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Estimating stepwise debromination pathways of polybrominated diphenyl ethers with an analogue Markov Chain Monte Carlo algorithm

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HIGHLIGHTS

- A stochastic process is proposed to simulate photolytic debromination of BDE209.
- The process is modeled efficiently by an analogue Markov Chain Monte Carlo (AMCMC) algorithm.
- Pathways are simulated such that the model fits measured congener patterns.
- Debromination activity is ortho > meta > para at 1 h, and mainly meta at 1–4 h.

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ABSTRACT

A stochastic process was developed to simulate the stepwise debromination pathways for polybrominated diphenyl ethers (PBDEs). The stochastic process uses an analogue Markov Chain Monte Carlo (AMCMC) algorithm to generate PBDE debromination profiles. The acceptance or rejection of the randomly drawn stepwise debromination reactions was determined by a maximum likelihood function. The experimental observations at certain time points were used as target profiles; therefore, the stochastic processes are capable of presenting the effects of reaction conditions on the selection of debromination pathways. The application of the model is illustrated by adopting the experimental results of decabromodiphenyl ether (BDE209) in hexane exposed to sunlight. Inferences that were not obvious from experimental data were suggested by model simulations. For example, BDE206 has much higher accumulation at the first 30 min of sunlight exposure. By contrast, model simulation suggests that, BDE206 and BDE207 had comparable yields from BDE209. The reason for the higher BDE206 level is that BDE207 has the highest depletion in producing octa products. Compared to a previous version of the stochastic model based on stochastic reaction sequences (SRS), the AMCMC approach was determined to be more efficient and robust. Due to the feature of only requiring experimental observations as input, the AMCMC model is expected to be applicable to a wide range of PBDE debromination processes, e.g. microbial, photolytic, or joint effects in natural environments.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants in a wide array of products for decades. Based on the bromine numbers and their occupations on the two phenyl rings, 209 BPDE congeners are identified. PBDEs were commercially available in terms of mixtures, and have now been banned in the European Union and were phased out by the end of 2012 in the United States (Hites, 2004; USEPA, 2009; Zou, 2011). The compositions of these mixtures are provided by La Guardia et al. (2006). Debromination of PBDEs in the environment is a concern due to the potentially higher bioaccumulation and toxicity of the reaction product congeners compared to the parent congeners (McDonald, 2002; Darnerud, 2003). For this reason, debromination of PBDE has undergone intensive study in the past decade. Most of the studies identified the major debromination products and explicitly reported debromination pathways based on experimental observations (Bezares-Cruz et al., 2004; He et al., 2006; Robrock et al., 2008; Tokarz et al., 2008; Davis and Stapleton, 2009; Zhuang et al.,

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2012). However, as has been reported in PCB dechlorination, the explicitly reported pathways likely represent only a subset of the possible pathways (Hughes et al., 2010). In order to uncover the missing information, experimental methods using advanced instruments have been developed to improve chemical detection. For example, the gas chromatographic (GC) separation of 180 PBDE congeners was optimized by Wei et al. (2010a, b, 2014). Even with these advances, experiments may be insufficient to trace the complete pathways due to rapid formation of daughter congeners (Davis and Stapleton, 2009), and the limitation of instrumental analysis caused by high detection limits, matrix effects, and/or co-elution of compounds from GC columns.

Modeling approaches provide valuable inferences by extending the knowledge obtained from experimental data (Vinu et al., 2012). Many studies have attempted to reveal PBDE debromination pathways and kinetics using quantitative structure–activity relationships (QSAR), which explore the links between the reaction parameters and molecular descriptors calculated based on quantum chemistry principles (Hu et al., 2005; Andersson et al., 2006; Niu et al., 2006; Zeng et al., 2008; Fang et al., 2009; Heimstad et al., 2009; Wang et al., 2012). QSAR models focus on the internal molecular structures and are not always reflective of external conditions (Davis and Stapleton, 2009). Stochastic modeling approaches have been applied to molecular level disordered reaction sequences in material synthesis (Petrov and Miller, 2012), pyrolysis (Vinu et al., 2012), bio-engineering and molecular biology (Subbian et al., 2005; Ribeiro et al., 2009; Oliveira et al., 2010; Chen et al., 2011). The approach of the stochastic model is based on computational statistics. Unlike molecular property based models, the statistical model does not necessarily need additional thermodynamic data. It draws feasible candidate reactions randomly and reconstructs the experimental measurements by conditionally accepting those random reactions. Markov Chain Monte Carlo (MCMC) is one of the most generally recognized stochastic modeling methods, and has been used in simulating chemical reactions for decades (Metropolis et al., 1953). However, to our knowledge its application to PBDE debromination has not been reported.

A previous version of the stochastic process, stochastic reaction sequences (SRS), was proposed and applied to anaerobic dechlorination of polychlorinated biphenyls (PCBs) (Imamoglu et al., 2004; Bzdusek et al., 2006a; Bzdusek et al., 2006b), and the photolytic debromination of PBDEs (Wei et al., 2013). Even with these successful applications, the advantages of using stochastic simulation of dehalogenation have not been well recognized. The SRS model for BDE209 debromination is relatively inefficient in that it randomly selects reaction sequences from possible homolog transitions consisting of only measured congeners. By contrast, the AMCMC method is working on executing reactions only in descending order of homologs, e.g., deca-to-nona, nona-to-octa, etc. Another important feature of the ACMCMC model is that it includes not only measured congeners, but all possible congeners, assuming zero concentrations of non-measured congeners. This provides information about possibly unexplored debromination pathways involving non-measured congeners. Therefore, the advantages of using the AMCMC algorithm, compare to SRSs, can be shown by reducing the simulation time, improving the robustness of the model results, and expanding the applicability to a wide range of dehalogenation studies. The main purpose of the model simulation is to infer the most likely debromination pathways while maintaining the best possible fit to the measured target PBDE profile.

2. Theory and method

The traditional Monte Carlo method draws independent samples from a desired probability distribution, whereas MCMC generates sequential samples such that future samples are dependent on the current ones (Bartoszynski and Niewiadomska-Bugaj, 2008). This property of Markov Chains agrees with the nature of PBDE debromination reactions, since the daughter product is dependent on the parent PBDE congener. There are certain other properties of Markov Chains imbedded in the stochastic debromination model, e.g. ergodicity, which means that all possible reactions will be executed during the model simulation; and stationarity, which means that the model generated PBDE profile at the end of the selected time period is relatively stable and similar to the experimental observation. However, some properties of Markov Chains are not valid in the proposed stochastic debromination process. First, the debromination reactions are unidirectional. No bromine can be added to turn the product congeners back to the initial identity of the parent, which contrasts with the property of recurrence. Second, the step selection is determined by a maximum likelihood function (MLF) other than a desired probability distribution. With respect to these differences, we would call the algorithm in the proposed stochastic debromination process an analogue MCMC (AMCMC) algorithm.

The 209 PBDE congeners (Table S1, Supporting information) and 837 debromination reactions (from deca to mono, 840 if from deca to diphenyl ether) (similar to PCBs, Hughes et al., 2010) (Table S2) are used as database for the model. An illustration of debromination pathways from deca to octa is shown in Fig. 1. These reactions are formulated in a stepwise cascade manner. The daughter congeners are determined by the position from which the bromine was broken off from one of the two phenyl rings of the parent congener. For example, the loss of a bromine from the ortho, meta, and para position of BDE209 generates BDEs 206, 207, or 208, respectively.

Given the initial PBDE profile, the stochastic debromination simulation mimics the debromination reactions to generate the target profile which is the debrominated profile experimentally determined at a certain time. How the model mimics the debromination reactions is the key feature. The two methods, SRS and AMCMC differ on how to draw the random candidate reactions. The procedures of the model execution are given in Table 1. For both methods, the acceptance or rejection of the proposed debromination reaction is determined by the MLF,

$$S = \sum_{i=1}^{m} \frac{(\hat{x}_i - x_i)^2}{\sigma_i^2} \tag{1}$$

where $\hat{x}_i$ is the model generated value and x_i is the measured, i.e. experimentally determined value for the molar concentrations of PBDE congener i, respectively, while m is the total number of PBDE congeners, and σ_i is the measurement error also in molar concentration for congener i. In this study, the σ_i is assigned the value 1 for all congeners estimated from the experimental results (Table S3) (Press et al., 2002).

For the SRS method, a collection of possible debromination reactions (a subset of reactions in Table S2) were preselected based on the debromination products detected at the times of measurement. The model randomly selects the debromination reaction from the subset of the reactions, and checks to determine if the candidate reaction is feasible or not. In SRS method, the candidate reaction is independent of the previous reaction. The same reaction sequence is repeated using updated congener numbers to ensure minimization of the objective function, Eq. (1), and that all possible congeners are populated. In contrast, for the AMCMC method, the model first identifies the mother congener, and then draws a candidate reaction based on the bromine occupation on the two phenyl rings of the mother congener. If the candidate reaction was accepted, then the model takes the daughter congener as a mother congener for the next step reaction. Therefore, the candidate reaction is dependent on the previous reaction in the AMCMC method.