



# Evidence for photochemical and microbial debromination of polybrominated diphenyl ether flame retardants in San Francisco Bay sediment



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## HIGHLIGHTS

- The analysis used a data set of 24 BDE congeners in 233 samples.
- Factor analysis resolved five factors.
- Two factors resembled the deca and penta commercial BDE formulations.
- Two factors contained di and tribromo congeners indicative of debromination.
- Photolytic and microbial debromination are thought to explain these two factors.

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## ABSTRACT

Brominated diphenyl ethers (BDEs) are flame retardant compounds that have been classified as persistent organic pollutants under the Stockholm Convention and targeted for phase-out. Despite their classification as persistent, PBDEs undergo debromination in the environment, via both microbial and photochemical pathways. We examined concentrations of 24 PBDE congeners in 233 sediment samples from San Francisco Bay using Positive Matrix Factorization (PMF). PMF analysis revealed five factors, two of which contained high proportions of congeners with two or three bromines, indicating that they are related to debromination processes. One of the factors included PBDE 15 (4,4'-dibromo diphenyl ether, comprising 20% of the factor); the other included PBDE 7 (2,4-dibromo diphenyl ether; 12%) and PBDE 17 (2,2',4-tribromo diphenyl ether; 16%). The debromination processes that produce these congeners are probably photochemical debromination and anaerobic microbial debromination, although other processes could also be responsible. Together, these two debromination factors represent about 8% of the mass and 13% of the moles of PBDEs in the data matrix, suggesting that PBDEs undergo measurable degradation in the environment.

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## 1. Introduction

Brominated diphenyl ethers (BDEs) are flame retardant compounds that have been widely used in consumer products since the 1970s, exhibit elevated concentrations in seafood and indoor dust, and may pose human health hazards at environmentally relevant concentrations (Domingo, 2012). As a result, PBDEs have been classified as persistent organic pollutants (POPs) under the Stockholm Convention and are targeted for phase-out (United

Nations Environment Program, 2009). Despite their classification as persistent, PBDEs undergo debromination via microbial and photochemical pathways that have been studied under laboratory conditions, but as yet there is little understanding of their importance for the environmental fate of PBDEs.

The photolysis of PBDEs, studied with multiple light sources and media, exhibits characteristic pathways and breakdown products (Sanchez-Prado et al., 2006; Fang et al., 2008; Sanchez-Prado et al., 2012; Wei et al., 2013 and references therein). Several researchers (Fang et al., 2008; Sanchez-Prado et al., 2012; Wei et al., 2013) have demonstrated that during photolysis, removal of bromines in the *ortho* position predominates. PBDE 15 (4,4'-dibromodiphenyl ether) is a major photolysis product, with PBDE 17 (2,2',4-tribromodiphenyl ether) sometimes reported as a

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minor product (Sanchez-Prado et al., 2012; Wei et al., 2013). Ahn et al. (2006) studied PBDE photolysis on clays, metal oxides, and sediments and concluded that the photolysis pathways were largely matrix independent.

Although the regiospecificity of microbial debromination of PBDEs is more complicated, certain breakdown products are observed. Using a biomimetic system, Tokarz et al. (2008) noted that PBDEs 17 (2,2',4-tribromo diphenyl ether) and 28 (2,4,4'-tribromo diphenyl ether) were major microbial debromination products of high molecular weight PBDEs in anaerobic sediment. Tokarz et al. (2008) also indicated that although microbial debromination at the *ortho* positions is possible, removal of the *meta* and *para* bromines predominates, especially for heavy congeners. Similarly, Robrock et al. (2008) and Ding et al. (2013) found that debromination of PBDEs by several cultures preferentially removed bromines at the *meta* and *para* positions, with formation of PBDE 17 as a major product. La Guardia et al. (2007) observed evidence of microbial debromination of PBDEs in sewage sludge and near wastewater outfalls. They measured PBDE 17 but could not detect PBDE 15 in sewage sludge. Davis et al. (2012) also detected PBDE 17 in biosolids. In contrast, Lee et al. (2011) studied the debromination of PBDE by a coculture consisting of *Dehalococcoides* and *Desulfovibrio* species, and found that debromination at the *ortho* position is preferred, with significant amounts of PBDE 15 formed. This echoes the regiospecificity of the microbial dechlorination of polychlorinated biphenyls (PCBs): dechlorination at the *meta* and *para* positions is preferred, but chlorines at the *ortho* position can be removed by some strains of bacteria (Bedard, 2003). For the PBDEs, it is not clear which set of pathways predominates in the environment, and indeed different regiospecificity might be observed in different environments.

The purpose of this work was to use factor analysis to examine the importance of these debromination processes in the environment. Data collected by the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) were analyzed using Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994). The RMP data set is a good choice for this investigation because it includes measurements of 50 PBDE congeners using high-resolution mass spectrometry in hundreds of sediment samples collected in San Francisco Bay (Oram et al., 2008; Klosterhaus et al., 2012). PMF is an advanced factor analysis method, described in detail by Paatero and Tapper (1994). Briefly, PMF defines the sample matrix as product of two unknown factor matrices with a residue matrix:

$$X = GF + E \quad (1)$$

The sample matrix ( $X$ ) includes  $n$  observed samples and  $m$  chemical species.  $F$  is a matrix of  $p$  chemical profiles. The  $G$  matrix describes the contribution of each factor to any given sample, while  $E$  is the matrix of residuals. The PMF solution (i.e.,  $G$  and  $F$  matrices) is obtained by minimizing the objective function  $Q$  through the iterative algorithm:

$$Q = \sum_{i=1}^n \sum_{j=1}^m (e_{ij}/s_{ij})^2 \quad (2)$$

$Q$  is the sum of the squares of the difference (i.e.,  $e_{ij}$ ) between the observations ( $X$ ) and the model ( $GF$ ), weighted by the measurement uncertainties ( $s_{ij}$ ).

PMF has several advantages over simpler factor analysis tools such as Principle Components Analysis (PCA). PMF allows only positive correlations, and because the model input includes a point-by-point uncertainty estimate, PMF allows the inclusion of missing or below detection limit data points, which are assigned an arbitrary concentration and then associated with a high uncertainty. PMF and other similar factor analysis methods have been used to

investigate the dehalogenation of PBDEs (Zou et al., 2013) as well as other POPs, including polychlorinated biphenyls (PCBs) (Magar et al., 2005; Bzdusek et al., 2006b; Rodenburg et al., 2010) and polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) (Barabas et al., 2004; Rodenburg et al., 2012). Like all factor analysis methods, however, PMF can only isolate the factors that make up the data set. It is up to the user to use her best judgment to understand what these factors mean.

## 2. Methods

### 2.1. Study site

San Francisco Bay (the Bay, Fig. 1) is one of the largest urbanized estuaries in the world, with a surrounding population of 7 million people. Bay hydrology is driven primarily by the tidal influence from the Pacific Ocean and the freshwater inflow from the Sacramento and San Joaquin Rivers, which drain an area of about 150,000 km<sup>2</sup> (Cloern, 1996), and enter the Bay at its northern end in Suisun Bay (Fig. 1). As a result of freshwater inflow and tidal mixing, the northern Bay (Suisun and San Pablo Bays) is relatively well flushed, whereas South Bay is less well flushed (Conomos, 1979). Treated wastewater discharge is released via 31 permitted outfalls distributed Baywide, totaling a dry weather permitted flow into the Bay of 788 MGD. Concentrations of many pollutants, including PBDEs, are highest in Central Bay, South Bay, and Lower South Bay sediment and tend to decline moving northward towards San Pablo and Suisun Bays (Oros et al., 2005; Davis et al., 2007; Klosterhaus et al., 2012).

The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) is an ongoing monitoring partnership established in 1993 between a regulatory agency, over 70 local regulated entities, and other local stakeholders (e.g., environmental NGOs), administered by an independent scientific organization (Hoenicke et al., 2003). RMP sediment monitoring employs a stratified design, in which eight probabilistic sites are collected annually from each of five Bay segments following a rotating panel design, with seven additional samples collected from fixed monitoring stations (Lowe et al., 2004). Every sample incorporates two to three homogenized subsamples, each collected by 0.1 m<sup>2</sup> Kynar<sup>®</sup> coated stainless steel Young-modified Van Veen grab. Trace clean techniques are employed, including quadruple rinsing of all equipment between each sampling event (SFEI, 2012). Beginning in 2002, fifty PBDE congeners were measured in the sediment by Axy's Analytical Services (British Columbia, Canada) using high resolution gas chromatography/mass spectrometry methods equivalent to EPA method 1614A (EPA, 2007).

### 2.2. Data matrix

Of the 50 congeners measured, only 24 were above the detection limit in more than 50% of the 403 sediment samples. These 24 congeners were retained for PMF analysis. Only samples with fewer than four non-detects were included in analysis. This resulted in 24 congeners measured in 233 samples, with adequate detection limits only occurring in sampling years 2005 through 2010.

### 2.3. PMF analysis

The data were analyzed using Positive Matrix Factorization (PMF), employing PMF2 software (YP-Tekniika KY Co., Helsinki, Finland).

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