

Development of multi-chemical food chain model: Application to PBDEs in Lake Ellasjøen, Bear Island, Norway

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Introduction

Mass balance models are useful tools for evaluating the mechanisms responsible for contaminant levels and trends in biota.^{1,2,3} However, most food web models have only been applied to contaminant, such as PCBs, that are not very susceptible to metabolic degradation in fish and invertebrates.^{1,2,3} For compounds, such as PBDEs, which are not as persistent in the environment, it is important to simultaneously track both the parent chemical and its degradation 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 However, this single-chemical approach is inappropriate because the connection is lost between the parent compound and its transformation products.

In this study, we present an extension of the food web model of Campfens and Mackay³ to simultaneously account for multiple, related chemicals by solving mass balance equations of chemicals of concern simultaneously using a matrix approach. Such an approach was suggested by Diamond et al.⁶ to track the movement of multiple interconverting metal species and was recently used by Fenner et al.^{7,8} and Cahill et al.⁹ for organic chemicals in the abiotic environment. The general model formulation developed here also addresses the need for estimating rates of biodegradation and bioformation of a family of compounds through a food web. We illustrate the model using PBDEs in the food web of Lake Ellasjøen, a high arctic lake located on Bear Island, Norway.

Model Development

In a fugacity-based food web model, Campfens and Mackay³ constructed one chemical mass balance equation for each taxonomic group. The simplified steady-state equation is

$$f_i = W_i(x_W f_W + x_S f_S) + \sum A_{ji} f_j \quad (1)$$

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 sediments, respectively, x is a respiration fraction, and the summation is for all taxonomic groups. W_i and A_{ji} are calculated as D_{Wj}/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 metabolic degradation.

In the Campfens and Mackay³ model, the set of p number of equation (1)'s (for p organisms) is converted into the matrix form of

$$\mathbf{A}\mathbf{f} = \mathbf{E} \quad (2)$$

where \mathbf{A} is the $p \times p$ food consumption or diet matrix, \mathbf{f} is the vector of organism fugacity, and \mathbf{E} is a respiration vector. If there are three organisms, for example, then equation 2 becomes

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

To extend the model for q inter-converting chemicals, we first construct p q set of equations, one for each of q chemicals in each of p organisms. The set of equations is then converted into a general matrix equation $\mathbf{A}\mathbf{f} = \mathbf{E}$. The expanded $(p \ q) \times (p \ q)$ \mathbf{A} -matrix includes a diet sub-matrix and a transformation sub-matrix. The dimensions of vectors \mathbf{f} and \mathbf{E} also expand from p to $p \ q$.

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

$$\mathbf{A}^a = \begin{bmatrix} (1-A_{11a}) & -A_{21a} & -A_{31a} \\ -A_{12a} & (1-A_{22a}) & -A_{32a} \\ -A_{13a} & -A_{23a} & (1-A_{33a}) \end{bmatrix} \quad \mathbf{A}^b = \begin{bmatrix} (1-A_{11b}) & -A_{21b} & -A_{31b} \\ -A_{12b} & (1-A_{22b}) & -A_{32b} \\ -A_{13b} & -A_{23b} & (1-A_{33b}) \end{bmatrix} \quad (4)$$

A_{ij} for the chemicals a and b are calculated as discussed earlier.

\mathbf{T}^{ba} and \mathbf{T}^{ab} are transformation sub-matrices for the conversion of chemical b to a and a to b , respectively, and are constructed as

$$\mathbf{T}^{ba} = \begin{bmatrix} -T_{ba1} & 0 & 0 \\ 0 & -T_{ba2} & 0 \\ 0 & 0 & -T_{ba3} \end{bmatrix} \quad \mathbf{T}^{ab} = \begin{bmatrix} -T_{ab1} & 0 & 0 \\ 0 & -T_{ab2} & 0 \\ 0 & 0 & -T_{ab3} \end{bmatrix} \quad (5)$$

where $T_{abi} = D_{Tabi}/D_{Totia}$ for a and b inter-converting chemicals with ab being conversion from chemical a to b in taxonomic group i . D_{Totia} includes D_{Tabi} for the transformation of chemical a into b in addition to D_{Mia} formetabolism. This allows opting for non-unity product yield, i.e., all the reactant does not necessarily transform into the chemicals that are being considered in the study and may possibly degrade or mineralize into other chemicals or elements outside of the mass balance.

The \mathbf{A} -matrix is then formulated as $\begin{bmatrix} A^a & T^{ba} \\ T^{ab} & A^b \end{bmatrix}$ (6)

Although the above illustrated equations are for three organisms and two chemicals, the equation developed here 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 multi-chemical food-web model developed here can be combined with previously developed multi-chemical abiotic fate models using one-step (integrated) or two-step (sequential) methods.

The Z and D values, which were originally defined by Campfens and Mackay³, were modified in this study to incorporate the recent developments of Arnot and Gobas¹.

Model Application

To illustrate this general model, we apply it to track the movement of four BDE congeners (47, 99, 100, 153) in a simple, high arctic food web. The results should be regarded as illustrative given the limited dataset.

Lake Ellasjøen is located on Bear Island, in the Norwegian high arctic (74°30'N, 19°0'E). The lake has a maximum depth of 34 m and a surface area of 0.72 km². Arctic char from this lake contain among the highest concentrations of POPs, including PBDEs, ever reported in the arctic, and concentrations are significantly higher than in nearby lakes.^{10,11}

We considered five taxonomic groups: zooplankton, chironomid, caddisfly, and small and large char within the food web. The model is parameterized similarly to Morrison et al.² and Arnot and Gobas¹. Based on results from Stapleton et al.¹² and assuming that debromination occurs by elimination of one bromine atom at a time and that there is no structural rearrangement during this transformation, we considered the debromination and bioformation path shown in Figure 1.

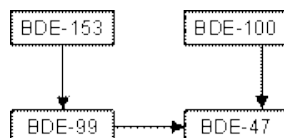


Figure 1: Debromination and bioformation path of the four BDE congeners considered in the model application.

In absence of measured degradation half-life of these congeners, we used the model to back-calculate these values for each congener specific to each taxonomic group.

Results and Discussion

Figure 2 compares measured versus modeled concentrations in the arctic char for various scenarios. The results illustrate how the model can account for bioformation of lower brominated congeners (e.g., BDE-47) and its effect on estimated concentrations. Further, with regards to degradation rate calculated using model calibrated half-lives, the model predictions for BDE-99, -100, and -153 tend to be more sensitive than for the predictions for BDE-47. This is occurring because concentrations of the more brominated congeners are much less than the concentrations of BDE-47 and therefore they can only contribute a limited amount to BDE-47 through bioformation, regardless of their degradation half-life.

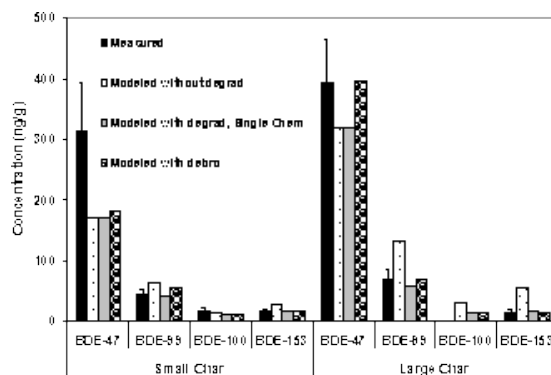


Figure 2: Measured vs model estimated BDE concentrations in small and large char

Based on model calibrated half-lives, the results (not shown here) suggest that bioformation supplies about 20 and 3650 ng/yr of BDE-47 to small and large arctic char, respectively, which correspond to 8 and 6% of total BDE-47 input. Metabolic degradation ranges from 20% (BDE-100) to 65% (BDE-153) of total loss rate in arctic char species. For congeners with a high potential for debromination, e.g. BDE-153 and BDE-99, degradation could become a major process of elimination within the aquatic food chain.

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