Environ. Sci. Technol. **2009,** *43,* 4200–4206

Brominated Flame Retardants in Children's Toys: Concentration, Composition, and Children's Exposure and Risk Assessment

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Received February 14, 2009. Revised manuscript received April 9, 2009. Accepted April 13, 2009.

Brominated flame retardants (BFRs), including polybrominated diphenyl ethers (PBDEs), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), and polybrominated biphenyls (PBBs) were found in children's toys purchased from South China. The median BFR concentrations in the hard plastic toys were 53 000, 5540 ng/g, 101.1 ng/g, and 27.9 ng/g, for total PBDEs, DBDPE, BTBPE, and PBBs, respectively, which were notably higher than values in other toys. The PBDE concentrations were below the threshold limit (1000 ppm) required by the European Commission's Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) directives in all of the toys, except for one hard plastic toy with a total PBDE concentration of 5 344 000 ng/g. The BFR profiles in the toys were consistent with the patterns of their current production and consumption in China, where PBDEs, specifically decaBDE product, were the dominant BFR, followed by the emerging DBDPE. The relatively high concentrations of octa- and nonaBDEs in the foam toys and the results of principal component analysis (PCA) may suggest the decomposition of highly brominated BDEs during the manufacturing processes of the toys. Daily total PBDE exposures associated with toys via inhalation, mouthing, dermal contact, and oral ingestion ranged from 82.6 to 8992 pg/kg bw-day for children of 3 months to 14 years of age. Higher exposures, predominantly contributed through the mouthing pathway, were observed for infants and toddlers than for the other subgroups. In most cases, children's BFR exposure via the toys likely accounts for a small proportion of their daily BFR exposure, and the hazard quotients for noncancer risk evaluation were far below 1. To the author's knowledge, this is the first study to examine the concentrations of BFRs in toys, and the potential exposures to children.

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Introduction

A number of brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A, hexabromocyclododecane, and novel decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), have been used to enhance the safety of a variety of commercial and consumer products (*1*). Over the past few decades much attention has been given to PBDEs in the environment and their effects on humans (*2*). Three PBDE technical mixtures were commercially available, that is, pentaBDE, octaBDE, and decaBDE, but the former two products have been banned or voluntarily withdrawn from use in some regions of the world (*3*−*5*) because of their ubiquitous presence, bioaccumulation, and potential toxicities (*2, 6*). DecaBDE, made up mostly of BDE209, has become controversial in recent years because of increasing evidence of its bioaccumulation (*7*) and tendency to break down into more toxic lower brominated congeners in the environment, as well as within the bodies of biota (*8*−*10*). DecaBDE has been banned in parts of the United States, and the European Union banned its use in electronic products on July 1, 2008 (*8, 11*). Recently, more concerns have arisen about novel non-PBDE BFRs, such as DBDPE and BTBPE, which are, respectively, used as replacements for deca and octaBDEs in a variety of products (*5, 12*). They have been detected in the environment and in wild species (*1, 12, 13*). It is expected that an increasing number of alternate BFRs will be consumed and consequently introduced into the environment due to the phase-out of PBDEs.

As additives, most of these BFRs are physically mixed into product applications, rather than chemically bound. As a result, they can be released from products into the ambient environment when they are used or disposed of. Therefore, the use of consumer products in the indoor environment can provide a potentially significant BFR exposure via inhalation, oral ingestion, and dermal contact. Many studies have raised particular concerns about BFR exposure in children, who are likely to receive greater exposure to hazardous chemicals via human milk, inhalation, food, and dust (*14*−*18*). In addition, children may differ from adults in their susceptibility to hazardous chemicals because of their lower body weight, reduced ability to excrete xenobiotic toxic chemicals, rapid growth, and structural and functional development of vital organ systems (*19, 20*).

The safety of children's toys became a key issue in 2007 because of the toy recalls by toy-makers (*21, 22*). Many countries have passed toy safety regulations, but few of them have limited the content of BFRs. In 2003, the European Commission's two directives, RoHS (Restriction of Hazardous Substances) and WEEE (Waste Electrical and Electronic Equipment), restricted the threshold values of PBDEs and PBBs to 1000 ppm in only certain electrical and electronic toys (*3, 23*). It was estimated that China manufactured more than 70% of the world's toys, of which approximately 70% are manufactured in Guangdong Province, South China. The United States imports 70−80% of its toys from China (*24*).

To date, however, there have been few studies concerning BFRs in toys and children's exposure to BFRs associated with toys. In this paper, the concentrations and compositions of BFRs in various children's toys made in China are examined. BFRs were assumed to have been flame retardant additives in the plastic, rubber, textile, or stuffing material of these toys. Children's exposure to BFRs via toys is also assessed. Because of extended periods of play, mouthing behavior,

10.1021/es9004834 CCC: $40.75
Published on Web 04/29/2009

and frequent hand-to-mouth contact, toys may pose a significant pathway of BFR exposure in children.

Methodology

Sample Collection. Sixty-nine toy samples were collected. Most of them were purchased from the two largest toy markets in Guangzhou City, which is the capital of Guangdong Province and also the largest toy trading center in China. Some of the toys were purchased from supermarkets in Guangzhou from October 2007 to April 2008. The toy samples were categorized into four types, according to their materials: hard plastic toys (such as racing cars, vehicles, weapons, action figures, and hand-held video game consoles; $n = 30$), foam toys (such as mats, puzzles, and swords; $n = 18$), rubber/soft plastic toys (such as Barbie dolls and teethers; $n = 15$), and textile and stuffed toys (such as animals, dolls, and Christmas toys; $n = 6$).

Materials. PBDE, including triBDEs (BDE28), tetraBDEs (BDE 47and 66), pentaBDEs (BDE99 and 100), hexaBDEs (BDE 138, 153, and 154), heptaBDE (BDE183), octaBDEs (BDE196, 197, and 203), nonaBDEs (BDE206, 207, 208), decaBDE (BDE 209), and PBB (BB153 and 209) standards were purchased from Accustandards Inc. (New Haven, CT). BTBPE and DBDPE solutions were obtained from Wellington Laboratories (Guelph, Canada). All organic solvents were redistilled using a glass system.

Sample Preparation and Analysis. Two to three pieces of matrix were excised from the main body of each toy. They were then cut into tiny fragments, and about 1 g of the homogeneous fragments was used for analysis. Toy samples were cleaned with distilled water and air-dried prior to the Soxhlet extraction with a mixture of acetone and hexane (1:1 v/v) for 24 h. The extracts were concentrated to 1−2 mL using a rotary evaporator and then further purified in a silica/alumina column. The effluent, eluted with 30 mL of hexane and 60 mL of hexane:methylene chloride (1:1), was finally condensed to 1 mL or 200 μL under a gentle stream of N_2.

The target compounds were analyzed by a Shimadzu 2010 gas chromatograph coupled with a mass spectrometer (GC-MS) using electron capture negative ionization (ECNI) in the selected ion monitoring (SIM) mode. A DB-XLB (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column was used for the determination of tri through heptaBDE congeners and PBB153. Initial column temperature was held at 110 °C for 1 min and then programmed to 180 at 8 °C/min (held for 1 min), to 240 at 2 °C/min (held for 5 min), to 280 at 2 °C/min (held for 15 min) and to 310 at 10 °C/min (held for 5 min). A CP-Sil 13 CB (12.5 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column was used to separate octa through decaBDEs, BTBPE, DBDPE, and PBB209. The column temperature was initiated at 110 °C (held for 5 min), increased to 200 at 20 °C /min (held for 4.5 min), and finally reached 310 at 10 °C /min (held for 15 min). Methane was used as a chemical ionization moderating gas at an ion source pressure of 2.4 × 10^3 Pa and helium as the carrier gas at a flow rate of 1 mL/min. The ion source and interface temperatures were set to 200 and 290 °C, respectively. Injection of 1 μL sample was conducted with an automatic sampler in the splitless mode. Ion fragments m/z 79 and 81 were monitored for all compounds except for BDE209 for which m/z 79, 81, 486.7, and 488.7 were recorded.

QA/QC. A procedural blank was run with each batch of samples. Trace amount of BDE28 and BDE209 (0.14 and 8.0 ng per sample, respectively) were found only in procedural blank for stuffed toy batch (with final volume of 200 μL), and they were subtracted from those in the sample extracts. The repeatability of analysis was assessed by analyzing six replicates. The relative standard deviation (RSD) was within 4.1−15.4% for PBDEs and BTBPE, and 35.2% for DBDPE. An instrumental daily calibration check standard containing the analytes was run every 10 samples. Samples were analyzed only when the RSD was less than 10%. The limit of detection, defined as a signal of 5 times the noise level ranged from 0.05 to 50 ng/g. Quantification of all the target compounds was carried out by external standard procedure.

Data Analysis. Principal component analysis (PCA) was conducted for PBDE congeners that occurred above the detection limit in over 50% of the samples. PCA can graphically represent the similarities, differences, and relationships of the congeners and provide a way to determine their origins. For congeners that were present below the limit of detection (LOD), a value of one-half of the LOD was assigned. All concentration data were logarithmically normalized before the PCA. Principal components whose eigenvalues exceed 1 were retained. The PCA was carried out with the statistical package SPSS 12.0.

Exposure and Risk Assessment. To understand the role of the toys in a child's daily exposure to BFRs, we assessed the daily exposure (picogram per kilogram body weight per day) of children at different age levels (3 months to 14 years) in four scenarios: inhalation, mouthing, dermal contact, and oral ingestion. The exposure was assessed primarily for PBDEs from hard plastic toys, because of the lack of key parameters (e.g., migration rate) for other BFRs in the assessment, and the low BFR concentrations in nonplastic toys.

Inhalation exposure occurs as a result of chemical emission from the toy to the room air and subsequent inhalation, which depends on the amount of PBDEs that are emitted to the room air, room volume and ventilation, exposure time, and the age of the child (specifically the inhalation rate and body weight). These input parameters and those thereafter in our assessment are summarized in Table S1 (Supporting Information). Currently, not much data are available with regard to BFR emission from toys to air. Kemmlein et al. (*25*) tested the area specific emission rates (SER) of PBDEs from used television set housings to chamber air. Even though PBDE concentrations in the television set housing was possibly higher than, or in the higher range of the concentrations in the hard plastic toys, the SER was used as the constant emission rate from toys to room air, in an attempt to give a reasonable worst-case estimate. The daily exposure can be estimated by the equation

$$E_{\text{inh}} = C \times \text{IR} \times t/\text{BW} \quad (3)$$

where E_{inh} is the daily exposure via inhalation (pg/kg bw-day), C is the PBDE concentrations in the room air (pg/m^3) resulting from emission from the toys (see Supporting Information), IR is the inhalation rate (m^3/h), t is the daily exposure time (h), and BW is the body weight of the exposed child (kg).

A key factor for BFR exposure via mouthing is the BFR migration rate from the toy into saliva. Likewise, no related information can be obtained from the literature; therefore the migration rates were measured in vivo (see Supporting Information). The exposure was thus estimated by the equation

$$E_{\text{mout}} = \text{MR} \times \text{CA} \times t/\text{BW} \quad (4)$$

where E_{mout} is the daily exposure via mouthing (pg/kg bw-day), MR is the migration rate from the toy into saliva, and CA is the contact area (cm^2).

Dermal contact exposure is a result of the transfer of BFRs from the toy and then adsorption to the dust, oil, or perspiration of the hand surface. Since there is no previously established migration rate, the SER of PBDEs from the television set housing was also used in this estimate. It is assumed that chemicals migrate to the hand surface in the same mode as migration to air, in the case of a child's hand-to-toy contact. In fact, PBDE congeners, particularly highly

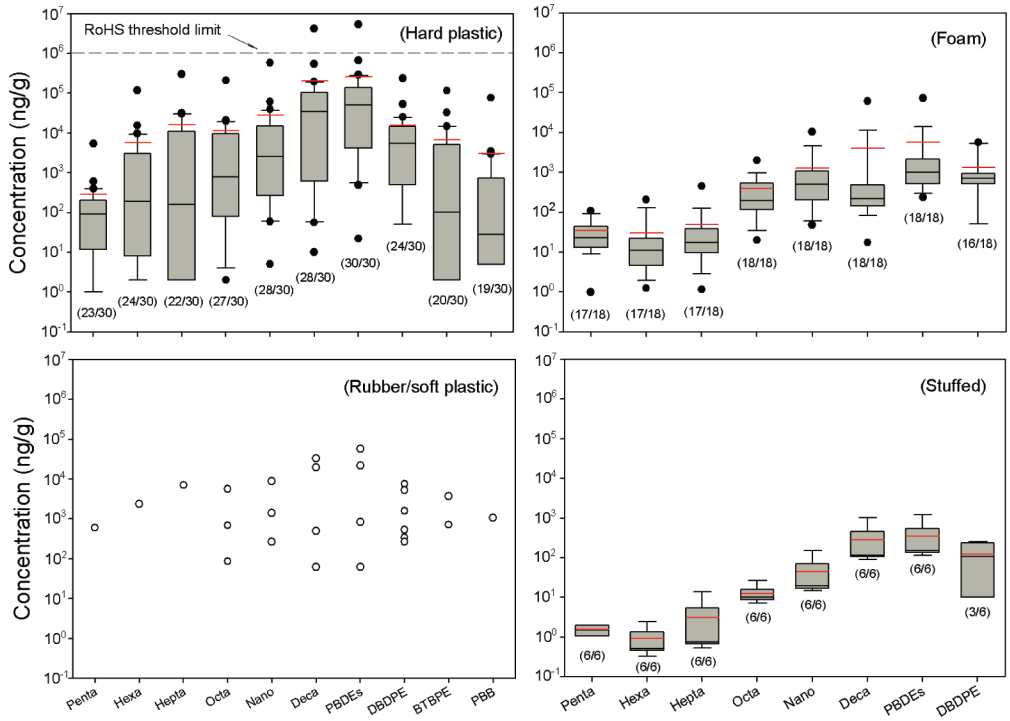

FIGURE 1. Concentrations (ng/g) of BFRs in each type of toy. The horizontal lines represent the 10th, 50th, and 90th percentiles; the box represent the 25−75th percentiles; the red lines represent the means; individual points are outliers; circles represent BFR concentrations in rubber/soft plastic toys; values in brackets are detection frequencies.

brominated ones, were predominantly found in the chamber walls, rather than in the air, in the test by Kemmlein et al. (*25*). Consequently, the dermal contact exposure can be calculated by the equation

$$E_{\text{derm}} = \text{MR} \times \text{CA} \times t/\text{BW} \quad (5)$$

where E_{derm} is the daily exposure due to dermal contact, and MR is the migration rate from the toy to the hand surface (ng/cm^2-h).

Given a child's predilection for hand-to-mouth contact behavior, a significant portion of the PBDEs loading on the hand surface can be orally ingested via dermal contact. The exposure from oral ingestion was estimated by the equation

$$E_{\text{oral}} = M \times \text{TE} \times \text{SA} \times \text{EF}/\text{BW} \quad (6)$$

where M is the PBDE mass available for transfer on the hands (ng/cm^2), TE is transfer efficiency or fraction of the PBDE mass transferred at each contact, SA is the hand surface area in contact within each event (cm^2), and EF is the frequency of contact (events/h). Here, it is assumed that the PBDEs will distribute uniformly on the palm surface, and hand washing will not be considered.

To estimate the noncancer risks of a child's BFR exposure, the congener-specific hazard quotient (HQ) was calculated by

$$\text{HQ}Q = (E_{\text{mout}} + E_{\text{oral}})/\text{RfD} \quad (7)$$

where the RfD is the reference dose of daily oral PBDE exposure that is likely to be without an appreciable risk of deleterious effects recommended by the United States Environmental Protection Agency's Integrated Risk Information System (U.S. EPA IRIS) Toxicological Evaluations. The RfD values were 0.1 μg/kg bw-day for BDE47 and 99, 0.2 μg/kg bw-day for BDE153, and 7 μg/kg bw-day for BDE209 (*26*). If an HQ value is <1, it can reasonably be assumed that the chemical exposure does not pose a significant risk. As HQ values increase above 1, the potential for a deleterious effect increases.

Results and Discussion

BFR Concentrations. The concentrations of BFRs measured in the different type of toys are summarized as box charts in Figure 1 and Table S2, Supporting Information. BFR concentrations in the hard plastic toys were generally higher than those in other toys. PBDEs were detected in all of the hard plastic toys with a median concentration of 53 000 ng/g (sum of the 16 congeners). DecaBDE had the highest concentration of 4 232 000 ng/g, with a median value of 34 300 ng/g. Other PBDE concentrations, in terms of median values, were present in the following decreasing order: nona- > octa- > hexa- ≈ hepta- > pentaBDEs (refers to the sum of tri through pentaBDEs). Deca-, nona-, and octaBDEs are the main ingredients in commercial decaBDE product; while hexa-, hepta-, and a part of octaBDEs largely originate from commercial octaBDE product. It is not surprising to find high concentrations of these congeners in hard plastic toys, since both of the products are usually used as additive flame retardants in thermoplastics (*27*). Generally, the lowest concentrations were observed for pentaBDEs, which are the main congeners of commercial penta product. This is expected, since the penta product is used almost exclusively in flame retardant flexible polyurethane foam (PUF) for furniture and upholstery in homes and vehicles (*28*). Non-PBDE BFRs, DBDPE, BTBPE, and PBBs, were also detected in the hard plastic toys with detection frequencies of 80.0%, 66.7%, and 63.3%, respectively. DBDPE, one of the major currently used novel BFR products in China, had a median value of 5540 ng/g. The median value of BTBPE, which is used only in minor quantities in China (*28*), was 101.1 ng/g. It was unexpected that PBBs were also found in over half of the hard plastic toys, with a median concentration of 27.9 ng/g. Since the 1970s, PBBs have been banned in the U.S. and were likely never produced in China. A plausible explanation is that some toys were manufactured using recycled plastic materials that contained PBBs.

PBDEs were also detected in all the foam toys and their total concentrations were 4−160-fold lower than the concentrations in the hard plastic toys and had a median value of 1012 ng/g (Figure 1). It is noteworthy that the values of nona- and octaBDEs exceeded those of the decaBDE in 14 of the 18 foam toys. Given that neither nona- nor octaBDEs are predominant congeners in commercial deca or octaBDE products (*30*), the relatively high concentrations in foam toys were likely a result of photo- or thermal-decomposition of decaBDE (*29, 30*). The median concentrations of PBDEs decreased in the order of nona- > deca- ≈ octa- > penta- > hepta- > hexaBDEs. DBDPE was found in 88.9% of the foam toys, with a median concentration of 719 ng/g, similar to the median concentration of nonaBDEs. However, BTBPE and PBBs were not found in the foam toys.

The detection frequencies of BFRs in the rubber/soft plastic toys were very low (26.7%, 40.0%, 13.3%, and 6.67%, for PBDEs, DBDPE, BTBPE, and PBBs, respectively). DBDPE was detected in all of the teethers, in which PBDEs were rarely found. Basically, BFR concentrations were substantially low in rubber/soft plastic toys, except for two samples (dolls) with relatively higher values of total PBDEs (21 600 and 57 600 ng/g, respectively). The absence of BFRs in most samples indicated their infrequent use in these types of toys.

PBDEs were found in all of the stuffed toys and DBDPE was detected in half of the stuffed toys. BTBPE and PBBs were not detected in any of the stuffed toys. The concentrations of total PBDEs and DBDPE (with median values of 150 and 108 ng/g, respectively) in the stuffed toys were generally the lowest among the four types of toys. It is likely that the BFRs in these toys were not additives but were a result of adsorption of the chemicals from the environment by the outer covering textiles or inner stuffing (PUF or floss) of the toys.

Overall, only one hard plastic toy had a total PBDE concentration (5 344 000 ng/g) exceeding the RoHS required threshold limit. None of the other BFR concentrations were above this limit in any of the toy samples.

Congener Profile and PCA. PBDEs were the predominant BFR and accounted for, on average, 77.6%, 60.3%, 78.8%, and 45.1% of the BFRs in the hard plastic, foam, rubber/soft plastic, and stuffed toys, respectively. DBDPE was the second most-prevalent BFR in the toys, with average contributions ranging from 16.4% to 53.7%. In contrast, the average contributions of BTBPE and PBBs were only 7.8% and 1.0%, respectively, in all of the toys. Of the PBDEs, congeners from decaBDE product (including octa-, nona-, and decaBDEs) were dominant in almost all of the toys, contributing over 72.0% of the total PBDEs in all of the toys, except for two hard plastic toys in which they were not detected. Conversely, congeners from octa- and pentaBDE products (tri through heptaBDEs) constituted small percentage distributions (<27.4% and <11.5%, respectively) of PBDEs in all of the toys except two. The BFR profiles in the toys were consistent with the patterns of their current production and consumption in China, where decaBDE is still the most widely used BFR and the demand for DBDPE, a replacement for decaBDE, has increased dramatically in recent years (*28*).

The congener profiles of penta-, octa-, and decaBDEs in each type of the toys and commercial products are illustrated in Figure S1 (Supporting Information). Surprisingly, the results show that the congener profiles varied greatly among the toys, and they did not exactly match the profiles of the corresponding commercial products (especially for octa and decaBDE products). For instance, there was an obviously elevated contribution of nonaBDEs in the foam toys compared to the octa- and decaBDE products. To demonstrate the relationship among the variables (congeners) and the similarities and differences in their origins, PCA was separately applied to the hard plastic, foam, and stuffed toys. For

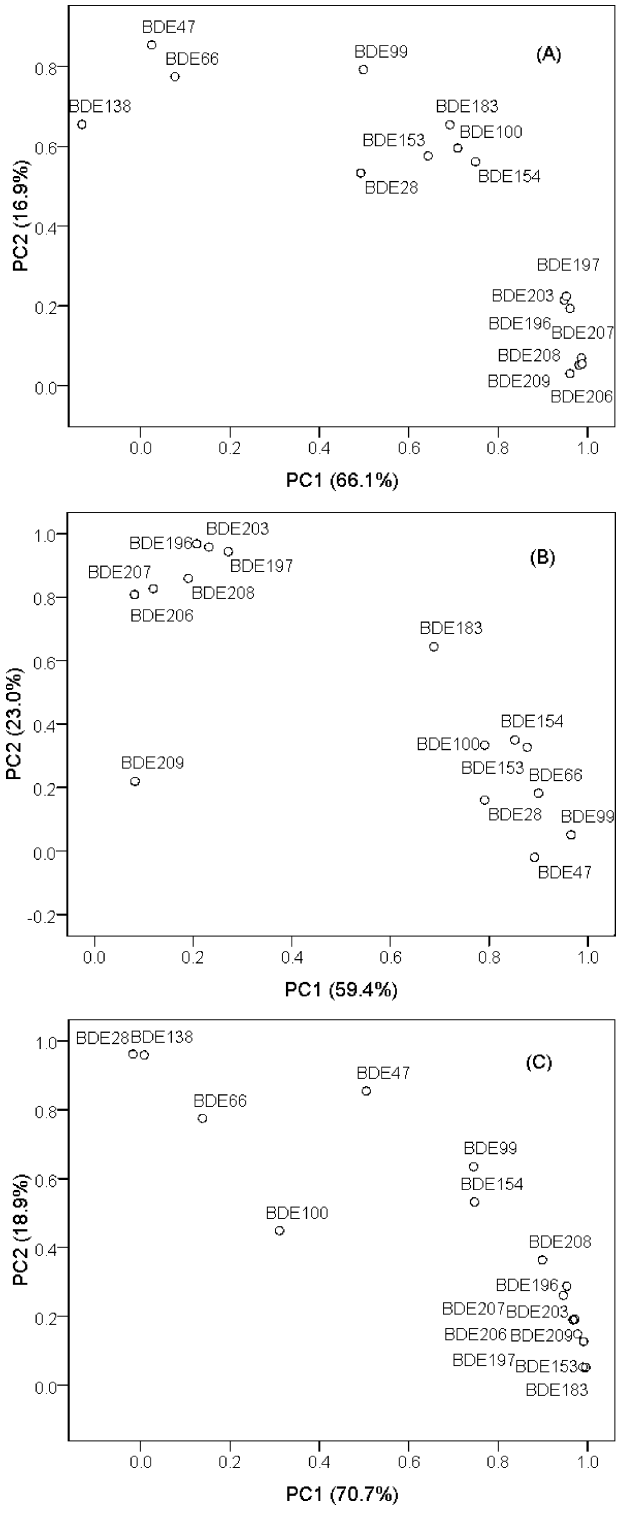

FIGURE 2. Loading plots of the principal component analysis (PCA) for each type of toy: A, hard plastic toy; B, foam toy; and C, stuffed toy.

the hard plastic toys, PCA classified the PBDE congeners into three distinct clusters, generally corresponding to deca-, octa-, and pentaBDE products, respectively (Figure 2A). Congeners related to decaBDE product had high loadings on PC1. BDE196, -197, and -203, ingredients of both octa- and decaBDE products, were located more closely to BDE209 than BDE183, implying a greater contribution from decaBDE products than from octaBDE products. It is noticeable that BDE28, -99, and -100, which were commonly derived from pentaBDE product, are grouped with BDE183 (a major

TABLE 1. Children's Daily Exposure to PBDEs via Toys

age group	exposure (pg/kg bw day)						
	penta[a]	hexa	hepta	octa	nona	deca	ΣPBDEs
inhalation							
3−12 months	17.5	2.20	8.27	2.76	1.47	0.55	32.7
1−3 years	65.2	8.23	30.9	10.3	5.49	2.06	122
3−5 years	47.7	6.02	22.6	7.53	4.02	1.51	89.3
5−9 years	34.6	4.37	16.4	5.47	2.92	1.09	64.9
9−14 years	27.8	3.51	13.2	4.39	2.34	0.88	52.1
mouthing							
3−18 months	5.88	109	400	1031	2370	5001	8916
19−36 months	0.52	9.58	35.1	90.4	208	439	782
dermal contact							
3−12 months	23.1	2.92	11.0	3.65	1.95	0.73	43.3
1−3 years	20.9	2.64	9.89	3.30	1.76	0.66	39.1
3−5 years	22.9	2.83	10.6	3.53	1.89	0.71	42.0
5−9 years	17.2	2.17	8.15	2.72	1.45	0.54	32.2
9−14 years	16.3	2.06	7.71	2.57	1.37	0.51	30.5
oral ingestion (hand-to-mouth)							
3−12 months	16.5	2.09	7.83	2.61	1.39	0.52	31.0
1−3 years	7.83	0.99	3.71	1.24	0.66	0.25	14.7
3−5 years	4.79	0.60	2.27	0.76	0.40	0.15	8.97
5−9 years	1.50	0.19	0.71	0.24	0.13	0.05	2.82
9−14 years	0.97	0.12	0.46	0.15	0.08	0.03	1.82

[a] Refers to the sum of tri- through pentaBDEs (BDE28, -47, -66, -100, and -99).

congener of octaBDE product) rather than BDE47 (a major congener of pentaBDE product). These results were probably indicative of both commercial and decomposition origins for these less brominated congeners. For instance, Rayne et al. (*31*) found that BDE99 was a primary photodegradation product of BDE153 in acetonitrile and water.

For the foam toys, the congeners originating from pentaBDE product are clustered in one group, indicating the similarities in their origins. However, the octa- and nonaBDE congeners separated from BDE209, as well as BDE183 (Figure 2B). In addition, as shown in Figure S1, Supporting Information, the octa- and nonaBDE profiles in foam toys are also different from those of the commercial products. These findings suggest that the highly brominated PBDEs in the foam toys may have been subject to degradation caused by complex physical and chemical processes during the manufacturing of the toys. The degradation of highly brominated BDE congeners in the environment remains controversial (*8*). Results of the present study suggest that some less brominated BDEs in the environment may be derived from the decomposition of higher brominated PBDEs in PBDE-containing products during manufacturing and/or the use in addition to degradation in the environment.

Finally, for the stuffed toys, the congeners (BDE196−209) stemming from the decaBDE product are grouped together, indicating a common source. However, no apparent grouping of the penta- and octaBDE commercially derived congeners was found in the loading plot for stuffed toys (Figure 2C), probably suggesting a minor contribution from these products. This result was in agreement with the previous findings in environmental samples in China, in which congeners from penta- and octaBDE products had substantially lower contributions than those from decaBDE product (*29, 33*), and may confirm the supposition that PBDEs in the stuffed toys may be a result of the toys' adsorption of contaminants from the environment. Further investigation is needed to confirm this explanation.

Children's Exposure and Risks. The daily exposures to PBDEs from toys for children at different ages (3 months to 14 years) via the pathways of inhalation, mouthing, dermal contact, and oral ingestion are summarized in Table 1. Our results showed that toys resulted in concentrations of 0.79 to 104.8 pg/m^3 for different PBDE congeners in room air, which were generally within, but toward the lower end of, the range of PBDE concentrations (0.3−11 470 pg/m^3) in the domestic air of Guangzhou (*32*). The daily exposures of total PBDEs via inhalation were estimated to be 32.7 to 122 pg/kg bw-day for children of 3 months to 14 years old. The highest exposures were found for BDE47 and 183 for children of 1−3 years old. Children's total inhalation exposures to PBDEs from the toys were generally much lower than those (30.3−6640 pg/kg bw-day) estimated based on the Guangzhou indoor PBDE concentrations from Chen et al. (*32*). This suggests that inhalation exposure associated with toys accounted for a small proportion of the daily inhalation exposure of PBDEs in the indoor environment.

The migration test in vivo showed that no BFR migration was observed from the teethers because of the low concentrations in this type of toy; however BFRs were found in the saliva samples associated with the hard plastic toy. The PBDE migration rates varied substantially among the volunteers and congeners, ranging from nonobservable to 2960 pg/cm^2-min (Table S3, Supporting Information). Migration rates were obviously high for one volunteer, especially for decaBDE and DBDPE. Mouthing exposures were estimated only for infants (3−18 months) and toddlers (1.5−3 years), because these children are more likely to be exposed to pollutants via this pathway than other children, because of their mouthing behavior. It is likely that BFR exposure from toys meant for mouthing (such as teethers and pacifiers) is negligible for young children. The total PBDE exposures via mouthing hard plastic toys were 8916 and 782 pg/kg bw-day for infants and toddlers, respectively, estimated by the median migration rates. However, it is noteworthy that the exposures were 65 180 pg/kg bw-day for infants and 5717 pg/kg bw-day for toddlers, calculated using the 95th percentile migration rates. The highest exposure was found for decaBDE, followed by nona and octaBDEs. Also worthy of mention is that children's mouthing behavior with hard plastic toys can also result in their exposure to BTBPE and DBDPE (not shown in Table 1). The exposures ranged from 24.2 to 822 pg/kg bw-day for BTBPE and from 1323 to 15 085 pg/kg bw-day for DBDPE. It is indeed very surprising to find children's exposure to these non-PBDE BFRs, given their expectable increasing

usage after the ban on PBDEs and the current lack of knowledge of their potential toxicities to young children.

The daily exposures resulting from dermal contact ranged from 30.5 to 43.3 pg/kg bw-day, on the basis of the assumption of 3 h of playtime with the toys and 2 h of real contact with the toys for all age groups. Approximately 6% to 72% of the PBDEs (1.82−30.1 pg/kg bw-day) on hand surfaces were ingested by children via hand-to-mouth contact, depending on the proportion of the contact area to the hand area in each event, and the child's contact frequency. The combined potential exposure to PBDEs associated with toys ranged from 56.6 to 8992 pg/kg bw-day. Much higher exposures were observed for infants and toddlers than in other subgroups, which was predominantly a result of exposures from mouthing toys. There is the potential for significant or substantial uncertainty in the exposure assessment, relating to the uncertainty of the input parameters used. For total exposure, the greatest uncertainty of the exposure will arise from the children's mouthing behavior. Long mouthing duration or occasional swallowing of small bit-off pieces, and high BFR concentrations in the toys mouthed would notably increase the child's exposure to BFRs.

The children's exposure via toys was comparable to the exposure via human milk (7100 pg/kg bw-day) for infants and was higher than that via fish consumption (110−395 pg/kg bw-day) and inhalation (230−343 pg/kg bw-day) for toddlers, recently reported by Meng et al. (*16*). Our results were comparable or lower than the median exposures via dust ingestion (4750−6990 pg/kg bw-day) and food (4330−6370 pg/kg bw-day) for British children (6−24 months) reported by Harrad et al. (*15*). For children more than 3 years old, however, their exposures to PBDEs were lower than that from fish consumption (110−395 pg/kg bw-day) and inhalation (230−343 pg/kg bw-day) (*16*), and much lower than the daily exposure (1380 ng/day) via hand-to-mouth contact for children (8−10 years old) assessed by Stapleton et al. (*17*). Most recently, Lorber (*33*) reported that overall exposure (from diet, inhalation, dust ingestion, and dermal contact) of American children to PBDEs ranged from 9.1 to 49.3 ng/kg bw-day, which was much greater than the values reported in this study.

The hazard quotients ranged from 4×10^{-9} to 8×10^{-3}, and higher values were observed for infants (Table S4, Supporting Information). Clearly, the hazard quotients for the four congeners were all far below 1, even calculated on the basis of the observed worst-case exposure, suggesting a low deleterious risk associated with children's toys with regard to BFRs. However, it is noteworthy that children can be exposed to a significant amount of non-PBDE BFRs, as well as highly brominated BDEs, in addition to BDE209 via toys. Toxicological data of these chemicals are currently very limited. Additionally, young children may be much more sensitive to xenobiotic toxic chemicals than adults, and the EPA's confidence in this RfD is low (*34*). Therefore, this exposure route is still of special concern and further work is required to allow for accurate evaluation.

Acknowledgments

This study was financially supported by the National Science Foundation of China (No. 40632012 and 40821003), the National Basic Research Program of China (No. 2009CB421604), and the Earmarked Fund of the State Key Laboratory of Organic Geochemistry (SKLOG2008A05). The authors thank Prof. Ling-Yan Zhu from Nankai University, China for kindly providing the BTBPE standard.

Supporting Information Available

Methodology section, including estimation of room air PBDE concentrations and in vivo test for BFR migration into human saliva, is described, Figure S1 depicting the PBDE congener profiles in the toys and commercial products, Figure S2 depicting the loading plot of PCA for foam toys (PC2 vs PC3), Table S1 summarizing the input parameters utilized in the exposure assessment, Table S2 listing the descriptive statistics for the BFR concentrations in toys, Table S3 listing the BFR migration rates from toys into saliva, Table S4 listing the hazard quotients of children's exposure to PBDEs via toys, and Table S5 listing full data for each example. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES9004834