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After the PBDE Phase-Out: A Broad Suite of Flame Retardants in Repeat House Dust Samples from California

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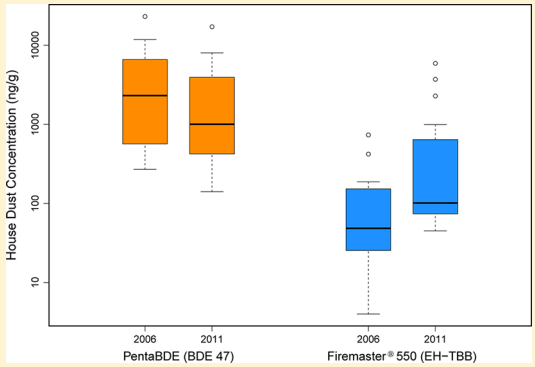
Supporting Information

ABSTRACT: Higher house dust levels of PBDE flame retardants (FRs) have been reported in California than other parts of the world, due to the state's furniture flammability standard. However, changing levels of these and other FRs have not been evaluated following the 2004 U.S. phase-out of PentaBDE and OctaBDE. We analyzed dust collected in 16 California homes in 2006 and again in 2011 for 62 FRs and organohalogens, which represents the broadest investigation of FRs in homes. Fifty-five compounds were detected in at least one sample; 41 in at least 50% of samples. Concentrations of chlorinated OPFRs, including two (TCEP and TDCIPP) listed as carcinogens under California's Proposition 65, were found up to 0.01% in dust, higher than previously reported in the U.S. In 75% of the homes, we detected TDBPP, or brominated "Tris," which was banned in children's sleepwear because of carcinogenicity. To our knowledge, this is the first report on TDBPP in house dust. Concentrations of Firemaster 550 components (EH-TBB, BEH-TEBP, and TPHP) were higher in 2011 than 2006, consistent with its use as a PentaBDE replacement. Results highlight the evolving nature of FR exposures and suggest that manufacturers continue to use hazardous chemicals and replace chemicals of concern with chemicals with uncharacterized toxicity.



INTRODUCTION

California house dust contains some of the highest concentrations of polybrominated diphenyl ether (PBDE) flame retardants (FRs) in the world due to a state-wide furniture flammability standard (Technical Bulletin 117).[1] PBDEs have been associated with thyroid and other endocrine system disruption and adverse neurological development (see Supporting Information (SI)). PBDEs in California homes and residents[2−6] often exceed risk-based levels for children,[4,7] raising concerns about exposures to the many other FRs that have not yet been well-characterized. For example, Great Lakes Chemical Corporation, the sole U.S. PBDE manufacturer, introduced Firemaster 550 to replace the PentaBDE commercial mixture in response to prospective bans in Europe and several U.S. states.[8] Little is known about the chemical composition, uses, exposure levels and health effects of this mixture or of other brominated, chlorinated, and organophosphate chemicals used as FRs. Because additive FRs shed from consumer products, they are found in house dust. Measuring dust concentrations over time can identify exposure trends that result from changes in product formulations.

House dust is the primary route of exposure for PBDEs,[9,10] contributing 82%, on average, of a U.S. adult resident's exposure.[10] Dust concentrations of PentaBDE were correlated with breast milk levels in 11 women.[11] Although diet may also contribute,[11] dust appears to be particularly important in areas, like California, with high concentrations in dust.[5] Dust is a direct exposure pathway through incidental ingestion, inhalation of resuspended particles, and dermal absorption, and it is a proxy for exposure from product use.

Commercial PentaBDE and OctaBDE mixtures were phased-out in 2004 in the U.S.[8] DecaBDE is banned in electrical and electronic applications in Europe,[12] and U.S. producers and importers (Chemtura, Albermarle, and ICL Industrial Products) committed to end production, import and sales by the end of 2013.[13]

As PBDEs were phased out due to health concerns, other brominated FRs (BFRs) and organophosphate flame retardants (OPFRs) were introduced as replacements.[14] Chemtura, formerly Great Lakes Chemical Corporation, replaced PentaBDE in polyurethane foam with Firemaster 550, a mixture of 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEH-TEBP), triphenyl phosphate (TPHP), and a yet-to-be-fully characterized triaryl phosphate isopropylated mixture.[15] Concerns are emerging about BEH-TEBP's environmental persistence and toxicity, since BEH-TEBP is the brominated

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Table 1. Concentrations (ng/g Dust) of Flame Retardants and Legacy Organohalogens in California House Dust from 16 Homes Sampled in 2006 and 2011

			2006 samples (round 1; n = 16)				2011 samples (round 2; n = 16)			
chemical name	abbreviation[a]	LOQ[b]	% > LOQ	min.	median	max.	% > LOQ	min.	median	max.
Polybrominated Diphenyl Ethers (PBDEs)										
2,4,4′-tribromodiphenyl ether	BDE 28	2	100	5	26	270	100	3	14	310
2,2′,4,4′-tetrabromodiphenyl ether	BDE 47	2	100	270	2300	23 000	100	140	1,000	17 000
2,3′,4,4′-tetrabromodiphenyl ether	BDE 66	2	100	8	64	520	100	4	23	1800
2,2′,3,4,4′-pentabromodiphenyl ether	BDE 85	3	100	13	110	1300	100	9	66	6000
2,2′,4,4′,5-pentabromodiphenyl ether	BDE 99	2	100	280	2200	24 000	100	190	1100	25 000
2,2′,4,4′,6-pentabromodiphenyl ether	BDE 100	2	100	56	520	4900	100	37	240	11 000
2,2′,4,4′,5,5′-hexabromodiphenyl ether	BDE 153	3	100	2	250	2400	100	21	150	7800
2,2′,4,4′,5,6′-hexabromodiphenyl ether	BDE 154	3	100	22	240	1800	100	17	110	6700
2,2′,3,4,4′,5′,6-heptabromodiphenyl ether	BDE 183	4	100	9	28	770	100	3	18	920
2,2′,3,3′,4,4′,5,6′-octabromodiphenyl ether	BDE 196	4	88	<4	7.5	240	56	<4	4	180
2,2′,3,3′,4,4′,6,6′-octabromodiphenyl ether	BDE 197	4	81	<4	9	530	56	<4	4	230
2,2′,3,4,4′,5,5′,6-octabromodiphenyl ether	BDE 203	4	81	<4	5	130	50	<4	2	110
decabromodiphenyl ether	BDE 209	10	100	580	1400	15 000	100	110	1200	8500
Firemaster 550										
2-ethylhexyl-2,3,4,5-tetrabromobenzoate	EH-TBB (or TBB)	2	100	4	48	740	100	45	100	5900
bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate	BEH-TEBP (or TBPH)	2	100	36	140	1900	94	<2	260	3800
triphenyl phosphate	TPHP	20	100	580	3000	14 000	100	790	2800	36 000
Tetrabromobisphenol A										
tetrabromobisphenol A	TBBPA	10	94	<10	260	3400	100	22	200	2000
Hexabromocyclododecane										
α-hexabromocyclododecane	α-HBCYD (or α-HBCD)	5	100	31	62	710	100	17	62	910
β-hexabromocyclododecane	β-HBCYD (or β-HBCD)	5	100	8	18	330	100	7	16	230
γ-hexabromocyclododecane	γ-HBCYD (or γ-HBCD)	5	100	29	94	6700	100	13	73	790
hexabromocyclododecane	Σ HBCYD (or HBCD)	5	100	82	190	6800	100	39	160	1800
Other Brominated Flame Retardants (BFRs)										
hexabromobenzene	HBB	2	50	<2	1	8	31	<2	<2	13
hexachlorocyclopentadienyl-dibromocyclooctane	DBHCTD (or HCDBCO)	5	6	<5	<5	9	25	<5	<5	72
1,2-bis(2,4,6-tribromophenoxy)ethane	BTBPE	2	100	7	30	220	100	3	12	130
decabromodiphenylethane	DBDPE	10	94	<10	51	430	100	18	140	2800
tetrabromobisphenol A - bis(2,3-dibromopropylether)	TBBPA-BDBPE (or TBBPA-dbpe)	10	75	<10	22	180	50	<10	7	560
α-1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane	α-DBE-DBCH (or α-TBECH)	2	6	<2	<2	13	19	<2	<2	25
β-1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane	β-DBE-DBCH (or β-TBECH)	2	6	<2	<2	11	12	<2	<2	16
γ-1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane	γ-DBE-DBCH (or γ-TBECH)	2	0	–	–	–	6	<2	<2	3
δ-1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane	δ-DBE-DBCH (or δ-TBECH)	2	0	–	–	–	0	–	–	–
2,4,6-tribromophenyl allyl ether	TBP-AE (or ATE)	2	0	–	–	–	0	–	–	–
2-bromoallyl-2,4,6-tribromophenyl ether	TBP-BAE (or BATE)	2	0	–	–	–	0	–	–	–
2,4,6-tribromophenyl 2,3-dibromopropyl ether	TBP-DBPE (or DPTE)	2	6	<2	<2	2	6	<2	<2	11
α-1,2,5,6-tetrabromocyclooctane	α-TBCO	2	6	<2	<2	2	0	–	–	–
β-1,2,5,6-tetrabromocyclooctane	β-TBCO	2	0	–	–	–	0	–	–	–
octabromo-1,3,3-trimethyl-1-phenylindane	OBTMPI (or OBIND)	5	44	<5	<5	130	25	<5	<5	62
Halogenated Organophosphate Flame Retardants (OPFRs)										
tris(2-chloroethyl)-phosphate	TCEP	20	100	610	5100	160 000	100	330	2700	110 000
tris(1-chloro-2-propyl)-phosphate	TCIPP (or TCPP)	20	100	340	2100	120 000	100	490	2200	140 000
tris(1,3-dichloro-isopropyl)-phosphate	TDCIPP (or TDCPP)	20	100	730	2800	24 000	100	920	2100	44 000
tris(2,3-dibromopropyl) phosphate	TDBPP	20	62	<20	35	8900	38	<20	<20	310
Nonhalogenated Organophosphate Flame Retardants (OPFRs)										
triethyl-phosphate	TEP	20	56	<20	28	410	31	<20	<20	250

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Table 1. continued

chemical name	abbreviation[a]	LOQ[b]	2006 samples (round 1; n = 16) % > LOQ	min.	median	max.	2011 samples (round 2; n = 16) % > LOQ	min.	median	max.
tri-n-propyl-phosphate	TnPP (or TPP)	20	0	–	–	–	0	–	–	–
tri-iso-butyl-phosphate	TIBP (or TiBP)	80	56	<80	84	180	19	<80	<80	120
tri-n-butyl-phosphate	TNBP (or TnBP)	80	50	<80	32	1800	38	<80	<80	1800
tri-(2-butoxyethyl)-phosphate	TBOEP (or TBEP)	300	100	2300	12 000	68 000	100	790	11 000	170 000
tri-(2-ethylhexyl)-phosphate	TEHP	200	19	<200	<200	3700	12	<200	<200	340
ethylhexyl diphenyl phosphate	EHDPP	100	100	180	610	3000	100	140	560	1500
tricresyl phosphate	TMPP (or TCP)	20	100	330	1000	4400	100	180	680	10 000
			Dechlorane Plus (DP)							
syn-Dechlorane Plus	syn-DP	2	81	<2	3	22	44	<2	<2	7
anti-Dechlorane Plus	anti-DP	2	100	3	7.5	35	75	<2	3	8
Dechlorane Plus	Σ DP	2	100	3	10	47	75	<2	4.5	15
			Legacy Compounds							
2,2′,4,4′,5,5′-hexachlorobiphenyl	CB 153	5	100	6	18	200	81	<5	9.5	130
2,2′,3,4,4′,5,5′-heptachlorobiphenyl	CB 180	5	94	<5	16	74	75	<5	8.5	90
3,3′,5,5′-tetrabromo biphenyl	BB 80	3	0	–	–	–	6	<3	<3	6
2,2′,4,5′,6-pentabromo biphenyl	BB 103	3	0	–	–	–	6	<3	<3	3
2,2′,4,4′,5,5′-hexabromo biphenyl	BB 153	3	56	<3	4.5	160	44	<3	<3	47
2,2′,3,4,4′,5,5′-heptabromo biphenyl	BB 180	5	0	–	–	–	0	–	–	–
decabromo biphenyl	BB 209	10	0	–	–	–	0	–	–	–
cis-chlordane	CC	5	94	<5	26	250	94	<5	17	180
trans-chlordane	TC	5	94	<5	34	280	100	5	22	220
trans-nonachlor	TN	5	94	<5	19	130	88	<5	11	140
1,1,1-trichloro-2,2-di(4-chlorophenyl) ethane	p,p′-DDT	10	100	44	530	4100	100	50	160	1500
1,1-bis-(4-chlorophenyl)-2,2-dichloroethene	p,p′-DDE	10	94	<10	74	430	88	<10	40	170
1,1-dichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane	p,p′-DDD	10	88	<10	36	240	75	<10	14	64

[a]Compounds were named following the newly proposed nomenclature presented by Bergman et al,[62] with the older name give in parentheses. [b]LOQ, limit of quantification; – indicates insufficient number of detects to calculate summary statistics.

version of bis(2-ethylhexyl)phthalate (DEHP) that adversely affects reproductive development.[16] The U.S. EPA recently announced plans to conduct risk assessments for BEH-TEBP and EH-TBB.[17]

Several OPFRs are used as PBDE replacements. In the late 1970s, tris(2,3-dibromopropyl) phosphate (TDBPP or brominated "Tris") was banned from children's pajamas because of its mutagenic and carcinogenic properties.[18,19] Exposure data are limited, although the toxic breakdown product, 2,3-dibromo-1-propanol, was detected in U.S. homes.[20] The chlorinated analog, tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), also a carcinogen,[14,21] has been found in U.S. house dust and baby products.[22,23] TDCIPP concentrations in U.S. house dust were recently associated with altered thyroid (free T4) and prolactin hormone levels in men.[24] Little information exists on exposure.[22,25]

Elevated PentaBDE concentrations in California relative to other parts of the U.S. and world have been well established; however, little is known about levels of other FRs. We expect that FRs used in polyurethane foam, including PentaBDE replacements, may be elevated due to the furniture flammability standard. Exposure patterns for FRs in other applications, such as electronics, are not known because of limited data, including for BDE 209.[5]

To provide data on a wider range of FRs and on changing exposure patterns, this study measured a broad array of FR chemicals in repeat dust samples collected from 16 California homes. Dust collected in California homes in 2006 and in the same homes in 2011 was analyzed for a broad suite of BFRs and OPFRs (n = 49). We also measured 13 "legacy" chemicals: persistent organochlorines (OCs) banned long ago (e.g., DDT). We expected OC concentrations to remain relatively constant or decrease between sampling dates.[26] Correlation and cluster analysis of simultaneous FR measurements were used to shed light on mixtures and potential sources. Measurement at two time periods allows for the investigation of changes in residential levels, which likely reflect patterns of use. This work contributes to the ongoing characterization of evolving exposures to FR chemicals in homes.

MATERIALS AND METHODS

Sample Collection. Dust samples were collected in 16 northern California homes in 2006 and again in the same homes with the same participants in 2011. These homes were a subset of 50 homes in two San Francisco Bay Area communities further described in Brody et al.[27] and Rudel et al.[28] Samples were collected by trained field staff using a Eureka Mighty-Mite vacuum cleaner fitted with a specially designed PTFE Teflon crevice tool attachment modified to collect dust into a cellulose extraction thimble (19 × 90 mm). Samples were collected by slowly dragging the crevice tool for approximately 30 min over surfaces in the living areas of the home. Samples were sieved to <150 μm prior to long-term storage (−16 °C ± 10 °C) and extraction. Residents were surveyed about the presence of furniture, carpets, and electronics, particularly if any

Table 2. Major Flame Retardant Classes Investigated in This Study, Their Uses, and Health Effects

FR class	≥ 1 M lbs produced/yr[b]	EPA action plan[c]	REACH SVHC[d]	uses	health concerns[a]			
					endocrine disruptor	cancer	neurotoxicity	lack of health studies
PBDEs								
PentaBDE[e]		•		polyurethane foams [41]	•		•	
				phase-out in U.S. in 2004				
OctaBDE[f]		•		plastic housings and office equipment[41]	•		•	
				phase-out in U.S. in 2004				
DecaBDE[g]	•	•		electrical equipment, textiles and fabric backings; 80% of total PBDE production[41]	•	•	•	
				volunteer phase-out in U.S. by 2014				
Firemaster 550	•			replacement for PentaBDE in foams	•			•
HBCYDs	•	•	•	thermoplastic (moldable) polymers and styrene resins;[41]	•		•	
				building insulation, upholstery textiles and electrical equipment housing[38]				
TBBPA	•			reactive in circuit boards; additive in polymers; most widely used flame retardant[41]	•		•	•
Other BFRs								
TBBPA- BDBPE	•			plastics, including pipes, water barriers, kitchen hoods and electronics[45]	•	•[h]		•
HBB				paper, wood, textiles, electronics and plastics; not used in Europe[45]			•	
BTBPE	•			replacement for OctaBDE[45]	•			•
DBDPE	•			alternative to DecaBDE[45]				•
Halogenated OPFRs								
TCEP	•		•	polyurethane foams, plastics, polyester resins, and textiles[25,52]		•	•	
				banned from children's products in NY in 2011[51]				
TCIPP	•			polyurethane foams[25]		•[h]	•[h]	•
TDCIPP	•			polyurethane foams, plastics, and textiles[25,52]	•	•	•	
TDBPP				polyurethane foams[25]		•		
				banned in 1977 for use in US children's clothing[19]				
Non-Halogenated OPFRs								
TEP	•			also used as plasticizer and in antifoam agents and lacquers[25,52]			•	•
TIBP				also used as plasticizer and in antifoam agents and lacquers[25,52]				•
TNBP	•			also used as plasticizer and as a lubricant in hydraulic fluids[25]		•		•
TBOEP	•			also used in floor wax, lacquers, rubber and plastics[25,52]			•	•
TEHP				clothing, also used as plasticizer and as a solvent[63]		•		•
TMPP	•			also used as plasticizer and as lubricants in hydraulic fluids [25]			•	•
DP	•			electronics[58]	•[h]			•

[a]References for health effects can be found in SI Table SI4. [b]Chemicals produced in the U.S. ≥ 1 million pounds per year are typically designated by the EPA as High Production Volume chemicals, a voluntary reporting program (data from 2006). [c]U.S. EPA Action Plans have been developed for 10 chemicals considered high priority for risk management. [d]The European Union's system of Registration, Evaluation, Authorization, and Restriction of Chemical substances (REACH) identifies Substances of Very High Concern (SVHC), which are public health hazards proposed for regulation under REACH. [e]Congeners BDE 28, BDE 47, BDE 66, BDE 85, BDE 99, BDE 100, BDE 153, and BDE 154.[64] [f]Congeners BDE 183, BDE 196, BDE 197, and BDE 203.[64] [g]Congener BDE 209.[64] [h]Based on structural considerations.

items were introduced to the home since the 2006 sample collection. Individual results will be reported to participants.

Analyte Selection. Analytes were selected based on previous research, current understanding of potential replacements for PBDEs, health concerns, and analytical capability. Based on production volumes, HBCYD and TBBPA are important BFRs. Other potential PBDE-replacements were included. The health effects of chlorinated and brominated OPFRs are of concern and recent work suggests they are found at levels similar to PBDEs.[22,25] Nonhalogenated FRs are expected to be used in various FR mixtures and may be pervasive given their many other uses in the home. Legacy OCs were included to evaluate concentration consistency over time. The 62 target chemicals are listed in Table 1.

Analytical Methods. Due to the comprehensive list of target analytes and differences in physical-chemical properties, two different sample preparation methods were used in four extracts per sample (two fractions per method) for chemical analysis. One sample preparation method, which was used to measure the bulk of BFRs, OCs, and OPFRs, involved

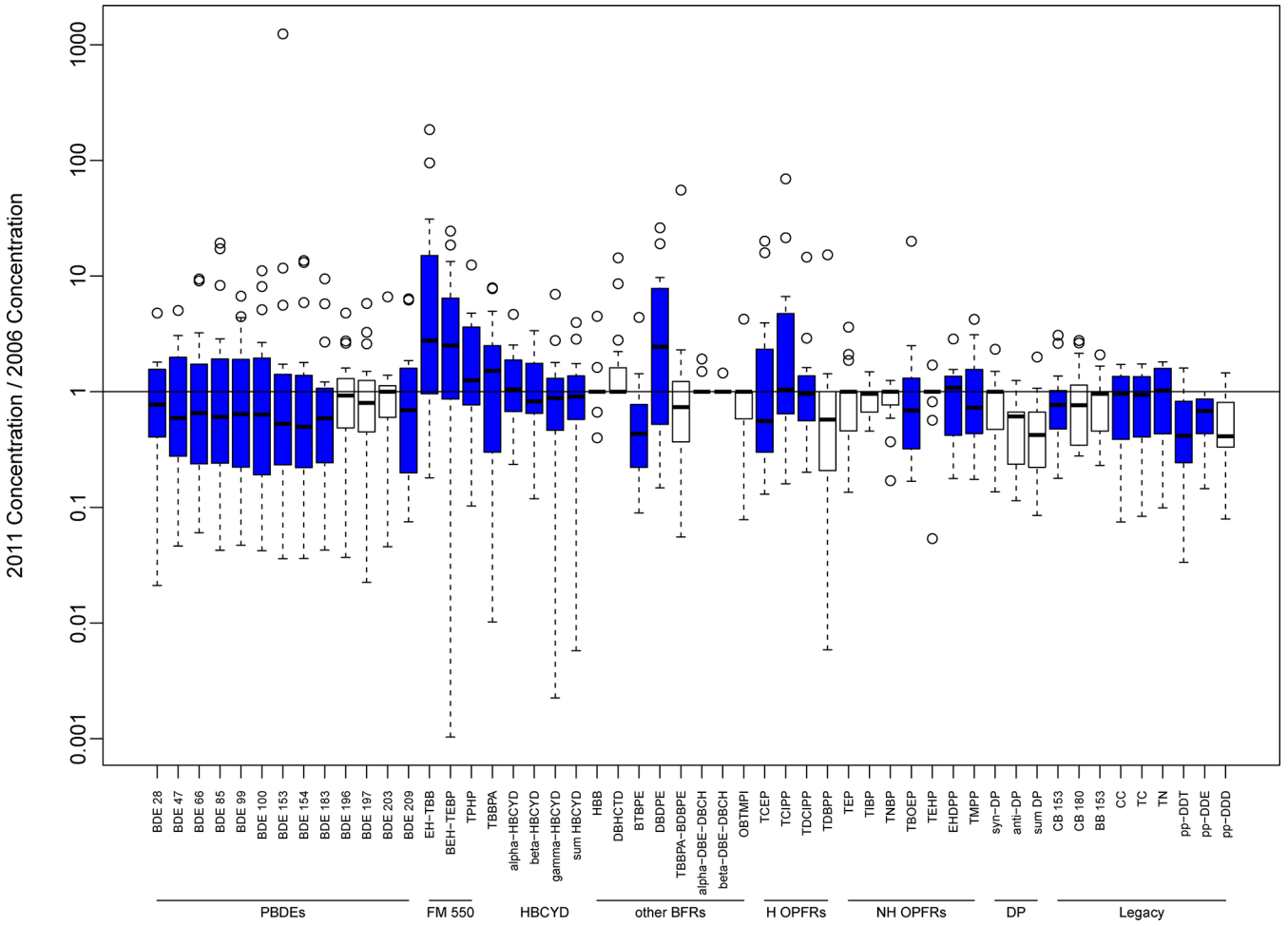

Figure 1. Distributions of concentration ratios (2011/2006) in dust collected from 16 homes. Nondetectable levels set to detection limit. Chemicals with median ratios above 1 were higher in 2011 samples compared with 2006 samples. Darker shaded boxes used for chemicals with >75% simultaneous detects.

extraction using Hex-Ac (3:1, v:v) and fractionation on Florisil.[29] The obtained fractions F1 and F2 were subjected to analysis by GC-ECNI/MS and GC-EI/MS (see SI Table SI1). A second sample preparation method,[30] involving similar extraction and fractionation on silica, was employed to measure HBCYDs, TBBPA, and to confirm PBDEs. The fraction containing PBDEs was subjected to GC-ECNI/MS and the fraction containing HBCYDs and TBBPA was subjected to LC-MS/MS analysis. Additional analytical details are in the SI.

Quality Control. Six procedural blanks were analyzed in the same batches as the samples and concentrations were blank-corrected by subtracting the mean blank values (in pg) from the raw analyte values. Method limits of quantification (LOQ) were calculated as 3 × standard deviation of blank values and divided by the amount of dust used for analysis (typically 50 mg). For compounds not detected in the blanks, the LOQ was calculated based on the signal-to-noise ratio 10/1. Since LOQs are compound-specific variables, they spanned a large range of concentrations. Certified reference material SRM 2585 (Organics in Indoor Dust) was used to test the accuracy. Additional details are in the SI.

Data Analysis. Summary statistics were calculated for all analytes within each sampling round. Nondetectable concentrations were left at zero for summary statistics, which results in lower values than if other replacement methods were used. Concentration ratios (2011/2006 concentrations) were calculated to evaluate changes between the two sampling periods. Nondetectable concentrations were set to the LOQ for concentration ratios. Ratios above 1 indicate higher concentrations in 2011 and ratios below 1 indicate higher 2006 concentrations. Spearman rank correlations were used to evaluate associations between absolute concentration differences between rounds (2011−2006 concentrations) and total number of reported new FR-relevant items (e.g., electronics, carpets) in 2011.

Kendall's tau rank correlation estimates were calculated to investigate relationships between analytes within each sampling round and for each analyte across rounds. These estimates were used in cluster analysis to elucidate common mixtures and potential sources. Additional details are in the SI. Data analysis was performed in R (version 2.15).

■ RESULTS AND DISCUSSION

Overall, 55 compounds were detected and 41 were found in at least 50% of the 32 samples (Table 1). Detected chemicals were 13 PBDE congeners, 3 components of Firemaster 550, 15 other BFRs, 4 halogenated OPFRs, 7 nonhalogenated OPFRs, and 2 Dechlorane-Plus isomers. Table 2 summarizes information on usage and health concerns of these FRs grouped by common formulations (related to exposure patterns) and chemical

structure (often related to use and toxicity). These FR group names are used throughout the paper.

The highest concentrations, greater than 0.1 mg/g or 0.01%, were for two chlorinated OPFRs, including TCEP, which is listed as a carcinogen under California's Proposition 65, and TCIPP, and one nonhalogenated OPFR (TBOEP). Over the five years between the sample collection periods, Firemaster 550 components increased, while PentaBDE levels decreased. Legacy pollutants like DDT also decreased, suggesting that the PBDE reduction may be due to decreased loading and/or possibly to differences in sample collection between 2006 and 2011. Figure 1 shows ratios of 2011/2006 concentrations; ratios >1 suggest increasing concentrations with time. Detailed findings are presented below by chemical group.

Concentrations in House Dust. *PBDEs.* We found all targeted PBDE congeners in at least 50% of samples, with the components of PentaBDE (BDE 47 and BDE 99) and DecaBDE (BDE 209) mixtures in 100% of samples. Median concentrations for all PBDE congeners decreased from 2006 to 2011 (Table 1); however, not all of the means decreased (data not shown), with exceptions likely driven by two homes with substantial increases in the congeners of PentaBDE mixture (SI Figure SI3). Exposed furniture foam was noted in one of these homes. Ratios of 2011/2006 concentrations are used to evaluate relative concentrations from the two sampling periods. Median concentration ratios were less than 1 for all congeners (Figure 1), suggesting a decrease in concentrations between 2006 and 2011, which could reflect decreased use. However, since we saw decreases for legacy OCs, which should generally have minimal changes between 2006 and 2011, the PBDE reduction may reflect some unidentified but systematic difference in sample collection (see Legacy Chemicals below).

Substantial decreases (up to 20-fold) in concentrations of PentaBDE were observed in three homes where participants reported remodeling or acquiring new furniture and/or rugs/carpet between 2006 and 2011. In fact, there was a significant statistical association between concentration reductions and participant-reported new furniture, electronics, and flooring ($p < 0.05$), suggesting that PentaBDE is no longer present in new household items. Reductions are likely the result of phase-outs (2004)[8] and bans (2006 in CA)[31] of PentaBDE and OctaBDE. Substantial decrease (14-fold) in BDE 209 was observed in a home where the participant did not report changes in electronics and furnishings; possibly some relevant changes were not reported.

We detected BDE 47 and BDE 99 at median concentrations >1000 ng/g in both sampling rounds, which is consistent with previous research showing higher PentaBDE concentrations in California than elsewhere due to the unique furniture flammability standard.[5] In comparison to other studies within California, the median concentration of BDE 47 in 2006 is similar (within 30%); whereas median concentrations of BDE 99 and 100 in 2006 (2,200 ng/g and 520 ng/g, respectively) were lower (up to 2×) than other California studies, which used slightly different vacuum sampling techniques.[4,32]

Correlation and cluster analysis were used to evaluate mixtures and common sources. SI Figures SI4 and SI5 show that PBDE congeners measured in each sampling round correlate/cluster together in the three commercial formulations (PentaBDE, OctaBDE, and DecaBDE). OctaBDE levels correlate between sampling rounds (along diagonal in SI Figure SI4), suggesting relatively stable concentrations in the homes over time; however, PentaBDE and DecaBDE levels were not significantly correlated over time, likely due to a few homes with substantial changes.

Firemaster 550. Chemtura introduced Firemaster 550 in 2004 as a replacement for PentaBDE in polyurethane foam.[15] Besides TPHP, the other constituents of Firemaster 550 were only recently identified as two brominated compounds: EH-TBB and BEH-TEBP.[15] Subsequently, Chemtura developed additional products, with undisclosed composition, including Firemaster 600, Firemaster 800, and Emerald Innovation, with claims of increased efficiency. Firemaster 550 is genotoxic[33] and TPHP was associated with altered prolactin levels and decreased sperm concentration in men.[24] To our knowledge, carcinogenicity, reproductive and development studies have not been conducted on the brominated components of Firemaster 550.

We detected EH-TBB, BEH-TEBP, and TPHP in all but one sample. Concentrations of EH-TBB and BEH-TEBP increased across rounds (median ratio >1; Figure 1), except in one home where BEH-TEBP was found at 1,935 ng/g in the 2006 sample and not detected (<2 ng/g) in 2011 (SI Figure SI3). This home also had lower 2011 EH-TBB and TPHP concentrations. The generally increasing trend for EH-TBB and BEH-TEBP suggests that Firemaster 550 is being used as a PentaBDE replacement.

We compared our 2006 results to two sets of dust samples collected in the Boston area (50 vacuum bag samples collected between 2002 and 2007 and 20 field technician collected dust samples collected in 2006)[15,22,24] and vacuum bag dust collected in Vancouver, Canada in 2007−2008.[34] The 2006 EH-TBB and BEH-TEBP levels in our study were similar to, if not slightly lower than, levels in Boston.[15,22] Our 2006 EH-TBB levels were lower than levels in Vancouver whereas the 2011 levels are comparable.[34] In contrast, the levels of BEH-TEBP at both time periods in our study were higher than those in Vancouver.[34] The concentrations in our 2006 samples of TPHP were lower than in Boston.[24]

EH-TBB and BEH-TEBP were significantly positively correlated within each sampling round (SI Figure SI4; tau = 0.4−0.5; $p < 0.05$), which is expected since they are both in Firemaster 550. We compared the observed ratio of EH-TBB/BEH-TEBP in our samples with the ratio of the commercial mixture and Boston-area samples to evaluate if Firemaster 550 is the sole source and if EH-TBB and BEH-TEBP have different fates once applied to a product. We observed a mean EH-TBB/BEH-TEBP ratio of 0.6 (0.04−3.1) in the 2006 samples and 1.5 (0.8−11) in the 2011 samples. These ratios are lower than the reported ratio in Firemaster 550 (4) and in Boston dust (mean 4.4; range 0.5−50).[15] This suggests other sources of BEH-TEBP in California or a different fate of the chemicals. TPHP, also present in Firemaster 550, was not significantly correlated with either EH-TBB or BEH-TEBP in either sampling round, although TPHP concentrations increased in homes with substantial increases in EH-TBB and BEH-TEBP. This suggests that, in addition to Firemaster 550, there are other sources of TPHP, for example, as a FR in other formulations or applications or as a plasticizer.

HBCYD. HBCYD, the third most used BFR, is used mostly in polystyrene foams in building materials and consumer products.[35] It is being considered for addition to the list of Persistent Organic Pollutants (POPs) under the Stockholm Convention, which would substantially limit its production and use.[36] In 2010, the U.S. EPA released an Action Plan for HBCYD citing its wide use, presence in humans, bioaccumu-

lation potential, persistence, toxicity to aquatic organisms and concerns about reproductive, neurological and developmental effects in humans.[35] The Action Plan was followed by a proposed Significant New Use Rule (SNUR) for HBCYD in textiles, where it is often used to meet furniture flammability standards. The SNUR would limit HBCYD in U.S. furnishings.

We detected all HBCYD isomers (α-, β-, and γ-HBCYD) in all samples, and they were significantly correlated (tau = 0.4−0.8; $p < 0.05$) within each sampling round. Total HBCYD (sum of three isomers) concentrations were similar across time periods, ranging from 82 to 6800 ng/g (median 190 ng/g) in the 2006 samples and 39 to 1800 ng/g (median 160 ng/g) in 2011. It is unclear whether the phase-out of PentaBDE and OctaBDE mixtures influenced the pattern of HBCYD use. Median concentrations were similar to those reported for U.S. and Canadian samples, but less than for UK samples.[34,37] However, our maxima (2006: 6800 ng/g; 2011: 1800 ng/g) were substantially lower than those reported in Boston living room dust (130 200 ng/g) and UK samples (110 000 ng/g).[15,37] Commercial mixtures of HBCYD mainly consist of γ-HBCYD (75−89%), while α- and β-HBCYD are found at lower amounts.[38] However, we observed relative abundances of 45−50%, 40−45%, and approximately 10% for γ-, α-, and β-HBCYD, respectively. This is likely the result of thermal rearrangement at high temperatures in production and processing of HBCYD-added materials[39] or photolysis.[40] This raises cautions about using only source composition information and not evaluating fate and transport of chemicals in products to evaluate potential exposures.

Tetrabromobisphenol A. Tetrabromobisphenol A (TBBPA), the most commonly used BFR,[41] is employed as a reactive FR in circuit boards, plastics, paper and textiles as a plasticizer, in coatings and adhesives, and as an intermediate in the synthesis of other FRs.[42] It has been associated with effects on the immune system, reproductive and development effects, and neurotoxicity (see SI Table SI4 for details and references). TBBPA was detected in nearly all homes in both rounds with concentrations ranging from <10 to 3400 ng/g in 2006 and from 22 to 2000 ng/g in 2011 (Table 1). We found a significant association between concentration reductions and new electronics suggesting that new electronics contain less TBBPA (rho = −0.69; $p = 0.003$). Concentrations are higher (17−22× at median) than reported in European homes[43] and similar to Michigan offices.[44]

Other Brominated Flame Retardants. Dust samples were analyzed for 15 other BFRs. BTBPE, in production since the 1970s and now used to replace OctaBDE,[45] and DBDPE, introduced in mid-1980s and available as a replacement for DecaBDE,[45] were detected in nearly 100% of samples. The concentrations of BTBPE, which has limited toxicity data (see SI Table SI4), were similar between 2006 and 2011. In contrast, concentrations of DBDPE, structurally similar to BDE 209 and associated with reproductive and developmental toxicities,[46] were generally higher in 2011 (Table 1 and Figure 1), and two homes had substantial (>20-fold) increases.

Another commonly detected FR was the TBBPA derivative tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-BDBPE), which is being studied by the National Toxicology Program (NTP) because of the structural similarity with the carcinogenic TDBPP (brominated "Tris"). Levels of TBBPA-BDBPE appear fairly stable over time (Table 1 and Figure 1) and lower than levels reported in Belgium.[47]

Hexabromobenzene (HBB), an additive FR used in paper, wood, textiles, plastics and electronics, and not used in Europe,[45] was detected in 50% of 2006 samples and 31% of 2011 samples. octabromo-1,3,3-trimethyl-1-phenylindane was infrequently detected and one home had substantial (10-fold) reductions over the 5 years. Studies on exposures and health effects of these BFRs are limited.

Halogenated Organophosphate Flame Retardants. Chlorinated and brominated OPFRs have a long history of use in polyurethane foam and textiles and an equally long history of concerns about health effects, particularly cancer.

TDBPP or brominated "Tris" was banned from children's sleepwear in the U.S. in 1977 due to carcinogenicity concerns and detection of its mutagenic metabolite in children.[18] It is listed as a carcinogen in California's Proposition 65. It is reported to be used as a FR in polyurethane and polystyrene foams, acrylic furnishings, polyvinyl and phenolic resins, paints and lacquers, styrene-butadiene rubber, and latexes.[48] We detected TDBPP in 62% of 2006 samples and 38% of 2011 samples. As far as we know, this is the first report of TDBPP in house dust, although we previously detected its mutagenic metabolite, 2,3-dibromo-1-propanol, in about 10% of indoor air samples from Cape Cod, MA.[20] Dust concentrations were much lower in 2011 (mean 40 ng/g; maximum 310 ng/g) compared with 2006 (mean 1000 ng/g; maximum 8900 ng/g), though this may be due to whatever factor led to lower concentrations of legacy pollutants (see below).

We also detected three chlorinated OPFRs: TCEP, TCIPP, and TDCIPP (chlorinated "Tris"), which are used in polyurethane foams as replacements for PentaBDE. TDCIPP was voluntarily withdrawn from children's pajamas after metabolites 1,3-dichloro-2-propanone and 1,3-dichloro-2-propanol were found to be mutagenic.[49] The Consumer Product Safety Commission (CPSC) said TDCIPP was a potential hazard to consumers, based on cancer and noncancer end points.[50] The CPSC estimate of children's exposure from treated furniture was 5× higher than the agency's acceptable daily intake, with most of the exposure from inhalation of the chemicals volatilized from treated furniture. TDCIPP was the most commonly detected FR (36%) in a U.S. sample of child care products.[23] Our reported concentrations of TDCIPP comprise tris(1,3-dichloro-2-propyl) phosphate, which makes up approximately 90−95% of TDCIPP, and tris(2,3-dibromopropyl) phosphate. Both TCEP and TDCIPP are listed as carcinogens under California's Proposition 65. TCEP is slated to be banned from children's products in New York by 2014, and a bill is currently being considered that would expand the ban to TDCIPP.[51] TCIPP is structurally similar to TCEP.

Median concentrations of all chlorinated OPFRs were above 1,000 ng/g, or 1 μg/g, in both sampling rounds, and maxima were >100 000 ng/g or 0.01%, making these the most abundant FRs in this study (Table 1). Levels in some homes changed dramatically. For example, between 2006 and 2011, one home with a new roof installed between sampling rounds had 20-fold increase in TCEP concentration and another home with substantial remodeling had a 14-fold increase in TDCIPP. TCIPP means (2006 mean 1200 ng/g; 2011 mean 1700 ng/g) and medians increased (Table 1), suggesting an increase in use between 2006 and 2011. People who reported new furniture between sampling rounds showed increases in TCIPP concentrations (rho = 0.6; $p = 0.02$), suggesting that TCIPP is a PentaBDE replacement.[52]

Based on limited comparison data, concentrations of chlorinated OPFRs observed in this study are some of the highest in the world; only concentrations in Japan are consistently higher.[53] Generally lower levels have been reported for homes in Boston,[22] Belgium,[25] Spain,[54] Sweden,[55] and Germany,[56] except for higher TCIPP in Spain[54] and TDCIPP in Sweden.[55] The highest concentrations of chlorinated OPFRs were found in a study of 41 Japanese homes, which reported median concentrations 2- to 25-fold higher than seen in our California samples.[53] The levels in Japan are likely a result of a voluntary phase-out of PentaPBDE in the early 1990s.[57]

TDCIPP concentrations were correlated across sampling rounds (tau = 0.54). Concentrations of the chlorinated OPFRs are not correlated with each other, likely because TCIPP has been reported as a replacement for TCEP and is often used in the same types of products as TDCIPP, which is typically used only when a more efficient FR is needed, since it is more expensive.[52]

Nonhalogenated Organophosphate Flame Retardants. Nonhalogenated OPFRs are used as FRs and often as plasticizers. We analyzed eight nonhalogenated OPFRs. The highest concentrations were for TBOEP, used as FR as well as in antifoam agents, floor polish, lacquers, plastics, rubbers, and solvents.[52] It had the highest median concentration, 2-fold higher than the next highest, of any analyte (2006: 12 000 ng/g; 2011: 11 000 ng/g) and the highest concentration of any analyte in 2011 (170 000 ng/g). In addition to TBOEP, we detected EHDPP and TMPP (sum of four isomers)—used in hydraulic fluids and PVC—in all samples. TBOEP and TMPP generally decreased, whereas EHDPP concentrations generally increased between sampling events (Figure 1).

Concentrations of TBOEP were higher than in dust samples collected in Belgian and Spanish homes, although lower than Japanese homes (1 570 000 ng/g).[25,53,54] TMPP concentrations were higher than those found in Belgian homes.[25] Concentrations of several nonhalogenated OPFRs (TBOEP, TEP, TNBP, and TMPP) were correlated across sampling rounds (tau = 0.37−0.69), indicating that these compounds have temporal stability.

Dechlorane-Plus. Dechlorane-Plus (DP), a chlorinated FR, is used in electronics and is an alternative to DecaBDE. It is pervasive in the environment and has high potential for long-range transport.[58,59] DP, measured as two isomers (syn and anti), was detected in all of the homes, although levels were lower than other FRs in this study and may have decreased over time. Total DP concentrations were generally lower than those reported in Ottawa in 2002−2003 and 2007 samples,[60] whereas concentrations of individual isomers are comparable to those reported in Vancouver in 2007−2008.[34]

Legacy Chemicals (PCBs, PBBs, Chlordane, DDT). To evaluate whether our dust collection methods produced consistent results between the two sampling rounds, we analyzed samples for several legacy compounds that were banned years ago. These chemicals would not be introduced in new products between sampling rounds, though they could possibly increase or decrease with a change in an old item. Despite being banned for many years, legacy compounds were frequently detected. PCBs, chlordane, and DDT were detected in almost all homes, with DDT at the highest concentration (2006 median 530 ng/g; 2011 median 160 ng/g). Polybrominated biphenyls (PBBs) were infrequently detected except for congener BB 153, which was detected in about half of the homes. Concentrations of legacy chemicals were generally significantly correlated across sampling rounds, indicating that the rank order was consistent over 5 years. However, the average concentration ratio (2011/2006) was 0.8, which means that 2006 concentrations were generally higher than 2011 concentrations. This may be due to degradation or depletion. However, it may also be due to some unidentified but systematic difference in sample collection between the two sampling rounds, which could also influence results for other chemicals. For example, PentaBDE levels went down between 2006 and 2011, which may reflect decreasing use or may simply be due to the same factor causing decrease in legacy pollutant concentrations. In light of this, the Firemaster 550 increase may be underestimated. Two homes had substantial (10−30×) decreases in DDT and DDD; one of these homes had significant renovations between rounds, while no explanation was identified for the other home.

Co-Occurrence of Flame Retardants. We were interested in learning which FRs co-occurred, suggesting common sources, so we conducted correlation analysis for analytes within each sampling round (SI Figure SI4), and also used these correlation estimates in cluster analysis to visualize relationships (SI Figure SI5). As expected, many compounds known to co-occur in commercial formulations were correlated in both rounds. We saw strong correlations for: PBDE congeners comprising the PentaBDE and OctaBDE mixtures, DDT and its breakdown products, the legacy pesticides *cis*- and *trans*-chlordane and *trans*-nonachlor, PCB 153 and PCB 180, and the DP isomers. Interestingly, the brominated Firemaster 550 chemicals, EH-TBB and BEH-TEBP, were also clustered consistently, but the third Firemaster 550 constituent, TPHP, did not cluster with them, suggesting other sources. TPHP was correlated with TDCIPP and PentaBDE congeners in 2006 samples. TPHP has reportedly been used in the PentaBDE commercial mixture.[52]

Limitations. As far as we know, this is the first study to analyze for such a broad range of FRs in house dust and to analyze samples collected in the same home at two different time periods. This design allowed us to evaluate time trends in concentrations; however, rigorous longitudinal analysis was not possible due to the small sample size (n = 16 pairs). The sample size also limits assessment of generalizability of our findings. Since our study began in 2006, we did not fully capture the effects of the 2004 PBDE phase-out, and although many participants reported some changes in their homes over the 5 year period, larger differences in FR concentration might be seen in a longer study. We observed differences in concentrations in many homes that reported acquiring furniture, carpets, and electronics; however, our ability to link chemical concentrations with characteristics of products and residences was limited, because our questionnaire relied on residents' recollections. Residents may have introduced additional chemical sources that were not identified by our questionnaire, removed major sources without replacing them with new items, or failed to report on changes that we did ask about. These limitations raise cautions about relying on questionnaires to classify FR exposures. Finally, while our analyte list is extensive, it is not exhaustive. There are probably additional FRs used in consumer products that are not included because they have not been disclosed by manufacturers.

FR Burden in California Homes. We found that PBDEs; components of Firemaster 550; other BFRs, such as HBCYD, TBBPA, BTBPE, DBDPE; and OPFRs, including the carcinogenic TCEP and TDCIPP, were abundant and

commonly detected, and we hypothesize that they are likely to be found in nearly all California homes. In our study, the levels of individual FRs in dust exceeded 0.01%, with a cumulative level of all FRs almost 0.03% in one home. Such concentration of FRs in dust is expected to lead to 30 μg/day FR ingestion in a typical child. The average total load of FRs in house dust was approximately 80−90 μg/g.

For six chemicals, dust concentrations exceeded risk-based screening levels for residential soil[60] in at least one of the homes, indicating exposure is potentially of health concern. Specifically, concentrations of BDE 47, BDE 99, TCEP, TDCIPP, BB 153, and DDT exceed screening levels, with 13 of 16 homes exceeding at least one chemical screening level in either sampling round. Exposure pathways for residential soil are similar to house dust. Screening levels provided in the SI.

Our previous work showed that elevated PentaBDE levels in California house dust and serum are likely the result of the state's unique furniture flammability standard.[1] The present study shows California homes still have higher levels of PentaBDEs than the rest of the world and that California also has some of the highest concentrations of halogenated OPFRs, which are also used in furniture foam. The only location with consistently higher OPFR concentrations is Japan, where the elevated OPFRs levels are likely due to the early phase-out of PentaBDE almost 20 years ago.[57] OPFR levels in Japan may foreshadow levels in California.

We also observed that Firemaster 550 concentrations are increasing in California homes, suggesting that Firemaster 550 is being used as a replacement for PentaBDE, which was phased-out in 2004, shortly before our first sample collection. Continued monitoring in California and other locations is warranted because we anticipate levels will continue to increase unless manufacturing practices change.

Policy Implications. Following the phase-out of PBDEs due to health concerns, other FRs with considerable evidence of toxicity appear to remain at high or increasing levels of use. Some FRs appear to be replaced by less-studied chemicals whose health implications are unknown. Chlorinated OPFRs, some of the most abundant FRs in our study, continue to be used despite evidence of carcinogenicity, listing as carcinogens under California's Proposition 65 and IARC, and structural similarity to brominated "Tris" (TDBPP), which was banned in children's sleepwear in 1977. Despite this ban, we detected TDBPP in approximately half of the homes. We detected HBCYD in all homes, even though it has been identified under Europe's REACH program as a Substance of Very High Concern and the U.S. EPA initiated a SNUR to limit its use citing its bioaccumulation potential, persistence, toxicity to aquatic organisms and concerns about human reproductive, neurological, and developmental effects. Publicly available health and toxicity information for the PBDE replacements, such as Firemaster 550 and BTBPE, is very limited. The continued use of FRs with established health concerns and introduction of replacement FRs with limited data highlights the need to modernize U.S. chemical policies to require more complete disclosure and safety testing of consumer product chemicals prior to sale.

■ ASSOCIATED CONTENT

Supporting Information

Specific details for analytical protocols, quality control (including results from interlaboratory tests), correlation/cluster analysis, and screening levels are in Supporting Information. Detailed use and health information for FRs, including references, is presented in Table SI4. Home-specific concentrations (Figure SI3), Kendall's tau correlation estimates (Figure SI4) and cluster analysis dendrograms (Figure SI5) are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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