CAN BIOTRANSFORMATION OF BDE-209 CAUSE BIOACCUMULATION OF MORE TOXIC, LOWER BDEs (e.g., BDE-47, -99) IN FISH OVER THE LONG TERM?

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Introduction

Lower brominated BDEs can be more toxic than higher BDEs. Although laboratory experiments have shown that debromination of BDE-209 resulted in accumulation of lower brominated BDEs down to hexa- and hepta-BDE congeners (e.g., BDE-183, BDE-154) in fish, the more toxic BDE-47 and -99 congeners were not formed [1,2]. However, these experiments are generally less than one year in length. In order to investigate the long-term impact of debromination of BDE-209 on the bioaccumulation of more toxic BDE-47 and -99, experiments need to be performed over several years, which is difficult in a laboratory setting. We previously investigated the extent and rate of BDE-209 debromination in fish using our calibrated multi-chemical, dynamic fugacity-based fish model [3] that was applied to the experimental data of Tomy et al. [4]. The calibrated model estimated approximate gut absorption efficiencies (GAE) and half-lives (HL) of 13 PBDE congeners in juvenile lake trout by reproducing observed concentrations for high and low doses applied to uptake and depuration phases for 168 days. In this study, we conduct a modelling analysis to examine the extent to which higher BDEs such as BDE 209 biotransform into lower BDEs over a long-term (i.e., 10-15 years).

Model details

We used our previously developed general dynamic multi-chemical fish model [3], which was calibrated by reproducing the observed PBDE concentrations in laboratory exposed juvenile lake trout in a six month study conducted by Tomy et al. [4], where important model input parameters such as diet concentrations, ingestion and growth were directly measured. The model was used in reverse model in order to back-calculate HL and GAE, which are chemical- and fish-species-specific and, in general, not well known for PBDEs [1,5,6]. In this model application to a life time of lake trout, we used laboratory measured as well literature values for model parameterization.

The physical-chemical properties of PBDEs were taken from Tomy and co-workers [7,8] and were all derived in the same laboratory which conducted the lake trout bioaccumulation experiment [4]. This increases the extent of consistency for these data.

For lipid content of the diet, density of fish and plankton were used for piscivorous and non-piscivorous fish, respectively. For the lake trout being modeled, we used 3% lipid [4], and assumed 20% non-lipid organic matter and 77% water. Growth rate and dietary consumption values for piscivorous lake trout (PLT) and non-piscivorous lake trout (NPLT) were obtained from Pazzia et al. [9] (Figure 1). Since the exponential curve did not result in a realistic consumption rate for the first 200 days of life of PLT, we assigned a consumption rate of 3% of the body weight for this initial life stage. By considering daily changes in fish volume, the model inherently accounts for contaminant loss due to the growth dilution.

We used a biotransformation path for the PBDE congeners suggested by Bhavsar et al. [3] (Figure 2) based on the following assumptions [3,10]: debromination constitutes 100% of biotransformation [11,12]; one bromine atom is removed at a time with no restructuring of the other bromine atoms [2,4]; and bromines in the ortho- and meta-positions are more susceptible to debromination [2,13,14]. This path also considers the heats of formation of the parent and product congeners as biodegradation/bioformation reactions favour more stable products, i.e. products with low heat of formation [13]. The model was run for only BDE-209 for the low and high dietary concentrations (3.4 and 27.5 ng/g ww respectively) used by Tomy et al. [4].

Results and Discussion

Here we present model results for the PLT runs. We first ran the model with a variable consumption rate as shown in Figure 1. For this scenario, size (i.e., weight) of the fish increases with time while the consumption rate (g/g/day) decreases. The combined effects of these two parameters as well as increasing accumulation of BDE-209 during the first 300 days raises the levels of BDE-209 to approximately 240 and 30 ng/g lipid for high and low doses, respectively (Fig. 3a,b). However, the relatively faster decrease in the consumption rate compared to growth rate decreases the concentrations by about 65% over 15 years (Fig. 3a,b). In order to understand the effect of variable consumption rate on the modeled BDE-209 concentrations, next we ran the model for the high dose with the constant consumption rate of 3% of the body weight. This results in a continuous increase in BDE-209 concentration beyond 300 days until it reaches a steady-state level of about 425 ng/g lipid in 3-4 years.

The modelling results suggest that juvenile fish may debrominate BDE-209 into nona-, octa-, hepta- and hexa-BDEs but none of the major penta (e.g., BDE 99, 100) and tetra (e.g., BDE 47) BDEs within 5-6 months (Fig. 3a,b,c; all results not shown). These results are in agreement of laboratory based experimental observations [1]. However, noticeable amounts of lower brominated congeners (BDE-47, -99, -100) start appearing after the first year of exposure (Fig. 3a,b,c). Loss of BDE-209 due to biotransformation may account for about 30% of dietary intake, while egestion is the major loss process (Fig. 3d).

The long-term (15 year) run of the model shows that the concentrations of BDE-47 and -99 would stabilize around 8 and 23 ng/g lipid for high dose (Fig. 3a) and 1 and 3 ng/g lipid for low dose (Fig. 3b). The corresponding concentrations for BDE-100 are similar to that for BDE-99. As such, based on draft USEPA tolerable daily intakes (TDIs) and these results, we can conclude that biotransformation of BDE-209 in lake trout over the long-term would not result in levels of BDE-47, -99 and -100 that would be of concern for human health via dietary exposure.

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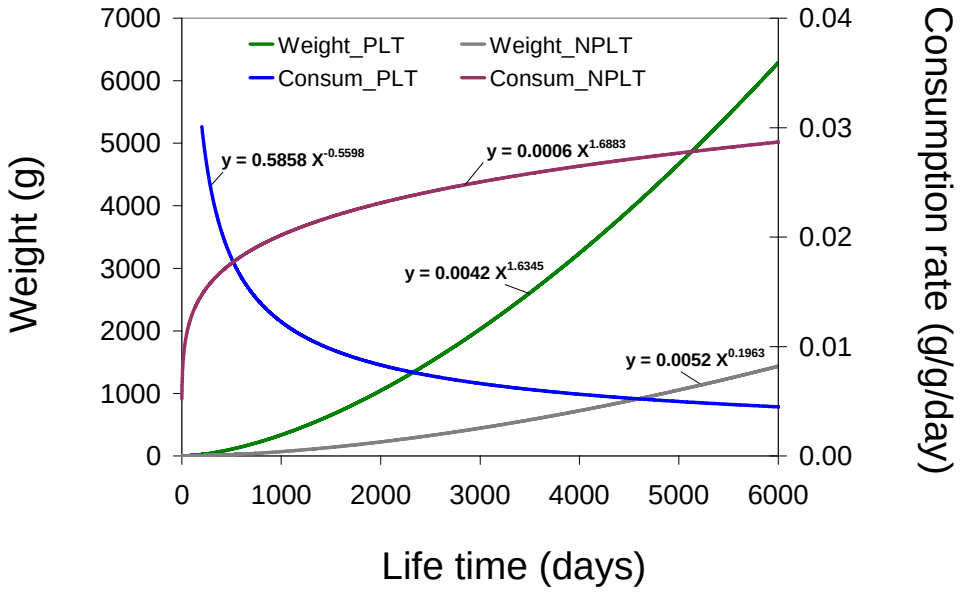

Figure 1. Growth rate and dietary consumption values for piscivorous lake trout (PLT) and non-piscivorous lake trout (NPLT). The values were obtained from Pazzia et al. [9].

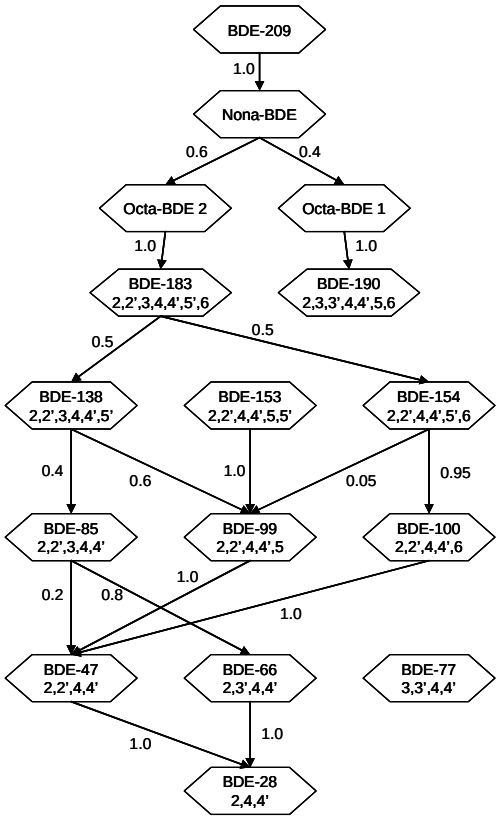

Figure 2. Biotransformation path considered in this dynamic, multi-chemical fish model application. The model calibrated fraction of which a debrominating congener contributes to a lower brominated congener is indicated by the number adjacent to the arrow.

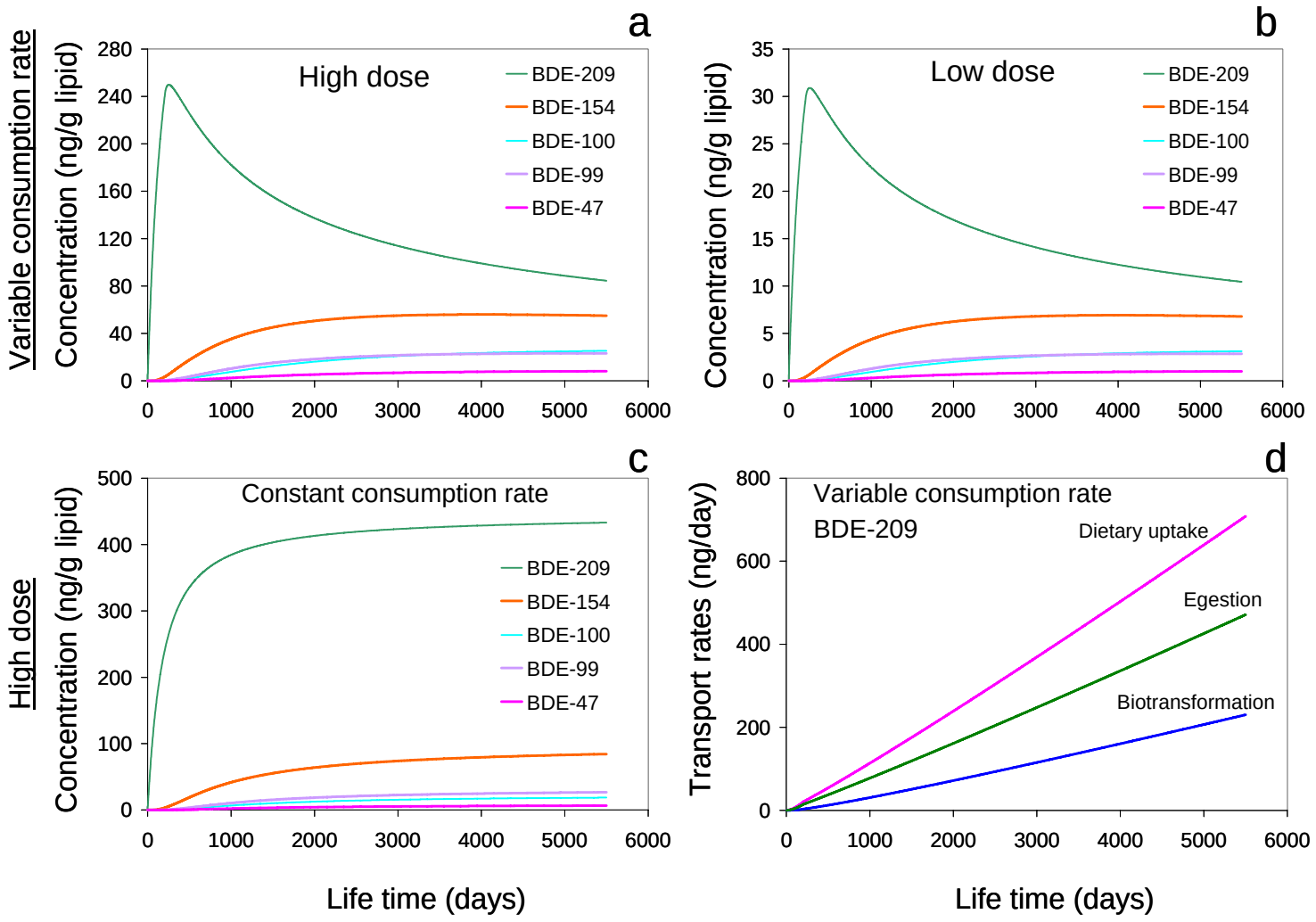

Figure 3. Modelled concentrations of various BDE congeners and transport rates of BDE-209 in piscivorous lake trout for high and low dietary doses of BDE-209 used by Tomy et al. [4]. A lipid content of 3% was used for the lake trout.