

Plastic-Mediated Photolysis of Flame Retardants

Kate Hebert, Xiomara Martinez, Hannah Olson, Claire Calhoun, Paul Chiarelli

Loyola University, Chicago, IL

Overview

Purpose

To understand the effects of microplastics on the photolysis of flame retardants, an emerging class of contaminants.

Method

Irradiation of flame retardants on microplastics in aqueous solution at 300 nm. Liquid-liquid and solid-liquid extractions followed. The samples were analyzed by gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS).

Results

A functional group with an acidic proton is necessary to achieve photolytic decomposition with flame retardants.

Introduction

Flame retardants are a group of chemicals often integrated into building materials, electronics, furnishings, upholstery in motorized vehicles, plastics, and textiles. The annual consumption of flame retardants is estimated to be around 2.25 million tons per year and worth \$7.09 billion in 2019 (1). These chemicals are released into the environment as early as their manufacturing process or when they are leached off from certain flame retardant containing materials during their breakdown. Polybrominated diphenyl ethers (PBDEs), a class of flame retardants, are known to be both endocrine disruptors and neurotoxins (2). In the presence of photons, flame retardants degrade into possibly more toxic compounds, for example, PBDEs degrade into dioxins (Figure 1). The dioxin product signifies environmental concern as the class of compounds is known to be extremely toxic and persistent, however, toxicity varies greatly within the dioxin class. In general, dioxins are known to cause issues with reproduction, development, the immune system, hormones, and are often carcinogenic (3). In general, the presence of flame retardants in the environment poses a concern, as they have been found to be cytotoxic, neurotoxic, genotoxic, and mutagenic (5). In water, flame retardants could accumulate on microplastics due to their insolubility in water. Microplastics arise from shampoos, toothpaste, cosmetics, and the breakdown of larger plastics in water—the use of such products has grown so much that in 2014 plastic waste surpassed 300 million metric tons per year (4). Marine organisms often confuse microplastics for food and consume it along with whatever insoluble compound accumulated on it. The microplastics and associated chemicals can then be biomagnified up the food chain to humans—bioaccumulating in adipose tissue, breast milk, placenta, blood, serum, and the brain. PBDE concentrations specifically have been found to be 40 times higher in North American than in Swedish women's breast milk. The deficit could be credited to a ban of polybrominated diphenyl ethers in the European Union while the United States remains the largest producer and user of the compound. The EPA has yet to include flame retardants on the Priority Toxic Pollutants List due to a lack of research supporting environmental and health concerns, thus, the goal of this study is to discover how flame retardants degrade in water in the presence of microplastics, with a focus on three types of flame retardants: 2,4,4-tetrabromodiphenyl ether (2,4,4-BDE), tetrachlorobisphenol A (TCBPA), and tetrabromobisphenol A (TBBPA) (2).

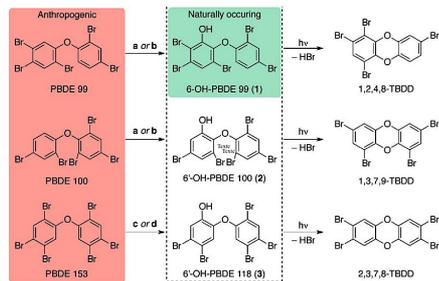


Figure 1 a: biotic hydroxylation b: +OH, -H•, c: (photolysis) hv + H₂O₂ -HBr; d: +OH, -H• s and other products of concern from hydroxylated polybrominated diphenyl ethers (OH-PBDEs).¹ Environmental science & technology 46 15 (2012): 8174-80.

Experimental

The samples were prepared using 10 mL of water, 100 µg of polyethylene plastic beads, and 50 µL of 2,4,4-BDE, 50 µL of TCBPA, or 50 µL of TBBPA in a 15 mL borosilicate tube. Blank samples prepared without plastics were also produced to act as a control. All samples were then placed in a Rayonet Photochemical Reactor and irradiated for various time intervals and varying intensities at a wavelength of 300 nm. All irradiated samples were then extracted via liquid-liquid extraction methodology with 3 mL of MTBE. The plastic beads in the irradiated samples were sonicated in 3 mL of MTBE for ten minutes. All extracted samples were stored over dry sodium sulfate until analysis. 1 mL of the samples was evaporated over nitrogen gas and reconstituted in 50 µL of methanol for the LC/MS.

Analysis

Samples were analyzed via GC/MS and LC/MS. Mass spectra of the aqueous and plastic extracts were analyzed using an Agilent 6890 GC-MS in positive EI mode and a helium gas mobile phase. A linear GC gradient was used (100 to 290°C) for separation, with a rate of 12°C per minute for a total run time of nineteen minutes. The source temperature was maintained at 280°C. One microliter was injected for analysis. The mass spectra was scanned from 50-800 m/z. For the LC/MS, a Thermo Finnigan LCQ advantage iontrap instrument was utilized. The reaction mixtures were analyzed via direct infusion at a rate of 50 µL per minute in negative ion mode.

Results and Discussion

Flame retardants were proposed to convert to dioxins during photolysis. However, there were no photoproducts formed with 2,4,4-BDE (Figure 2), perhaps due to lack of a hydroxyl group to initiate decomposition. With other contaminants such as triclosan and methyltriclosan, the hydroxyl group donates a proton to initiate degradation. Thus, we hypothesized that a functional group with an acidic proton such as a hydroxyl group is necessary to achieve photolytic decomposition in flame retardants. To test this hypothesis, we did preliminary investigations of tetrachlorobisphenol A (Figure 3) and tetrabromobisphenol A (Figure 4) two flame retardants with hydroxyl groups. We found that both compounds undergo degradation when adsorbed to plastic and irradiated for thirty to forty minutes (Figures 5 and 6). The spectra for the photoproduct from the tetrachlorobisphenol A at m/z 195 m/z allows us to propose an molecular formula for the product of C₂H₄OCl₂. The photoproduct at 195 m/z then undergoes further degradation to m/z 161 due to the loss of a chlorine atom, thus the molecular formula of this photoproduct becomes (Figure 8): C₂H₄OCl.

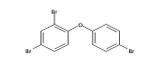


Figure 2: Structure of 2,4,4-BDE



Figure 3: Structure of TBBPA

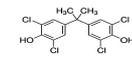


Figure 4: Structure of TCBPA

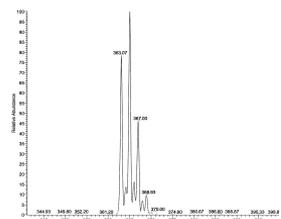


Figure 5: Spectrum of tetrachlorobisphenol a; acquired on LC/MS

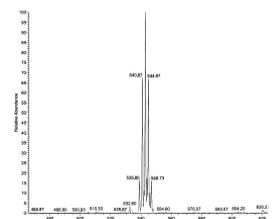


Figure 6: Spectrum of tetrabromobisphenol a; acquired on LC/MS

