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Quantifying Uncertainty in the Trophic Magnification Factor Related to Spatial Movements of Organisms in a Food Web

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ABSTRACT

Trophic magnification factors (TMFs) provide a method of assessing chemical biomagnification in food webs and are increasingly being used by policy makers to screen emerging chemicals. Recent reviews have encouraged the use of bioaccumulation models as screening tools for assessing TMFs for emerging chemicals of concern. The present study used a food web bioaccumulation model to estimate TMFs for polychlorinated biphenyls (PCBs) in a riverine system. The uncertainty associated with model predicted TMFs was evaluated against realistic ranges for model inputs (water and sediment PCB contamination) and variation in environmental, physiological, and ecological parameters included within the model. Finally, the model was used to explore interactions between spatial heterogeneity in water and sediment contaminant concentrations and theoretical movement profiles of different fish species included in the model. The model predictions of magnitude of TMFs conformed to empirical studies. There were differences in the relationship between the TMF and the octanol–water partitioning coefficient (K_{OW}) depending on the modeling approach used; a parabolic relationship was predicted under deterministic scenarios, whereas a linear TMF–K_{OW} relationship was predicted when the model was run stochastically. Incorporating spatial movements by fish had a major influence on the magnitude and variation of TMFs. Under conditions where organisms are collected exclusively from clean locations in highly heterogeneous systems, the results showed bias toward higher TMF estimates, for example the TMF for PCB 153 increased from 2.7 to 5.6 when fish movement was included. Small underestimations of TMFs were found where organisms were exclusively sampled in contaminated regions, although the model was found to be more robust to this sampling condition than the former for this system. *Integr Environ Assess Manag* 2015;11:306–318. © 2014 SETAC

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INTRODUCTION

New and existing chemicals are assessed by regulatory agencies based on their potential to persist (P) in the environment, to bioaccumulate (B), and exert toxic (T) effects in biota (USEPA 1976; Environment Canada 2003; Council of the European Union 2006). If a chemical, for example, is considered bioaccumulative it may be subject to regulatory control or to suggestion for further testing. Generally, bioaccumulation is assessed by calculating a bioaccumulation factor (BAF), by expressing the ratio of the chemical concentration in field-collected organisms to the water concentration, used as the reference. Evaluation of chemicals for bioaccumulation hazard assessment can be made difficult due to substantial uncertainty associated with water contamination, including a high degree of spatial and temporal variation in water contamination (Burkhard 2003 Drouillard et al. 2013), and site-specific or chemical property interactions that influence chemical bioavailability (Gobas and Morrison 2000). Furthermore, BAFs do not explicitly quantify chemical biomagnification (or change in concentration relative to the diet), a process of regulatory interest.

Trophic magnification factors (TMFs) provide a method of assessing chemical biomagnification in food webs through the integration of bioaccumulation processes occurring across individuals, species, and trophic levels in an ecosystem (Fisk et al. 2001; Jardine et al. 2006). TMFs are increasingly being used by policy makers to screen emerging chemicals as they provide a metric of the average extent of food web biomagnification of a given pollutant (Houde et al. 2008; Kelly et al. 2009; Borgå et al. 2012a). The TMF approach was

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amended to Annex XIII of the European Union Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) to be used in a weight of evidence approach of bioaccumulation assessment. Recent publications address specific concerns about the application of TMFs as a regulatory tool used for assessing chemicals under B-hazard assessment (Conder et al. 2012).

Relative to other bioaccumulation metrics such as BAFs, bioconcentration factors (BCFs), biota-sediment accumulation factors (BSAFs), and biomagnification factors (BMFs), which address chemical accumulation in selected indicator species, TMFs provide an integrated measure of bioaccumulation across multiple organisms in a food web (Gobas et al. 2009). This suggests the TMF is a bioaccumulation metric that is potentially more robust to errors compared to others that require the estimation of the bioavailable fraction of chemical in abiotic media (e.g., BCF and BSAF metrics) (Ditoro et al. 1991; Kelly and Gobas 2001) or accurate diet matching to establish a representative whole diet concentration BMF estimate (Flint et al. 1988). Furthermore, by simultaneously measuring chemical concentrations across multiple organisms, the TMF incorporates taxa- and species-specific differences in metabolic biotransformation capacities for a given contaminant (Mackintosh et al. 2004).

Recent studies have attempted to characterize the separate effects of chemical, physiological, ecological, and environmental characteristics on persistent organic pollutant (POP) bioaccumulation (Selck et al. 2012) and TMFs (Borgå et al. 2012b). Some common issues related to the TMF approach that have been identified include the need to standardize tissue analyses (e.g., muscle, whole body, or other tissues) across trophic levels, the use of appropriate concentration units (dry weight, wet weight, or lipid equivalents) for a given contaminant of study (McGoldrick et al. 2014), and the need for robust sampling efforts across multiple trophic levels (Condor et al. 2011; Borgå et al. 2012b). An issue that has received less attention concerning the application of TMFs is the consideration of differences in spatial scales of animal foraging ranges among organisms collected as part of a TMF evaluation (Burkhard et al. 2013). It is apparent that more mobile top predators can act as ecological integrators (McCann et al. 2005) by consuming prey items over large spatial dimensions relative to the diet items (e.g., benthic invertebrates) they consume. These differences in animal foraging ranges can interact with spatial scale heterogeneity of water and sediment contamination leading to under- or overestimates of TMFs depending on where animals are collected as part of a TMF estimation. For example, high degrees of spatial heterogeneity for chemical concentrations in water and sediments have been demonstrated for the Detroit River (Drouillard et al. 2006, 2013) and Hudson River (Bopp et al. 1981). Under such circumstances, it can by hypothesized that collection of benthic prey items exclusively in contaminated locations will lower the TMF because benthic organisms typically have limited mobility (Zsolt and Ciborowski 1989) compared to more mobile top predators that integrate food items from a combination of clean and contaminated areas.

In the present study, a food web bioaccumulation model described by Arnot and Gobas (2004) was used to estimate TMFs for polychlorinated biphenyls (PCBs) in a riverine system. Model modifications were made to allow for stochastic variation in model parameters and parameter ranges as described for single species bioaccumulation models described by Selck et al. (2012). The modified model was used to explore the relative importance of model parameters categorized as environmental parameters (chemical concentrations in water and sediments), physiological parameters (species-specific biological attributes) and ecological parameters (diet matrix, effective trophic position, and foraging range) on the magnitude and uncertainty of model predicted PCB TMFs. Although several studies have documented uncertainty propagation in food web bioaccumulation model output for bioaccumulative chemicals such as PCBs (MacLeod et al. 2002; Nfon and Cousins 2007; de Laender et al. 2010; Selck et al. 2012), this is, to our knowledge, the first study that specifically interprets how uncertainty propagates to model based estimates of TMF.

To test the interaction between spatial heterogeneity of chemical contamination and animal movement on TMFs, the model was adapted to the Detroit River. The Detroit River has been documented to have substantial spatial heterogeneity in water and sediment contamination (Drouillard et al. 2006; Szalinska et al. 2011; Drouillard et al. 2013) and has a well-characterized food web in which the biomagnification of pollutants such as PCBs has been demonstrated (Russell et al. 1999). By choosing a well-characterized system such as the Detroit River, realistic values and variation in key model inputs (water and sediment PCB concentrations) could be applied in conjunction with hypothetical animal movement profiles to test how robust TMFs may be toward spatial integration artifacts related to the location of animal or food web item collections. Thus, although the study goals did not include an explicit model validation component to it, the intention of the study was to provide a rigorous evaluation of model behavior with respect to TMF predictions under a variety of model scenarios incorporating parameter uncertainty and ecological considerations (e.g., fish movements) rarely incorporated within food web bioaccumulation models. Specifically, the objectives for this study were to determine: 1) the ability of the food web bioaccumulation model to predict appropriate magnitude and hydrophobicity trends of TMFs for PCBs, 2) how variation in environmental, physiological, and ecological parameters contribute to uncertainty of model predicted TMFs, 3) the influence of sampling strategies and sampling intensity on TMF uncertainty, and 4) how spatial heterogeneity in water and sediment contaminant concentrations and different foraging ranges of fish interact to influence the magnitude and uncertainty of model predicted TMFs.

METHODS

Study site

The model was adapted to explore a hypothetical food web based on contaminant concentrations empirically measured in the Detroit River. The Detroit River is a 52 km connecting channel linking Lake Huron and Lake Erie via the St. Clair River and Lake St. Clair. The Detroit River was designated an International Joint Commission Great Lakes Area of Concern in 1987 based on an assessment of a series of beneficial use impairments, several of which were evaluated as impaired (UGLCCS 1988; McCrea et al. 2003). Among these include fish consumption advisories for the Detroit River issued by both Michigan and Ontario that continue to be present today and are driven primarily by the bioaccumulation of PCBs in commonly consumed sport fish (OMOE 2009; Kashian et al. 2014). Furthermore, the Detroit River has been intensively

sampled to determine spatial and temporal patterns of water and sediment PCB contamination (Drouillard et al. 2006, 2013; Szalinska et al. 2011). These studies have demonstrated major spatial differences in PCB concentrations along the river width and length because of channelization of the river by fast flowing shipping channels and several islands that effectively separate past and ongoing US and Canadian sources of pollution along the river length (Drouillard et al. 2006). Given the size and delineation of contamination zones and plausibility of food web compartmentalization, the system was considered an ideal system to explore how spatial heterogeneity of contamination might interact with animal movements causing variation in TMFs.

Food web model

Model simulations were performed using a well-established food web bioaccumulation model developed for nonionized, hydrophobic organic contaminants as described by Arnot and Gobas (2004). This model builds on the general concepts provided by Thomann and Connolly (1984) integrating predictive algorithms and parameter estimates provided by numerous subsequent studies (Clark et al. 1990; Gobas 1993; Morrison et al. 1997). In the current simulations, it was assumed that the metabolic biotransformation of simulated PCB congeners was negligible (Elskus et al. 1994). Thus, biotransformation was not considered as a factor contributing to uncertainty of PCB TMFs but is likely to be more relevant for other chemicals of interest. A summary of the food web bioaccumulation model equations, parameters and inputs is provided in the Supplemental Data (Supplemental Data Section 1).

Environmental inputs used in the model include congener-specific PCB concentrations in water (ng/mL) and sediments (ng/g organic C), and these are referred to as model inputs to distinguish from other model parameters. The model outputs included congener-specific, lipid equivalent PCB concentrations in different organisms included in the food web ($n = 37$ study species, 9 of which were invertebrates; see Supplemental Data Table S5). This information was used in conjunction with trophic level designated by the feeding matrix of a given simulation to compute TMF (described below). The model was run both deterministically as well as under stochastic simulation conditions. In deterministic simulations, the model yields one output value for a given simulation scenario using the best, or recommended, values for each model input and parameter. Under stochastic simulations, the model was run via Monte Carlo simulations (Crystal Ball Software), over 10 000 iterations, with the output of each iteration saved to generate a distribution of model outcomes. During each iteration, model inputs or parameters were allowed to vary, either in isolation or all together (combined stochastic simulation), according to a specified distribution. The distribution of outputs from the stochastic simulations were considered representative of model uncertainty and reflect the range of potential model predictions under conditions of error or variable ranges associated with model inputs and model parameters. For the purposes of the present study, model sensitivity was evaluated under single parameter perturbations, i.e., only 1 model input or parameter was allowed to vary stochastically across model iterations whereas all other input and parameters were held constant. Model sensitivity was quantified by calculating the coefficient of variation of model outputs for a given simulation. Model uncertainty was evaluated when all model inputs and parameters were allowed to vary stochastically during each model iteration. The model uncertainty was quantified as the 95% confidence interval (95% CI) surrounding the mean model prediction of TMF for a given simulation.

Table 1 provides a description of model inputs and parameters that were allowed to vary under various stochastic simulations. A total of 17 parameters were allowed to vary, affecting 7 submodels, with the exception of chemical-specific properties including: octanol-water partition coefficient (K_{OW}), organic carbon-water partition coefficient (K_{OC}), and the proportionality constant of nonlipid organic matter (NLOM) relative to lipids (ϕ_{NLOM}). These coefficients were fixed for a given PCB congener because they reflect physical constants and do not vary among organisms. This enabled the investigation to focus on uncertainty contributions provided by environmental, physiological, and ecological parameters. Previous food web bioaccumulation modeling studies demonstrated the contributions of error in chemical partition coefficient estimates to overall model uncertainty (Nfon and Cousins 2007). Assumptions about the error distributions of parameters and error ranges attributed to each variable are also described in the Supplemental Data.

Under deterministic simulations, the feeding matrix describing the proportion of diet items included in any given animal diet, was predefined using literature estimates (Morrison et al. 1997) for the simulated organisms. The diet proportions were then used to calculate the trophic level of the organism using the following equation:

$$TL = 1 + \sum_{i=1}^{n} (p_i \times TL_i) \quad (1)$$

where p_i is proportion of diet item I, and TL_i is trophic level of organism i. Sediment and phytoplankton were assigned fixed TL values of 1, whereas zooplankton was assigned a fixed TL value of 2. All other species had TLs estimated according to Equation 1 based on the proportion of diet items used in the simulation. Under stochastic simulations, where variation in the feeding matrix was introduced, the trophic level of each organism was estimated during each model iteration and used to establish a distribution of values for animal trophic position across model trials. The latter was used to interpret how variability in organism feeding ecology contributed to uncertainty in TMFs. TMFs were estimated by performing linear regressions on the log-transformed, lipid-equivalent PCB concentrations against organism trophic level according to Equations 2 and 3:

$$\log(PCB_{lipid}) = b + (m \times TL) \quad (2)$$

$$TMF = 10^m \quad (3)$$

where b and m are the intercept and slope, respectively, of the regression line.

Model simulations

Four sets of model simulations were used to address the different objectives related to the study.

i) Baseline (deterministic) food web bioaccumulation model. The first simulation used the river-wide average water and sediment concentrations for the Detroit River and the recommended literature estimates for each model

Table 1. List of model parameters and descriptions

Parameter	Parameter description	Value
Under direct manipulation[a]		
T	Detroit River temperature	10.34 ± 8.39
BW	Organism body weight	Table A.3
C_w	Concentration of chemical in water	Table A.1
C_{sed}	Concentration of chemical in sediment	Table A.1
f_{OC}	Fraction organic C in sediment	Table A.4
$p_{(o,w)}$	Fraction of respired overlying water	Table A.2
$p_{(p,w)}$	Fraction of respired porewater	Table A.2
p_i	Proportion of diet item i's	Table A.5
AE_{lip}	Dietary assimilation efficiency for lipid	Table A.2
AE_{NLOM}	Dietary assimilation efficiency for NLOM	Table A.2
AE_W	Dietary assimilation efficiency for water	Table A.2
$p_{lip,\ diet\ i}$	Proportion of lipid in diet item i	Table A.3
$p_{NLOM,\ diet\ i}$	Proportion of NLOM in diet item i	Table A.3
p_{lip}	Proportion of lipid in the organism	Table A.3
p_{NLOM}	Proportion of NLOM in the organism	Table A.3
Submodels affected by manipulations[b]		
C_{O2}	Concentration of oxygen in water	
G_d	Organism feeding rate	
G_v	Organism gill ventilation rate	
E_W	Chemical absorption efficiency from water	
E_D	Chemical absorption efficiency from food	
$C_{w(p,w)}$	Concentration of contaminant in pore water	
G_{gro}	Organism growth rate	
Fixed		
D_{sed}	Sediment density	1.2
$p_{w,\ diet\ i}$	Proportion of water in diet item i	Table A.3
ϕ_{NLOM}	NLOM partitioning equivalent in the organism compared to octanol	0.05
p_w	Proportion of water in the organism	Table A.3
K_{OW}	The octanol–water partitioning coefficient	Table A.1
K_{OC}	The organic carbon–water partitioning coefficient	$= 0.35 \times K_{OW}$

[a]Constant causing E_W to vary according to a triangular distribution between 0.11 and 0.6, with empirically calculated E_W as the peak (Selck et al. 2012).
[b]Constant causing E_D to vary according to a triangular distribution between 0.23 (or the empirically calculated E_D if it was lower) and 1.01 with the empirically calculated E_D as the peak (Selck et al. 2012).

parameter to provide deterministic TMF estimates for 35 PCB congeners. The 35 PCB congeners were selected based on the availability of empirical input data on river-wide water and sediment concentrations and included the following congeners: (IUPAC numbers: 31/28, 42/47, 44, 64/41/71, 66/95, 70/76, 74, 97, 99, 101, 105, 110/77, 118, 129, 138/163, 141, 146, 149, 151, 153/132, 158, 170/190, 171/202, 172, 174, 180, 182/187, 183, 185, 194, 195/208, 196/203, 200, 201 and 206). The above simulation is herein referred to as the baseline simulation and forms the basis on which to compare the magnitude and pattern of model TMF estimates against generally

reported empirical trends of PCB TMFs from the literature. It should be noted that the intention of this study was not to provide a formalized model validation, or assess the accuracy of model predictions against measured chemical concentrations in different organisms from the Detroit River, which is the focus of a different study. Instead the intention was to evaluate if the pattern and overall magnitude of model output generally conforms to empirical observations of PCB TMFs in the river.

ii) Sensitivity of food web bioaccumulation model.
The next set of simulations served as a sensitivity analysis where model inputs and parameters were allowed to vary under a series of Monte Carlo simulations. In model sensitivity simulations, only a single model input or parameter was allowed to vary with each model iteration whereas the others were held constant. For model inputs, the empirically derived mean and standard deviation of the Detroit River water or sediment concentration was used in conjunction with Monte Carlo simulations. For model parameters, variation around their recommended values were assigned as described by Selck et al. (2012). All stochastic simulations were performed for 10 000 iterations in which the specified parameter was allowed to vary randomly within specified constraints and according to the distribution as described in Supplemental Data (Tables S1, S2, S3, S4, and S5). For each model iteration, the model calculates and stores an estimate of TMF. The coefficient of variation (CV; %) was calculated based on the distribution of model estimated TMFs for a given sensitivity trial as a measure of model sensitivity to a given input or parameter. CVs for each sensitivity trial were compared to determine which parameters or model inputs contributed to the greatest variation in model predicted TMFs. The purpose of sensitivity simulations was to determine how each model input or parameter contributed to uncertainty in the estimated TMF, and to identify the model parameters that illicit the most change in the TMF given realistic constraints in the variable range.

iii) Effect of sampling intensity on TMF variation.
A combined uncertainty simulation was generated such that all model inputs and the 17 model parameters identified as variables were allowed to vary simultaneously during each model iteration. Here, random values for individual parameters were chosen in the Monte Carlo analysis, such that the choice of one value for a given parameter was independent of values assigned to other parameters under stochastic choice. It should be noted here that the 5 submodels that incorporate multiple parameters under stochastic choice retained their logical relationships to one another for the parameters they have in common. However, they could be decoupled in output from one another when they included different sets of parameters from one another. For example, feeding rate and growth submodels were under a common influence of stochastic change in body weight for each trial iteration. Feeding rate was also influenced by stochastic variation in temperature whereas growth was not influenced. These features are inherent to the model structure as published in Arnot and Gobas (2004). The model output for each iteration of the combined trial was stored independently. Randomly selected subsets of the above distributions were then selected to determine how sampling intensity (number of species sampled and number of replicates per species) contributes to estimates of variation surrounding TMF by the model.
Six sampling strategies were compared to characterize how the number of species sampled, and number of replicates taken per species changes, estimates of uncertainty surrounding TMFs. The first strategy calculated the TMFs and 95% CI around TMFs that would occur under high resolution sampling, i.e., if all 37 species included in the model were sampled with a replication effort of 10 000 replicates per species. This effectively represents the slope and confidence interval generated from a plot of 370 000 log-transformed animal concentrations against trophic level, reflecting of the full output across all model iterations. The second sampling strategy used a more realistic sampling intensity considered comparable to empirical TMF sampling programs, which sample fewer species (<10) (Martin et al. 2004; Tomy et al. 2004, 2007; Law et al. 2009). In this case, a subset of 25 species (or organism type) was randomly selected from 37 species included in the full simulation set, still with 10 000 replicate sampling values associated with each species. The third sampling strategy used the same 25 randomly selected species with only 5 replicate sampling values associated with each species. Thus, 5 independently chosen random model iterations were selected from the model output. The plot of 125 (25 species × 5 replicates) selected log transformed animal concentrations against trophic level was then used to generate the slope and confidence interval surrounding the TMF estimate. For the second and third sampling strategy, the following organisms were used based on a randomized selection process: alewife, black crappie, bluegill, bowfin, brook silverside, crayfish, freshwater drum, *Gammarus*, gar pike, largemouth bass, mayfly, muskellunge, oligochaetes, phytoplankton, redhorse sucker, round goby, small white sucker, smelt, spottail shiner, stone cat, white sucker, yellow perch, young of the year (YOY) fish, dresseinid mussels, and zooplankton. The fourth sampling strategy randomly selected 15 species, with at least 1 organism selected from each trophic level, with only 5 replicate sampling values associated with each species. The randomly selected organisms for this sampling strategy were alewife, brook silverside, chironomids, crayfish, freshwater drum, largemouth bass, oligochaetes, redhorse sucker, rock bass, round goby, stone cat, white perch, white sucker, dresseinid mussels, and zooplankton. The fifth sampling strategy randomly selected 10 species, again with at least one organism selected from each trophic level, and only 5 replicate sampling values for each species. The species randomly selected for this strategy were bluegill, chironomid, crayfish, gizzard shad, largemouth bass, northern pike, rock bass, white sucker, young of the year fish, and dresseinid mussels. The sixth, and final sampling strategy randomly selected 5 species (chironomids, oligochaetes, walleye, white perch, and white sucker) with only 5 replicate sampling values for each species.

iv) Effect of spatial variability on TMF uncertainty.
A final set of simulations was performed to address the interaction between spatial variation in model inputs and fish movements on TMF estimates. To facilitate this comparison, 3 sets of combined uncertainty simulations were performed. The first used the final result from simulation set (iii) that established a river-wide TMF and

error estimate surrounding TMF based on the reduced species ($n = 25$) and sampling ($n = 5$/species) intensity scenario. In the second set of simulations, the Detroit River was divided into 6 food web zones (Figure 1) demonstrated to exhibit significant differences in sediment and water contaminant concentrations (Drouillard et al. 2006, 2013). Here, it was assumed that all organisms within a given food web zone lived their entire lives within the confines of that zone. The model was run independently for each zone to generate a zone-specific estimate of TMF and error range in TMF. Similar to the first simulation, these simulations adopted the reduced species and sampling intensity scenario considered more representative of an empirical TMF survey. Neither the first or second simulation sets allow for animal movements between zones. Thus, differences in TMFs that occur between the first 2 simulations are due to compartmentalization of the food webs and differences in the magnitude of contaminant inputs between the zones.

In the third simulation set, movement between different food web zones was permitted for some fish. For these simulations, phytoplankton, zooplankton, and benthos were assumed to remain within a given food web zone over their entire lifespan. In contrast, fish were allowed to move between zones as established through a literature review of species-specific foraging ranges described in Kashian et al. (2010). This third simulation type was generated for each food web zone using the reduced sampling intensity scenario adopted for the first 2 simulations. For each zone, fish-foraging ranges were incorporated into the model by calculating the weighted average PCB concentration in diet items from across its foraging range generated by means of a foraging coefficient. Essentially, the foraging coefficient is used to specify the proportion of time a fish from a given zone spends in other zones. This proportion was calculated based on a literature review of migration behavior and home ranges of all 17 fish species included in the model (Kashian et al. 2010). Kashian et al. (2010) developed zone-specific adjustment probabilities for each species based on the above migration habits, movement rates, and home ranges with a comparison to the width and length of each zone in the Detroit River. This arrangement results in the fish always spending more time in the zone from which it is captured (i.e., its primary zone) followed by smaller proportions of time spent in adjacent zones and the least amount of time spent in the most distant zones. The fish is assumed to have access to all food items and consume them in proportion to the feeding matrix for a given simulation trial, for all zones from which it feeds. In these simulations, the sum proportion of diet items was allowed to vary as described in Supplemental Data Table S5, and the species-specific foraging coefficients were allowed to vary on a lognormal distribution ± 25% of the mean foraging potential. Hence, for these simulations the amount of a specific diet item consumed in each zone varies as well as the foraging range of the organism under each simulation trial.

The observations generated from the third simulation series were compared against the first 2 simulation sets by contrasting the magnitude and uncertainty in TMFs across simulations and between zones. For example, simulation series 1 presents an idealized case of TMF where the entire Detroit River food web is homogeneously distributed and contamination is equally distributed throughout the ecosystem. Simulation series 2 presents a scenario where food webs are isolated from one another. Simulation series 3 presents the scenario where fish differentially integrate chemical signatures from among adjacent and their home zones. Finally, by comparing TMFs across zones in simulation series 3, the predicted bias due to sampling all organisms in one zone under a condition of differential foraging movement by different species can be evaluated.

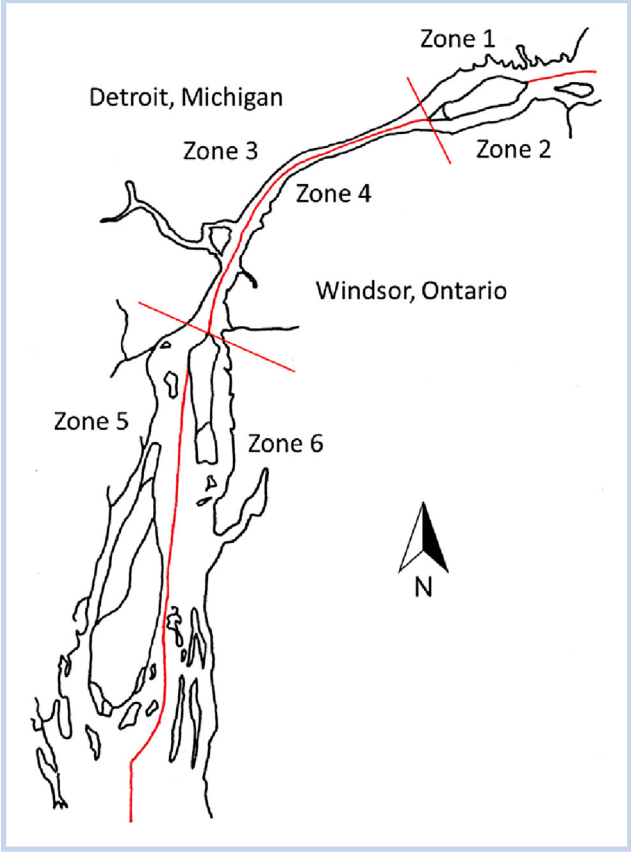

Figure 1. Map of the Detroit River divided into the 6 zones used in the model simulations, where the Michigan side of the river (Zones 1, 3, and 5) have higher contamination than the Ontario side of the river (Zones 2, 4, and 6).

RESULTS AND DISCUSSION

Baseline (deterministic) food web bioaccumulation model

The baseline model output of predicted organism concentrations yielded significant relationships between lipid-equivalent PCB concentrations and animal trophic level ($R^2 > 0.7$ for individual log linear regression fits) for each PCB simulated. The relationship between log concentration and trophic level is presented for 3 selected chemicals representing different homologue groups, PCB 31/28, 153, and 194 in Figure 2. Although a log linear regression provided a satisfactory fit to the data, a breakpoint in the regression slope was apparent between trophic levels 1 to 3 and tropic levels 3 to 4.3. This apparent breakpoint appears to be related to higher growth dilution of smaller organisms as predicted by the growth submodel contributing to lower bioaccumulation potentials of <1 g animals.

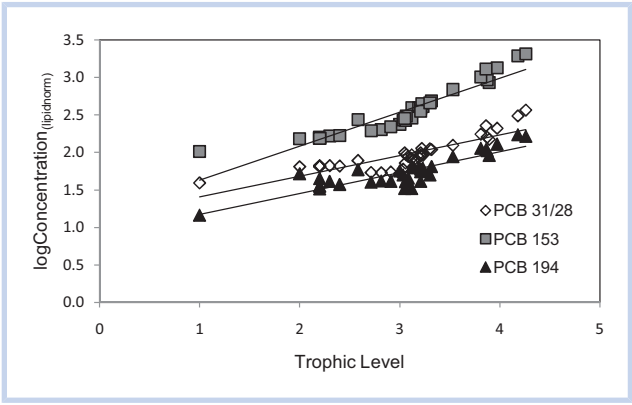

Figure 2. Deterministic model predictions for lipid-equivalent PCB concentrations against trophic level for a Detroit River food web. Each slope has an R^2 greater than 0.7 (0.73, 0.87, and 0.75 for PCB 31/28, 153, and 194, respectively).

Figure 3 presents simulated TMFs as a function of log K_{OW} for all 35 PCB congeners from the deterministic model (diamonds) and the combined uncertainty simulation (squares). The deterministic model generated a pronounced parabolic relationship between TMF and chemical hydrophobicity with a maximum TMF of 3.0 predicted for PCB 146 ($\log K_{OW} = 6.76$). Smaller amounts of noise between congeners of similar K_{OW} are apparent in the figure and are related to differences in the ratio of sediment–water contamination between individual congeners used as model inputs. In this case, congeners with higher sediment–water concentrations ratios generated slightly lower TMF estimates. Across the individual PCBs, sediment–water fugacity ratios varied by 211-fold between compounds. However, it is apparent from Figure 3 that chemical hydrophobicity, as opposed to the magnitude of sediment–water concentration ratio, provided the stronger regulator of TMF in model simulations given the model parameterization.

Sensitivity of food web bioaccumulation model

Table 2 summarizes the results of model sensitivity trials by presenting the CV surrounding TMF estimates for 3 selected PCB congeners where individual model inputs or parameters were allowed to vary in isolation. All single variable uncertainty simulations produced TMFs with CVs less than 10%, with the exception of temperature simulations where TMFs CVs ranged from 11% to 28% among selected chemicals. These results suggest that model predictions of TMF were surprisingly robust given the best estimates of parameter constraints and realistic variation in model inputs. Temperature was the most important parameter contributing to model sensitivity across selected congeners, and the role of temperature as a contributor to model uncertainty increased with chemical hydrophobicity. Temperature is an important term that modifies the magnitude of organism feeding rates. It also influences the saturation concentration of O_2 in the water, which in turn affects the gill ventilation rate (Table 1). As temperature increases, feeding rate and gill ventilation rate will both increase. However, feeding rate is more sensitive to temperature change than gill ventilation rate, leading to higher bioaccumulation estimates for iterations with higher temperature. As log K_{OW} increases, food sources become the more dominant exposure route for PCBs, combined with the positive relationship between % CVs and log K_{OW} suggests that temperature has a greater effect on feeding rate than gill ventilation rate.

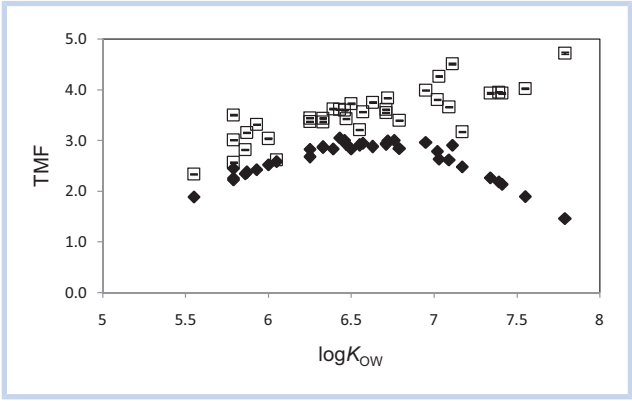

Figure 3. Relationship between model predicted TMFs versus chemical log K_{OW} for 35 PCB congeners. Diamonds indicate deterministic simulations (37 species), open squares represent river-wide combined uncertainty simulations (37 species, $n = 10\,000$) with error bars included, however, due to high replication efforts the errors are very low.

For the remaining variables, the mid K_{OW} congeners (represented by PCB 153), were generally more robust to the sensitivity analyses then the low and high K_{OW} congeners, with lower TMF CVs (ranging from 0%–2.8% for PCB 153 vs 0%–3.0% for PCB 31/28 and 0%–7.7% for PCB 194). However, commonalities in the major parameters contributing to model sensitivity were apparent across the selected congeners. After temperature, the chemical absorption efficiency from food (E_D) contributed most strongly to variation in TMF estimates across congeners. This agrees with previous analyses that have identified E_D as a key driver of uncertainty in model generated biomagnification estimates applied and validated against empirical measurements completed for several food web items in Lake Ontario (MacLeod et al. 2002). The proportion of overlying water respired by organisms relative to sediment porewater, $p_{(o,w)}$, was the third strongest contributor to variation in TMF estimates (PCBs 31/28 and 153) and fourth strongest contributor for PCB 194. This parameter deviates from a value of 100% respiration of overlying water, $p_{(o,w)}$, only for benthic invertebrates and benthic feeding fish. When $p_{(o,w)}$ is low for a given benthic organism, pollutant exposure becomes primarily a function of sediment fugacity and the potential for elimination across respiratory surfaces decreases, especially when sediment-water fugacity ratios are much greater than 1. This condition leads to higher variation in predicted chemical concentrations in benthic invertebrates relative to phytoplankton and zooplankton. This added variation around the TMF intercept (i.e., concentration in baseline organisms) translates into increased variation of individual TMF estimates during model uncertainty propagation.

Although the present study is focused on using a food web bioaccumulation model to examine model sensitivity and uncertainty in TMF predictions, past studies have used similar approaches to estimate uncertainty in model predicted PCB concentrations in different animals being simulated. For instance, previous research has demonstrated that variation in sediment and water PCB concentrations provide a great contribution to model sensitivity relative to organismal concentrations (MacLeod et al. 2002; de Laender et al. 2010). Selck et al. (2012) demonstrated that sediment and food concentration constituted the greatest input flux of

Table 2. A comparison of single-variable river-wide uncertainty simulations reported as coefficients of variation (%)

Parameter	Classification	PCB 31/28	PCB 153	PCB 194
C_{wat}	Environmental	1.57	2.16	0.082
C_{sed}	Environmental	1.19	1.15	1.05
f_{oc}	Environmental	0.04	0.12	0.30
Temperature	Environmental	11.38	15.08	28.06
E_W	Physiological	2.22	0.79	2.44
E_D	Physiological	2.96	2.75	7.67
% Lipids	Physiological	1.78	1.94	2.20
% NLOM	Physiological	0.84	0.78	2.14
BW	Physiological	1.54	0.8	0.81
AE_{lip}	Physiological	0.56	0.88	0.56
AE_{NLOM}	Physiological	0.36	0.91	0.63
AE_w	Physiological	0.01	0.07	0.12
$p_{(o,w)}$	Physiological	2.30	2.01	2.61
Dietary proportions	Ecological	0.56	0.58	0.75

The parameters are as follows: contaminant concentration in water and sediment (C_w, C_{sed}), chemical absorption efficiency from water and diet (E_W, E_D), the dietary assimilation efficiency for lipid, nonlipid organic matter (NLOM; AE_{lip}, AE_{NLOM}), and fraction of overlying respired porewater ($p_{(o,w)}$).

PCB153 among 4 aquatic (mayfly larvae, polychaetes, fish) and terrestrial (little owl) taxa with environmental parameters including diet composition and concentration greatly contributing to variation in model predicted organismal concentrations. Finally, in a similar study by Nfon and Cousins (2007) log K_{OW} was found to be the single most sensitive parameter. This parameter, however, was omitted in the present set of simulations, as discussed previously. Ultimately, the observations from our study suggest that model sensitivity to parameters and inputs differ depending on the desired model output (i.e., organism concentrations vs integrated biomagnification measures).

After completion of model sensitivity trials, a combined uncertainty trial was performed that allowed all model inputs and parameters to vary at the same time during each model iteration. TMFs generated by the combined uncertainty simulation are provided in Figure 3 and are contrasted against the deterministic simulation discussed previously (diamonds). Notably, the deterministic model predicted a parabolic relationship between TMF and K_{OW}, however, the combined uncertainty simulation predicts a positive linear relationship between TMF and chemical hydrophobicity.

The parabolic trend predicted for TMF with increasing K_{OW} from the deterministic model mirrors that predicted for individual animal BMFs and is dictated by competing processes of uptake and elimination for each organism of simulation (Gobas et al. 1988). Among uptake processes, uptake flux is dominated by food for most PCBs. However, uptake flux via food becomes progressively more important than water up to a log K_{OW} of approximately 6.8 at which point decreases in E_D occur at a pace that parallels the decrease in K_{BW} with further increases in chemical K_{OW} (note E_w is mostly insensitive to changes in K_{OW} over the hydrophobicity range of PCBs). Similar patterns are apparent for elimination processes. In this case, water dominates elimination flux up until a log K_{OW} of approximately 5.5, followed by an increasing dominance of fecal losses up until log K_{OW} of 6.8. Beyond log K_{OW} 6.8, growth dilution begins to exert an increasing level of importance to the total chemical elimination due to further hydrophobicity-related decreases in elimination to water and feces. These transitions regulate the shape of the TMF versus K_{OW} curve and specify the K_{OW} associated with peak TMF. For example, if E_W drops to zero, TMF becomes independent of chemical K_{OW}. Likewise, if E_D is increased by a value of 25% above the current submodel prediction, TMF approaches a saturation value beyond log K_{OW} of 7. Under the combined uncertainty trials, variation in E_W, E_D, and BW (that modifies growth among other variables) alter the transition points of competing uptake and elimination processes changing the K_{OW} at which peak TMF occurs. For example, higher values of E_D and of BW (resulting in lower growth dilution) can serve to increase the K_{OW} value at which peak TMFs occurs to one beyond the hydrophobicity range of PCBs. Because single parameter sensitivity trials showed little evidence for pronounced differences in the effect of E_D, E_W, or BW (Table 2) this suggests that the linearized trend of TMF with chemical K_{OW} were produced by interactions of multiple parameters under variation.

Unfortunately, there are limited case studies that have specifically examined the TMF–K_{OW} relationship for PCBs in the field. Kidd et al. (1998) demonstrated a positive relationship between TMF and log K_{OW}, with TMFs ranging from just over 1 for the low K_{OW} congeners (log K_{OW} of 5.9) to 1.5 for high log K_{OW} congeners (log K_{OW} of 6.9). Further positive correlations were found in other field studies examining the relationship between TMFs of PCBs and log K_{OW} (Fisk et al. 2001; Hoekstra et al. 2003; Walters et al. 2011). This positive relationship was more recently confirmed for brominated

flame retardants but over a wider log K_{OW} range of 5.0 to 10.0, and with TMF ranging from 1.0 to 6.5 (Toyoshima et al. 2009). Notably, the above field studies produced linear TMF–K_{OW} relationships consistent with our combined uncertainty simulation. Alternatively, in a study documenting biomagnification factors in laboratory exposed organisms Fisk et al. (1998) shown parabolic BMF versus K_{OW} relationships more consistent with the deterministic simulations. Interestingly, in a subsequent study, Fisk et al. (2001) noted an increasing positive relationship between TMFs and log K_{OW}s, and a parabolic BMF versus K_{OW} relationship for the same congeners and organisms. These simulations provide support for a hypothesis that differences between laboratory BMF and field TMF observations across chemicals are related to differences in the degree of control of toxicokinetic, physiological, and ecological variables affecting exposures by organisms in the field compared to the laboratory. For example, Liu et al. (2010) demonstrated large variation in the magnitude of dietary absorption efficiencies of PCBs in fish across different food items as well as differences in the E_D versus log K_{OW} relationship generated for different foods. In contrast, laboratory-exposed fish in bioaccumulation studies are more commonly subject to a single food type and thus variation in E_D is likely to be minimized. Other researchers have called into question the use of single values of E_W (Sijm et al. 1994; Drouillard et al. 2009) and growth (Jackson 1996; Paterson et al. 2006, 2007a, 2007b) across species, age and size classes, and between seasonal temperature shifts.

Effect of sampling intensity on TMF variation

Empirically generated TMFs are calculated by collecting replicate samples from multiple species of a given ecosystem. The statistical power related to detection of a TMF greater than 1 is therefore strongly influenced by the range and number of trophic levels sampled, number of species sampled and replication effort performed for each species (Borga et al. 2012b). Figure 4 contrasts mean values and variation around TMF estimates from the combined uncertainty simulation using the full simulation data set (i.e., 37 species and $n = 10\,000$ samples per species = high resolution sampling) against 5 different, sampling strategies (25 species and $n = 10\,000$ samples per species, 25 species and $n = 5$ samples per species, 15 species and $n = 5$ samples per species, 10 species and $n = 5$ samples per species, and finally 5 species and $n = 5$ samples per species). Although the species were chosen randomly, it was ensured that a species from each trophic level was selected. Data for the baseline (deterministic) simulation are also provided on Figure 4 to provide context (37 species).

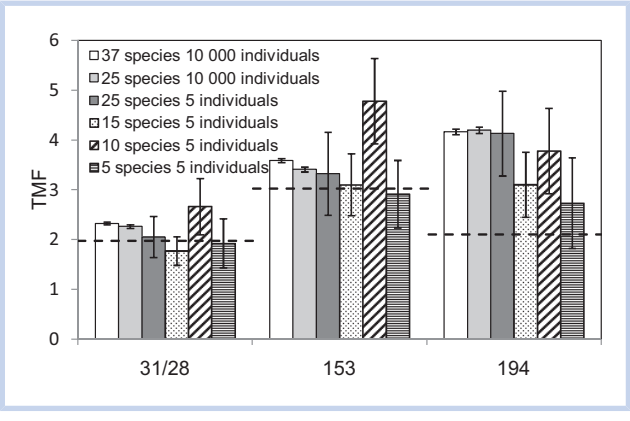

Figure 4. Comparison of river-wide combined uncertainty model predicted TMFs and 6 different sampling strategies for different PCB congeners. The sampling strategies have 37 species, 25 species, 15 species, 10 species, and 5 species randomly selected, as well as 10 000 or 5 individuals of each species depending on the sampling strategy. Error bars represent the 95% confidence intervals for the TMF regression. Horizontal dashed lines represent the river-wide deterministic TMF estimate.

For each of the selected chemicals, stochastic simulations produced mean TMF values that exceeded the baseline TMF estimates with the exception of 15 species ($n = 5$) for PCB 28/31 and 5 species ($n = 5$) for PCB 28/31 and PCB 153; although the effect was much more pronounced for PCB 194 compared to PCBs 28/31 and 153. In the case of the high resolution sampling TMF estimates, the 95% CI surrounding the mean TMF estimate were very small such that there was no overlap between the 95% CI and the TMF generated by the deterministic model. However, in the restricted sampling simulations, the 95% CI showed overlap with the mean TMFs generated by both the deterministic model (exception: 10 species; $n = 5$/species) and high resolution uncertainty model for PCBs 31/28 (exception: 15 species; $n = 5$/species) and PCB 153 (exception: 10 species; $n = 5$/species). However, for PCB 194, the 95% CI surrounding the restricted sampling TMF overlapped only the mean TMF estimate from the high resolution model but not that of the deterministic model except for the lowest resolution sampling method (5 species; $n = 5$/species) where overlap in the 95% CI occurred with the deterministic simulation and in the 15 species; $n = 5$/species simulation that did not overlap with the high resolution samplings. This reinforces earlier observations comparing TMF-K_{OW} trends between the deterministic and combined uncertainty simulations, implying that the differences in parabolic versus linear trends in TMF would be significant even under reduced statistical power associated with a more realistic sampling strategy unless very low sampling intensities are employed. The later exception is related to poor statistical power and random effects related to the choice of organisms sampled as part of the TMF estimate.

Finally, all congeners, including the least hydrophobic PCB (PCB 31/28), exhibited 95% CI TMF estimates that exceeded a value of 1. This suggests that uncertainty propagation by the model generates PCB TMF estimates that can be statistically distinguished from a value of unity even under realistic and undersampled sampling strategies.

Effect of spatial variability on TMF uncertainty

Figure 5 provides a comparison of TMFs from the 3 model scenarios for the selected chemicals in the 6 model zones using the restricted sampling strategy described previously (note that river-wide simulation is identical for each of the zones and replicated on each figure for context). The multizone TMFs exhibited 95% CI that overlapped with the CIs of the river-wide model for all zones and selected PCBs except for Zone 6 where differences between the 2 models were apparent for PCBs 31/28 and 153 but not for 194. These differences were relatively small, with only a small difference apparent between the lower CI of the multizone model and upper CI of the river-wide model. This was likely an artifact of the restricted sampling strategy. With the exception of PCBs 31/28 and 153 in one zone, the results support the common assumption that changes in background contaminant concentrations do not significantly affect food web-specific TMFs (Broman et al. 1992).

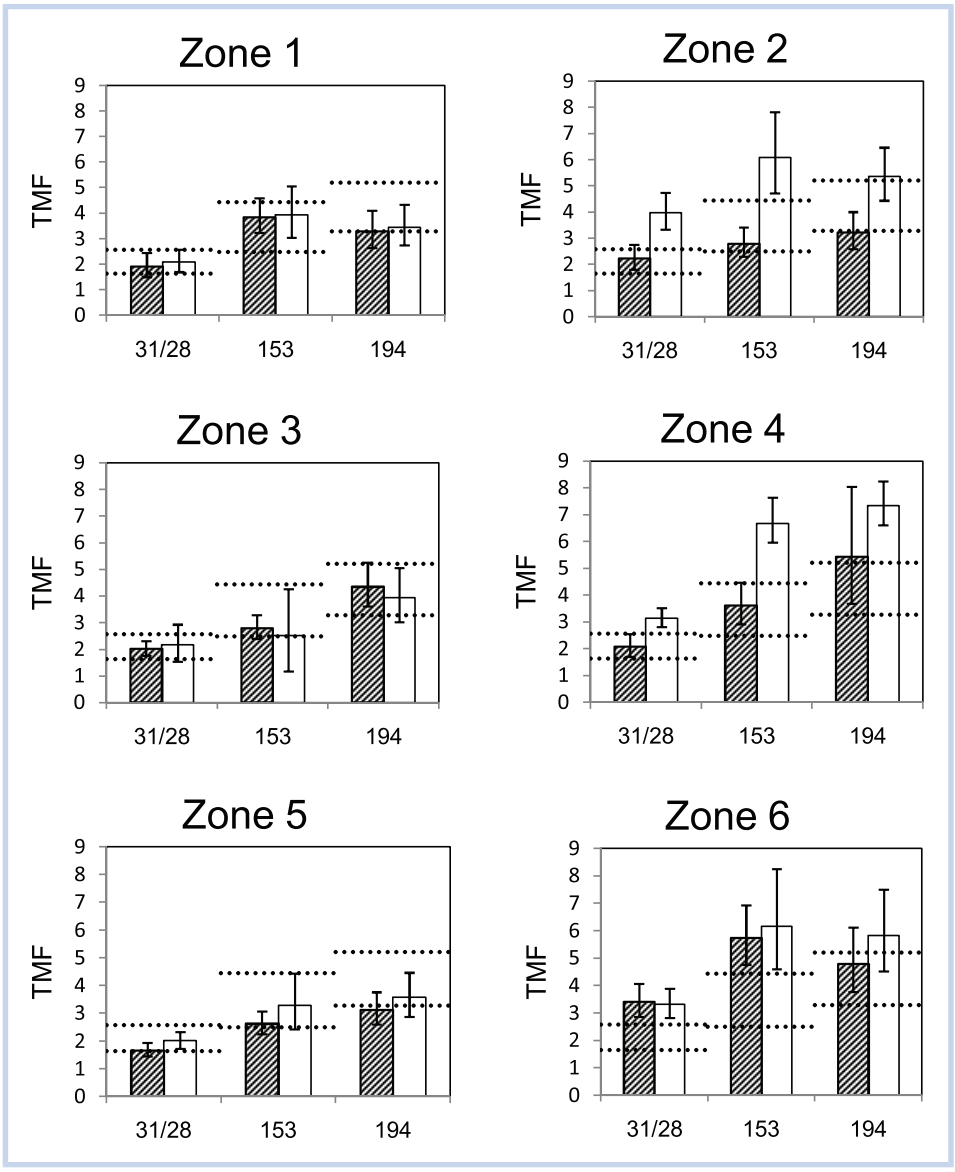

Figure 5. Comparison between TMFs for the multizone model (thatched bars), and the fish movement model (white bars) based on a reduced sampling effort (25 random species with 5 replicates per species). Error bars represent 95% CIs for the TMF regressions. Horizontal dashed lines represent the 95% CIs for the river-wide combined uncertainty model based on the same sampling strategy (25 random species with 5 replicates per species).

The fish movement simulations yielded different results. The less contaminated zones (represented by zones 2, 4, and 6) on the southeastern side of the Detroit River generally exhibit higher TMFs than either the river-wide output or the multizone output (Figure 5). This was clear for PCBs 31/28 and 153 in Zones 2 and 4 where the 95% CI around the fish movement TMF showed no overlap with confidence intervals around the river-wide or multizone simulations. For Zone 6, TMF estimates for PCB 31/28 and 153 under the fish movement scenario exceeded the estimates from the river-wide combined uncertainty simulation but were comparable to the multizone simulation. For PCB 194, the magnitude of TMF under the fish movement scenario was always higher than the averages generated for the multizone estimates, but there was overlap in the confidence intervals between the different simulation estimates. These observations are partially consistent with expectations. PCB half-lives increase with congener K_{OW}, so consuming a highly contaminated meal once will have a more pronounced effect for these higher K_{OW} congeners (Paterson et al. 2007a, 2007b). Under the fish movement scenario, sampling all animals exclusively from cleaner areas of the river elicits higher TMF estimates due to exposure of upper trophic level fish to more contaminated prey in adjacent contaminated zones. The smaller effect of movement in Zone 6 is attributed to a smaller gradient in contamination between US and Canadian zones in this region of the river and the large surface area of zone 6 that decreases the extent of fish movement between zones.

For the more contaminated zones 1, 3, and 5 located on the northwestern side of the river, TMFs from the fish movement scenarios yielded no consistent trends relative to river-wide combined uncertainty and multizone TMF estimates. In all cases, the 95% confidence interval ranges for fish movement simulations overlapped with the CI ranges of multizone and river-wide combined uncertainty TMF simulations. These results did not conform to initial predictions where it was expected that TMFs for animals collected exclusively in contaminated zones would be reduced because of increase in

the TMF intercept due to high contamination of baseline organisms.

The above spatial movement simulations have implications to the development of appropriate sampling strategies for establishing empirical TMFs in natural systems. In our simulations, allowing for fish movement contributed the greatest effect on TMF estimates and uncertainty propagation, but only under the condition where all the organisms were sampled exclusively in noncontaminated zones. This led to biasing TMF estimates to higher values compared to a baseline scenario or stochastic river-wide scenario. Interestingly, the fish movement effect interacted with and reinforced the effect of introducing model uncertainty over deterministic simulations. In other words, there was a synergistic effect of allowing for model uncertainty propagation, while at the same time exclusively sampling animals in clean areas, that leads to large overestimates in TMF over the baseline model prediction. Alternatively, when organisms are exclusively sampled within contaminated zones, the model demonstrated surprising robustness to the effect of fish movement. In this case, model uncertainty propagation still generates a deviation between the pattern of TMF with K_{OW} between deterministic and stochastic scenarios, but the effect is pronounced mainly for highly hydrophobic chemicals (biased high) and less so for moderate to low K_{OW} compounds. Taken together, the combined simulations used in this specific riverine model reveal that the risk of misclassifying chemicals in empirical TMF studies are more strongly biased toward overestimating TMFs resulting in the misclassification of nonbiomagnifying chemicals as opposed to the opposite (misclassification of biomagnifying chemicals as nonbioaccumulative). Thus, the simulation provides evidence supporting the use of TMF as a conservative estimate of food web biomagnification.

Although the present work was confined to model simulations, it would be difficult to empirically determine the effects of fish movement without the ability to empirically quantify the movement history of animals sampled in a TMF field study. However, models do offer a platform to generate hypotheses about complex interactions taking place in natural environments. It is acknowledged that the fish movement simulations incorporated in the present research force a number of simplifying assumptions that may not be representative of real environments. For example, it was assumed that fish spend a majority of their time in their home zone (reflective of their site of capture) and attenuated amounts of time in more distant zones depending on the distance from the location of capture. Another simplifying assumption forced into the model was that a given fish consumed the same diet items in similar proportions in adjacent zones as the home zone. Clearly, habitat differences, toxicity, and benthic community structure interactions are likely to impact diet composition over spatial scales (Vander et al. 1999), in addition to diet item concentrations considered by the model. In addition, all model simulations were constrained by the empirical spatial distribution of PCBs in water and sediments measured for the Detroit River. Other environments with different spatial gradients of contamination coupled with different scenarios of fish movements are likely to generate different results than presented here.

Despite the above noted simplifications, the model does reinforce a need for consideration of the spatial scale of sampling when generating data to calculate field TMFs. Rather than focusing efforts on collecting organisms from a single area, organisms having limited habitat ranges should be collected across multiple locations consistent with the foraging range of top predators sampled as part of the study. Such considerations are rarely incorporated into empirical TMF sampling designs.

CONCLUSIONS

A commonly used food web bioaccumulation model was used to provide estimates of PCB TMFs for a riverine system using realistic gradients in water and sediment contamination generated for the Detroit River, North America. The model predictions generally conformed to the pattern and magnitude of TMFs observed in empirical studies. Differences were noted between the TMF versus K_{OW} relationship depending on whether deterministic or stochastic modeling approaches were used, with deterministic models producing TMF relationships that appear to conform to laboratory based biomagnification observations and stochastic models producing TMF relationships more consistent with what has been observed in the field. It is hypothesized that interactions of parameter uncertainties and variabilities under both simulated and natural conditions contribute to the above noted laboratory versus field observation differences. A second major observation from the study was that spatial scale heterogeneity of water and sediment contamination is likely to interact with spatial movements of predators influencing the magnitude and variation of TMF. The simulations performed suggest that TMFs are more likely to show bias toward higher TMF estimates when organisms are exclusively collected in clean locations in a system demonstrating gradients of chemical contamination. In comparison, TMF estimates were more robust to change when animals were collected from the more contaminated regions of the system. These effects lead to the TMF approach being a conservative measure of biomagnification potential with a higher bias toward misclassifying nonbioaccumulative chemicals as biomagnifying in this hypothetical food web within the Detroit River. However, there could be some cases where the reverse is also valid. Hence, although the TMF is determined exclusively from biological samples, information for chemical distributions in the environment is needed to address and quantify uncertainty in the TMF calculation. Field studies testing the hypotheses generated by the modeling approach adopted in the present research are needed for model validation, to better address measurement error and sampling artifacts in the field TMF approach.

SUPPLEMENTAL DATA

Model Information

Table S1. Parameter values for concentration of contaminant in water.

Table S2. Assimilation efficiency and pore and water values used in model simulations.

Table S3. Species specific model parameters where the uncertainty simulations had lognormal distributions for both body weight and lipid content parameter selections.

Table S4. Proportion of mean foraging time spent in each zone for each species.

Table S5. Species specific diet matrix where each percentage has a lognormal distribution.

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