

CHARACTERIZATION OF ORGANOPHOSPHORUS CHEMICALS IN A PENTABDE REPLACEMENT MIXTURE AND THEIR DETECTION IN BIOSOLIDS

Klosterhaus, Susan¹; Konstantinov, Alex²; Davis, Elizabeth³; Klein, Jeffery²; and Stapleton, Heather³

1 San Francisco Estuary Institute, Oakland, CA, USA.

2 Wellington Laboratories Inc., Guelph, Ontario, Canada.

3 Duke University, Nicholas School of the Environment & Earth Sciences, Durham, NC, USA.

Abstract

The phosphate components of Firemaster 550 (FM 550), a high volume commercial flame retardant, were characterized and quantified in biosolids collected from San Francisco Bay and North Carolina municipal wastewater treatment plants (WWTPs).

Introduction

Worldwide restrictions on the use of PentaBDE have led to the use of new flame retardant mixtures to meet flammability standards. Assessments to determine if the chemicals in these mixtures are accumulating in indoor and outdoor environments have thus far not been possible because for many of them the structural identities are not readily available. In our study, the phosphate components of Firemaster 550 (FM-550), a commercial mixture used in high volumes to meet the California furniture flammability standard, were characterized and quantified in biosolids collected from two municipal wastewater treatment plants (WWTPs) that discharge effluent to San Francisco Bay. The analysis of biosolids was conducted to determine if these compounds are migrating out of consumer products. This study augments previous work which identified the brominated chemicals in FM-550¹.

Materials and Methods

Firemaster 550® Chemical Analyses

Triphenyl phosphate (TPP) was purchased from Aldrich. Tri *o*-tolyl phosphate was purchased from Fisher Scientific. Tris(2-isopropylphenyl) phosphate (TIPP), tris(3,5-dimethylphenyl) phosphate, and tris(4-tert-butylphenyl) phosphate were purchased from ChemBridge Corporation. 2-Ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethyl-1-hexyl) tetrabromophthalate (TBPH) were from Wellington Laboratories.

A sample of Firemaster 550® was provided by Chemtura. Low resolution electron impact (EI) 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 done in splitless mode. All experiments were performed using the following GC conditions:

- Helium carrier gas flow at 1.0 ml/minute.
- Injector temperature at 250°C.
- GC oven temperature program: initial oven temperature was 100°C for 5 minutes; 10°C/minute to 325°C ; hold for 20 minutes.
- Spectra (50 to 1000 u) were obtained in positive ion, electron impact mode (EI+).

High resolution analyses were performed on an Agilent 6890N HRGC / Waters Autospec Ultima HRMS equipped with a J&W 60 m DB-5 (0.25 mm ID, 0.25 µm film) column.

The following conditions were used:

- Helium carrier gas with constant flow at 1.0 ml/minute.
- Injector, source and transfer line at 280°C.
- GC oven temperature program: initial oven temperature was 100°C for 2 minutes; 25°C/minute to 250°C; 10°C/minute to 325°C; hold for 15 minutes.
- Data were acquired using SIM monitoring at a resolution of 10,000 in EI+ mode.

¹H-NMR analyses were performed on a 600 MHz Bruker instrument using deuterated methylene chloride (CDN isotopes) as the solvent.

Biosolid Analyses

- Collected in February 2008 from two WWTPs that discharge effluent to San Francisco Bay
- Extracted using pressurized fluid extraction (3X with 100% dichloromethane)

TBB, TBPH, and PBDE Extract Clean-up and Analysis

- Extracts purified using 8.0 g of 2.5% deactivated Florisil; rinsed with 50 mL of 50:50 hexane:dichloromethane.
- Analyzed using GC/ECNI-MS; 0.25 mm (I.D.) x15 m fused silica capillary column coated with 5% phenyl methylpolysiloxane (0.25 µm film thickness).
- PTV injection; inlet temperature 50 °C for 0.3 minutes and then a 700 °C/min ramp to 275 °C.
- GC oven temperature program: hold at 40 °C for 1 min, ramp of 18 °C /min to 250 °C, ramp of 1.5°C/min to 260 °C, ramp of 25 °C/min to 300 °C, 20 min. hold.
- Transfer line and ion source temperature: 300 °C and 200°C respectively.
- Molecular fragments quantified: m/z 484.6 and 486.6 (BDE 209); m/z 494.6 and 496.6 (13C BDE-209); m/z 357 (Quantitative) and 471 (Qualitative) (TBB); m/z 463 (Quantitative) and 515 (Qualitative) (TBPH).
- Quantification standards: F-BDE-160 and ¹³C-BDE-209.

TPP Extract Clean-up and Analysis

- Extracts purified using 4.0 g of 6.0% deactivated alumina; rinsed with 50 mL of 50:50 hexane:dichloromethane.
- Extracts blown to dryness under a N₂ stream, reconstituted in dichloromethane.
- Purified by using a GPC column (Envirogel™ GPC Cleanup 90x300 mm column, dichloromethane mobile phase, flow rate of 5 mL/min). The first 60 mL of eluate were discarded, and the following 40 mL were collected.
- Extract was solvent-switched to hexane.
- Quantification standard: ¹³C-CDE 141.
- Analyzed using GC/MS (EI); 0.25 mm (I.D.) x 15 m fused silica capillary column coated with 5% phenyl methylpolysiloxane (0.25 µm film thickness).
- PTV injection; inlet temperature 80 °C for 0.3 minutes and then a 600 °C/min ramp to 300 °C.
- GC oven temperature program: hold at 80 °C for 2 min, ramp of 20 °C /min to 250 °C, ramp of 1.5°C/min to 260 °C, ramp of 25 °C/min to 300 °C, 12 min. hold.
- Transfer line and ion source temperature: 300 °C and 200°C respectively.
- TPP was quantified using ion fragments m/z 326 (quantitative) and 325 (qualitative).

Results and Discussion

Characterization of Organophosphorus Compounds in Firemaster 550®

Identification: At least 24 alkylated phenyl phosphates were present in the FM-550 technical mixture according to gas chromatography-mass spectrometry (GC-MS). To make identification feasible, a large sample of FM-550 was subjected to preparative TLC separation. Separation yielded five TLC bands. The band with the lowest R_f value was triphenyl phosphate (TPP; 14% by weight), followed by three bands containing mono-, di-, and tri- isopropylphenyl phosphates (iPPs), respectively. The fifth TLC band (46% by weight) contained the brominated components of the mixture: 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethyl-1-hexyl) tetrabromophthalate (TBPH).

In addition to the analysis of ¹H NMR data, analysis of TLC bands two, three and four by ¹³C NMR (JMOD experiment) indicated an absence of CH₂ signals and isolated CH₃ groups, which is consistent with isopropyl-only alkyl groups. Examination of ¹³C chemical shifts for the second TLC band allowed for identification of ortho-, meta- and para-monoisopropyl isomers in FM-550. The assignments were made by comparison of the chemical shift values for the methyl and isopropyl carbons to those of the corresponding

isopropyl phenols in the NMR Library². The assignments were additionally confirmed by ¹H NMR data comparisons. The ortho isomer was the major isomer, followed by the meta and para isomers. For the remaining bands, identification by NMR analysis was not possible as the high structural similarity resulted in signal overlaps. Additionally, tris (2-isopropylphenyl) phosphate (T2iPP) was identified as a minor component in FM-550 (FIGURE 1).

Quantification: Relative response factors (RRFs) for various alkylated phenyl phosphates on GC-MS were also measured. The RRFs for TPP and T2iPP were found to be very similar and, in the absence of other isopropylated phenyl phosphate standards, the isopropyl aryl phosphates in FM 550 were quantified using commercially available T2iPP as a standard. Using a four point calibration (BDE-126 as an injection standard; RSD lower than 10%) and assuming an equal response for all isopropylated phenyl phosphates, the concentrations of the components of FM 550 were: TPP – 18%, Mono-iPP – 32%, Di-iPP – 10%, Tri-iPP – 2.4%, Tetra-iPP – 0.4%, TBB – 29.6%, and TBPH – 8.6%. There were also several co-elutions obvious from HRGC/HRMS data.

Organophosphorus Compounds in Biosolids

TPP was detected in the biosolids in concentrations ranging from 530-2630 ng/g dry weight, with mean concentrations of 2048 ± 544 and 945 for each of the WWTPs (FIGURE 2). At WWTP #1, the ratio of TPP to the other FM 550 components (TBB and TBPH) was fairly similar to the ratio found in the commercial mixture (FIGURE 1).

However, for WWTP #2, the mean TPP concentration was higher than TBB. TPP is a high volume chemical which has been used for decades as a plasticizer in several applications³; thus FM-550 is not the only potential source of TPP to the biosolids. At both WWTPs, TPP was comparable in concentration to BDE 209. Detection in biosolids suggests that TPP, a moderately hydrophobic compound (log K_{ow} 4.59)⁴, has the potential to be released to the environment via wastewater effluent and accumulate in aquatic environments.

Implications for Organophosphorus Compounds in the Environment

In addition to the detection of TPP in biosolids in this study, TPP was also recently found in house dust at concentrations similar or higher than that of PBDEs⁵. It has also been detected in indoor air, wastewater effluents, and surface waters³. This information suggests that TPP can migrate out of consumer products, in a manner similar to BFRs⁶.

The US Consumer Product Safety Commission has concluded that both TPP and iPPs are ‘possibly toxic’ to humans based on limited evidence of neurotoxicity in animal studies⁷. US EPA considers TPP a high hazard concern for ecotoxicity⁸. Potential exposure to humans and wildlife warrants further assessment of TPP environmental fate and toxicity due to the potential increased use of TPP in flame retardant mixtures as a replacement for PentaBDE.

References

- 1 Klosterhaus S., Konstantinov A., Stapleton H. 2008. 10th Annual Workshop on Brominated Flame Retardants. Victoria, British Columbia. June 3 and 4, 2008.
- 2 http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi
- 3 Marklund A., Andersson B., and Haglund P. *Chemosphere* 2003; 53:1137.
- 4 Reemtsma T., Quintanab J. B., Rodilc R., Garcia-López M., and Rodriguez I. *TrAC* 2008; 27: 727.
- 5 Stapleton H.M, Klosterhaus S., Fuh J., Eagle S., Meeker J., Blum A., and Webster T. 2009. 11th Annual Workshop on Brominated Flame Retardants. Ottawa, Ontario. May 19 and 20, 2009.
- 6 Webster T. F., Harrad S., Millette J.R., Holbrook R.D., Davis J.M, Stapleton H. M., Allen J. G, McClean M. D., Ibarra C., Abdallah M. A.-E., and Covaci A. *ES&T* 2009; 43:3067.
- 7 Babich, M. A. 2006. CPSC Staff Preliminary Risk Assessment of Flame Retardant (FR) Chemicals in Upholstered Furniture Foam. US CPSC Bethesda, MD 20814.
- 8 US EPA. 2005. Furniture Flame Retardancy Partnership: Environmental Profiles of Chemical Flame Retardant Alternatives. 742-R-05-002A.

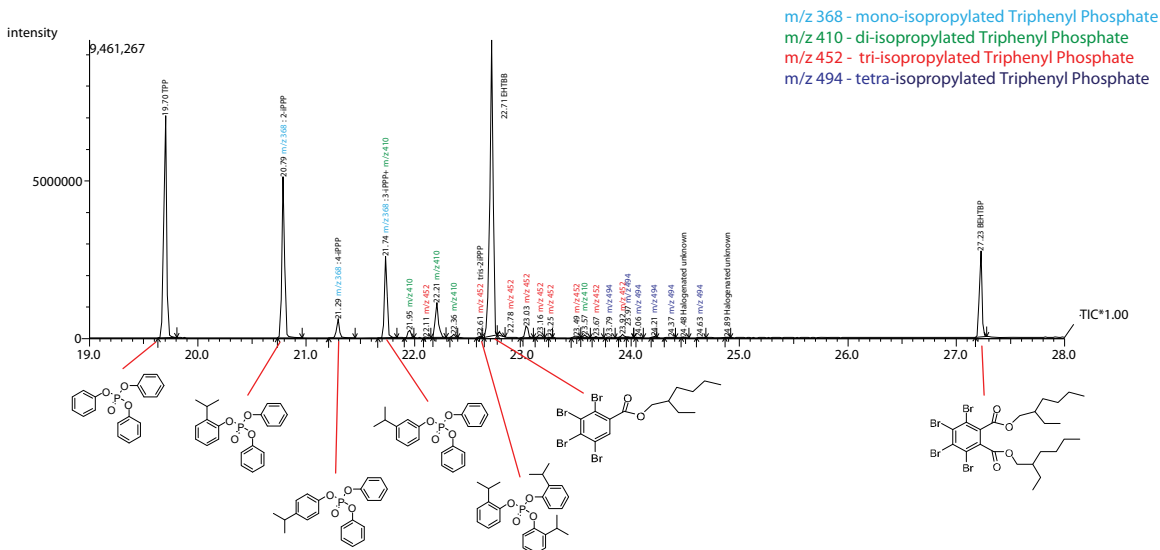


Figure 1. Identified Components in Firemaster 550: HRGC/LRMS Data.

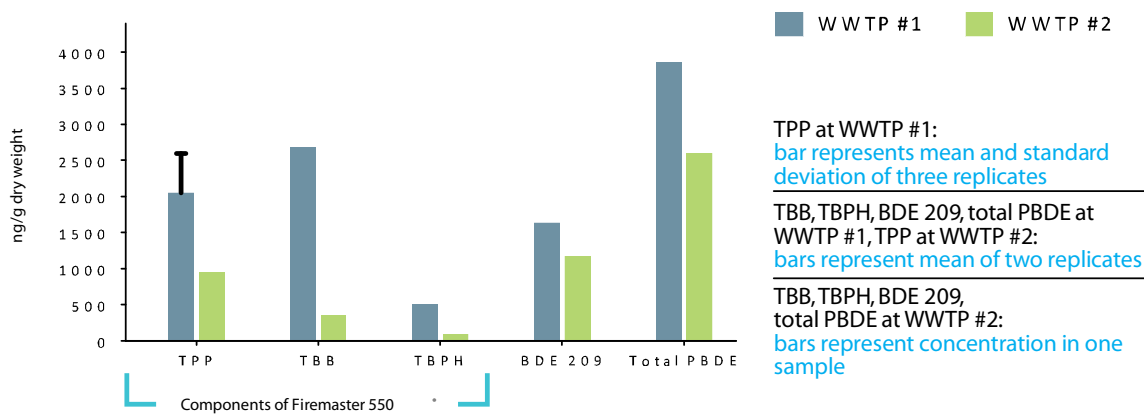


Figure 2. Concentrations of Flame Retardant Chemicals in Biosolids Collected from San Francisco Bay Area Wastewater Treatment Plants