Characterization of the Brominated Chemicals in a PentaBDE Replacement Mixture and their Detection in Biosolids Collected from Two San Francisco Bay Area Wastewater Treatment Plants

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Introduction

Worldwide restrictions on the use of PentaBDE have led to the use of new brominated flame retardant mixtures to meet flammability standards. Assessments to determine if the chemicals in some of these mixtures are accumulating in the environment have thus far not been possible because the structural identities of these compounds are not readily available. In our study, the brominated components of Great Lakes Chemical's Firemaster 550[®] (FM 550), a commercial mixture used as a replacement product for PentaBDE (1) and also reportedly used in the highest volumes to meet the California furniture flammability standard, were characterized using GC/MS and ¹H-NMR spectroscopy. Using this information, the brominated compounds of FM 550 were then quantified in biosolids collected from two municipal wastewater treatment plants (WWTPs) that discharge effluent to San Francisco Bay. The analysis of biosolids was used as a screening step to determine if these brominated compounds are migrating out of consumer products and thus potentially accumulating in San Francisco Bay sediments and wildlife.

Materials and Methods

Firemaster 550[®] Chemical Analyses

A sample of Firemaster 550[®] was provided by Chemtura for this study. El analyses were performed on a Shimadzu GC/MS-QP2010 using a J&W 30m DB-5 column (0.25 mm ID, 0.25 µm film). All injections were conducted in splitless mode. All experiments were done with the following GC conditions: helium carrier gas flow at 1.0 ml/minute, injector temperature at 250°C, temperature program set to the following parameters: initial oven temperature at 100°C, hold for 5 minute, ramp at 10°C/minute to 325°C, hold for 20 minutes. Spectra (50 to 1000 u) were obtained in positive ion, electron impact mode (EI+). ¹H-NMR analyses were performed on a 600 MHz Bruker instrument using deuterated methylene chloride (CDN Isotopes) as the solvent.

Characterization of Brominated Chemicals in Firemaster[®] 550

In the EI GC-MS analysis, Firemaster 550[®] appeared as a complex mixture containing at least 14 phosphate compounds of various concentrations (triphenyl phosphate was identified as the second major) and two brominated compounds (FIGURE 1). Of the two brominated compounds, the last eluting peak was identified as bis(2-ethylhexyl) 3,4,5,6-tetrabromophthalate (TBPH) by a comparison with an authentic standard (Wellington Laboratories). The major brominated component was isolated by preparative TLC and its structure was determined by GC/EI-MS, GC/NCI-MS, and ¹H-NMR spectroscopy along with ¹³C JMOD and INADEQUATE NMR data.

In EI GC-MS both TBPH and the unknown exhibited no molecular ion peaks with the most prominent peaks due to the loss of the iso-octyl chain (m/z 112). For TBPH both peaks resulting from consecutive iso-octyl losses were observed, though very small. One distinct feature of TBPH fragmentation in El mode was the formation of tetrabromophthalic anhydride (m/z 465) (FIGURE 2 A).



The EI GC-MS of the unknown compound displayed several fragments each containing four bromines at m/z 391, 421 and 438 (FIGURE 2B).

The information necessary for the structure elucidation of the unknown came from the NMR data (FIGURE 3A and B). A JMOD experiment (J-modulated spin-echo) provides a spectrum in which the quaternary and methylene signals have opposite phases to those of methine and methyl resonances. Thus in FIGURE 3A the peaks orientated upwards correspond to C and CH₂ moieties and those orientated downwards to CH and CH₂ groups.

FIGURE 1

When this information is taken in conjunction with the results of a 2D INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment) experiment: a clear picture of the structure emerges. In this experiment one bond correlations via spin-spin coupling of ¹³C carbons are observed. It is a very insensitive technique as 0.01% of the carbons are excited at natural abundance so about 25 mg material per carbon is needed to obtain data. Signals from coupled carbons are located on the same horizontal planes. For example, in FIGURE 3A, carbon 11 at about 38 ppm is coupled to carbon 10 at 68 ppm and to carbons 12 and 16. Further 'tracing' of the couplings allows for the construction of an iso-octyl chain. FIGURE 3B represents the aromatic region of the 'unknown'. JOMD data reveal the presence of a proton on the aromatic ring (Carbon 6) and coupling between the signals from carbon 1 and carbon 6 proves that the proton is next to the carbon bearing the carbonyl group thus solving the structure of the unknown as 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB).



FM 550 was also analyzed using GC/ENCI-MS to monitor bromide ion clusters as an indication of bromine content. ENCI-MS analyses were performed using an Agilent GC/MS (Models 6890 and 5975, respectively) using a J&W 15m DB-5 column (0.25 mm ID, 0.25 µm film). All injections were performed using a programmable temperature vaporizer (PTV) injector operated in pulsed splitless mode. The GC conditions are reported below under biosolid analysis.

Biosolids

Biosolids were collected in February 2008 from two WWTP that discharge effluent to San Francisco Bay. Biosolids (3 replicates per WWTP) were extracted using pressurized fluid extraction (3X with 100% dichloromethane at a temperature of 100°C and at 1500 psi). The final extract was reduced in volume to ~1.0 mL using an automated nitrogen evaporation system. Extracts were then purified by elution through a column containing 8.0 g of 2.5% deactivated Florisil. Hexabromocyclododecane (HBCD), BDE-209, TBB and TBPH were eluted with 50 mL of a 50:50 mixture of hexane:dichloromethane. The final extract was again reduced in volume to 0.5 mL and then spiked with 50 ng of the quantification standards, F-BDE-160 and ¹³C-labeled BDE-209.

Biosolid extracts were analyzed using GC/ECNI-MS and separated using a 0.25 mm (I.D.) x 15 m fused silica capillary column coated with 5% phenyl methylpolysiloxane (0.25 µm film thickness). Pressurized temperature vaporization (PTV) injection was used with the inlet set to a temperature of 50 °C for 0.3 minutes and then a 700 °C/min ramp to 275 °C. The GC oven temperature program was held at 40 °C for 1 min followed by a temperature ramp of 18 °C /min to 250 °C, followed by a temperature ramp of 1.5°C /min to a temperature of 260 °C, followed by a final temperature ramp of 25 °C/min to 300 °C which was held for an additional 20 min. The transfer line temperature was maintained at 300 °C and the ion source was held at 200°C. HBCD was quantified by monitoring bromide ions (m/z 79 and 81) and BDE-209 was quantified by monitoring molecular fragments (m/z 484.6 and 486.6). ¹³C BDE-209 was monitored through m/z 494.6 and 496.6. TBB was quantified using ion fragments (m/z) 357 (Quantitative) and 471 (Qualitative) while TBPH was quantified using ion fragments (m/z) 463 (Quantitative) and 515 (Qualitative).

All sample measurements were blank corrected by subtracting the average level measured in the laboratory blanks. Method detection limits were calculated by taking three times the standard deviation of the blank levels. Matrix spikes were prepared by adding approximately 100 ng of α -HBCD, TBB, and TBPH to cells filled with sodium sulfate powder. Matrix spikes were extracted alongside the biosolids samples and examined for percent recovery of the target compounds. TBB and TBPH in biosolids were quantified using the commercial mixture.





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Use, Applications, and Further Study of TBPH

To our knowledge, this study and a recent study on brominated flame retardants in house dust (2) are the first to report the detection of 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl) 3,4,5,6-tetrabromophthalate (TBPH) in environmental samples. Further investigation revealed that TBPH (CAS# 26040-51-7) is a high production volume chemical with 1-10 million pounds manufactured or imported in the US in 1990, 1994, 1998, and 2002 (US EPA TSCA Inventory Update Rule). This suggests that TBPH has been used in other applications since the production of FM 550 began in 2003. TBPH has reportedly been used as a plasticizer in polyvinylchloride (PVC) and neoprene (3) and is currently marketed for use as a flame retardant plasticizer for PVC applications such as wire and cable insulation, coated fabrics, film and sheeting (4).

Further study of these chemicals should be a high priority, especially because toxicity information is not readily available. The US EPA has provided some screening level toxicology and exposure information (as proprietary chemicals) (5), though much basic information on chronic toxicity and environmental fate is unknown. Work is underway to quantify TBB, TBPH, and several other chemicals that could potentially be used as PBDE replacements in San Francisco Bay biota and sediments. Results from this study will provide much needed information on the bioaccumulation potential of these chemicals and will also allow us to determine if management actions are needed to reduce exposure and risk in San Francisco Bay wildlife.

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