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Development of a Multichemical Food Web Model: Application to PBDEs in Lake Ellasjøen, Bear Island, Norway

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A multichemical food web model has been developed to estimate the biomagnification of interconverting chemicals in aquatic food webs. We extended a fugacity-based food web model for single chemicals to account for reversible and irreversible biotransformation among a parent chemical and transformation products, by simultaneously solving mass balance equations of the chemicals using a matrix solution. The model can be applied to any number of chemicals and organisms or taxonomic groups in a food web. The model was illustratively applied to four PBDE congeners, BDE-47, -99, -100, and -153, in the food web of Lake Ellasjøen, Bear Island, Norway. In Ellasjøen arctic char (*Salvelinus alpinus*), the multichemical model estimated PBDE biotransformation from higher to lower brominated congeners and improved the correspondence between estimated and measured concentrations in comparison to estimates from the single-chemical food web model. The underestimation of BDE-47, even after considering bioformation due to biotransformation of the other three congeners, suggests its formation from additional biotransformation pathways not considered in this application. The model estimates approximate values for congener-specific biotransformation half-lives of 5.7, 0.8, 1.14, and 0.45 years for BDE-47, -99, -100, and -153, respectively, in large arctic char (*S. alpinus*) of Lake Ellasjøen.

Introduction

Mass balance models are useful tools for evaluating the mechanisms responsible for contaminant levels and trends in biota (*1*−*3*). Most food web models have been applied to contaminants, such as PCBs, that undergo minimal metabolic degradation, or biotransformation, in fish and invertebrates (*1*−*3*). For compounds that are less persistent in the environment, it may be important to simultaneously track both the parent chemical and its transformation products in order to fully assess risk (*4*). Traditionally, separate mass balance equations for the parent chemical and its transformation products have been used to estimate fate (*5*). In situations where compartment-specific chemical transformation rates are poorly known, these single-chemical models are calibrated until the predicted concentrations correspond to the measured data. However, this single-chemical approach can be inappropriate because the connection is lost between the parent compound and its transformation products. Rather, it is more appropriate to construct one mass balance equation for each parent and transformed chemical in all environmental media, including consideration of chemical interconversion, and then to solve the equations simultaneously.

This approach was used by Diamond et al. (*6*), who developed the multispecies aquivalence method to account for interconversion of chemical species in an aquatic system. For metals, the interconversion of species can be very fast compared to their residence time in the medium. In addition, interconversion rates for the species are rarely known. As such, Diamond et al. (*6*) combined all the chemical-specific equations for one medium to obtain a pseudo-single-component mass balance equation, in which intermedia conversion rates cancel. These rates can be obtained a posteriori after solving all equations for the system. However, if the chemical interconversion rates are known and are comparable to the residence time of the chemicals in the media, these multispecies equations should be solved explicitly and simultaneously. The successful implementation of this approach was demonstrated by Fenner et al. (*7*, *8*) and Cahill et al. (*9*), where they applied their models to organic contaminants in abiotic systems. Although multichemical models are necessary to understand the dynamics of contaminants susceptible to biotransformation in aquatic food webs (*10*), such models have not yet been developed.

This paper extends the multiple chemical approach to food webs using the food web model of Campfens and Mackay (*3*) as its basis. This extended formulation accounts for multiple, related chemicals by solving mass balance equations of chemicals of concern simultaneously using a matrix approach. The formulation explicitly considers the biotransformation of all chemicals in the system. We illustrate the model using PBDEs in the food web of Lake Ellasjøen, a high arctic lake located on Bear Island, Norway.

PBDEs are a group of chemicals that have been used extensively as flame retardants in a wide variety of combustible materials (*11*, *12*) and are ubiquitous, having been detected throughout the world, including the arctic (*11*−*14*). Concentrations have been increasing in the environment and concerns mount regarding their potential toxicity (*15*−*17*). In response to these concerns, Europe and North America have moved to ban the penta- and octa-BDE mixtures (*11*) and industry in North America has voluntarily stopped production of these mixtures. PBDEs have similar structures and physical−chemical properties as polychlorinated biphenyls (PCBs) (e.g., *18*, *19*) and, as a result, show a similar ability to partition among environmental compartments and bioaccumulate in biota (*11*, *18*, *20*). However, a major difference between these two groups of contaminants is that PBDEs are more susceptible to biotransformation in organisms due to the weaker carbon−bromine bond compared with the carbon−chlorine bond in PCBs. PBDE biotransformation has been observed in the common carp (*Cyprinus carpio*) (*21*, *22*), rainbow trout (*Oncorhynchus mykiss*) (*23*,

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TABLE 1. Definitions of *Z* and *D* Values[a]

	***Z* values (mol/m³·Pa)**	
water	$Z_W = 1/H$ or C^S/P^S	H = Henry's law constant (Pa·m³/mol) C^S = water solubility (mol/m³) P^S = vapor pressure (Pa)
solid sorbent (e.g. sediment)	$Z_S = K_P \cdot \rho_S / H$	K_P = partition coefficient (L/kg) ρ_S = solid density (kg/L)
octanol or lipid	$Z_O = K_{OW}/H$	K_{OW} = octanol−water partition coefficient
nonlipid organic matter	$Z_N = 0.035 \cdot K_{OW}/H$	The constant 0.035 is from Gobas et al. (*53*) and expresses the sorptive capacity of nonlipid organic matter compared with lipid.
fish or organism	$Z_B = F_L Z_O + F_N Z_N + F_W Z_W$	F_L = lipid fraction of organism F_N = nonlipid organic fraction of organism F_W = water fraction of organism
diet	$Z_D = F_{LD} Z_O + F_{ND} Z_N + F_{WD} Z_W$	F_{LD} = lipid fraction of diet F_{ND} = nonlipid organic fraction of diet F_{WD} = water fraction of diet
gut	$Z_G = F_{LG} Z_O + F_{NG} Z_N + F_{WG} Z_W$	F_{LD} = lipid fraction of gut F_{ND} = nonlipid organic fraction of gut F_{WD} = water fraction of gut
	***D* values (mol/Pa·h)**	
chemical exchange through respiration from water	$D_W = G_W E_W Z_W$	G_W = gill ventilation rate (m³/h) E_W = efficiency of chemical transfer across gills
net chemical uptake from food	$D_D = E_D G_D Z_D$	E_D = gut absorption efficiency G_D = food ingestion rate (m³/h)
chemical loss by egestion	$D_F = D_D(1-\beta)/K_{DG}$	β = fraction of ingested diet absorbed by the organism K_{DG} = diet to GIT partition coefficient (equals Z_D/Z_G)
growth dilution term	$D_G = V_B Z_B k_g$	k_g = growth rate constant (1/h)
biotransformation term for chemical interconversion	$D_{Txy} = V_B Z_{Bx} k_{Rxy}$ or $D_{Txy} = V_B Z_{Bx} \nu_{xy} k_{TR}$	V_B = volume of organism (m³) Z_{Bx} = *Z* value of chemical *x* in organism k_{Rxy} = first-order reaction rate constant (1/h) for conversion of chemical *x* into *y* ν_{xy} = fraction of chemical *x* converting into another chemical *y* explicitly included in the mass balance k_{TR} = overall first-order degradation rate constant of *x* (1/h)
chemical loss by biotransformation	$D_{Mx} = V_B Z_{Bx}(1 - \sum_{y=1}^{n} \nu_{xy}) k_{TR}$	n = number of chemicals explicitly included in the mass balance, where $\sum \nu_{xy} \leq 1$

[a] The *Z* value for organism (Z_B), organism diet (Z_D), and gut (Z_G) are derived from information in Kelly and Gobas (*52*). The derivation of the *D* value for fecal egestion (D_F) is shown in the Supporting Information. All other *Z* and *D* values are from Campfens and Mackay (*3*).

24), and lake trout (*Salvelinus namaycush*) (*10*). The rates of PBDE biotransformation, which presumably differ for each congener in each organism, are poorly known (*10*, *22*, *25*). Knowledge of these rates would result in a better understanding of field data and would improve risk assessments and other regulatory assessments by accounting for the relationship among parent and transformation products. For PBDEs, this is important since the less brominated congeners are often more toxic and persistent than the parent compounds (*26*, *27*) and the three formulations have been subject to different regulatory actions. To address this need, the model is used to back-calculate biotransformation rates of PBDE congeners in the Lake Ellasjøen food web by calibrating the model so that the modeled concentrations correspond to measured data.

Model Development

Fugacity-based models have been used extensively to evaluate the fate and transport of contaminants in environments such as lakes (e.g., *28*) and food webs (e.g., *3*). A detailed theoretical explanation of the modeling framework is provided by Mackay (*29*). Briefly, fugacity (*f*, Pa) is linearly related to concentration (*C*, mol/m³) through fugacity capacity (*Z*, mol/Pa m³), denoted as $C = fZ$. *Z* values are calculated using partition coefficients, e.g., K_{OW} (as shown in Table 1). *D* values (mol/Pa h) for transport and transformation processes are subsequently calculated by multiplying *Z* and *G* (m³/h) values (Table 1). A chemical mass balance equation is set up for each environmental compartment or taxonomic group considered in the model as follows

$$VZ\, df_A/dt = f_B D_{BA} - f_A D_{A-Out} \quad (1)$$

where *V* (m³) is the volume of the environmental medium or taxonomic group, subscripts A and B refer to media, with BA denoting inputs from B to A and A-Out as the sum of all *D* values that are responsible for the loss of the chemical from compartment A.

For steady-state conditions, $df_A/dt = 0$. The set of equations, one per medium or taxonomic group, are then solved for the fugacities of the chemical in all media. Chemical concentrations and transport rates ($N = fD$, mol/h) can then be calculated.

In their fugacity-based food web model, Campfens and Mackay (*3*) constructed one chemical mass balance equation for each taxonomic group. The simplified steady-state equation is

$$f_i = W_i(x_W f_W + x_S f_S) + \sum A_{ji} f_j \quad (2)$$

where *i* is the organism (predator), *j* is a prey, W_i and A_{ji} are fugacity factors for respiration of water and uptake from food, respectively, subscripts W and S are for water and sediment, respectively, *x* is a respiration fraction, and the summation is across all taxonomic groups. W_i and A_{ji} are calculated as D_{Wi}/D_{Toti} and D_{Aji}/D_{Toti}, respectively, where D_{Toti} is the sum of the *D* values describing chemical elimination from fish gills to water and through fecal egestion, growth dilution, and biotransformation. The *Z* and *D* values, which were originally defined by Campfens and Mackay (*3*), were modified to incorporate the recent developments of Arnot and Gobas (*1*) and are summarized in Table 1.

In the Campfens and Mackay (*3*) model, the set of *p* numbers of eq 2 (one for each *p* taxonomic group) is converted into the matrix form of

$$\mathbf{Af} = \mathbf{E} \quad (3)$$

where **A** is the $p \times p$ food consumption or diet matrix, **f** is the vector of taxonomic group fugacity, and **E** is a respiration vector. If there are three taxonomic groups, for example, then eq 3 becomes

$$\begin{bmatrix}(1-A_{11}) & -A_{21} & -A_{31}\\ -A_{12} & (1-A_{22}) & -A_{32}\\ -A_{13} & -A_{23} & (1-A_{33})\end{bmatrix}\begin{bmatrix}f_1\\ f_2\\ f_3\end{bmatrix}=\begin{bmatrix}W_1(x_{1W}f_W+x_{1S}f_S)\\ W_2(x_{2W}f_W+x_{2S}f_S)\\ W_3(x_{3W}f_W+x_{3S}f_S)\end{bmatrix} \quad (4)$$

To extend the model for q interconverting chemicals, we first construct pq sets of equations, one for each of q chemicals in each of p taxonomic groups. The set of equations is then converted into a general matrix equation $\mathbf{Af} = \mathbf{E}$. The expanded $(pq) \times (pq)$ **A** matrix includes a diet submatrix and a biotransformation submatrix. The dimensions of vectors **f** and **E** also expand from p to pq.

For illustrative purposes, we consider three organisms 1, 2 and 3, and two interconverting chemicals a and b. Then, $\mathbf{A}^a$ and $\mathbf{A}^b$ are diet submatrices for the chemicals a and b, respectively, and can be constructed as follows

$$\mathbf{A}^a=\begin{bmatrix}(1-A_{11a}) & -A_{21a} & -A_{31a}\\ -A_{12a} & (1-A_{22a}) & -A_{32a}\\ -A_{13a} & -A_{23a} & (1-A_{33a})\end{bmatrix}$$

$$\mathbf{A}^b=\begin{bmatrix}(1-A_{11b}) & -A_{21b} & -A_{31b}\\ -A_{12b} & (1-A_{22b}) & -A_{32b}\\ -A_{13b} & -A_{23b} & (1-A_{33b})\end{bmatrix}$$

Values of A_{ji} for the chemicals a and b are calculated as discussed earlier.

$\mathbf{T}^{ba}$ and $\mathbf{T}^{ab}$ are biotransformation submatrices for the conversion of chemical b to a and a to b, respectively, and are constructed as

$$\mathbf{T}^{ba}=\begin{bmatrix}-T_{ba1} & 0 & 0\\ 0 & -T_{ba2} & 0\\ 0 & 0 & -T_{ba3}\end{bmatrix}$$

$$\mathbf{T}^{ab}=\begin{bmatrix}-T_{ab1} & 0 & 0\\ 0 & -T_{ab2} & 0\\ 0 & 0 & -T_{ab3}\end{bmatrix}$$

where $T_{abi} = D_{\mathrm{T}abi}/D_{\mathrm{Tot}ia}$ is for a and b interconverting chemicals with ab being conversion from a to b in taxonomic group i. $D_{\mathrm{Tot}ia}$ includes both $D_{\mathrm{T}abi}$ for the biotransformation of chemical a into b where both chemicals are explicitly included in the mass balance equations, as well as $D_{\mathrm{M}ia}$, which is for biotransformation loss of chemical a from the system. As such, $D_{\mathrm{M}ia}$ represents biotransformation into products (e.g., mineralized compounds) that are of no interest to the study and are not part of the chemical mass balance. This allows opting for nonunity product yield, i.e., all the reactant does not necessarily biotransform into the chemicals that are being explicitly included in the mass balance.

The **A** matrix is then

$$\begin{bmatrix}A^a & T^{ba}\\ T^{ab} & A^b\end{bmatrix}$$

Thus eq 3 becomes

$$\begin{bmatrix}(1-A_{11a}) & -A_{21a} & -A_{31a} & -T_{ba1} & 0 & 0\\ -A_{12a} & (1-A_{22a}) & -A_{32a} & 0 & -T_{ba2} & 0\\ -A_{13a} & -A_{23a} & (1-A_{33a}) & 0 & 0 & -T_{ba3}\\ -T_{ab1} & 0 & 0 & (1-A_{11b}) & -A_{21b} & -A_{31b}\\ 0 & -T_{ab2} & 0 & -A_{12b} & (1-A_{22b}) & -A_{32b}\\ 0 & 0 & -T_{ab3} & -A_{13b} & -A_{23b} & (1-A_{33b})\end{bmatrix}\begin{bmatrix}f_{1a}\\ f_{2a}\\ f_{3a}\\ f_{1b}\\ f_{2b}\\ f_{3b}\end{bmatrix}=\begin{bmatrix}W_{1a}(x_{1Wa}f_{Wa}+x_{1Sa}f_{Sa})\\ W_{2a}(x_{2Wa}f_{Wa}+x_{2Sa}f_{Sa})\\ W_{3a}(x_{3Wa}f_{Wa}+x_{3Sa}f_{Sa})\\ W_{1b}(x_{1Wb}f_{Wb}+x_{1Sb}f_{Sb})\\ W_{2b}(x_{2Wb}f_{Wb}+x_{2Sb}f_{Sb})\\ W_{3b}(x_{3Wb}f_{Wb}+x_{3Sb}f_{Sb})\end{bmatrix} \quad (5)$$

Equation 5 can be expanded to any number of organisms and chemicals that can be supported by the computing tool. In addition, this general model formulation can be used to describe all types of interactions among the chemicals, i.e., simple or complex reaction pathways including reversible reactions. This model formulation can also be used for dynamic situations. The multichemical food web model developed here can be combined with previously developed multichemical abiotic fate models using one-step (integrated) or two-step (sequential) methods.

A major assumption of the food web model is that the chemical is homogeneously distributed according to phase partitioning within the organism, which can be considered as a single compartment. This is justified for applications where changes in chemical concentration for a whole organism are relatively slow compared with its life span. Internal, physiologically based pharmacokinetic (PBPK) models, such as those developed by Nichols and co-workers (*30*), can best describe the organ-specific bioaccumulation process. However, use of these models is often hampered by a lack of data, such as the rates of biotransformation within various compartments (e.g., blood, liver, or muscles).

Model Application

To illustrate this general model, we applied it to track the food web transfer and biotransformation of four PBDE congeners in Lake Ellasjøen, which is located in the high arctic and contains a simple food web. We used the model to estimate first-order rate constants for biotransformation, which, in this case, is the debromination of a higher brominated congener and subsequent bioformation of a lower brominated congeners according to a specified biotransformation pathway. Although we chose this application due to the availability of data, sample sizes are small (Table S-4, Supporting Information) (*31*). As such, the results should be regarded as illustrative. Further model evaluation is underway using more comprehensive datasets.

Study Site. Lake Ellasjøen is located on Bear Island, in the Norwegian high arctic (74°30′N, 19°0′E) and has a maximum depth and surface area of 34 m and 0.72 km^2, respectively. Arctic char (*Salvelinus alpinus*) is the only fish species present in this lake. The large char (length > 250 mm) become cannibalistic and we thus considered contaminant accumulation in large and small char. The large char have among the highest concentrations of persistent organic pollutants, including PBDEs, ever reported in arctic fish, and concentrations are significantly higher than in nearby lakes (*31*, *32*).

Model Parametrization. The symbols used in the model parametrization are defined in Table S-1, the parameters are described in Table S-2, and the diet matrix (which illustrates dietary preferences of the organisms in the food web) is shown in Table S-3 (see the Supporting Information).

PBDE Data and Properties. The PBDE concentrations in biota were obtained from Evenset et al. (*31*) (Table S-4, Supporting Information). Sediment and water concentrations are used as input parameters to the model. Sediment concentrations were obtained from Christensen et al. (*33*), who analyzed a surface sample collected at the deepest part of the lake (Table S-4). Procedures for analyzing the PBDEs have been described previously (*31*, *33*). Since water con-

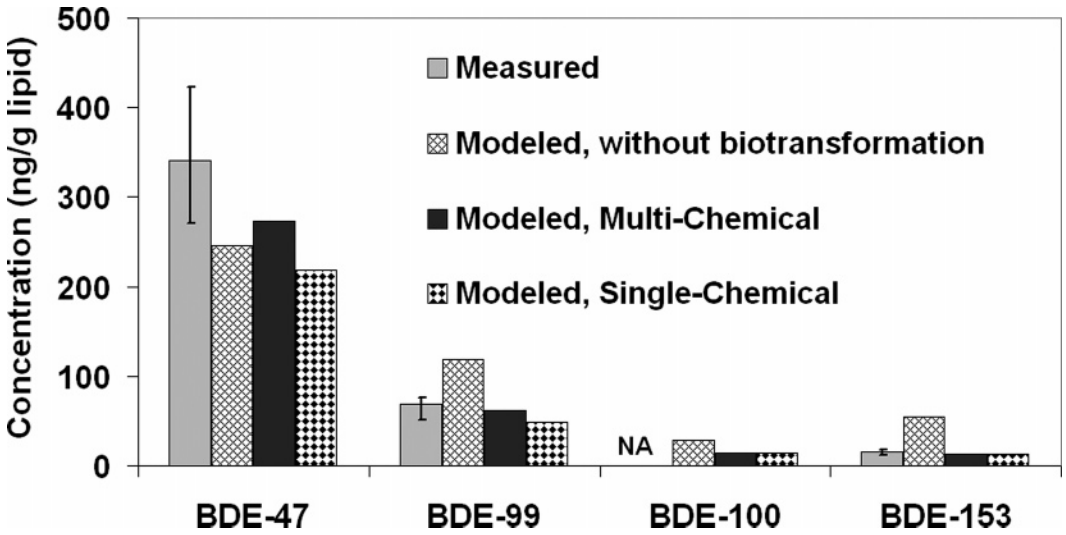

FIGURE 1. Measured and modeled concentrations (ng/g lipid) of four PBDE congeners, BDE-47, -99, -100, and -153, in Lake Ellasjøen large arctic char. Error bars represent ±1 standard error of the mean. NA denotes sample not analyzed for the PBDE congener in question. "Modeled, without biotransformation" refers to concentrations predicted assuming no biotransformation. "Modeled, multichemical" refers to concentrations predicted accounting for biotransformation through both biodegradation and bioformation. "Modeled, single-chemical" refers to concentrations predicted accounting for biodegradation but not bioformation input.

centrations were not measured, they were calculated from zooplankton concentrations by assuming equilibrium between zooplankton and water.

The model was applied to four PBDE congeners, BDE-47, -99, -100, and -153, as the concentrations of these congeners, out of the 18 congeners analyzed, consistently exceeded the detection limit in most of the organisms analyzed (*31*). Further, these congeners tend to dominate other food web studies due to their abundance in commercial penta- and octa-BDE technical mixtures (*13*, *20*, *34*). The physical−chemical properties of these congeners were obtained from Wania and Dugani (*18*) and are summarized in Table S-5 (Supporting Information).

Results and Discussion

Model without Metabolic Degradation. To evaluate the parametrization of this multichemical food web model, we first applied it to six PCB congeners in the Lake Ellasjøen food web. In this model application, interchemical conversions were not accounted for and the rate of chemical biotransformation was set to zero, similarly to model applications to Lake Ontario (*1*, *3*). For the most part, predicted PCB concentrations were within the error associated with the measured data and were identical to the results published in a previous study (*35*, *36*). The performance of the model application to PCBs is discussed further by Gewurtz et al. (*35*−*37*).

We then applied the model to PBDEs, similarly to its application to PCBs, by considering each congener separately, assuming no biotransformation, and setting fractions of interchemical conversions to zero. BDE-47 in large arctic char was underestimated by 30%, whereas BDE-99 and -153 were overestimated by 75 and 250%, respectively (Figure 1, modeled, without biotransformation). For large artic char, a measured concentration of BDE-100 was not available. The results obtained from the model are consistent with the observations of Stapleton et al. (*22*, *38*) in that BDE-99 and -153 are biotransformed (debrominated) to products that include BDE-47.

Multichemical Model. We next ran our multichemical model accounting for PBDE biotransformation. There is minimal or no information on the biotransformation half-lives of PBDE congeners and transformed products, although it is believed that the extent of biotransformation through debromination increases with greater bromination (*10*, *20*, *25*). The metabolic index (MI) provides empirical evidence of biotransformation and is calculated as the ratio between the relative presence of a congener in predator and prey expressed as a percent of PCB-153 (*13*, *39*)

$$\mathrm{MI} = \frac{\mathrm{predator}(\mathrm{BDE}_X/\mathrm{PCB}_{153})}{\mathrm{prey}(\mathrm{BDE}_X/\mathrm{PCB}_{153})} \quad (6)$$

where BDE_X and PCB_{153} are concentrations (ng/g lipid) of the PBDE congener of interest and PCB-153, respectively. PCB-153 is used as a reference compound because it is one of the most persistent of the PCB congeners (*39*). Concentrations of PCB-153 were measured in the same fish extracted for the PBDEs used in this study and have been previously reported by Evenset et al. (*32*). Assuming PCBs and PBDEs behave similarly (e.g., gut absorption efficiency, fecal elimination), except for differences in their susceptibility to biotransformation, MI < 1 suggests that biotransformation is occurring. One criticism of using this approach is that since bromine atoms are larger than chlorine atoms, PBDE uptake from diet as a result of passive diffusion may be less than that of PCBs (*40*) and could cause MI values to overpredict the extent of PBDE biotransformation. However, Burreau et al. (*41*) found that uptake from diet occurs as a result of both passive and mediated diffusion and that differences in the uptake efficiencies between the two classes of chemicals are less than previously assumed. Metabolic indices of BDE-47, -99, -100, and -153 for large arctic char are 0.25, 0.15, 0.25, and 0.06, respectively. This suggests that the char biotransforms these PBDE congeners with BDE-153 having the fastest rate, followed by BDE-99, with BDE-100 and -47 having slower rates.

We used the relative values of MI to guide the choice of congener- and organism-specific biotransformation half-lives during calibration. The model was calibrated by adjusting these biotransformation rate constants to maximize the correspondence between the modeled and measured concentrations of all congeners in small and large char. The only exception to our use of the MI to guide the choice of biotransformation rate constants was for BDE-47, where we assumed significantly slower biotranformation than for BDE-100, which is opposite to what was suggested by the MI values.

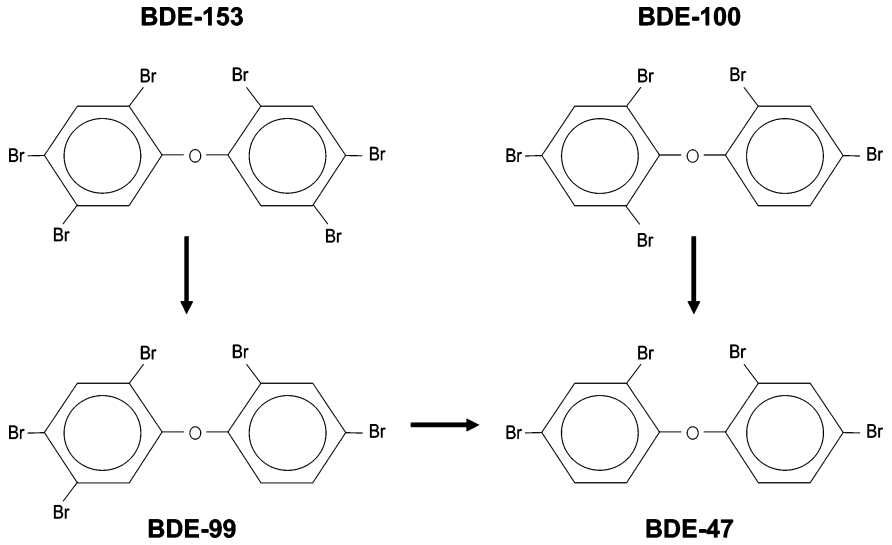

FIGURE 2. Biotransformation path of the four PBDE congeners, BDE-47, -99, -100, and -153, considered in the multichemical food web model.

This limitation in model parametrization was imposed by the absence of measured concentrations of possible biotransformation products of BDE-47 (e.g., BDE-28).

Four assumptions governed our calibration of the model for PBDEs in the Ellasjøen food web. First, we assumed that biotransformation of PBDEs occurs in fish only via reductive debromination (*10*, *21*, *22*) and not in invertebrates as a result of the poorly developed metabolic capabilities of the latter (*42*, *43*). Second, we assumed that debromination constitutes 100% of biotransformation (*44*, *45*). Third, we assumed that one Br atom is removed at a time without any restructuring of the other Br atoms (*10*, *21*). Finally, we assumed that bromines in the ortho- and meta-positions are more susceptible to debromination than those in the para-positions (*46*). According to these assumptions, the biotransformation or debromination pathway for the four PBDE congeners considered in this model run is shown in Figure 2, where BDE-153 debrominates into BDE-47 via BDE-99 while BDE-100 directly debrominates into BDE-47. As noted above, biotransformation products of BDE-47 are not considered in the mass balance.

The multichemical food web model calibrated biotransformation half-lives for BDE-47, -99, -100, and 153 in large char were 5.7, 0.8, 1.14, and 0.45 years, respectively. These half-lives are based on limited data and should be viewed as preliminary. As expected, the correspondence between modeled and measured concentrations improved when the multichemical model was used, compared to the model run without biotransformation (Figure 1, modeled, multichemical and modeled, without biotransformation). In large char, the concentrations of BDE-153, -100, and -99 decreased by 75%, 48%, and 48%, respectively, due to loss through biotransformation. In contrast, the concentration of BDE-47 increased due to bioformation resulting from biotransformation through debromination of the other three higher brominated congeners.

Modeled BDE-47 concentrations in large arctic char remained about 20% less than the mean measured value, even after we considered bioformation using our multichemical model (Figure 1, modeled, multichemical). In addition, we assumed relatively slow biotransformation (5.7-year half-life) of BDE-47, even though the MI suggests that the biotransformation of this congener is comparable to or greater than that of BDE-100, consideration of which would have further decreased the estimated concentration. Although we have limited measurements ($n = 6$) to confirm the underestimation of BDE-47, we believe that congeners in addition to BDE-99, -100, and -153 considered here are debrominating into BDE-47 and hence the bioformation of BDE-47 may be greater than that accounted for in the model.

The model estimates that an additional input via bioformation of 2300 and 330 ng/year of BDE-47 is necessary to match measured and modeled concentrations in large and small char, respectively. For large char, this additional input is comparable to the model estimate of 3604 ng/year of BDE-47 formed through the debromination path shown in Figure 2. In contrast, for small char, the additional input is more than an order of magnitude greater than the estimated BDE-47 bioformation of 24 ng/year (Figure 2). Since sediment tends to be enriched with higher brominated congeners such as BDE-209 (*47*−*49*) and because sediment is an important route of contaminant accumulation in the Ellasjøen food web (*35*), this shortfall of BDE-47 in small and large char could be due to biotransformation of higher brominated congeners not considered here. Although the debromination of BDE-209 to BDE-47 is possible (*50*), to our knowledge, it has not yet been demonstrated in fish (e.g., *21*).

An overestimation of the loss of BDE-47 due to fecal egestion, respiration, and growth dilution would also cause the model to underestimate BDE-47 in large char. However, since we successfully evaluated this model with PCBs by setting the rate of chemical biotransformation to zero, we believe that the parametrization for these three loss processes is reasonable.

Single-Chemical Model. Finally, we ran the model in single-chemical mode in order to compare the results with those of our multichemical model. The single-chemical model was run for each individual congener considering loss due to biotransformation but no bioformation input for the transformed products (Figure 1, modeled, single-chemical). Since BDE-153 and -100 are the parent compounds for the biotransformation pathway considered in this application (Figure 2), the estimated concentrations of these congeners in large arctic char remained unchanged compared to the multichemical model run (Figure 1). In contrast, the estimated concentrations of BDE-47 and -99 decreased by about 20% due to the omission of bioformation resulting from the debromination of BDE-100 and BDE-153, thereby reducing the correspondence between modeled and measured concentrations. This analysis illustrates the importance of considering bioformation input through the multichemical model while assessing the dynamics of PBDE congeners in aquatic food webs.

Chemical Fate and Transport Rates. To illustrate the relative importance of various chemical transport rates, we present the results for the multichemical model run in Figure

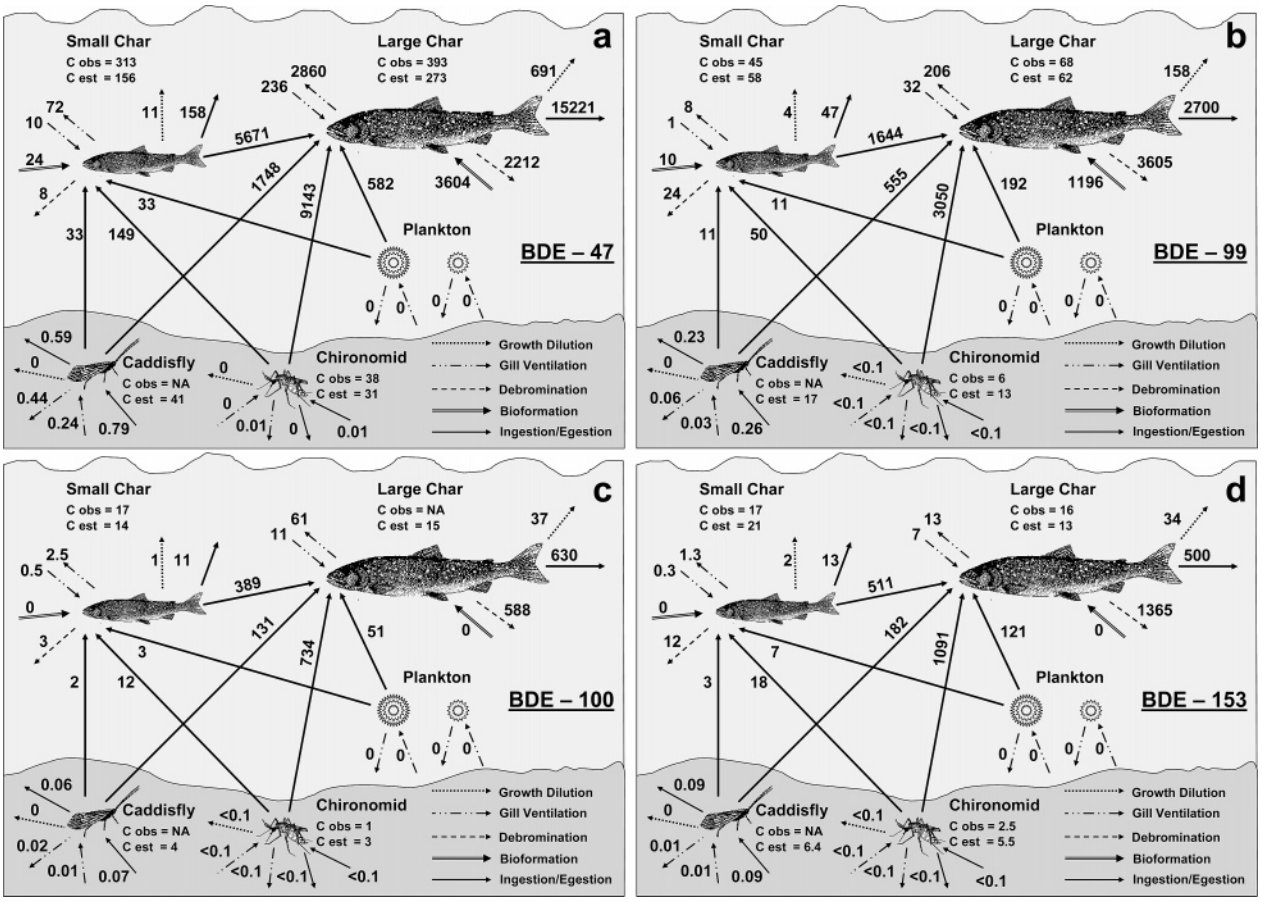

FIGURE 3. Schematic diagram of measured and modeled (multichemical food web) concentrations (ng/g lipid) and estimated chemical transport rates (ng/year) of (a) BDE-47, (b) BDE-99, (c) BDE-100, and (d) BDE-153 considering the biotransformation path shown in Figure 2. NA denotes sample not analyzed for the PBDE congener in question.

3. On the basis of model calibrated biotransformation half-lives, the results suggest that biotransformation input supplies a minimum of ~24 and 3600 ng/year of BDE-47 to small and large arctic char, respectively, which corresponds to ~10 and 17% of total BDE-47 input to these organisms. Debromination ranges from 3% (BDE-47) to 41% (BDE-153) and 10% (BDE-47) to 70% (BDE-153) of total loss in small and large arctic char, respectively. For congeners with a high potential for biotransformation through debromination, e.g., BDE-153 and BDE-99, biotransformation could become the major process of elimination within the aquatic food web. The model results support laboratory studies showing that the concentrations of PBDE congeners in fish are a product of direct trophic transfer, as occurs for persistent compounds, as well as bioformation resulting from biotransformation of higher brominated congeners (*10*, *21*, *22*). For chironomids, the model overestimated PBDE concentrations by a factor of 1.2−3 (Figure 3). However, the correspondence between modeled and measured concentrations for chironomids is still well within the range of the predictions of most food web models (e.g., *2*, *3*, *51*).

Sensitivity Analysis. We conducted a sensitivity analysis in order to evaluate the sensitivity of modeled PBDE concentrations to five selected parameters: water and sediment concentrations, fecal elimination, organism lipid content, and metabolic half-lives. These parameters were selected because we expected them to be highly uncertain and/or influential, on the basis of the results of a previous study (*37*). The sensitivity analysis was performed by doubling and halving each parameter value for all the congeners and organisms. Figure 4 presents the resulting percentage change

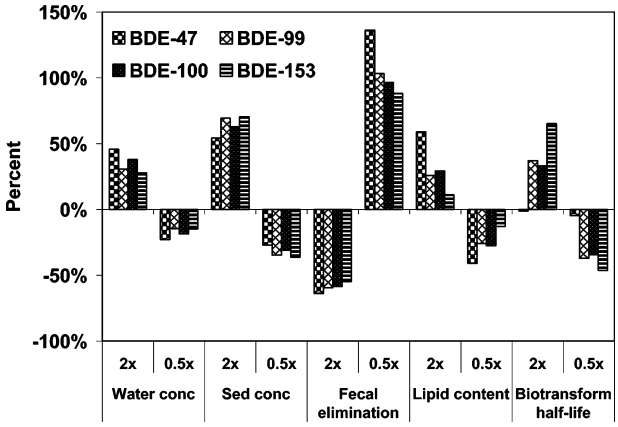

FIGURE 4. An evaluation of the sensitivity of the multichemical food web model expressed as the percentage change in modeled fish concentrations on a lipid basis due to a doubling and halving of each parameter value evaluated relative to the base case (Figure 1, modeled, multichemical).

in large char concentrations compared to concentrations obtained from the multichemical model run (Figure 1).

Of the parameters considered in this analysis, fecal elimination was the most influential, with a doubling and halving of the rate decreasing and increasing char concentrations by approximately 50% and 100%, respectively. This result is important because the mechanism of fecal elimination, and hence biomagnification, is not completely understood (*37*). Gewurtz et al. (*37*) also found that fecal elimination was one of the most influential parameters in the single-

chemical version of the model and provided a mechanistic explanation for this result. Fecal elimination was particularly influential for BDE-47, because this congener has the highest efficiency of transfer between the gut and the organism (Table S-2).

Since water concentrations were not available, we used values calculated from PBDE concentrations in zooplankton. Depending on the PBDE congener, the doubling and halving of water concentrations increased and decreased fish concentrations by 28−46% and by 15−23%, respectively, and the doubling and halving of sediment concentrations increased and decreased fish concentrations by 54−70% and by 27−36%, respectively. The increase and decrease in lipid content increased and decreased modeled fish concentrations by 11−59% and by 13−41%, respectively. However, in comparison to the other parameters, measured lipid values are relatively certain.

For BDE-99, -100, and -153, doubling and halving biotransformation half-lives increased and decreased concentrations by 33−65% and by 34−46%, respectively. The results for BDE-47 differed from those for the other congeners. An increase in the biotransformation half-lives decreased BDE-47 loss through biotransformation but also decreased bioformation input due to lower biotransformation of the other congeners. The combined effect resulted in a minimal (1%) decrease in the BDE-47 fish concentration. A similar mechanism was responsible for the minimal 5% decrease in BDE-47 concentrations that occurred when biotransformation half-lives were halved. It would be challenging to tease out such effects of biotransformation on chemical dynamics through experimental studies, as discussed by Tomy et al. (*10*).

In conclusion, we have developed a model that tracks parent compounds and their biotransformation products through a food web. The formulation is general to persistent organic chemicals and can be adapted to any number of organisms and reaction pathways. The model, when calibrated to field data, provides quantitative estimates of congener specific biotransformation half-lives and transport rates. As such, this model is an improvement over existing food web models, as it expands their applicability to contaminants, such as PBDEs, which are susceptible to biotransformation and bioformation in aquatic food webs.

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Supporting Information Available

The derivation of D_F, the symbols used in model parametrization (Table S-1), the input parameters and equations used in the model (Table S-2), the dietary preferences of organisms of the Lake Ellasjøen food web (Table S-3), the concentrations of the PBDE congeners in Ellasjøen sediment and biota (Table S-4), and the physical−chemical properties of the PBDE congeners used in model simulations (Table S-5). This material is available free of charge via the Internet at http://pubs.acs.org.

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