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Prevalence of historical and replacement brominated flame retardant chemicals in New York City homes

Whitney J. Cowell [a, b], Heather M. Stapleton [c], Darrell Holmes [b], Lehyla Calero [b], Catherine Tobon [b], Matthew Perzanowski [a], Julie B. Herbstman [a, b, *]

[a] Department of Environmental Health Sciences, Mailman School of Public Health, Columbia University, New York, NY 10032, United States
[b] Columbia Center for Children's Environmental Health, Mailman School of Public Health, Columbia University, New York, NY 10032, United States
[c] Nicholas School of the Environment, Duke University, Durham, NC 27708, United States

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ABSTRACT

Background: Until their phase-out between 2005 and 2013, polybrominated diphenyl ethers (PBDEs) were added to household products including furniture, rugs, and electronics to meet flammability standards. Replacement brominated flame retardant (BFR) chemicals, including 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl) 2,3,4,5-tetrabromophthalate (TBPH), which are components of the Firemaster 550® commercial mixture, are now being used to meet some flammability standards in furniture. The objective of this analysis was to evaluate the extent to which mothers and their children living in New York City are exposed to PBDEs, TBB, and TBPH.
Methods: We measured PBDEs, TBB, and TBPH using gas chromatography mass spectrometry in dust ($n = 25$) and handwipe ($n = 11$) samples collected between 2012 and 2013 from mothers and children living in New York City. We defined dust as enriched if the proportional distribution for a given BFR exceeded two-thirds of the total BFR content.
Results: We detected PBDEs and TBPH in 100% of dust and handwipe samples and TBB in 100% of dust samples and 95% of handwipe samples. Dust from approximately two-thirds of households was enriched for either PBDEs ($n = 9$) or for TBB + TBPH ($n = 8$). Overall, the median house dust concentration of TBB + TBPH (1318 ng/g dust) was higher than that of ΣPentaBDE (802 ng/g dust) and BDE-209 (1171 ng/g dust). Children generally had higher BFR handwipe concentrations compared to mothers (ΣPentaBDE: 73%, BDE-209: 64%, TBB + TBPH: 55%) and within households, BFR concentrations from paired maternal-child handwipes were highly correlated. Among mothers, we found a significant positive relation between house dust and handwipe BDE-209 and TBB + TBPH concentrations.
Conclusion: PBDEs, TBB and TBPH are ubiquitous in house dust and handwipes in a sample of mother-child pairs residing in New York City.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardant (BFR) chemicals that were widely added to furniture, textiles, electronics and other consumer products manufactured in the United States to meet fire safety standards passed in the 1970s [1]. Notably, while these standards do not mandate the use of PBDEs, they can be difficult to pass without the addition of flame retardant chemicals. Between 2004 and 2013, the three major commercial PBDE formulations (PentaBDE, OctaBDE and DecaBDE) were phased out of production in the United States owing to their environmental persistence and mounting evidence demonstrating their association with human health toxicity [2–5]. In 2013, residential fire safety standards were amended to allow upholstered furniture to pass a smolder test rather than the previously required open-flame test [6]. While compliance with the new standard is feasible without the use of flame retardant chemicals, research suggests manufacturers have sought out

* Corresponding author. Columbia Center for Children's Environmental Health, 12th Fl, Mailman School of Public Health, 722 West 168th St, New York, NY 10032, United States.
E-mail address: jh2678@cumc.columbia.edu (J.B. Herbstman).
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Abbreviations

BFR	brominated flame retardant
MLD	method limit of detection
PBDE	polybrominated diphenyl ether
TBB	2-ethylhexyl-2,3,4,5- tetrabromobenzoate
TBPH	bis(2-ethylhexyl) 2,3,4,5-tetrabromophthalate

alternative flame retardants for use in residential furniture and furnishings. For example, proximate to the PentaBDE phase-out, Chemtura introduced Firemaster 550®, a commercial mixture comprised of several chemicals, including two brominated compounds: 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB: 35%) and bis(2-ethylhexyl) 2,3,4,5-tetrabromophthalate (TBPH: 15%). Studies examining the flame retardant content of furniture manufactured in the 2000s suggest Firemaster 550® was introduced as a replacement following the PBDE phase-out [7].

During manufacturing, PBDEs and Firemaster 550® are added, rather than chemically bound, to the consumer products that they are intended to protect. Over time these chemicals are released into the indoor environment where they sorb to house dust [8]. Young children have been shown to have higher serum PBDE concentrations compared to adults living in the same household; this pattern has been partially attributed to children's increased time spent on the floor and their frequent hand-to-mouth activity, which both lead to increased incidental ingestion of house dust [9]. Based on their shared chemical properties and commercial applications, we similarly expect TBB and TBPH to partition in dust; however, data supporting environmental transport and exposure patterns among young children are limited.

Our primary objectives of this study were to examine the associations between concentrations of PBDEs and alternative BFRs (TBB/TBPH) measured in house dust and handwipes collected from maternal-child pairs and to examine the relation between concentrations of these BFRs and several lifestyle and household factors. This is the first comparison of PBDEs, TBB and TBPH in dust and paired maternal-child handwipe samples. This study adds information about how adult versus child BFR exposure pathways may vary and whether TBB/TBPH exposure pathways parallel PBDE exposure pathways. The later have been previously well characterized, however, it is not known whether recommendations developed to minimize PBDE exposure from the indoor environment may also apply to TBB/TBPH.

2. Materials and methods

2.1. Study population

The study population consists of mothers and children enrolled in the Sibling-Hermanos birth cohort. Beginning in 2008, pregnant women were recruited from participants previously enrolled in the Columbia Center for Children's Environmental Health Mothers and Newborns Study, a prospective birth cohort started in 1998 [10]. At enrollment in the 2008 cohort women were between the ages of 27–44 years old. The cohort was originally established to study the effects of prenatal and childhood exposure to several environmental chemicals, therefore, for feasibility, information was collected only on the mother-child dyad. The study protocol was approved by the Institutional Review Board of the Columbia University Medical Center.

2.2. Household dust and handwipe sample collection

From February 2012 to January 2013, when children were approximately 3-years old, we collected dust and handwipe samples from 25 households located in Manhattan and the Bronx. Fig. 1 presents a schematic of all study samples collected.

At the beginning of each study visit mothers gave written informed consent for themselves and for their child. Detailed sample collection methods are published elsewhere [11]. Briefly, a trained field technician vacuumed the surface area of the main living space using a commercial-grade Eureka canister vacuum cleaner fitted with a specially designed cellulose extraction thimble for dust collection. After 10–15 min (mean: 13 min, SD: 2.4 min), thimbles were removed, wrapped in aluminum foil and sealed in polyurethane bags until further processing. We collected dust field blanks in every 5th household by vacuuming 5 g of sodium sulfate powder from a clean aluminum foil surface. In the laboratory, we sieved dust samples to collect particles <500 μm in size, which we stored in clean amber glass jars at room temperature.

Detailed handwipe sample collection methods have been previously described [12]. Briefly, we wiped the entire palm and back surface of both hands from the base of the fingernails to the wrist with a 3×3 sterile gauze pad saturated with 3 mL of isopropyl alcohol. We replaced the used handwipe in a glass vial in an aluminum foil packet, covered it in bubble wrap and stored in a cooler for transport to our laboratory where samples were stored at −20 °C. We collected field blanks at 10% of randomly selected households by saturating a sterile gauze pad with isopropyl alcohol and placing it directly into an aluminum foil packet.

2.3. Household dust and handwipe analysis

Household dust ($n = 25$) and handwipe ($n = 11$) samples were analyzed for TBB, TBPH and 28 PBDE congeners using methods that have been previously reported [12,13]. Briefly, dust samples and handwipes were extracted with 50:50 hexane:dichloromethane and then purified using Florisil solid-phase extraction cartridges. Samples were spiked with isotopically labeled internal standards prior to extraction. Final analytic concentrations were determined using gas chromatography-mass spectrometry operated in electron capture negative ionization mode (GC/ECNI-MS). Laboratory blanks were included with each analytic run. Method limits of detection (MLD) were calculated using 3 times the standard deviation (SD) of the field blanks or as the laboratory limit of quantification (signal to noise ratio of 3) for congeners not detected in field blanks. Handwipes were only analyzed from a subset of participants due to resource constraints. The handwipes selected for analysis were collected between February and May 2012; these were the first 11 of the 25 households included in the study.

2.4. Questionnaire

At the time of sample collection, we conducted a structured interview to obtain information about personal characteristics (race/ethnicity, maternal age, marital status), lifestyle habits (maternal employment, smoking status, cleaning patterns, maternal-reported minutes since last hand wash) and household factors (clutter, type of floor covering, living conditions, material hardship). We additionally recorded the season that samples were collected.

2.5. Data analysis

To account for size differences in mother's versus children's hands, we normalized handwipe concentrations by hand surface