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A DYNAMIC MULTIMEDIA ENVIRONMENTAL AND BIOACCUMULATION MODEL FOR BROMINATED FLAME RETARDANTS IN LAKE HURON AND LAKE ERIE, USA

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Abstract—Polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) may pose a worldwide pollution problem because of their persistence, long-range transport capability, and predisposition to bioaccumulate. The ubiquitous presence of PBBs and PBDEs has heightened interest in determination of their fate. We report results for a fugacity-based dynamic environmental and bioaccumulation model of the fate of hexabromobiphenyl (hexaBB) discharged into the Saginaw Bay region of Lake Huron, USA. We calculated transient fugacity profiles of hexaBB in Lake Huron and Lake Erie water and sediment during the 1970s, 1980s, and 1990s. The hexaBB concentrations in the environmental compartments were used as inputs for a dynamic bioaccumulation model of Lake Huron and Lake Erie aquatic biota. The model results indicate that the sediment compartments of Lakes Huron and Erie serve as reservoirs for the accumulation and slow transfer of hexaBB to the food web constituents of these lakes. We present bioaccumulation factors (BAFs) and compare the predicted hexaBB concentrations in lake trout from the bioaccumulation model with measurements during the period 1980 to 2000. An uncertainty analysis for this model suggests that errors associated with input parameter uncertainty can be reduced by refining estimates of the sediment degradation half-life of hexaBB. The corroborated PBB model has carryover application for modeling the fate of polybrominated diphenyl ether (PBDE) contaminants in the Great Lakes. By fitting model outputs to field measurement data using the transformed least square fit method, we report estimations of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) emission rates into the Lake Huron and Lake Erie watershed areas. Environ. Toxicol. Chem. 2011;30:1018–1025. © 2011 SETAC

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INTRODUCTION

Brominated flame retardants (BFRs) are an important class of emerging contaminants that have bioaccumulated at exponentially growing levels over the last 30 years in humans, marine mammals, birds, and fish in North America. Polybrominated diphenyl ethers (PBDEs) are a widely used class of BFRs that are named by number and position of bromines, analogously to polychlorinated biphenyls (PCBs) [1]. The ubiquitous presence of PBDEs in consumer goods and rising concern over their dramatically increasing environmental concentrations and possible role as endocrine disruptors have heightened interest in determining the fate of BFR emissions [2]. It is generally accepted that exposure to indoor dust and consumer products such as sofa, mattress, and chair foams is a main route for human exposure to BFRs [3,4]. Consumption of fish has also been suggested as a significant route of human exposure of BFRs [5], so a predictive model is sought to relate BFR emissions to BFR concentration in predatory fish in contaminated waters.

Sampling data for multimedia PBDE concentrations of the Great Lakes region (USA) were not collected until very recently. Environmental concentrations are, however, available over a longer time period for polybrominated biphenyls (PBBs), a related class of BFRs, and these may be used for development of a Great Lakes region BFR fate model. Polybrominated biphenyls are structurally similar to PBDEs and were used as

flame retardants in commercial products such as FireMaster BP-6 until their production was halted in 1979, following a 1973 livestock contamination episode in which a PBB-containing product was mistakenly mixed into cattle feed as an additive [6]. After this incident, a cohort of 4,000 individuals was tracked for observations of the chronic effects of PBB exposure, and field sampling of PBB concentrations in environmental media and wildlife populations commenced in areas near PBB manufacturing facilities in Michigan, USA.

Fugacity-based mass balance models have been widely accepted as valuable tools for predicting chemical fate in the environment [7]. Steady-state, nonequilibrium, level III fugacity models have been applied for both regional-scale assessment and near-field evaluation of chemical fate [8,9]. Nonequilibrium, nonsteady-state fugacity models (level IV) can account for time-varying emissions to environmental media to yield estimated recovery times for contaminated regions [10,11]. Fugacity-based approaches have also been used to evaluate bioaccumulation of hydrophobic substances in aquatic food webs [12]. The degree of bioaccumulation is described in terms of the bioaccumulation factor (BAF), the ratio of the chemical concentration in an organism to that of the surrounding water, expressed on a wet weight basis as liters per kilogram. Bioaccumulation factor represents accumulation in organisms arising from water and dietary sources [13].

In the present study, a nonequilibrium, nonsteady-state, fugacity-based, coupled multimedia environmental and bioaccumulation model was developed to assess the fate of BFR emissions in the Lake Huron and Lake Erie watersheds and to estimate BFR bioaccumulation in predatory Great Lakes fish. The dynamic model predicted the fate of hexabromobiphenyl (hexaBB) in the food chains of the Great Lakes. The predicted

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hexaBB concentrations in lake trout were then compared with measured hexaBB concentrations during the period from 1980 to 2000. Furthermore, we describe herein, for the first time, an application for the estimation of the emission rate of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) into Lake Huron and Lake Erie based on measured BDE-47 concentrations in the top predator level of the Lake Huron and Lake Erie food webs.

MODELING METHODS

Fugacity-based, multimedia and bioaccumulation models

The nonequilibrium, nonsteady-state model (level IV) [14] used in the present study included four environmental compartments: air, water, soil, and sediment. The BFR mass balance equation for each compartment is shown in Supplemental Data, S1.1 and Figure S1.

The mass balance equation of the food web model assumes chemical uptake from the consumption of food and water intake and chemical elimination from metabolism, egestion, discharge through gills, and organism growth. The transient bioaccumulation of BFRs at different trophic levels is correspondingly modeled for each organism in the present study as

$$V_F Z_F \frac{df_F}{dt} = (D_A f_A + D_w f_w) - f_F (D_W + D_M + D_E + D_G) \quad (1)$$

where the subscript F represents the organism; A and W denote uptake, respectively, from food and water (or sediment); and M, E, and G denote elimination by metabolism, egestion, and growth dilution, respectively. Among the loss terms, growth dilution and egestion can be important for hydrophobic chemicals that are not biotransformed [15]. The basic concept of the fugacity approach and a detailed description of how the D values for the model are calculated have been reported by Mackay [10] and Sweetman et al. [11]. With environmental input parameters and physicochemical properties of hexaBB in Supplemental Data, Tables S1 and S2, respectively, D values were computed using the steady-state, fugacity-based level III model (version 2.80) and food web model available at the Canadian Center for Environmental Modelling and Chemistry ([16]; http://www.trentu.ca/academic/aminss/envmodel/models/models.html). With environmental emissions of BFRs, time-dependent BFR concentrations in Great Lakes aquatic biota were calculated from multimedia fugacity model values for the water and sediment compartments using Equation 1 and equations given in Supplemental Data, S1–S4. Polymath 6.10 (Polymath Software) with the stiff solver (the Rosenbrock method) was used to solve the set of coupled ordinary differential equations.

Model structure and inputs

The boundary of the study areas for the Lake Huron and Lake Erie multimedia models encloses lake areas and their watersheds (Supplemental Data, Fig. S2). Lake Erie is linked to Lake Huron, so our model assumed that 100% of the advection losses through the water and sediment compartments of Lake Huron enter Lake Erie as the PBB emission source for the Lake Erie watershed. However, 50% of the advection loss through the air compartment of the Lake Huron watershed was assumed to enter the Lake Erie watershed. More information on this assumption is discussed in Supplemental Data, Figures S2 and S3.

Hexabromobiphenyl was the principal BFR constituent of FireMaster BP-6, a commercial product manufactured by Michigan Chemical from 1970 and 1974 [17,18]. HexaBB has a high octanol–water partition coefficient (log $K_{OW} = 6.4$) and readily bioaccumulates in food chains [19]. Degradation half-lives of hexaBB in air, water, soil, and sediment were obtained from EPIWIN ([20]; http://www.epa.gov/oppt/exposure/). A complete listing of the environmental input parameters and transport velocities and the physicochemical input parameters are shown in Supplemental Data, Tables S1 and S2, respectively. Calculations of important input parameters are discussed in Supplemental Data, S1.2.

As shown in Figure 1, eight species for the Lake Huron and Lake Erie food webs were selected using information from Fish
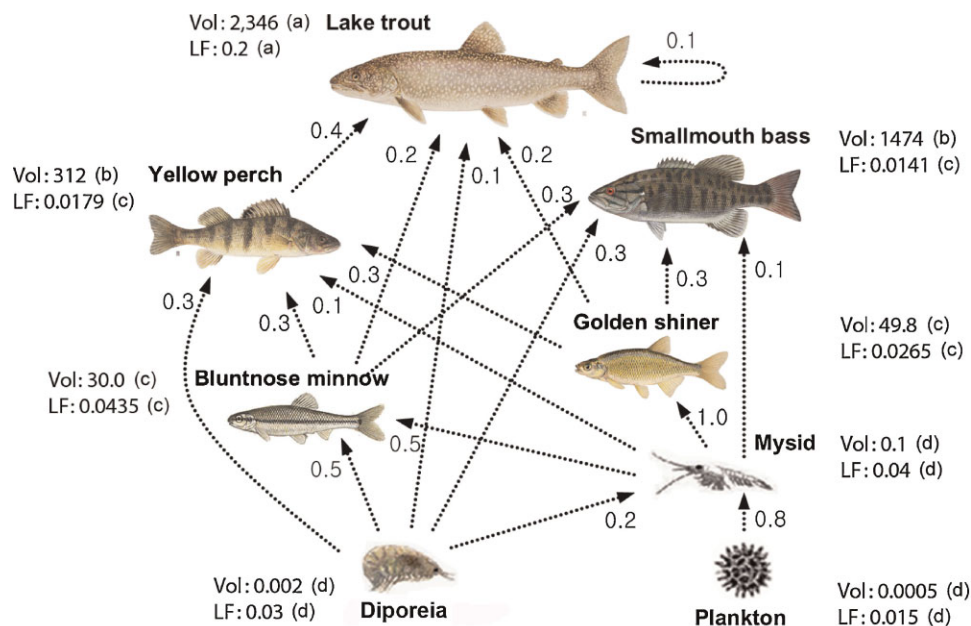

Fig. 1. Schematic diagram of Lake Huron and Lake Erie, USA, food webs and dietary preferences. Vol and LF refer to organism volume (cm^3) and lipid volume fraction, respectively. The dietary preferences are described as fractions marked at the end of arrows (for example, the diet of smallmouth bass consists of 10% mysid, 30% diporeia, 30% bluntnose minnow, and 30% golden shiner). a: Luross et al. [22]; b: Wisconsin Sea Grant [21]; c: Blasland, Bouck & Lee and Quantitative Environmental Analysis [23]; d: Canadian Centre for Environmental Modelling and Chemistry [16]. [Color figure can be seen in the online version of this article, available at wileyonlinelibrary.com]

of the Great Lakes ([21]; http://www.seagrant.wisc.edu/great-lakesfish/LakeHuron.html). The same food webs were used for both lakes and included both benthic (diporeia) and pelagic (plankton, fish) organisms and one species (mysid) that respires in both water and sediment. Input parameters for the dynamic bioaccumulation model (Supplemental Data, Table S3) were obtained from the steady-state food web fugacity model [15,16], with the volumes and lipid fractions of the aquatic organisms adjusted (Fig. 1) according to current information on the species found in Lake Huron and Lake Erie ([21–23]; http://www.epa.gov/ne/ge/thesite/restofriver-reports.html).

Emission rate profile

In this work, the source of environmental PBB emission is presumed to arise principally from historic production in the Saginaw Bay region of Michigan, USA. Although production of PBBs at Michigan Chemical Corporation ceased in 1974, releases into air and water continued until 1977 [17]. From 1970 to 1977, 5,352 metric tons of FireMaster BP-6 were produced in Michigan [17]. Of this amount, it was estimated that 273.0 metric tons were released into the environment. The hexabromobiphenyl content in BP-6 varied, ranging from 60 to 90% [17]. The content of individual PBB congeners in BP-6 was not precisely quantified, but BP-6 was known to contain isomeric tetrabromobiphenyls, pentabromobiphenyls, hexabromobiphenyls, heptabromobiphenyls, and an octabromobiphenyl [17]. Hass et al. [24] reported 63% hexaBBs, 33% heptabromobiphenyls, and 4% pentabromobiphenyls in BP-6, according to their fractional areas in a gas chromatography–mass spectrometry analysis. Hence, most (96%) of the BP-6 product was composed of hexa- and heptabromophenyls. Lighter PBB congeners can be formed in the environment from the debromination of heavier congener species. In the present study, it was assumed that all of the heptaBB congeners released to the environment produced hexaBBs upon debromination. Therefore, the emission rate of hexaBB into the Lake Huron watershed was assumed to be equal to the quantity of BP-6 released to the environment (273.0 metric tons) as reported by Di Carlo et al. [17].

It was calculated that 0.07, 1,000, and 50,000 kg were released into air, water, and soil, respectively, per 10^6 kg of total PBB production at this site [17,18]. The emission contributions from in-use and landfilled products treated with PBBs were small relative to direct PBB emissions from production and are thus disregarded (more discussion in Supplemental Data, S1.3).

Annual PBB production, totaling 5,079 metric tons from 1970 to 1974, is reported in Supplemental Data, Table S4. For the additional 273.1 metric tons manufactured from 1975 to 1977, production figures are not available, so it is assumed, based on the PBB production stop in 1974, that 96%, 3%, and 1% of this amount was produced in 1975, 1976, and 1977, respectively. These percentages were estimated from PBB loading rates discharged into the Pine River during 1975 to 1977 by the Michigan Chemical Corporation [18]. Using the data from Supplemental Data, Table S4, the emission rate E (kg/h) was fitted to the following equation [25].

$$E(\text{kg/h}) = \left(4E_{\max} \exp\left(\frac{t_{\max}-t}{A}\right)\right) \Big/ \left(1 + \exp\left(\frac{t_{\max}-t}{A}\right)\right)^2 \quad (2)$$

where $E_{\max}$ is maximum emission rate (kg/h) occurring in year $t_{\max}$, and A is time (year) for which the emission rate decreases to 80% of its maximum. The values of $E_{\max}$ in 1974

for emission into air, water, and soil are 1.77×10^{-5}, 2.53×10^{-1}, and 1.26×10^1 kg/h, respectively. In Equation 2, $A = 0.4$ for $t < t_{\max}$ and 0.85 for $t > t_{\max}$.

Uncertainty analysis

The degradation half-lives are typically much less well known than other physicochemical properties [26]. The uncertainty associated with the EPIwin estimation of degradation half-lives of persistent organic pollutants (POPs) may be more than a factor of 10 [27,28]. In the present study, Monte Carlo analysis was applied to determine the range of the model outputs depending on the uncertainty associated with EPIWIN [20]. Using an assumed log-normal shape distribution for each degradation half-life value, 5th and 95th percentiles of the model outputs were determined based on the confidence factors (Cf) of 2, 5, and 10 for the degradation half-lives of hexaBB in the environmental compartments. A Cf of 2.0, for example, conveys that 95% of the trial values for an input parameter lie between one-half and twice the median [29]. One thousand sets of simultaneously randomly chosen values of the four degradation half-lives were used to determine 5th and 95th percentiles of the model outputs. This Monte Carlo analysis was carried out using Crystal Ball 7® (Decisioneering). Standard deviations of the lognormal distributions of the degradation half-lives depending on different Cf values are presented in the Supplemental Data, Table S5.

Application to brominated diphenyl ether emissions

The BDE-47 is one of the most widely distributed PBDE congeners in the environment [1], and, along with BDE-99, another congener in the penta-BDE flame retardant product, mostly BDE-47 and BDE-99, is among the most bioaccumulative ([30]; http://assets.panda.org/downloads/newpopsfinal. pdf; [31]; http://www.ec.gc.ca/CEPARegistry/documents/ subs_list/PBDE_draft/PBDE_TOC.cfm; [32]). The physicochemical properties and degradation half-lives of BDE-47 are shown in Supplemental Data, Table S2. The measured BDE-47 concentrations in top-level predators were obtained from Lake Huron lake trout [22,33] and Lake Erie walleye [34] and converted into nanograms per gram of lipid based on lipid content [22,34].

The same geographical compartments and food web model used in the PBB fate model were used for estimation of BDE-47 emissions into Lake Huron and Lake Erie. An input emission profile that produces the best fitting of the model outputs to the measured data was determined by using the transformed least square fit method. The best fitting is achieved by minimizing the sum of the squared difference between a natural log-transformed predicted value and a measured value. Matlab® version 7.0 (The MathWorks) with the stiff solver ode23tb was used to solve the set of coupled ordinary differential equations.

RESULTS AND DISCUSSION

PBB contamination

Figure 2A reports the time-dependent hexaBB fugacities in the Lake Huron environmental compartments in response to the PBB emission forced into the Lake Huron watershed soil compartment. The soil fugacity profile mirrors that of the soil emission profile, with approximately one-year offset in the soil compartment response. The persistence of hexaBB is most sustained, however, in the sediment compartment, even in the absence of direct emission to sediment. Because of the
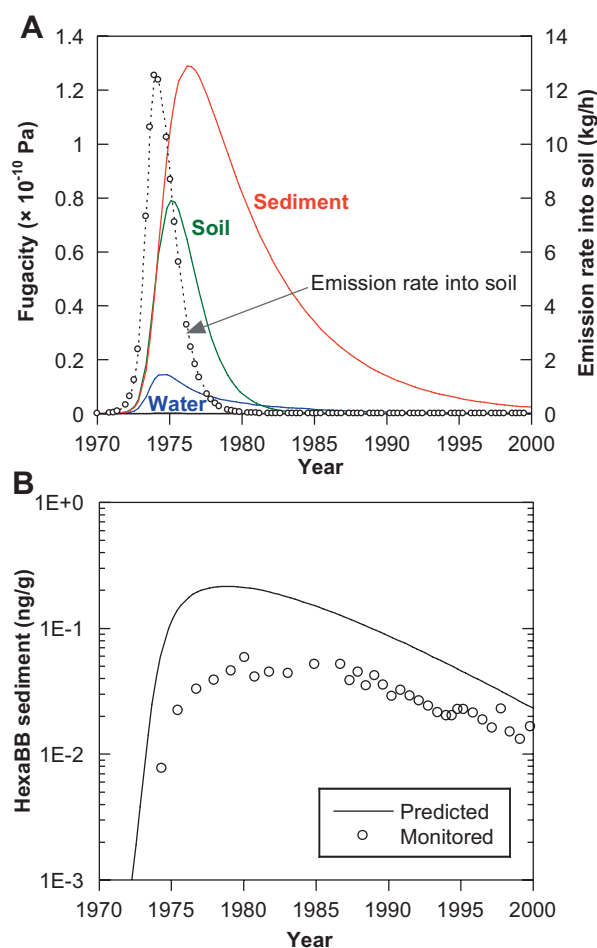
Fig. 2. (**A**) Time variation of hexabromobiphenyl (hexaBB) fugacities in Lake Huron environmental compartments and PBB emission rate into Lake Huron watershed soil compartment. The air compartment fugacity is small and is not visible on the scale of the figure (maximum air fugacity = 1.66×10^{-13} Pa in 1974). (**B**) Comparison between measured [35] and predicted hexaBB sediment concentrations in Lake Erie, USA. [Color figure can be seen in the online version of this article, available at wileyonlinelibrary.com]

shorter hexaBB half-life in soil and the smaller organic matter content of soil compared with sediment, hexaBB uptake by soil is relatively transient compared with that by sediment, whereas lingering hexaBB accumulation in sediment poses a concern to the aquatic food web. After hexaBB uptake by sediment during the hexaBB emission period from 1970 to 1978, the sediment compartment serves as a source of hexaBB release to the aquatic environment and its resident organisms from the early 1980s until 2000. Similar dynamics have been observed in the modeling of polychlorinated biphenyl (PCB) fate in the United Kingdom [11], in which PCB emissions to atmospheric air transferred to soil, which then functioned as a source for re-emission of PCBs over protracted periods.

Figure 2B shows a comparison of hexaBB sediment concentrations between moel predictions and measured data [35] in Lake Erie. The concentration trends agreed well; however, predicted hexaBB concentrations ranged from 0.8 to 6.1 times higher than the reported concentrations. Given that a one or two order of magnitude difference between field measurements and model results has been deemed acceptable in previous environmental compartment modeling studies [11], the agreement between predicted and observed sediment concentrations in Lake Erie is satisfactory. It should further be noted that the measured data were obtained from the eastern part of Lake Erie

(latitude N45°10.704′, longitude W86°22.521′ [35]), which has lower contamination levels for many pollutants compared with the western portion of Lake Erie (see Supplemental Data, Section 2.1). Concentrations of PBDE [36] and PCB [37] in the sampled eastern region are, for example, approximately nine and five times lower, respectively, than in the western part of Lake Erie (Supplemental Data, Fig. S4). Taking into account the well-mixed, homogeneous compartment assumption in this model, the prediction of hexaBB sediment concentrations in Lake Erie agrees adequately with the measured data for the purpose of model validation.

The hexaBB fugacity profile for lake trout, the organism at the top of the bioaccumulation model for Lake Huron, is responsive to sediment re-emission forcing, as observed by comparing Supplemental Data, Figure S5, and Figure 2A. According to the dynamic bioaccumulation model, the peak hexaBB fugacity in lake trout occurs in 1978 (Supplemental Data, Fig. S5), four years after the maximum single-year PBB emission in 1974 (Fig. 2A). The time lag is attributable to the slow transfer of PBB emissions from soil to water to sediment, followed by transmission of PBBs to lake trout, typically by way of one or two trophic level intermediates. The time lag may be longer than four years if the degradation half-life of hexaBB in soil obtained from EPIWIN [20] was underestimated. Although EPIWIN [20] estimated a soil half-life of 8,640 h (or ~360 d), Jacobs et al. [38] reported that PBBs may remain in soil for many years because of their nonvolatility and resistance to bacterial degradation. Jacobs et al. [39] also reported that there was no detectable degradation of two major PBB isomer (hexa- and heptabromobiphenyls) in soils in one year.

In a steady-state bioaccumulation model, fugacities generally increase with trophic level [15]. However, in our dynamic bioaccumulation model, the environmental compartments remain in a nonequilibrium state, and the fugacity of the top-level predator, lake trout, is lower than the fugacities of lower trophic level organisms (smallmouth bass, yellow perch, and diporeia) as shown in Supplemental Data, Figure S5. The smaller organisms approach equilibrium and steady state with environment faster than the larger trout species. This partially explains why the trout has the highest hexaBB concentration but not the highest hexaBB fugacity. For pre-1982 conditions, hexaBB concentrations (mg/m³ whole organism) are generally larger for organisms at higher trophic levels (Supplemental Data, Figure S6), although two organisms that populate lower trophic levels, diporeia and bluntnose minnow, exhibit higher hexaBB concentrations than all other organisms except for lake trout. Because diporeia is a sediment-dwelling organism and is consumed principally by bluntnose minnow, a fish with relatively high lipid content (4.35%), hexaBB fugacities in these two species considerably surpass the water compartment fugacity. On account of differences in lipid content and gut absorption efficiency parameters for organic matter (GAO), there are significant differences in the hexaBB concentrations among the species. The capacity of an organism to store hydrophobic organic chemicals increases as its lipid content increases [12], whereas the chemical absorption efficiency of an organism decreases with increasing GAO value. With their small GAO and large lipid content, lake trout are predisposed to bioaccumulate hydrophobic compounds [40].

Bioaccumulation factor analysis

In Figure 3, hexaBB BAFs for the Lake Huron and Lake Erie food web organisms were calculated from the time-dependent
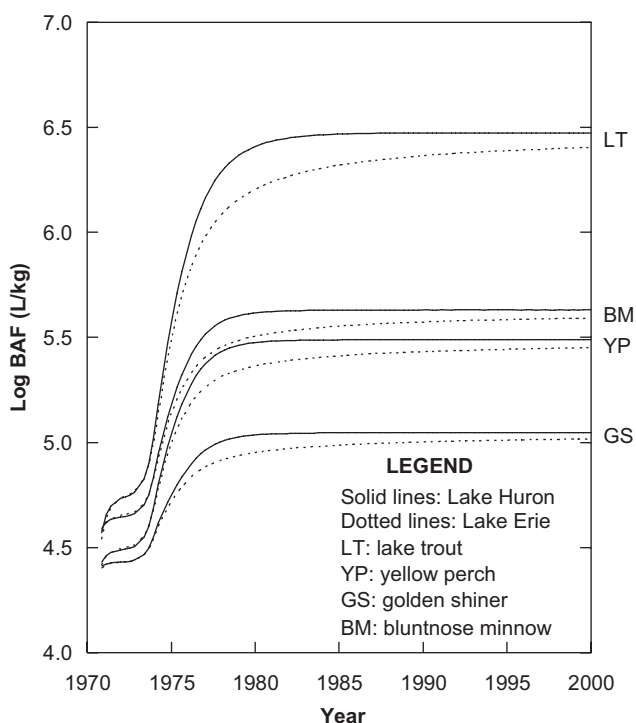
Fig. 3. Bioaccumulation factors (BAFs) of hexabromobiphenyl (hexaBB) over time in organisms in the food webs of Lake Huron and Lake Erie, USA.

hexaBB concentrations of the organisms and lake water. The temporal pattern of the BAFs was due to the fluctuation of concentrations of hexaBB in water, which is in the denominator of the BAF calculation. Bioaccumulation factors in both lakes started to increase dramatically in 1974 when PBB emissions peaked. In Lake Huron, BAFs reached the stable level in the early 1980 s following cessation of PBB emissions; however, BAFs in Lake Erie continued to increase moderately into the 1980 s and reached the stable level in the early 2000 s. This is due to the slow transfer of suspended sediments, bearing long-lived hexaBB accumulations, from Lake Huron to Lake Erie.

Arnot and Gobas [12] reported that log BAF measurements in 1,012 sampled fish range between 4.0 and 7.0 for 108

chemical substances with log K_{OW} values between 6.2 and 6.5. Given the log K_{OW} value of hexaBB (log $K_{OW} = 6.39$), the calculated log BAFs for hexaBB of 6.4 and 6.5 for Lake Erie and Lake Huron, respectively, in the year 2000 agree fairly well with the data from Arnot and Gobas [12]. The calculated data also agree fairly well with the log BAF values of 5.46 to 7.65 reported for chemicals with log K_{OW} ranging from 6.2 to 6.5 [19]. As indicated in Figure 3, BAFs increase at higher trophic levels for all species except for bluntnose minnow, which shows a higher BAF than yellow perch and golden shiner. This can be partially attributed to the higher lipid content in bluntnose minnow than in perch or shiner. Arnot and Gobas [12] observed that organisms with higher lipid content have a greater capacity to store hydrophobic organic chemicals and therefore can exhibit a higher BAF [12]. The ability to metabolize an acquired substance also influences the species BAF. If organisms at higher trophic levels are capable of metabolizing more of a substance than organisms at lower trophic levels, then trophic dilution can occur and BAFs in the higher level organisms can be smaller than those in lower trophic levels [12].

Comparison with measurements

In Figure 4A and B, model predictions are compared with measured concentrations [22,33,41,42] of BB-153, the predominant congener of hexaBB (except for Jaffe et al. [41] measuring total PBBs in 1983) in Lake Huron lake trout collected from Saginaw Bay (Michigan, USA), Point Edward (Ontario, Canada), Port Austin (Michigan, USA), and Rockport (Michigan, USA) and in Lake Erie lake trout from Dunkirk (New York, USA) and Lake Erie walleye (another top-level predator) from Middle Bass Island (Ohio, USA). HexaBB concentrations in various units were converted into nanograms of hexaBB per gram of lipid based on the weight and lipid content of lake trout. Model predictions agree moderately well with measured data, especially for Lake Erie. For both lakes, the model results are within an order of magnitude of the measured values. It should be duly acknowledged that the hexaBB concentrations measured in lake trout at different sampling locations and at different times are unlikely to be exactly reproduced by a fugacity model in which each environ-
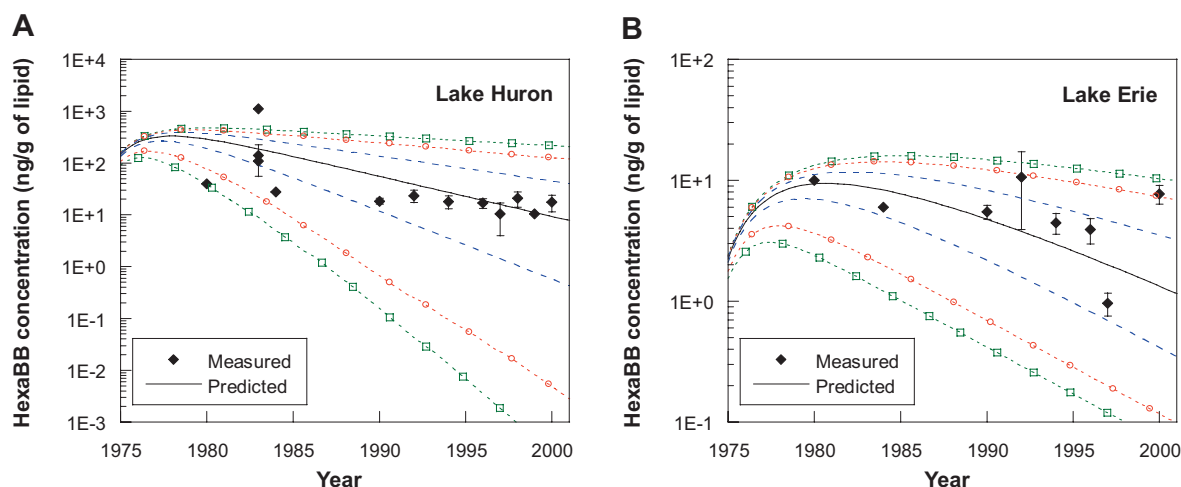

Fig. 4. Comparison of measured and predicted hexabromobiphenyl (hexaBB) concentrations of lake trout in Lake Huron (**A**) and Lake Erie (**B**), showing 5th and 95th percentiles of the predicted values with confidence factors of 2 (dashed lines), 5 (dashed lines with open circles), and 10 (dashed lines with open squares). The error bars in the measured data represent standard deviations. [Color figure can be seen in the online version of this article, available at wileyonlinelibrary. com]

mental medium and food web constituent is represented as a single homogeneous compartment. When appropriate, and if the requisite input data are available, spatial refinement of the model predictions can be achieved by using multicompartment models in which the environmental media in the study region are segmented laterally and vertically according to geography or other considerations [43]. Also, consideration of seasonal variations in temperature and organism characteristics (e.g., size, lipid content, dietary preference) will refine the prediction of the BFR fate, but the present study assumed that temperature was invariant over time as was done in previous studies [11,15,29,44–46].

Figure 4A and B show the uncertainty of the predicted hexaBB concentrations of lake trout associated with EPIWIN estimates of hexaBB degradation half-lives. Most of the measured data lie between 5th and 95th percentiles of the predicted outputs with $Cf = 2$. As uncertainty of the degradation half-life increases, the range between 5th and 95th percentiles of the model outputs is significantly broadened.

The uncertainty shown in Figure 4A and B was determined using simultaneously randomly chosen values of the four degradation half-lives as described in the *Modeling methods* section. To investigate the impact of each half-life on the model outputs, dynamic calculations were conducted with the fixed values for the half-lives in all compartments except for one. As

shown in Figure 5, for all time periods, the predicted lake trout hexaBB concentration was far more sensitive to the hexaBB sediment degradation half-life than to the half-lives in other environmental compartments. In the year 2000 in Lake Huron, for example, the range of the 5th and 95th percentiles of the model outputs calculated for a sediment-phase degradation half-life uncertainty of $Cf = 5$ is 13, 190, 17, and 9 times larger, respectively, than the corresponding uncertainty ranges calculated for the air, water, and soil degradation half-lives for the same Cf value. The smaller percentile range for the effect of uncertainty in the Lake Erie soil degradation half-life can be attributed to the absence of direct PBB emissions or advection inputs into the Lake Erie soil compartment. Uncertainty in the hexaBB half-life in air has very little effect on the predicted hexaBB concentration in lake trout. In future modeling efforts, more attention should thus be devoted to refining estimates for the hexaBB sediment degradation half-life than for those in air, water, or soil. Although the present study did not thoroughly investigate uncertainties associated with biotransformation half-lives in food web species, octanol–water partition coefficients (K_{OW}), or organism properties such as the lipid content and gut absorption parameter, it is acknowledged that these parameters are also significant factors that could affect the outcomes reported for our bioaccumulation model.
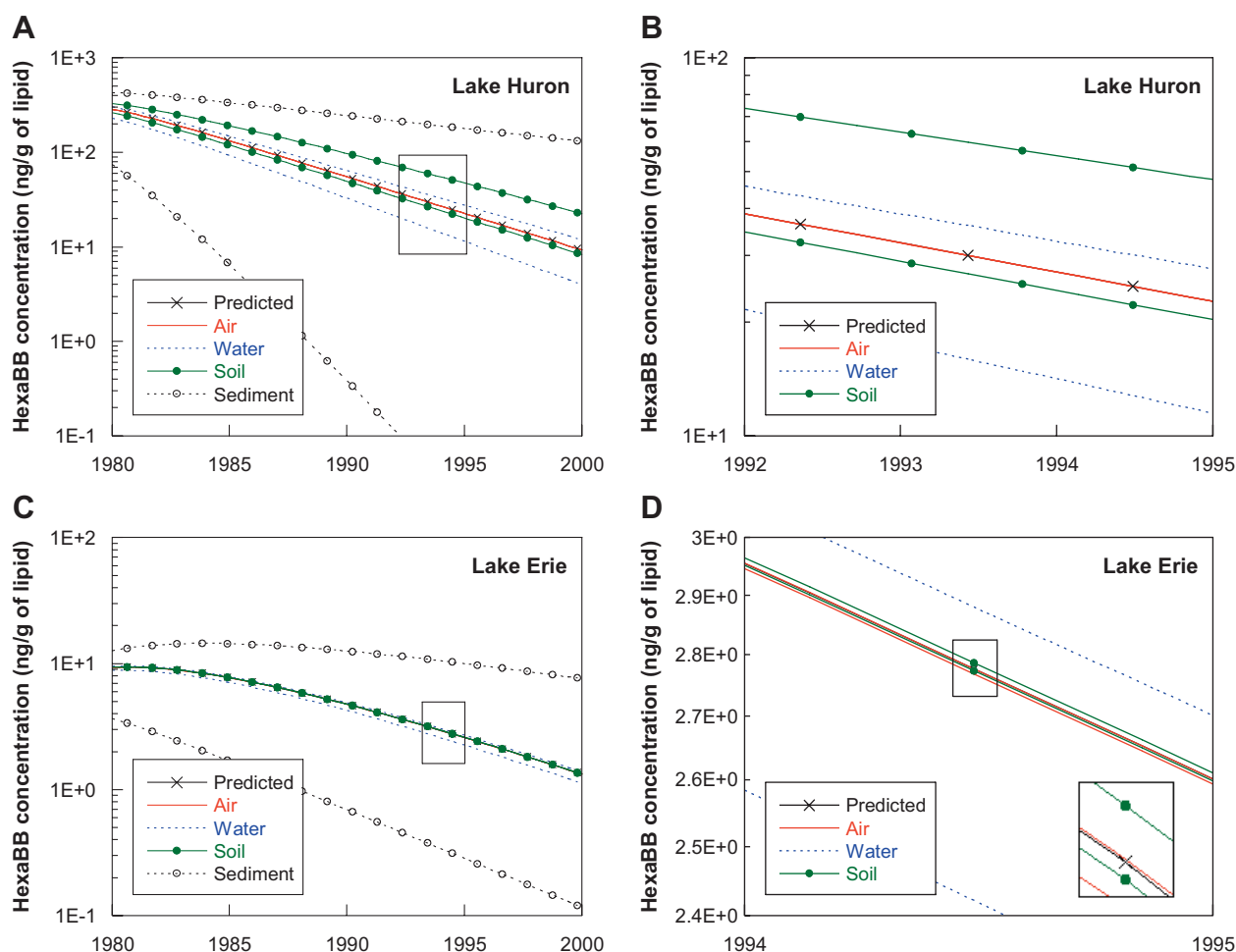

Fig. 5. Impact of uncertainty in the individual hexabromobiphenyl (hexaBB) half-lives in air, water, soil, and sediment, on the 5th and 95th percentiles of the model outputs. A confidence factor of 5 is assumed for each half-life. Detailed model outputs enclosed by a rectangle in Lake Huron (**A**) and Lake Erie (**C**) are shown in (**B**) and (**D**), respectively. In D, detailed outputs enclosed by a rectangle are shown in the **inset**. [Color figure can be seen in the online version of this article, available at wileyonlinelibrary.com]
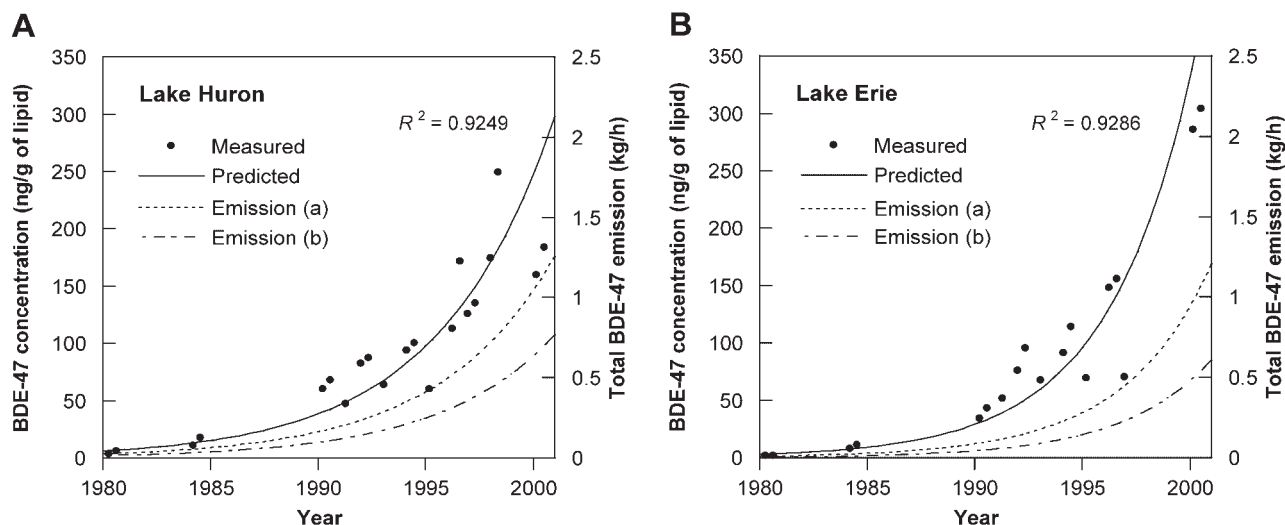
Fig. 6. Estimation of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) emission rates into the environment of Lake Huron (**A**) and Lake Erie (**B**). Emission a represents an assumed scenario of BDE-47 emission into the air (80%), water (10%), and soil (10%). Emission b represents emissions equally into the air, water, and soil (each 33.3%). Predicted represents the best fitted predicted values based on the emission a scenario (little difference exists between the best fit trends of the two emission scenarios).

Application to brominated diphenyl ether emissions

Unlike the manufacturing-based PBB point source emissions, PBDE emissions in the Great Lakes area are more likely attributed to volatilization from flame-resistant products in use [32,47]. The total emissions of BDE-47 into the environment of Switzerland, simulated using a dynamic substance flow analysis (SFA) model [48], were contributed mostly by emissions released into the air (~80%). Thus, considering the relatively larger fractions of water compartment in the present study, we employed two scenarios of BDE-47 emission into Lake Huron and Lake Erie. Emission a assumes emissions into the air (80%), water (10%), and soil (10%); emission b assumes emissions equally into the air, water, and soil (each 33.3%). Considering that the commercial pentaBDE and octaBDE mixture production in the United States was discontinued at the end of 2004 ([49]; http://www.epa.gov/opptintr/pbde/) and that the atmospheric BDE-47 emission patterns estimated in Europe showed a rapid decline after peak emissions in 1997 [50], we assumed that the BDE-47 emission exponentially increased in the United States until 2000.

Estimated emission rates of BDE-47 into the Lake Huron and Lake Erie environments are shown in Figure 6A and B. As the fraction of the BDE-47 air emission increases, the estimated total emission rate becomes larger (emission a > emission b) because of the lowest residence time of BDE-47 in the air compared with that in other compartments. Results of BDE-47 emission estimations by two more different emission scenarios are shown in Supplemental Data, Figure S7. Emission c and d scenarios assume most of emission (80%) into the water and the soil, respectively, with equal fractions of the rest of the compartments (each 10%). Emission into the water compartment causes the most direct, and greatest, impact on the BDE-47 concentration in the aquatic organisms among emissions into the compartments. This is due to the more direct exposure pathway of the chemical to the aquatic organisms. Thus, emission c scenario estimates the smallest emission rate among the four emission scenarios (Supplemental Data, Fig. S7). On the other hand, the emission d scenario, including the largest fraction of emission into the soil compartment, estimates the greatest

emission rate. This is due to the stagnant characteristics of the soil compartment, which does not convey the pollutant from the soil to the water through compartment movement, and the relatively small values of the pollutant transport velocities (Supplemental Data, Table S1). Although both emission c and emission d scenarios are unlikely to occur in a real environment, because BDE-47 emissions are attributed mostly to the air [48], they help to explain the characteristics of the developed dynamic model. The fitted trend lines of moderate exponential increases in the BDE-47 emissions to both lakes show good agreement with estimated BDE-47 emission rate trends into air in North America [32], in which emission rates were calculated by considering both primary sources from in-use products and secondary sources from landfilled or recycled goods.

Input sources of BDE-47 into the Lake Erie watershed originated from both the direct emissions from Lake Erie's watershed and the advection inputs delivered from Lake Huron. Contribution fractions of emission sources to the total BDE-47 emission into Lake Erie are shown and discussed in Supplemental Data, Figure S8. In both emission a and emission b scenarios shown in Supplemental Data, Figure S8, among the BDE-47 input sources, the largest input source to Lake Erie is direct emission from within the watershed boundary into the Lake Erie air compartment.

As previously mentioned, in this model, the formation of lighter PBDE congeners by debromination of heavier PBDEs [51] is not explicitly considered. This could result in an overestimation of the BDE-47 emission rate.

The study reported herein demonstrates that a fugacity-based dynamic model may be reliably used to predict the fate of emerging BFR contaminants in regional areas with local emission profile. It is anticipated that the multimedia environmental model and bioaccumulation analysis developed and validated for hexaBB in the present study can be applied to the investigation of BFR fate and transport in other geographic regions.

SUPPLEMENTAL DATA

Figures S1–S8.
Tables S1–S5. (557 KB DOC)

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