeling approaches based on equilibrium partitioning theory that assumes thermodynamic equilibrium between the lipids in biota, the organic carbon phase of the sediments and water (Brown et al., 1982; Bierman, 1990; Di Toro et al., 1991; van der Kooij et al., 1991; Endicott and Cook, 1994; Landrum et al., 1994; Meador et al., 1997; Wang et al., 1997). Thompson et al. (2000) found that the equilibrium partitioning model could not explain the accumulation of three PAHs (i.e., phenanthrene, pyrene, and chrysene) in oysters from a high salinity estuary. Instead, they fitted Weibull and lognormal distributions to lipid normalized tissue concentrations and organic carbon normalized sediment concentrations and found the Weibull distribution to fit the data well. They also investigated probability models for the ratio of the two concentrations, the biota-sediment ratio, and found that these could be represented equally well by the loglogistic or lognormal distribution.

Models based upon mass balances track the flow of chemical(s) between compartments formulated as sets of ordinary differential equations which can be simplified under steady-state conditions (McElroy and Means, 1988; Barber et al., 1991; Thomann et al., 1992; Gobas, 1993; Abbott et al., 1995; Wang et al., 1996; Means and McElroy, 1997). Burkhard (1998) compared the steady-state models of Gobas (1993) and Thomann et al. (1992) and performed extensive sensitivity and uncertainty analyses on these models. Predictions made by the two models were found to be similar except for compounds with log K_{ow} ranging from 6.5 to 6.9. Abbott et al. (1995) validated RIVER/FISH, a PC based dynamic simulation model, using data collected in an experimental stream setting.

Carrer et al. (2000) modelled dioxins and dibenzofurans in clams, mussels, and fish by linking a trophic network model (Ecopath) based on energy flows in an ecosystem to a bioaccumulation model based on Thomann (1989) and Thomann et al. (1992). Outputs of the Ecopath model (e.g., production:biomass, consumption:biomass, respiration, diet matrix) were used as inputs into the bioaccumulation model to provide a better representation of these parameters in modeling bioaccumulation. Their model predictions were within one order of magnitude for the clams and mussels and two orders of magnitude for the fish.

Wang et al. (1996) used the Boltzman equation to describe organism growth in their study of aquatic organism bioconcentration. Using non-linear regression, they fitted their model to the data of Gobas et al. (1991), Mailhot (1987), Geyer et al. (1984), and Ellgehausen et al. (1980). They found the ratio of bioconcentration

factors (previous studies:current study) to range from 0.28 to 2.82 for several different hydrophobic organic contaminants and organisms.

Models based on fugacity include Booty and Wong (1996), Campfens and Mackay (1997), and Gobas et al. (1999). The model described by Campfens and Mackay (1997) is an equivalent reformulation of a concentration-based model. Its main advantage is that the fugacity factors (similar to partition coefficients although not necessarily at equilibrium conditions) have similar values for chemicals of similar octanol–water partition coefficient. Campfens and Mackay demonstrated their model using data from the Lake Ontario salmonid food web described by Gobas (1993), and calculated fugacity parameters from the concentrations and rate constants described by Gobas. Their results were consistently higher than the observations.

Others (Norstrom et al., 1976; Madenjian and Carpenter, 1993; Eby et al., 1997; Luk and Brockway, 1997) incorporated bioengergetics into the bioaccumulation equations. Madenjian and Carpenter (1993) described an individual-based model of Lake Trout bioaccumulation where three sub-models were combined to address the observed population variability in PCB concentration. They used a bioenergetics based submodel (Stewart et al., 1983) to describe fish growth, a predator–prey submodel, and a PCB bioaccumulation submodel (Thomann, 1989). Individual fish of a particular size were simulated and their daily encounters with prey were allowed to vary randomly.

We formulated our model with assumptions based on the work of several investigators in the study of food web bioaccumulation of hydrophobic organic contaminants in aquatic systems (Landrum et al., 1992; Thomann et al., 1992; Gobas, 1993; Iannuzzi et al., 1996; Morrison et al., 1996; Thomann and Komlos, 1999). In these earlier models, input parameters (e.g., environmental conditions, kinetic rate constants, and physiological parameters) were treated as known constants, and no attempt was made to quantify the uncertainty and variability in the model predictions. Recently, the United States Environmental Protection Agency (U.S. EPA, 2001) recommended probabilistic modeling approaches (e.g., Bayesian analysis, one- and two-dimensional Monte Carlo) to characterize uncertainty and variability in risk assessment. Our study uses a probilistic Bayesian approach to provide a framework for understanding the transfer of PAHs in the spotted gar food web of this wetlands ecosystem, and demonstrates a method to quantify the combined uncertainty and variability in model predictions.

In this study, we account for variability and uncertainty in the data using a hierarchical statistical model and Markov Chain Monte Carlo simulation (Gelman et al., 1995; Bois et al., 1996b) to estimate sediment and water PAH concentrations, water organic matter concentration, sediment organic carbon fraction, and unobservable, kinetic rate constants in fish. Prior distributions, assigned to variable and uncertain parameters, are multiplied by the likelihood of the data to yield an unnormalized, joint posterior distribution of the parameters conditional upon the data. The marginal posterior distributions of the parameters of interest can then be examined and used to simulate distributions of model predictions.

In related studies, Bayesian techniques were used to estimate parameters of: (1) an ocean ecosystem model using simulated data (Harmon and Challenor, 1997); (2) a microbial substrate model using simulated data (Omlin and Reichert, 1999); and (3) a water quality model using data from an 18 lake survey (Aldenberg et al., 1995). The Revised Baseline Modeling Report, Hudson River PCBs Reassessment RI/FS (U.S. EPA, 2000b) used Bayesian updating with FISHRAND, an aquatic food-web bioaccumulation model based on Gobas (1993) and Gobas et al. (1995) that incorporates probability distributions for model parameters. Linkov et al. (1999) used Bayesian updating to reduce uncertainty in predicting the distribution of ^{137}Cs in a coniferous forest. Later, Linkov et al. (2001) performed a two-dimensional Monte Carlo uncertainty analysis for PCB bioaccumulation in an osprey (*Pandion haliaetus*) food chain model based upon the models of Gobas (1993) and Gobas et al. (1995).

Of 50 semi-volatile contaminants analyzed in tissues, we focus on three PAHs that were detected at measureable levels: naphthalene; phenanthrene; and benzanthracene. Their octanol–water partition coefficients (K_{ow}) range from $10^{3.3}$ to $10^{5.6}$ and the U.S. EPA (2000a) recommends these compounds, with the exception of naphthalene, for fish tissue screening of PAHs. Based on K_{ow}, the bioaccumulation potential of these PAHs is highest for benzanthracene comprised of four fused rings, followed by phenanthrene comprised of three fused rings and is lowest for naphthalene comprised of two fused rings. While naphthalene has

the lowest potential for bioaccumulation of the three PAHs, it is nevertheless one of the most ubiquitous PAHs found in the environment from both combustion sources and petroleum spills. It and other PAHs are metabolized by many vertebrates (ATSDR, 1995; 1National Toxicology Program, 2000; Schreiner, 2003; van der Oost et al., 2003), and the metabolites may be more toxic than the parent compounds. In this study, we estimate the kinetic rate constants in fish (i.e., dietary uptake, uptake from water, and total elimination) and other uncertain/variable environmental parameters from field-collected and reference literature data.

2. Methods

Our primary objective is to estimate the kinetic rate constants in fish and other uncertain/variable environmental parameters (water and sediment PAH concentration, water organic matter concentration, and sediment organic carbon fraction) using Bayesian techniques of Markov Chain Monte Carlo simulation and a hierarchical statistical model. These parameters are used in computing bioconcentration, biomagnification, and biota-sediment accumulation factors (Means and McElroy, 1997) typically from single-value estimates of the rate constants or measured environmental parameters (Ellgehausen et al., 1980; Geyer et al., 1984; Bierman, 1990; Di Toro et al., 1991; van der Kooij et al., 1991; Landrum et al., 1992; Amyot and Pinel-Alloul, 1994; Endicott and Cook, 1994; Landrum et al., 1994; Meador et al., 1995; Sijm et al., 1995; Sijm and van der Linde, 1995;van Bavel et al., 1996; Means and McMillin, 1997; Wang et al., 1997; Thomann and Komlos, 1999; Bailer et al., 2000; Berglund et al., 2000; Clarke and McFarland, 2000; Gewurtz et al., 2000). Here, we extend previous methods to determine distributions of these parameters utilizing methodology that yields: (1) a collection of parameter vectors obtained from their joint posterior distribution; (2) a distribution of model predictions; and (3) quantification of the combined uncertainty and variability in the population through a hierarchical statistical model and Markov Chain Monte Carlo simulation. In the next sections we describe the food-web bioaccumulation model, the measured data, and the statistical methods used to estimate the unknown parameters.

2.1. Bioaccumulation model formulation

The food-web model (Fig. 1) is based on the assumptions of Gobas (1993) who modeled bioaccumulation of hydrophobic organic contaminants in the food web of Lake Ontario salmonids. Gobas describes for each type of organism, a time-dependent, ordinary differential equation, but ultimately uses a steady-state formulation. The following equations describe the concentration of contaminant in each type of organism. We assume that the concentration of contaminant in terrestrial insects and arthropods, C_{ti}, is zero.

Eq. (1) describes the dissolved water concentration, C_{wd}, calculated from the total water concentration, C_{wt}, the octanol–water partition coefficient, K_{ow}, the water organic matter concentration, C_{om}, and the density of the organic matter, d_{om}.

$$C_{wd} = \frac{C_{wt}}{1 + K_{ow} C_{om}/d_{om}} \tag{1}$$

In plankton and aquatic insects, bioaccumulation is determined by partitioning of the contaminant between the water and the lipids in the organism.

$$C_a = L_a K_{ow} C_{wd} \tag{2}$$

where C_a is the whole body concentration and L_a the lipid fraction of the organism.

Crayfish and grass shrimp are assumed to be in equilibrium with the organic carbon fraction of the sediment as described by Eq. (3).

$$C_b = \frac{C_s d_{oc} L_b}{f_{oc} d_l} \tag{3}$$

where C_b is the whole body concentration in the crayfish or shrimp, C_s the sediment concentration, d_{oc} the density of organic carbon, L_b the lipid fraction, f_{oc} the organic carbon fraction of the sediment and d_l the density of lipids.

The concentration of toxicant in fish, C_f, is

$$C_f = \frac{k_{uf} C_{wd} + k_{df} C_{df}}{k_{elim}} \tag{4}$$

where k_{uf} is the rate constant for uptake through the gills, k_{df} the dietary uptake rate constant, and k_{elim} the total elimination rate constant including elimination through the gills, fecal egestion, dilution due to growth,

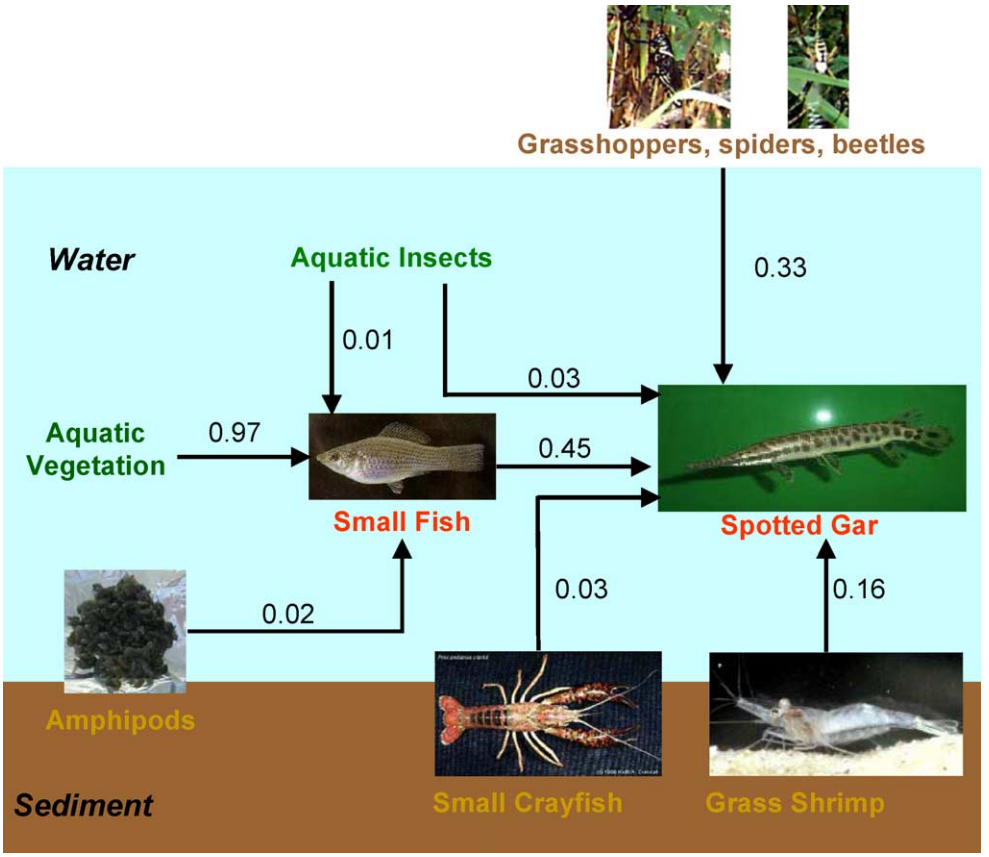

Fig. 1. Spotted gar food web based upon stomach contents analysis. The numbers associated with each arrow indicate the diet fraction for each prey item.

and metabolism. C_{df} is the concentration of contaminant in the diet calculated as $\sum_m p_m C_m$, where p_m is the fraction of the fish diet made up of prey m and C_m the chemical concentration in prey m.

Food web structure and feeding preferences were determined from the gut content analyses of 14 spotted gar and 298 small fish (*Cyprinodon variegatus*, *Gambusia affinis*, *Poecilia latipinna*) collected in Bayou Trepagnier from 1996 to 1997. Prior to dissection and content analysis, gar stomachs were removed on the day of capture and fixed in 10% formalin solution, and small fish were fixed whole in the field. Stomach contents were identified to the lowest taxonomic level. Diet fractions for spotted gar were computed as the ratio of the number of prey type m to the total number of prey found in the stomachs (Fig. 1). Diet fractions for small fish were determined by combining data from all three species and weighting the number of prey type m, n_m, by the number of stomachs containing prey type m, s_m.

$$\frac{n_m s_m}{\sum n_m s_m} \tag{5}$$

This method of summary was used for the small fish because unequal numbers of stomachs were examined for each of the species. Weighting the number of prey m by the number of stomachs containing prey m adjusts for species-specific preferences. Terrestrial insects and arthropods were also found in gar stomachs, however, since these organisms are not aquatic, they were assumed to be free of contamination for modeling purposes.

2.2. Site-specific data

In 1996 and 1997, several site-specific measurements of the model input parameters were made by different investigators under the auspices of the Tulane/Xavier Center for Bioenvironmental Research (CBR). In addition to individual investigator studies, the CBR supported core groups to facilitate field sampling and laboratory analysis. Site-specific measurements used to determine model input prior distributions included PAH concentrations in water and sediment, sediment total carbon fraction (TCF) used as the upper bound on sediment organic carbon fraction, and the concentration of total suspended particulates (TSP) used as the upper bound for the concentration of suspended organic matter. When site-specific measurements were unavailable, data from the literature (e.g., lipid density and lipid fractions) were used as model inputs (Table 1). Some of the organism lipid fractions were measured in a recent study and are used in this investigation.

Concentrations of individual PAHs in water and sediment samples were measured by the CBR Analytical Core. The concentrations of individual PAHs in gar fish tissue were determined by Dr. Means' analytical laboratory for 11 spotted gar (Table 2) captured at different sites in Bayou Trepagnier between September 1996 and March 1997. Details of these procedures are outlined below.

2.2.1. Water and sediment analysis

Concentrations of individual PAHs in water were measured by gas chromatography and mass spectrometry (GC/MS) after extraction using a liquid–liquid separatory funnel method based on U.S. EPA SW-846 Method 3510B (U.S. EPA, 1998). 1.0 l water samples were placed in a 2 l separatory funnel; 5.0 μl of surrogate standard (M-8270-SS from Accustandard, Inc., New Haven, CT, USA) was added; and 60 ml of methylene chloride was added. Samples were mechanically shaken for a minimum of 2 min after which the methylene chloride phase was removed. This procedure was repeated three times for a total extraction volume of 180 ml of methylene chloride. Emulsions were broken up either mechanically or by the addition of sodium sulfate. GC grade methylene chloride and sodium sulfate were purchased from Fisher Scientific. Samples were concentrated and analyzed as described below.

Concentrations of individual PAHs in sediment were measured by GC/MS after extraction using an accelerated solvent extractor (ASE-200) purchased from Dionex Corporation (Sunnyvale, CA, USA) based on SW-846 proposed Method 3545 (U.S. EPA, 1998). Eight grams of sediment were added to a 100 ml beaker;

Table 1
Input parameters treated as constant and data sources

Input description	Variable	Value	Source
Constant parameters			
Lipid density	d_l	0.9 kg/l	Gobas (1993)
Organic carbon density	d_{oc}	0.9 kg/l	Gobas (1993)
Organic matter density	d_{om}	1.0 kg/l	Gobas (1993)
Octanol–water partition coefficients			
Naphthalene	K_{ow}	2.00×10^3	Hazardous Substances Data Bank (HSDB)
Phenanthrene		3.72×10^4	HSDB
Benzanthracene		4.07×10^5	HSDB
Lipid fractions			
Amphipod	L_{am}	1.8%	Average of values for a mixture of amphipods (Gewurtz et al., 2000), *R. abronius* (Meador et al., 1997), and *G. fasciatus* (Morrison et al., 1996)
Aquatic vegetation	L_{av}	1.6%	Average for algae (Gobas et al., 1991) and plankton (Morrison et al., 1996)
Aquatic insect	L_{ai}	5.0%	Upper bound based on insect lipid content (Chapman, 1982)
Grass shrimp	L_{sh}	2.2%	H. Lin
Small crayfish	L_{cr}	2.1%	H. Lin
Feeding preferences	P_{feed}		
Spotted gar			P. Martinat
Small fish			P. Atkins, M. Kunas and H. Bart Jr.

Table 2
Measured gar tissue PAH concentrations (Dr. Means' laboratory)

Subject	ID	Concentration (ng/g)					
		Naphthalene (C_{na})	Ln(C_{na})	Phenanthrene (C_{ph})	Ln(C_{ph})	Benzanthracene (C_{bz})	Ln(C_{bz})
1	2288	7.87	2.06	3.71	1.31	11.1	2.41
2	2278	6.19	1.82	2.91	1.07	10.8	2.38
3	2279	12.1	2.50	3.53	1.26	10.8	2.38
4	525	6.58	1.88	5.96	1.78	11.6	2.45
5	538	10.9	2.39	9.65	2.27	11.0	2.39
6	2276	5.98	1.79	2.76	1.01	11.0	2.39
7	2277	3.84	1.35	3.90	1.36	11.1	2.41
8	2282	12.2	2.50	3.74	1.32	10.6	2.36
9	2284	10.8	2.38	3.95	1.37	10.8	2.38
10	2287	2.98	1.09	3.66	1.30	1.12[a]	0.11[a]
11	1887	5.12	1.63	3.91	1.36	10.88	2.39

[a] Value not used because of a transcription error resulting in an order of magnitude difference in the concentration.

5 μl of surrogate standard was added; 6 g of hydromatrix was added; and the mixture was thoroughly stirred prior to transferring to a 33 ml Dionex Cell that contained a 1.91 cm cellulose paper at the bottom. Hydromatrix and cellulose papers were purchased from Dionex Corporation. Hydromatrix was used to fill any remaining volume in the cell. The ASE was then used to extract the sample with methylene chloride. The extract was collected in a 60 ml vial, concentrated and analyzed as described below.

Sample extracts (from either water or sediment) were transferred to RapidVap beakers and placed in the RapidVap. The RapidVap was operated at 55 °C with nitrogen purge gas. Samples were concentrated to approximately 0.5 ml and then quantitatively transferred to a 1.0 ml volumetric tube. Final sample volume was adjusted to 1.0 ml either by further concentrating with a gentle stream of nitrogen or by adding additional methylene chloride. 5.0 μl of internal standard was added (Z-14J from Accustandard, Inc., New Haven, CT, USA). The sample was then transferred to a GC autosampler vial for analysis.

GC/MS analysis was performed on an Agilent 6890 GC with liquid autosampler and J&W Scientific DB-5-MS column interfaced to an Agilent 5972 mass selective detector. The GC inlet temperature was 280 °C, initial oven temperature was 40 °C and transfer line was 280 °C. After a 2 min initial hold time, the GC oven was ramped at 10 °C per minute to 320 °C and held for 20 min. A splitless injection of 2 μl of extract was used. The mass spectrometer was tuned using decafluorotriphenylphosphine (DFTPP). After a 10 min solvent delay, the mass spectrometer was operated in the positive electron ionization mode using a selected ion monitoring program for increased sensitivity. Peaks were identified by comparison to retention time and ion ratios. A linear five-point calibration curve based on relative response factors was used to quantify the individual PAHs in the sample extract.

2.2.2. Tissue analysis

Fish tissue samples ranging in wet weight mass from 0.4 to 0.9 g were extracted for PAHs using a matrix solid phase dispersion (MSPD) method (Barker 1et al., 1993). Briefly, the tissue was weighed and combined with 5 g of dry, pre-cleaned C-18 solid phase material (Varian, Inc. Scientific Instruments, Walnut Creek, CA, USA) in a glass mortar, spiked with 25 μl of a solution containing 40 μg/ml each of five deuterated surrogate standards (Ultra Scientific, Inc., North Kingstown, RI, USA) and then thoroughly ground into a homogeneous powder with a glass pestle. The C-18 was then transferred quantitatively into the barrel of a disposable 10 ml plastic syringe plugged at the end with a 4 mm glass fiber filter and a small amount of inactivated glass wool. The MSPD columns were then eluted as follows: the column bed was first saturated with approximately 2 ml of dichloromethane (Baker Scientific, Phillipsburg, NJ) and allowed to stand for 20 min. Then, an additional 8 ml of dichloromethane followed by 8 ml of pesticide grade hexane was passed through each MSPD column and allowed to elute

by gravity into a 40 ml glass vial. In some cases the solvent was slowly forced through the column using the plunger of the syringe. The solvent eluant was then evaporated to approximately 2 ml under a stream of pure nitrogen, transferred quantitatively to a 4 ml amber glass vial and further evaporated under nitrogen to a final volume of 200 μl. Samples were then stored at −20 °C until analyzed by GC/MS.

The individual PAH as well as isomer group sums were quantified by the multiple selected ion monitoring GC/MS method adapted from Means (1998). Analysis was performed on 2 μl samples of the extracts using a Hewlett-Packard (AG) 5890A gas chromatograph equipped with the capillary column (AG DB-5MS) (30 m × 0.025 mm i.d.) directly interfaced to an H-P 5970 mass selective detector (MSD), equipped with an autosampler. A temperature program for the GC oven using a series of linear temperature ramps from 50 to 300 °C was developed in order to optimize the separation of the analytes. The mass spectrometer was tuned daily and/or after each 16 h of analysis using perfluorotributylamine (PFTBA). An initial five-point calibration curve was prepared and continuing calibrations for all analytes were run at the beginning and end of each analysis group. A multiple selected ion monitoring method (SIM) was developed which employed monitoring of up to 18 ions in each of 16 retention time windows. This method included ions selected to allow for quantification of over 60 individual PAHs using authentic individual standards or mixtures (Chiron AS, Trondheim, Norway). Internal standard, 4,4′-dibromo-octafluoro biphenyl (DBOFP, Ultra Scientific, Inc., North Kingstown, RI, USA) and spike recoveries for tissues typically ranged from 80 to 100%.

Detection limits for each analyte in the sample matrix type were estimated from statistical information derived from standard calibration curves used to determine instrument detection limits, corrected for the type-of-sample concentration factor. Triplicate analyses of a five-point standard calibration curve were used to obtain a mean standard deviation for each analyte. This value was then multiplied by a factor of 3 (Taylor, 1987), to obtain an instrument detection limit in units of ng on-column. The use of the 3× multiplier has the advantage of maximizing the amount of numerical values reported in data sets obtained in research projects. The instrument detection limits were then corrected for average concentration factors to obtain a sample detection limit for the fish samples of typically 4–10 ng/g wet wt (ppb). Samples were spiked immediately before injection with 10 μl of a 100 μg/ml solution of DBOFP as an internal standard.

2.3. Hierarchical model and parameter estimation

The hierarchical framework for parameter estimation is illustrated in Fig. 2. It has two components: the individual level and the population level. In this model, φ_{ij}, and θ_{ij}, denote known model parameters treated as constants, and uncertain or variable model parameters, respectively for parameter, i, and individual, j, treated as random variables. Table 3 describes the prior distributions used for the uncertain parameters that were determined from a broad knowledge base or historic site-specific measurements. In this study, the random variables can be divided into three categories: (1) inputs which were measured with temporal or spatial variability; (2) a site-specific measurement providing information about a model input parameter, such as an upper or lower bound; and (3) unobservable model parameters. The first category describes the sediment and water PAH concentrations where measurement uncertainty, temporal and spatial variability exist. We used site-specific measurements and determined the prior distribution from these data collected over the project period. The second category includes values of sediment organic carbon fraction and the concentration of suspended organic matter, which were not directly measured, but are required by the model. Sediment total carbon fraction and total suspended particulates were measured and were used as upper bounds for the sediment organic carbon fraction and the concentration of suspended organic matter in water. Unobservable model parameters in the third category include the uptake rate constant, k_{uf}, the dietary uptake rate constant, k_{df}, and the total elimination rate constant, k_{elim}, from Eq. (4) for small fish and spotted gar.

Gar tissue PAH concentrations (C_{gar}) were measured in individual fish captured at different locations in the LaBranche Wetlands. A lognormal likelihood was assigned to the data with the geometric mean of the gar tissue concentration predicted by the food-web bioaccumulation model and the variance sampled from an inverse-gamma distribution (the conjugate prior for a normal model with known mean but unknown variance).

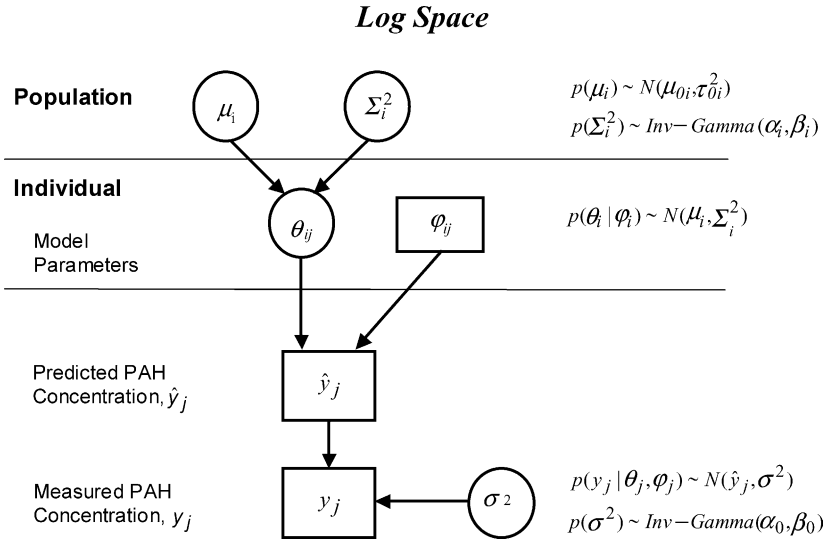

Fig. 2. Diagram of a statistical model describing the dependence between model variables. Circular nodes represent unknown variable parameters, and square nodes represent observed (or experimental) data. The arrows show the dependence between model parameters and observed data. The prior sampling distributions listed were used after natural log-transformation of the raw data.

2.3.1. Variable input parameters

The variable input parameters (θ_i) are the kinetic rate constants for the small fish and spotted gar (i.e., k_{uf}, k_{df}, and k_{elim}) from Eq. (4), sediment and water PAH concentration, concentration of suspended organic matter in water, and the sediment organic carbon fraction. At the individual level, the rate constants, sediment and water concentrations were sampled from lognormal distributions with geometric means and geometric standard deviations sampled from population-level or hyperprior distributions. The organic matter concentration and sediment organic carbon fraction were sampled uniformly with their respective upper bounds of total suspended particulates and sediment total carbon fraction, respectively, sampled from a lognormal distribution.

Vague prior distributions were assigned to k_{uf} and k_{elim} by considering the data on these parameters from all types of aquatic systems (i.e., marine, estuarine, and freshwater), for all species of fish, and for all PAHs. The rationale for using a vague prior is that measured gar concentrations will improve the estimate of the rate constants for this species and the PAHs of interest. At the population level, the means (μ_i) of the uptake and elimination rate constants were sampled from a lognormal distribution with geometric mean and geometric standard deviation based on values reported in the literature for uptake (Spacie et al., 1983; Djomo et al., 1996; Baussant et al., 2001) and elimination (Niimi, 1987; Niimi and Dookhran, 1989; Baussant et al., 2001) rate constants. Total elimination rate constants were either reported as such or determined from the reported half-life, where k_{elim} is $0.693/t_{1/2}$. If a half-life was reported as less than a value, X, the value X was used in calculating the geometric mean and geometric standard deviation of the lognormal distribution. The hyperprior variances (Σ_i^2) were sampled from inverse-gamma distributions following Bernillon and Bois (2000) and Gelman et al. (1995) with a shape parameter, α, equal to two and the scale parameter, β, equal to the sample variance after log-transformation.

Data for the dietary uptake rate constant, k_{df}, were not found explicitly in the literature so the hyperprior distribution was determined using the correlation described by Gobas (1993) based upon octanol–water partition coefficient, site-specific, measured, fish weights (for *G. affinis*, one of the small fish found in the gar diet and *L. oculatus*) and water temperatures.

$$k_{df} = \frac{0.022\, e^{0.06T_w}}{(2.3 + 5.3 \times 10^{-8} K_{ow}) V_f^{0.15}} \quad (6)$$

Table 3
Population-level prior distribution parameters and posterior parameters obtained through Markov Chain Monte Carlo simulation

Parameter	Variable	Prior for μ[a]		Prior for Σ^{2}[b]		Posterior for μ[a]		Posterior Σ^{2}
		Mean	S	α	β	Mean	S	Median[b]
Total water concentration, C_{wt} (Coordinated Instrumentation Facility)								
Naphthalene		0.13	0.36	2	1.2	0.01	9.8×10^{-3}	0.42
Phenanthrene		0.03	0.02	2	0.49	0.01	9.0×10^{-3}	0.22
Benzanthracene		0.05	0.01	2	0.09	0.05	0.01	0.052
Sediment concentration, C_s (Coordinated Instrumentation Facility)								
Naphthalene		48	30	2	0.34	49	31	0.23
Phenanthrene		58	31	2	0.29	51	35	0.18
Benzanthracene		95	67	2	0.67	94	61	0.37
Water total suspended particulates, TSP[c] (T. Bianchi, personal communication)								
Naphthalene		2.0×10^{-4}	8.0×10^{-5}			1.9×10^{-4}	6.0×10^{-5}	
Phenanthrene		2.0×10^{-4}	8.0×10^{-5}			1.8×10^{-4}	5.7×10^{-5}	
Benzanthracene		2.0×10^{-4}	8.0×10^{-5}			1.8×10^{-4}	6.9×10^{-5}	
Sediment total carbon fraction[d], TCF (G. Flowers, personal communication)								
All PAHs		0.08	0.02			0.07	0.02	
Water uptake rate constant, k_{uf}, for gar/small fish (Spacie et al., 1983; Djomo et al., 1996; Baussant et al., 2001)								
Naphthalene		929/929	686/686	2/2	0.82/0.82	799/1111	630/1294	0.36/0.57
Phenanthrene		929/929	686/686	2/2	0.82/0.82	541/862	383/685	0.33/0.49
Benzanthracene		929/929	686/686	2/2	0.82/0.82	1382/1187	1062/1273	0.42/0.58
Dietary uptake rate constant, k_{df}, for gar/small fish (Gobas, 1993)[e]								
Napthalene		0.05/0.18	0.02/0.06	2/2	0.19/0.16	0.04/0.18	0.02/0.06	0.13/0.10
Phenanthrene		0.05/0.18	0.02/0.06	2/2	0.19/0.16	0.05/0.18	0.03/0.08	0.11/0.11
Benzanthracene		0.05/0.18	0.02/0.06	2/2	0.19/0.16	0.05/0.20	0.02/0.07	0.12/0.10
Total elimination rate constant, k_{elim}, for gar/small fish (Niimi, 1987; Niimi and Dookhran, 1989; Baussant et al., 2001)								
Naphthalene		0.50/0.50	0.29/0.29	2/2	0.60/0.60	0.96/0.5	0.79/0.50	0.25/0.39
Phenanthrene		0.50/0.50	0.29/0.29	2/2	0.60/0.60	0.63/0.47	0.38/0.37	0.22/0.37
Benzanthracene		0.50/0.50	0.29/0.29	2/2	0.60/0.60	0.35/0.46	0.18/0.34	0.22/0.36

Mean and standard deviation (S) for μ reported in natural space and β is the sample variance after log-transformation of the data. Source of prior data cited.

[a] Mean and sample standard deviation, S, in natural space. Lognormal distributions were used to sample the parameters.

[b] Inverse-gamma distribution used to sample the population-level variances. When the shape parameter, $\alpha = 2$, the scale parameter, β is equal to the expected value of the random variate. Values reported in log-space.

[c] Measured total suspended particulates sampled at the population level according to a lognormal distribution, then used as the upper bound for uniformly sampling the suspended organic matter concentration in water at the individual level.

[d] Measured total carbon fraction sampled at the population-level according to a lognormal distribution, then used as the upper bound for uniformly sampling the sediment organic carbon fraction at the individual level. Posterior means and standard deviations were the same for all PAHs.

[e] Dietary uptake rate constant correlation used with site-specific water temperature and fish weights.

where T_w is the water temperature in degrees centigrade and V_f the fish weight in kilograms. Water temperature and fish weights used in Eq. (6) were measured in the LaBranche Wetlands over the 1996–1997 sampling period. Similar to the other rate constants, the hyperprior variance (Σ_i^2) was sampled from an inverse-gamma distribution.

Measurements of total water and sediment PAH concentrations were made at different sampling locations in January, March and May 1997. Thirty water concentration measurements from four different sites in Bayou Trepagnier were used to define the hyperprior parameters of the lognormal distribution for the total water concentration. The hyperprior parameters for the

sediment PAH concentrations were based upon 13 measurements made at six different sites over the same time period.

Prior data for the site-specific concentration of water suspended organic matter and sediment organic carbon fraction were unavailable, but TSP in water (T. Bianchi, personal communication) and TCF in the sediment (G. Flowers, personal communication) were measured and used as upper bounds. Based upon the data throughout the bayou, the population-level prior distributions for these were found to be lognormal, and the randomly sampled values were used as the upper bound to sampling the actual model input parameters (C_{om} and f_{oc}) at the individual level from uniform distributions. Eleven measurements of TSP from four different locations in September 1996, February and May 1997 were used to determine the geometric mean and geometric standard deviation of the hyperprior, lognormal distribution. The randomly sampled value of TSP was then used as an upper bound on the concentration of suspended organic matter in water sampled uniformly at the individual level. In summer 1995, Flowers measured TCF at 15 sites in Bayou Trepagnier, which were used to define the hyperprior parameters of the lognormal distribution. Similar to the method of sampling C_{om}, f_{oc} was sampled from a uniform distribution using the sampled TCF value as the upper bound.

We used the Metropolis-Hastings algorithm in MCSim (Bois and Maszle, 1997) to perform the MCMC simulations. The advantage of using this algorithm over the Gibbs sampler, for example, is that the full conditional distributions of the parameters do not need to be defined. It is also efficient for complex probability models and hierarchical models (Gelman et al., 1995). The posterior parameter distribution was obtained by first running an initial sequence of 500 iterations for each of four separate chains, checking for convergence, and restarting the chain to perform subsequent increments of 5000 iterations saving the last 3000 iterations to monitor convergence. Each chain was initialized by a random selection of parameters using a different random seed.

There is some debate in the literature over which points comprise a representative sample from the stationary posterior distribution. A chain must be run long enough to reach a stationary distribution, but some argue that after the "burn-in" period one long chain is sufficient (Geyer, 1992) and others (Bois et al., 1996b; Gelman and Rubin, 1996) recommend the use of multiple chains. We chose to monitor the convergence of our Markov chains by the scale reduction method described in Gelman et al. (1995), which compares the variance between and within sequences using an Excel macro we developed in Microsoft Visual Basic for Applications. As recommended by Gelman, values between 1.0 and 1.2 indicate acceptable convergence and served as our criteria in this study.

3. Results

3.1. Parameter estimation

The distributions in Fig. 2 were used to sample the parameters after logarithmic transformation of the data. Each naphthalene chain required 15,000 iterations to converge in contrast to phenanthrene and benzanthracene which required 25,000 iterations per chain. Table 3 lists the posterior mean and standard deviation in natural space for the population-level random variables. Unlike the median, the mean cannot be transformed directly from log to natural space by exponentiation because the transformation is non-linear. For example, we found posterior parameter means that were lower than the prior in log-space, but upon exponentiation of the individual values to natural space and recalculation of the mean, the posterior mean (in natural space) was found to be higher than the prior mean. Thus, we report the mean and standard deviations calculated after exponentiation of the 12,000 posterior parameter values.

The posterior naphthalene total water concentration was an order of magnitude lower than the prior mean value, but the phenanthrene and benzanthracene mean concentrations were fairly close to the prior mean. Sediment mean concentrations and standard deviations for the three PAHs were close to the prior values.

TSP was measured at three different sites in September 1996, February and May 1997. The posterior means for all PAHs are comparable and consistent with expectations since this is an environmental, location-specific parameter and not a chemical dependent one. Slight decreases in the posterior means and standard deviations were found. TSP was used as an upper bound for sampling the concentration of organic matter at the

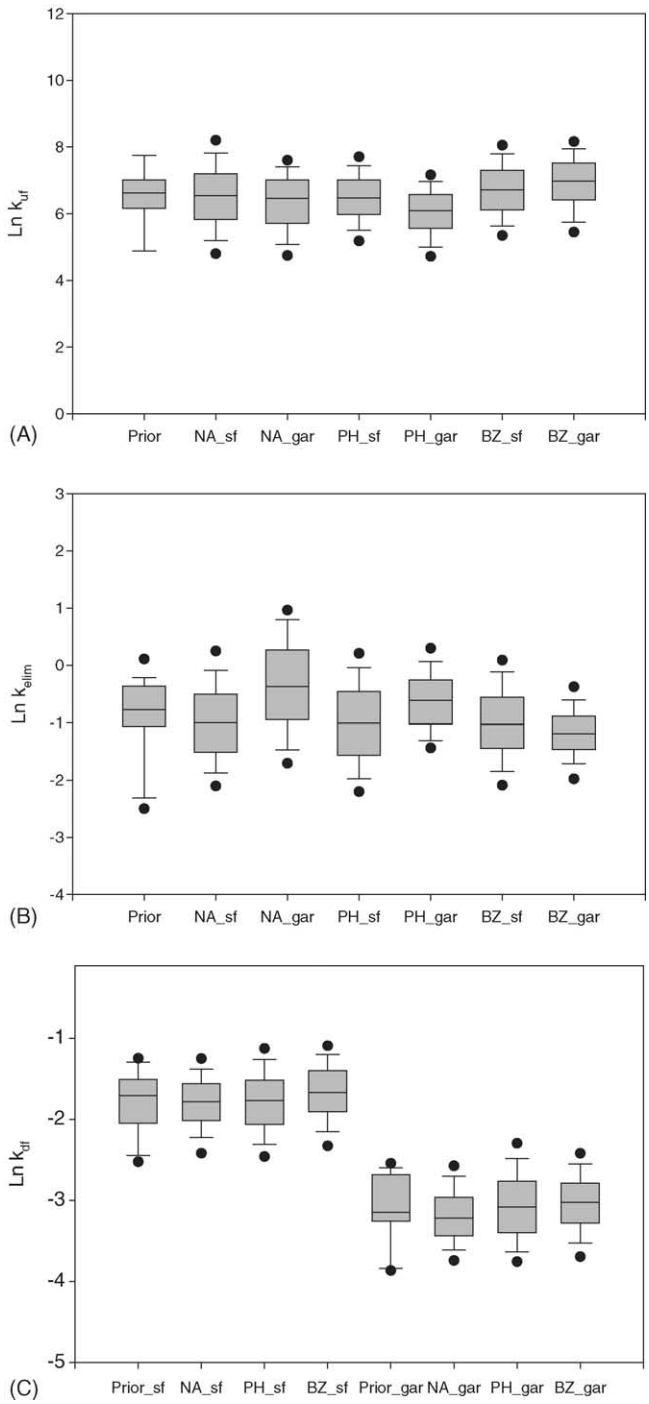

Fig. 3. Box plots of the data used to determine the prior distribution and the posterior distributions for (A) the uptake rate constant, k_{uf}; (B) the elimination rate constant k_{elim}; and (C) the dietary ingestion rate constant, k_{df}. The mid-line of the box represents the median, the outer edges represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentiles, and the filled circles encompass the 5th and 95th percentiles. NA: naphthalene, PH: phenanthrene, BZ: benzanthracene, sf: small fish and gar: spotted gar.

individual level whose posterior mean over all iterations and individuals by chemical ranged from $9.4 \times 10^{-5} \pm 6.0 \times 10^{-5}$ for naphthalene to $9.5 \times 10^{-5} \pm 6.0 \times 10^{-5}$ for phenanthrene and benzanthracene.

Similarly, TCF was used as the upper bound for sampling the sediment organic carbon fraction. Its posterior mean decreased from 0.08 to 0.07 and the variance remained the same. Sediment organic carbon fraction ranged from 0.035 ± 0.02 for benzanthracene to 0.037 ± 0.02 for naphthalene and phenanthrene.

Fig. 3 contains box plots of the population-level posterior distributions for the water uptake (Fig. 3A), total elimination (Fig. 3B), and dietary uptake (Fig. 3C) rate constants including plots of the data that were used to determine the population-level prior distributions. Differences in the posterior distributions between small fish and gar for each chemical can be seen, particularly in the elimination and dietary uptake rate constants. The posterior medians of the water uptake rate constants for naphthalene and phenanthrene are 6.5 and 6.1 (in natural space, 693 and 443 l/kg per day), respectively, slightly lower than the prior. Baussant et al. (2001) reported uptake rate constants in juvenile turbot of 6.0 (396 l/kg per day) for naphthalene and 6.5 (646 l/kg per day) for phenanthrene. In zebrafish, Djomo et al. (1996) found the uptake rate constant to be 7.7 (2280 l/kg per day) for phenanthrene. For benzanthracene, the posterior medians are slightly higher than the prior, 6.7 (823 l/kg per day) for small fish, and 7.0 (1076 l/kg per day) for gar.

The elimination rate constants for all PAHs in small fish were updated from a prior median of -0.78 (in natural space, $0.46\,\text{day}^{-1}$) to a posterior median of -1.0 ($0.37\,\text{day}^{-1}$). In gar, the median for naphthalene was the highest at -0.37 ($0.69\,\text{day}^{-1}$) and benzanthracene was found to be the lowest at -1.2 ($0.30\,\text{day}^{-1}$). The posterior gar naphthalene and benzanthracene elimination rate constants are consistent with values reported by Niimi (1987) of -0.37 ($0.69\,\text{day}^{-1}$) in trout, salmon and minnow via water exposure, and -1.1 ($0.35\,\text{day}^{-1}$) in trout via dietary exposure, respectively. Our median posterior elimination rate constant for phenanthrene in gar was -0.61 ($0.54\,\text{day}^{-1}$), which falls between the values reported by Niimi (1987) of -2.6 ($0.077\,\text{day}^{-1}$) for trout via dietary exposure and -0.37 ($0.69\,\text{day}^{-1}$) in minnow via water exposure. Baussant et al. (2001) reported values measured in juvenile turbot through water exposure of -0.062 ($0.94\,\text{day}^{-1}$) for naphthalene and -0.37 ($0.69\,\text{day}^{-1}$) for phenanthrene.

The posterior medians of the dietary uptake rate constants are essentially equal to the prior means with significant differences between the values for small fish and gar (Fig. 3C). In small fish, the posterior medians ranged from -1.8 (0.17 kg/kg per day) for

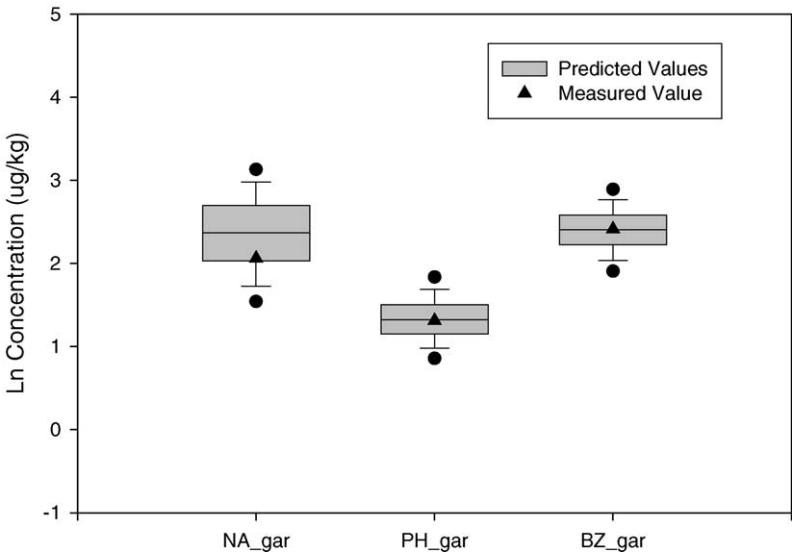

Fig. 4. The predicted PAH concentrations in gar, subject 1, using the 12,000 posterior parameter vectors obtained through MCMC simulation.

naphthalene and phenanthrene to −1.7 (0.18 kg/kg per day) for benzanthracene. Gar posterior medians ranged from −3.2 (0.041 kg/kg per day) for naphthalene to −3.0 (0.050 kg/kg per day) for benzanthracene.

In Table 3, gar posterior water uptake and elimination rate constants show greater changes in the posterior means than the small fish. As noted earlier, the dietary uptake rate constants were only slightly changed for both gar and small fish.

Median posterior population-level variances were all less than the sample variances (β) used in the prior distributions. In natural space (Σ^2 median in Table 3 exponentiated), all of the dietary uptake rate constant variances for both gar and small fish are equal to 1.1. Across all PAHs, the uptake rate constant variances ranged from 1.3 to 1.5 for gar and 1.6 to 1.8 for small fish. Similarly, the total elimination rate constant variances were approximately 1.2–1.3 for gar and 1.4–1.5 for small fish. Differences across PAHs exist for the estimated variances of total water concentration and sediment concentration.

3.2. Predictions of organism concentrations

Fig. 4 shows predicted concentrations using the 12,000 posterior parameter vectors obtained for the first gar out of 11 analyzed in this study. The predicted naphthalene concentration distribution encompasses the measured concentration at approximately the 25th percentile. For phenanthrene and benzanthracene, the measured value is the median of the predicted concentrations.

4. Discussion

4.1. Parameter estimation

We demonstrated a Bayesian approach to estimating parameters in a food-web bioaccumulation model. The method is feasible and appropriate for use in environmental studies where temporal, spatial, and inter-individual variability and uncertainty cannot be controlled or minimized. Rather, they are real characteristics of the system, which do not need to be averaged as inputs into a mathematical model. One advantage of this approach is that as new data become available, parameter estimates can be updated without starting over. That is, the current posterior parameter distribution can be used as the prior for simulations based on the likelihood of the new data. In particular, estimates of the small fish rate constants could be refined with measurements of small fish tissue concentrations, tissue measurement in the other food web organisms could also reduce the variability in the parameter estimate and subsequent predictions. Other model parameters treated as constants could also be allowed to vary given sufficient prior information. A disadvantage of the Bayesian approach is that it requires a large amount of data, but as demonstrated here, the method is capable of refining estimates starting with vague or uninformative priors and site-specific data.

The steady-state bioaccumulation model used here, like the equilibrium partitioning approach, will often oversimplify natural ecosystem dynamics in contrast to time-dependent model formulations. An advantage of the hierarchical model and Markov Chain Monte Carlo simulations we used to estimate the model parameters is that it can be applied to a set of ordinary differential equations (ODEs) describing time-dependent, ecosystem dynamics. This technique has been used in estimating parameters for physiologically based pharmacokinetic models, which are formulated as sets of ODEs (Bois et al., 1996a,b; Bernillon and Bois, 2000).

4.2. Environmental conditions

The water naphthalene posterior mean concentration decreased by an order of magnitude. Of the 30 water concentrations that determined the parameters of the prior distribution for naphthalene, 28 of them ranged between 0.01 and 0.09 μg/l with two values of 1.3 and 1.6 μg/l. Thus, posterior mean value of 0.01 is a reasonable value for the naphthalene total water concentration. Water concentrations for the other compounds did not show outliers of the magnitude seen with naphthalene.

At the individual level, there were no significant differences in the water and sediment PAH concentrations, water suspended organic matter, and sediment organic carbon fractions. The gar were captured at different locations within the LaBranche Wetlands, but they likely do not remain in one location throughout their lifetime. It is reasonable that the water concentration distributions obtained for individual gar do not show variation with capture location because measure-

ments actually show little spatial dependence. In contrast, the prior sediment concentrations have order of magnitude, site-specific differences, but the gar tissue concentration depends upon the sediment concentration only through benthic prey in its diet. This is also true for the sediment organic carbon fraction dependence. Thus, having PAH concentration measurement in benthic organisms should lead to sediment concentrations that reflect sampling location variability.

4.3. Kinetic rate constants

Kinetic rate constants in the literature were measured under different conditions, in different species of fish, and serve as a reference point for comparison with our findings for small fish and spotted gar. Essentially, all previously reported uptake and elimination rate constants fall between the 25th and 75th percentile (within the box in Fig. 3) of the small fish and spotted gar distributions indicating that these differences are not statistically significant given our level of uncertainty. Exceptions include an uptake rate constant for phenanthrene in zebrafish (Djomo et al., 1996) which is near the 95th percentile of our estimate for small fish and outside the 95th percentile for gar. Compared to our small fish elimination rate constant distributions: (1) the values reported by Niimi for water naphthalene exposure fall between the 75th and 90th percentile whereas Baussant et al. report a value that is between the 90th and 95th percentile; and (2) for phenanthrene exposure by water only, Niimi and Baussant et al. report values of 0.68 day^{-1} for turbot and minnow that lie between the 75th and 90th percentile. An elimination rate constant in trout exposed through their diet of 0.077 day^{-1} (Niimi, 1987) falls far below the 5th percentile of our distributions for small fish and gar.

Our small fish rate constants are often far from measured values primarily in other small fish, and more measurements of PAH concentrations are needed to better estimate these. In contrast, our estimates of the gar kinetic rate constants are consistent with previously reported values.

5. Conclusions

Markov Chain Monte Carlo is a useful technique for estimating parameters in a hierarchical model. Given a prior distribution for naphthalene water concentration that started far from the posterior, we were able to estimate the parameter at a more reasonable level that was consistent with the prior data when two outliers were removed. We also obtained kinetic uptake and elimination rate constants in gar that are consistent with values published in the literature for each PAH of interest after starting with a vague prior that included data measured in different fish species from estuarine, marine, and freshwater systems for all PAHs. This study demonstrated the utility of the Markov Chain Monte Carlo approach in estimating parameters from a food-web bioaccumulation model and provides a method for quantifying uncertainty and variability in parameter estimates and in model predictions.

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