Flame Retardant Transfers from U.S. Households (Dust and Laundry Wastewater) to the Aquatic Environment

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Ⓢ Supporting Information

ABSTRACT: Levels of flame retardants in house dust and a transport pathway from homes to the outdoor environment were investigated in communities near the Columbia River in Washington state (WA). Residential house dust and laundry wastewater were collected from 20 homes in Vancouver and Longview, WA and analyzed for a suite of flame retardants to test the hypothesis that dust collecting on clothing and transferring to laundry water is a source of flame retardants to wastewater treatment plants (WWTPs) and subsequently to waterways. Influent and effluent from two WWTPs servicing these communities were also analyzed for flame retardants. A total of 21 compounds were detected in house dust, including polybrominated diphenyl ethers (PBDEs), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB or EH-TBB), bis(2-ethylhexyl) 3,4,5,6-tetrabromophthalate (TBPH), 1,2-bis(2,4,6,-tribromophenoxy)ethane (BTBPE) and decabromodiphenylethane (DBDPE), hexabromocyclododecane (HBCD or HBCDD), tetrabromobisphenol A (TBBPA), and three chlorinated organophosphate flame retardants (ClOPFRs), tris(1,3-dichloro-2-propyl)phosphate (TDCPP or TDCIPP), tris(1-chloro-2-propyl)phosphate (TCPP or TCIPP), and tris(2-chloroethyl)phosphate (TCEP). Levels ranged from 3.6 to 82,700 ng g^{-1} (dry weight). Of the 21 compounds detected in dust, 18 were also detected in laundry wastewater. Levels ranged from 47.1 to 561,000 ng L^{-1}. ClOPFRs were present at the highest concentrations in both dust and laundry wastewater, making up 72% of total flame retardant mass in dust and 92% in laundry wastewater. Comparison of flame retardant levels in WWTP influents to estimates based on laundry wastewater levels indicated that laundry wastewater may be the primary source to these WWTPs. Mass loadings to the Columbia River from each treatment plant were by far the highest for the ClOPFRs and ranged up to 114 kg/yr for TCPP.

INTRODUCTION

The global use of flame retardants (FRs) in consumer and building products, including in polyurethane foam items such as couch cushions, in plastics such as television housings, in electronics, and in building materials including insulation, has led to their accumulation throughout the environment.[1−3] With the exception of known discharges from manufacturing, recycling, and wastewater treatment, the mechanisms by which FRs are transported from indoor to outdoor environments are poorly understood.[4,5] FRs have been detected in air, water, sediments, surface films, and tree bark, indicating that once released from associated materials, they can enter the environment through multiple pathways.[6−9] A recent report detected a broad suite of 62 FRs in indoor dust, and several reports have detected many of these compounds on surface wipes, hands, hair, and in clothes dryer lint, indicating their mobility within the indoor environment.[2,10−12] Incidental ingestion of dust is believed to be a significant pathway for human exposure to FRs. In addition to detections in humans, including in breast milk, adipose tissue, and serum, a number of

FRs have been detected in shell- and finfish and marine mammals including orcas, indicating their potential to accumulate in the aquatic environment.[13,14] Some FRs have been linked to toxic effects including cancer, hormone disruption, neurotoxicity, and reproductive impacts.[3,15]

Because of their heavy use in polyurethane foam as well as in household plastics, polybrominated diphenyl ethers (PBDEs) were the dominant FR analyzed in U.S. household dust until recently.[1,16] Industry ended U.S. production of the penta formulation of PBDEs at the end of 2004 and sales of the deca-BDE formulation at the end of 2013.[17,18] Recent tests of foam-containing products and of dust in U.S. homes indicate increased use of chlorinated organophosphate flame retardants (ClOPFRs) such as tris(1,3-dichloro-2-propyl)phosphate (TDCPP) and tris(1-chloro-2-propyl)phosphate (TCPP), as

well as components of the FR Firemaster 550 (Chemtura, PA, USA): triphenyl phosphate (TPP), bis(2-ethylhexyl) 3,4,5,6-tetrabromophthalate (TBPH), and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB).[2,19] Other FRs known to be found extensively in consumer and building products include tetrabromobisphenol A (TBBPA), used in electronics, and hexabromocyclododecane (HBCD), used primarily in insulation and to a lesser extent on textiles.[20,21] Due to growing environmental and human health concerns, the U.S. Environmental Protection Agency (USEPA) is now evaluating these and 13 other FRs under the Toxic Substances Control Act.[22]

PBDEs were phased out largely because of their ability to persist in the environment and build up in the food chain along with evidence of toxicity.[23] In the Columbia River, USA and Canada, PBDEs have been detected in the bodies and stomach contents of juvenile salmon, with the highest concentrations in more industrialized areas of the lower Columbia.[24] Some FRs such as HBCD share PBDEs' characteristic as persistent bioaccumulative compounds.[3] These hydrophobic compounds partition preferentially to sewage sludge, with more than 90% of PBDEs in wastewater treatment found in sludge.[25,26] Others, such as ClOPFRs, are more hydrophilic and pass through WWTPs, partitioning to effluent rather than sludge.[15] A U.S. Geological Survey study found two ClOPFRs (TCEP and TDCPP) in effluent from each of nine WWTPs discharging into the Columbia River at levels ranging from 120 to 690 ng L^{-1}.[27] No data have been published on levels of ClOPFRs in Columbia River surface water. However, Kolpin et al. found TCEP in 58% of 85 U.S. streams sampled in 1999 and 2000, at a median level of 100 ng L^{-1}.[28] European studies have also investigated ClOPFRs in surface water: TCEP, TDCPP, and TCPP were detected in urban and rural surface waters in Germany.[29,30] ClOPFRs have been detected in biota including mollusks, fish, birds, and bird eggs.[15,31]

This study tested the hypothesis that clothing, and the dust it carries, creates a pathway for chemicals used in household products to travel to waterways. In this pathway, chemicals such as FRs escape from household products and accumulate in house dust and on clothing. When that clothing is washed, the FRs and/or particulate matter including FRs enter laundry wastewater and make their way to wastewater treatment facilities. Depending on the chemical, a certain percentage of the load survives treatment and is then discharged to a waterway. This study focused on homes associated with treatment plants in Washington state (WA), USA, that discharge to the lower Columbia River.

■ EXPERIMENTAL SECTION

A convenience sample of 20 households in Longview and Vancouver, WA was recruited via newsletters, electronic mailing lists, local businesses, and organizations. Researchers visited homes to collect dust and laundry wastewater in 2011 and 2012. The homes sampled were all single family homes, 90% in suburban and 10% in rural areas.

Dust was collected using a Eureka Mighty-Mite (model 3670G) vacuum fitted with a cellulose filter (Whatman 2800-199) held in the crevice tool with a stainless steel ring.[16] Researchers collected dust from primary living areas including kitchen, living room, bedroom, office, and dining room by moving the crevice tool slowly across bare floor and carpet. A sample of sodium sulfate was collected in the same manner from a clean surface in place of a field blank; no FRs were detected (>1 ng g^{-1}) in this sample.[11]

Participants prepared a full load of laundry to primarily include clothing worn around the house, with type and number of items tracked (i.e., pajamas, jeans; none appeared to be specialty FR-treated work clothes). The home washing machine was used to wash the clothing using Natural 2X Concentrated Liquid Laundry Detergent (Seventh Generation, Burlington, VT, USA) and warm water (detergent was separately analyzed for FRs and none were detected). Samples (1 L) of the laundry wastewater were collected in amber glass bottles at the end of the agitation cycle, placed on dry ice in the field, and stored at <4 °C until analyzed. Blank water samples were collected prior to addition of clothing and detergent.

A single grab sample (1 L) of influent and effluent was collected in amber glass bottles from the Three Rivers Regional Wastewater Treatment Plant in Longview, WA, and the Marine Park Wastewater Treatment Plant in Vancouver, WA. Collection of influent and effluent was timed so effluent was collected after the estimated residence time, collecting a "plug" before and after treatment. Samples were stored on dry ice until placement in a freezer (<4 °C).

Analysis of the Brominated FRs (BFRs). PBDEs (BDE-28, -47, -66, -85, -99, -100, -153, -154, -183, -206, -209), alternative-BFRs (alt-BFRs: BTBPE, DBDPE, TBB and TBPH), and HBCD isomers (α-, β-, γ-HBCD) by ultra-performance liquid chromatography (UPLC)-atmospheric pressure photoionization (APPI) tandem mass spectrometry (MS/MS) described by La Guardia et al.[32] was modified for this study to include TBBPA and the ClOPFRs (TCEP, TCPP, and TDCPP).[32] (Targeted analyte names, acronyms, and chemical formulas are listed in Supporting Information, Table S1, along with methodology and instrument setting.) Briefly, ~1 g (dry weight) sieved (300 μm) dust sample was subjected to accelerated solvent extraction (ASE 200, Dionex, Sunnyvale, CA, USA) with dichloromethane (DCM). Surrogate standards (200 ng of 2,3,4,4',5,6-hexabromodiphenyl ether (BDE-166); Cambridge Isotope Laboratories, Inc., Andover, MA, USA and 1000 ng of deuterated triphenyl phosphate (d_{15}-TPP); Sigma-Aldrich, St. Louis, MO, USA) were added to each sample prior to extraction. Extracts were purified by size exclusion chromatography (SEC, Envirosep-ABC, 350 mm × 21.1 mm. column; Phenomenex, Torrance, CA, USA). Each post-SEC extract was solvent exchanged to hexane, reduced in volume, and added to the top of a solid phase extraction (SPE) glass column containing 2 g of silica (Isolute, International Sorbent Tech.; Hengoed Mid Glamorgan, U.K.). Each column was eluted with 3.5 mL hexane (fraction one), followed by 6.5 mL of 60:40 hexane/DCM, 8 mL DCM (fraction two), and 5 mL 50:50 acetone/DCM (fraction three). The second fraction, containing PBDEs, alt-BFRs, and HBCD, and the third fraction, containing ClOPFRs and TBBPA, were reduced and solvent exchanged to methanol, and the internal standard decachlorodiphenyl ether (DCDE, 400 ng; Ultra Scientific, North Kingston, RI, USA) was added to both fractions prior to UPLC-APPI-MS/MS analysis.

FR Liquid Determination (Laundry Wastewater, WWTP Influent and Effluent). Each sample (~1 L) was liquid/liquid extracted three times with DCM, 200 mL total. Surrogate standards (200 ng BDE-166 and 1000 ng d_{15}-TPP) were added prior to extraction. The three extracts were combined, solvent exchanged to hexane, and reduced in volume (<1 mL). Post-extracts were purified by SPE, as noted for the dust samples. Internal standard (DCDE, 400 ng) was added to
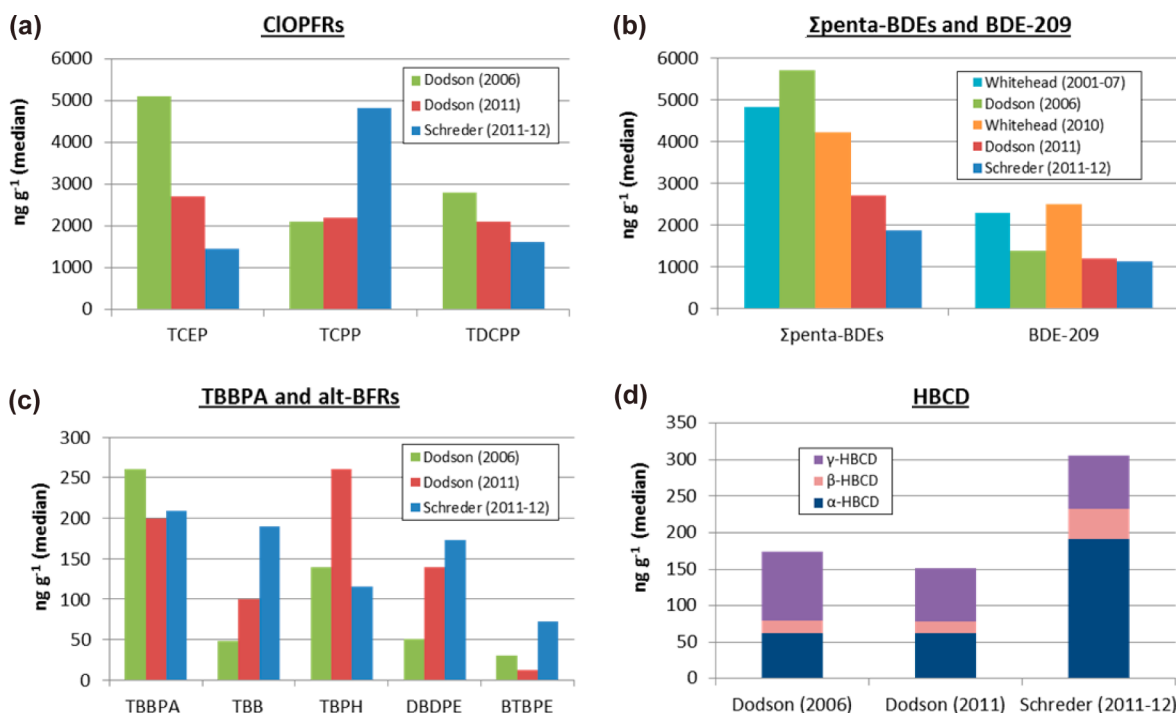
Figure 1. (a−d) Household dust flame retardant median concentrations (ng g^{-1}, dry weight) and comparison results from previous studies. (Sample collection dates).

each SPE fraction (two and three), and these were analyzed for BFRs and ClOPFRs by UPLC- APPI-MS/MS.

Analytes in purified extracts were chromatographically separated by UPLC (Acquity UPLC, Waters Corporation, Milford, MA, USA) operated in gradient mode (100% methanol (A1) and 100% water (B1)), equipped with a C18 UPLC analytical column (Acquity UPLC BEH C18, 1.7 μm, 2.1 mm × 150 mm, Waters Corp.). Analytes were ionized by APPI; dopant (acetone) was introduced (150 μL/min) by a liquid chromatography pump (LC-20AD, Shimadzu Corporation, Kyoto, Japan). Product and transition ions were detected by triple quadrupole mass spectrometer (3200 QTrap, AB Sciex, Framingham, MA, USA) operated in the multiple reaction monitoring (MRM) mode. Quantitation ions for BFRs (mass to charge ratio, m/z) were m/z 79 ($[^{79}Br]^{-}$) and 81($[^{81}Br]^{-}$), and m/z 35 ($[^{35}Cl]^{-}$), 37($[^{37}Cl]^{-}$) for ClOPFRs and DCDE. Positive ions m/z 342 and 343 were monitored for d_{15}-TPP quantitation. (Additional sample preparation and UPLC-APPI-MS/MS operating conditions can be found in Supporting Information).

Method validation was established by performance-based QA/QC including method blanks, surrogate, duplicate, and matrix spike analysis. (Surrogate recoveries are listed with the sample results in Supplementary Tables S3, S5, S7, and S8). A National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) #2585 (house dust) was also analyzed; SRM #2585 mean % recoveries for $\sum$PBDEs, $\sum$alt-BFRs, $\sum$HBCDs, $\sum$ClOPFRs, and TBBPA range 50−91%; individual recoveries range 38−143%, Supplementary Table S10). In laboratory blanks, FRs were not observed above detection limits (>1 ng g^{-1}) in the first batch (samples 01 to 09). However, trace amounts of TBB (4.2 ng g^{-1}), TBPH (7.7 ng g^{-1}), and TDCPP (16 ng g^{-1}) were detected in the blank of the second batch. These amounts were subtracted from results 10−20 for TBB and TBPH, as they were >10% of the lowest

detections (Quality assurance procedures including duplicate and matrix spike results can be found in Supporting Information, results in Supplementary Table S9).

RESULTS AND DISCUSSION

Household Dust and Laundry Wastewater. Levels of FRs in household dust were obtained for 20 homes. A total of 21 FRs were detected; 16 were detected in 95% or more of the homes. Laundry wastewater was also obtained from 19 of these homes (one sample was lost during storage), and of the 21 compounds detected in dust, 18 were also detected in laundry wastewater. Whereas the FR contribution to dust was dominated by the three ClOPFRs, which contributed 72% of the total (followed by $\sum$PBDEs 19%, TBBPA 3.7%, $\sum$alt-BFRs 2.9%, and $\sum$HBCDs 2.5%), ClOPFRs were even more dominant in laundry wastewater, at 92% of the total (followed by BDE-47 at 2.5% and BDE-99 at 2.0%). This shift can be attributed to these compounds' hydrophilic nature together with higher solubility and lower partitioning coefficients compared to other targeted FRs (see Supplementary Table S1 for log K_{ow} values). Each of the three ClOPFRs, two PBDE congeners (BDE-47 and -209), TBB, and TBPH were detected in 100% of laundry wastewater samples; other compounds detected included seven additional PBDE congeners, BTBPE, DBDPE, and HBCDs. TBBPA was not detected (>1 ng L^{-1}) in laundry wastewater samples. Dust results are presented in Figure 1, and composition of PBDEs and ClOPFRs in dust and laundry wastewater is presented in Figure 2.

Laundry wastewater field blanks were collected from 14 of the 20 homes. Of the 22 analytes, TCEP (sample 8), TCPP (samples 3, 8, and 18), and BDE-209 were detected in blanks, but only BDE-209 was detected at levels >10% of the corresponding laundry wastewater sample, in three blanks at 18%, 12%, and 21%. These values were subtracted from the laundry wastewater analysis values for samples 8, 9, and 10. No
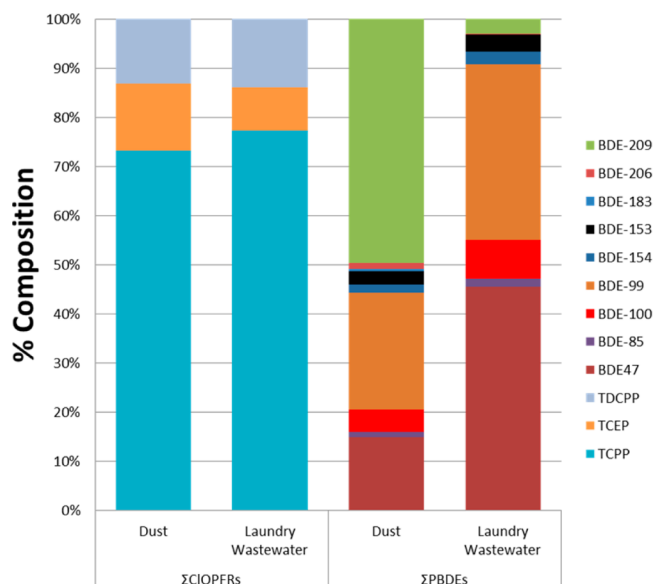
Figure 2. ClOPFRs and PBDEs in dust and laundry wastewater, percent composition (mean).

analytes were detected in the surrogate field blank. Individual dust and corresponding laundry wastewater results by home and analyte are listed in the Supporting Information, Supplementary Tables S3–6.

Chlorinated Organophosphate Flame Retardants (ClOPFRs). TCPP and TDCPP were detected in all dust samples, and TCEP was detected in 95% of homes (ClOPFRs dust results were obtained for 19 of the 20 homes due to analytical issues). According to USEPA's 2012 Chemical Data Reporting (CDR), 4,500–22,700 tons/year of TDCPP were manufactured or imported into the U.S. in 2010 and 2011; TCPP was reported at 25,000 tons/year. According to the CDR, TDCPP production has changed little since 1998; TCPP volumes appear to have risen since 2006.[15,33] However, ICL Industrial Products, a major U.S. producer of TDCPP, announced in 2012 that it would cease production of TDCPP in 2015.[34] TCEP production fell between 2006 and 2012, but TCEP was also found at a level of 14% in the FR Antiblaze V6 (2,2-bis(chloromethyl)propane-1,3-diyl tetrakis-(2-chloroethyl)bis(phosphate) (Albemarle, Baton Rouge, LA).[35] This product is primarily in automobile foam, with production dating back to 1990 but levels not reported to CDR for 2006 or 2012.[35]

Of the 22 targeted FRs, TCPP was present in dust at the highest level of any single chemical with a median level of 4,820 ng g^{-1} and a maximum of 82,700 ng g^{-1}. The primary use of TCPP in homes is likely in polyurethane and polyisocyanate insulation, and it has been found in the foam of some children's products such as car seats and changing pads.[36–39] TDCPP, in dust samples at a median level of 1,620 ng g^{-1}, has recently been widely found in furniture foam as well as in children's products, although its use in children's sleepwear was withdrawn in 1977 due to its mutagenicity.[1,40,41] The median dust level of TCEP (1,380 ng g^{-1}) was similar to that of TDCPP. Median levels of TDCPP and TCEP were about half of those reported in a 2011 California dust study by Dodson et al., while TCPP levels were about twice as high as in the California samples (Figure 1a).[2] Dodson et al. sampled the same homes in 2006 (median levels 2,800, 5,100 and 2,100 ng

g^{-1} for TDCPP, TCEP and TCPP, respectively), suggesting a decline for TDCPP and TCEP but a rise in TCPP exposure (Figure 1a).

ClOPFRs were the FRs found at the highest levels in laundry wastewater, and all three were detected in laundry wastewater from every home. As with household dust, TCPP was found at the highest levels, with a maximum of 561,000 ng L^{-1} and a median value of 43,500 ng L^{-1}, followed by TDCPP with a maximum of 65,600 ng L^{-1} and a median value of 13,500 ng L^{-1}, and TCEP, with a maximum of 42,800 ng L^{-1} and median value of 7,680 ng L^{-1}. The contribution of the individual ClOPFRs to mean $\sum$ClOPFRs was similar in dust and laundry wastewater, with TCPP contributing 73% and 77%, respectively, followed by TCEP (14% and 9%) and TDCPP (13% and 14%) (Figure 2). The similarity in profiles in dust and laundry wastewater may indicate that once released to the indoor environment, these ClOPFRs have equal ability to collect on clothing via dust and/or air. Clothing may then be acting as a quasi-passive sampler, as previously suggested in several FR studies of clothes dryer lint, transferring FRs, particularly those that are more hydrophilic or water-soluble, to wastewater when washed.[10,11,42] TCPP was also the most abundant ClOPFR observed in several indoor passive air sampler studies.[43]

Polybrominated Diphenyl Ethers (PBDEs). After the ClOPFRs, PBDEs were the next highest in dust samples ($n = 20$): $\sum$PBDEs ranged from 311 to 19,700 ng g^{-1}. BDE 209 was the dominant congener in most samples. Total PBDE levels were similar to those in 50 Boston homes sampled between 2002 and 2008 and those observed by Dodson et al. in 2011.[2,44] The median level of the penta-BDE formulation, which includes congeners with 4–6 bromines, was about one-third that of the 2006 samples tested by Dodson et al. (Figure 1b). A larger study of 292 California dust samples collected between 2001 and 2007 and then again in 2010, however, reported little change in concentration (Figure 1b).[45]

The median level of BDE-209 (1140 ng g^{-1}), the major PBDE in the deca formulation, was consistent with the 2006 and 2011 Dodson et al. report (1,400 and 1,200 ng g^{-1}, respectively) and about half of levels reported in the larger California study, 2,300 and 2,500 ng g^{-1} for 2001–07 and 2010, respectively (Figure 1b).[2,45]

Two PBDE congeners, BDE-47 and BDE-209, were detected in laundry wastewater from every home, with median levels of 1,230 ng L^{-1} for BDE-47 and 140 ng L^{-1} for BDE-209. $\sum$PBDEs were detected in laundry wastewater at a median level of 2,550 ng L^{-1}. Unlike the ClOPFR profiles, the PBDE dust and laundry wastewater profiles were disproportional. The dust profile favored the higher brominated, lipophilic PBDE congener BDE-209, used primarily in television and electronics casings, making up 50% of the mean $\sum$PBDEs (Figure 2). The laundry wastewater profile, however, favored the lower brominated, less lipophilic congeners of the penta formulation, particularly BDE-47 and -99, which contributed 46% and 36% of the mean, respectively. The penta formulation was used primarily in polyurethane foam, which can degrade and produce low-density fragments.[46] These penta-BDE-containing particulates may then become airborne, explaining the dominance of penta-BDE congeners reported in passive sampling of indoor air.[47–49] This may also explain their accumulation on clothing, whereas BDE-209 has been observed to reside primarily in settled dust.[48,49]

Tetrabromobisphenol A (TBBPA). TBBPA is used primarily as a reactive FR (i.e., chemically bound to the polymer) in

printed circuit boards, with approximately 18% used as an additive FR (no chemical bond) in acrylonitrile butadiene styrene (ABS) resins and possibly in high impact polystyrene (HIPS).[21,50] TBBPA was detected in 95% of dust samples ($n = 19$), with a median level of 209 ng g^{-1}. Levels were highly variable, with the maximum detection (6560 ng g^{-1}) exceeding those of BDE-47 (2600 ng g^{-1}) and -99 (5810 ng g^{-1}) and several other FRs in the dust samples. Dodson et al. also detected TBBPA in 100% of their 2011 and 94% of 2006 dust samples.[2] Median levels were similar to our 2012 samples, at 200 ng g^{-1} in the 2011 samples and 260 ng g^{-1} in the 2006 samples (Figure 1c). TBBPA is considered the most heavily used brominated FR, making up 59% of the total 2001 market, with U.S. imports and production nearly tripling over the past 11 years (to 53,450 tons in 2012).[33,51] Despite its high usage and 95% detection rate in the dust samples, TBBPA was not detected in the laundry water samples. This may be explained by the Abdallah et al. observation, with a modified passive air sampler collecting both gaseous and particulate phases. They detected TBBPA at levels approaching those of BDE-47, but only in the particulate phase, whereas the lower brominated BDEs as well as HBCD were detected in both particulate and gaseous phases.[47] Batterman et al. also detected TBBPA in 90% of office dust samples, but only in 30% of office air samples.[48] This may be related to TBBPA's lower vapor pressure, compared to PBDEs and HBCD, as well as product usage: since its primary use is reactive, the chemical bond may restrict its mobility once incorporated into products.

Alternative Brominated Flame Retardants (TBB, TBPH, DBDPE, and BTBPE). TBB and TBPH were detected in each of the dust samples ($n = 20$), a detection rate nearly double that of a 2002−2007 study of Boston homes.[1] Median levels of TBB and TBPH, 190 and 115 ng g^{-1}, respectively, were similar to those in the 2011 California samples taken by Dodson et al., but the maximum levels were much higher in the California study (for TBB, 5900 compared to 1430 ng g^{-1}, and for TBPH, 3800 compared to 435 ng g^{-1}) (Figure 1c). TBB and TBPH are components of Chemtura products Firemaster 550 and BZ-54, used in polyurethane foam; another Chemtura product, DP-45, is used in PVC plastic and other applications and contains TBPH.[52−54] TBB and TBPH were also detected in 100% of laundry wastewater samples. Median concentrations were 363 ng L^{-1} for TBB and 445 ng L^{-1} for TBPH. The TBB-related fraction (f_{tbb}) of the total concentration of TBB plus TBPH (f_{tbb} = TBB/(TBB + TBPH) was lower in the laundry wastewater ($f_{tbb} = 0.45$) than in the dust samples ($f_{tbb} = 0.69$) but similar to that observed in the air over the Great Lakes, which ranged from 0.26 to 0.54, possibly indicating that TBB and TBPH on clothing are associated with air levels.[52]

A 2012 study of 102 couch foam samples collected from U.S. households found these FRs in 13 samples, primarily from couches purchased after the penta-BDE phaseout.[19] Three studies tested foam from children's products and found TBB and TBPH in 17% of 101 items currently in use in 2011, in 5% of 20 products newly purchased in 2011, and in 52% of products newly purchased in 2013, indicating this combination is becoming one of the primary replacements for penta-BDE in children's products.[36,37,55]

DBDPE, structurally similar to BDE-209, has been marketed as the replacement for the deca-BDE formulation used as an additive FR in HIPS, ABS, and polypropylene plastics and in textiles.[56] Its 2012 U.S. production volume was reported at 22,700−45,400 tons.[33] DBDPE was detected in house dust from all homes sampled (range 18−490 ng g^{-1}, median 173 ng g^{-1}), in the same range as for TBB and TBPH. Dodson et al. also detected DBDPE in all samples, with median values nearly tripling between 2006 and 2011 (from 51 to 140 ng g^{-1}) (Figure 1c).[2] BTBPE, another PBDE replacement product (for octa-BDE), was first introduced in the 1970s and is now used in ABS, HIPS, thermoplastics, thermoset resins, polycarbonate, and coatings.[56] Its metabolism may yield the neurotoxic compound tribromophenol.[57] BTBPE was detected in 80% of the dust samples, with a range of <1 to 361 ng g^{-1}, somewhat higher than levels observed by Dodson et al., which ranged from 3 to 130 ng g^{-1}.[2]

Although both DBDPE and BTBPE compounds were found in household dust from 80% or more of homes and DBDPE was detected in 74% of laundry wastewater samples, BTBPE was detected in only 5% of the samples. Median levels of DBDPE in dust were approximately twice those of BTBPE. A Swedish dust and air study of five households detected BTBPE in each dust sample and DBDPE in four but detected DBDPE in only one air sample.[49]

Hexabromocyclododecane (HBCD). The three isomers of HBCD (α-, β-, and γ-HBCD) were detected in 95% of dust samples, at levels approximately 1 order of magnitude lower than PBDEs or ClOPFRs, but higher than other FRs. $\sum$HBCD concentrations ranged from <1 to 3160 ng g^{-1}, with a median concentration of 300 ng g^{-1}, nearly double the Dodson et al. median values of 190 ng g^{-1} (2006) and 160 ng g^{-1} (2011) (Figure 1d).[2] In the California study, the dominant diastereomer detected was γ-HBCD, with median levels 49% and 46% of median $\sum$HBCD in 2006 and 2011, respectively; in our samples, α-HBCD dominated (64% of $\sum$HBCD) (Figure 1d). The technical product is dominated by the γ-isomer (>90%), but enrichment to α-HBCD occurs following exposure of HBCD-treated thermoplastics and textiles to elevated temperatures (>160 °C), which can occur during product manufacturing or through biotransformation.[5,58] The primary uses of HBCD in the home are likely in expanded and extruded polystyrene foam insulation (EPS and XPS) and to a lesser extent on upholstery textiles.[20] A signficant shift from γ- to α-HBCD in dust samples has been observed after exposure to natural light.[59] Also, spatial variability can affect isomer profiles, with decreasing γ-HBCD and increasing α-HBCD concentrations with distance from HBCD-containing products.[60] Therefore, collection techniques and light exposure may have contributed to profile variability between these studies.

HBCDs were detected in only 26% of laundry wastewater samples, with $\sum$HBCD levels ranging from <1 to 1,270 ng L^{-1}. The stereoisomer profile of one laundry wastewater sample was dominated by the γ isomer, contributing 80% to $\sum$HBCD in that sample (Home 4, Supplementary Table S6). This was considered an outlier, and when it was removed from the data set, we observed similar isomer profiles in dust and laundry wastewater, with α-HBCD contributing 69% and 63% to mean $\sum$HBCD, respectively.

HBCD has been added to the Stockholm Convention on persistent organic pollutants because of its persistence, bioaccumulation, and toxicity, with phaseout under the Stockholm Convention beginning in 2014.[61,62] The United States is not a party to the Convention, but the USEPA initiated an action plan on HBCD in 2010 and recently released a draft Alternatives Assessment.[63]
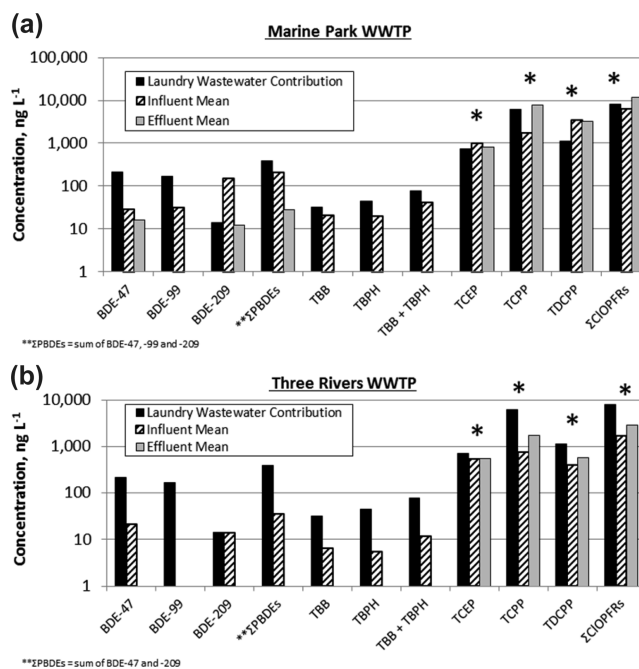
Wastewater Treatment Plants. To evaluate laundry wastewater contributions of FRs to the aquatic environment,

influent and effluent were collected from two WWTPs, Marine Park and Three Rivers, WA, and analyzed for FRs. These WWTPs serve predominantly households (>80%), with some industry discharges, none of which are known FRs dischargers, and service the communities where the dust and laundry wastewater samples were collected. Both utilize activated sludge treatment and process approximately 10 million gallons per day. Three PBDE congeners ($\sum_3$PBDE: BDE-47, -99, and -209), TBB, TBPH, DBDPE, and three ClOPFRs (TCEP, TCPP, and TDCPP) were detected in influents. The ClOPFRs were present at by far the highest levels, with mean influent levels of individual compounds ranging from 393 to 3,440 ng L^{-1}; $\sum$ClOPFRs were 6,140 ng L^{-1} at Marine Park and 1,680 ng L^{-1} at Three Rivers. $\sum_3$PBDEs were detected in influent at 206 ng L^{-1} at Marine Park and 35.0 ng L^{-1} at Three Rivers. In effluent, two PBDEs ($\sum_2$PBDE: BDE-47 and -209), TCEP, TCPP, and TDCPP were detected. Effluent $\sum_2$PBDE levels were 28.2 ng L^{-1} at Marine Park and below detection at Three Rivers. Effluent $\sum$ClOPFRs were 11,800 ng L^{-1} at Marine Park and 2,900 ng L^{-1} at Three Rivers (Supplementary Tables S7 and S8).

These levels of ClOPFRs are somewhat higher than those found by the USGS at nine WWTPs discharging to the Columbia River in 2008−09. TCEP in those effluents ranged from 160 to 650 ng L^{-1}, compared to our results of 814 and 563 ng L^{-1} at Marine Park and Three Rivers, respectively (Supplementary Tables S7 and S8). TDCPP in USGS samples ranged from 120 to 690 ng L^{-1}, compared to our results of 3,250 and 579 ng L^{-1} (Supplementary Tables S7 and S8). The USGS study did not include TCPP, but it was measured in WWTP effluents and surface water of the Rhine Valley in Germany.[30] Effluent levels of ClOPFRs in that study typically ranged from 5 to 400 ng L^{-1}, with TCPP at the highest concentrations, and surface water samples varied from 13 to 310 ng L^{-1}, with TCPP again at the highest concentrations. TCEP and TCPP were also detected along California's San Francisco Bay and the Southern California Bight, with mean concentrations of 410 and 7.6 ng L^{-1}, respectively.[64] Indicating resilience to treatment, these ClOPFRs were also detected in the source water and finished drinking water of eight U.S. water utilities, with median drinking water concentrations of TCEP and TCPP at 120 and 210 ng L^{-1}, respectively.[65]

PBDE concentrations were substantially lower in effluent than in influent; previous studies indicate that PBDEs partition primarily to sewage sludge.[26] No PBDEs were detected in the effluent from the Three Rivers plant, and the Marine Park plant showed an 86% removal rate (Figure 3; Supplementary Table S7). High removal rates (100%) were also observed for TBB, TBPH, and DBDPE. By contrast, there was an increase in TCEP, TDCPP, and TCPP levels at Three Rivers; at Marine Park, TCPP increased, and TCEP and TDCPP decreased slightly (Figure 3; Supplementary Tables S7 and S8). Although treatment retention times were taken into account during collection, similar observations have been reported and presumed to result from fluctuations in influent concentrations.[66−68] Alternative explanations could include analytical interference from the complex influent matrix.

To gain a general understanding of the importance of laundry water in contributing FRs to WWTP influent, estimates were generated of expected levels of FRs if laundry wastewater were the sole source. To create these estimates, we multiplied the median level of the compound by 7.8% to account for the proportion of influent from laundry water and by 81%

(a)

Marine Park WWTP

(b)

Three Rivers WWTP

Figure 3. (a,b) Flame retardants in wastewater treatment plant influent and effluent and estimated flame retardant contribution of laundry wastewater to influent (* removal rate < 16%).

(obtained from each WWTP) to account for the proportion of influent from residences.[69−71] Interestingly, the estimates generated are comparable to measured mean influent concentrations at the two WWTPs (Figure 3a,b; Supplementary Tables S7 and S8). Based on these observations, laundry wastewater may well be a primary source of these FRs to WWTP influent and for ClOPFRs, with their ability to resist treatment, to the aquatic environment.

Estimated mass loadings to the Columbia River were calculated using average yearly discharge from the WWTPs sampled. The highest estimated loadings were for TCPP, at 114 and 22.1 kg/year, and TDCPP, at 48 and 7.3 kg/year, followed by TCEP, at 12 and 7.1 kg/year, from Marine Park and Three Rivers, respectively. Considering that the U.S. generates more than 85 trillion liters of wastewater annually, if the effluent levels detected at these plants represent WWTP loadings nationally, approximately 402,000 kg of TCPP, or 2% of its annual production, and 174,000 kg of TDCPP, or 1−4% of its annual production, are being discharged annually to the aquatic environment. This was also observed in a Swedish study, reporting influent loadings representing up to 5% of compounds' reported use.[66]

While PBDE levels in house dust were approximately one-third of ClOPFR levels, PBDEs were present at comparatively low levels in laundry wastewater and WWTP influent and even lower in effluent. ClOPFRs, on the other hand, were found at the highest concentrations in house dust and were also present at relatively high levels in laundry wastewater as well as WWTP influent and effluent. These data indicate that several factors affect the transfer of FRs from products in the home to WWTP effluent and ultimately waterways. First, use patterns determine the extent to which the compound is present in the household dust and air. Second, our results suggest that hydrophilic compounds accumulate at a higher rate in laundry wastewater. Finally, a number of studies have demonstrated that compounds that are highly soluble, resilient to microbial

degradation, or with low partitioning coefficients (e.g., log K_{ow} < 2) are inefficiently removed during wastewater treatment and thus discharged into aquatic environments.[26,72]

The three ClOPFRs identified here, the compounds found at by far the highest levels in the wastewater effluent, combine all of these factors, making them more likely to be present in discharges to the environment. Some are high production volume compounds, used in many products in the home in an additive fashion, and have been shown to be resilient to wastewater treatment.

While this study was somewhat limited in sample size, with 20 homes sampled, the variety of compounds analyzed provided an opportunity to investigate factors affecting transfer of a range of FRs with varying chemical properties including solubility. These findings should inform public policy on use of FRs in products in the home by highlighting transfer of these compounds to waterways such as the Columbia River.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Detailed instrument methodology, QC/QA, and individual FR results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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