Modelling of flame retardants in typical urban indoor environments in China during 2010-2030: influence of policy and decoration and implications for human exposure

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Abstract

Novel flame retardants (FRs) are of increasing concern, given growing evidence of health effects and use to replace polybrominated diphenyl ethers (PBDEs). This study modelled combined effects of use policies and decoration on indoor FRs and human exposure for 18 widely used PBDEs, organophosphate esters (OPEs) and novel brominated flame retardants in typical urban indoor environments in China. The current estimated indoor emission rates, average concentrations in air and dust of the 18 FRs were 10^2 - 10^3 ng/h, 561 ng/m^3 and 1.5×10^4 ng/g, respectively, with seven OPEs dominant (>69%). Different use patterns exist between China and the US, Europe. Scenarios modelled over 2010-2030 suggested that decoration would affect indoor concentrations of FRs more than use policies, and use policies were mainly responsible for shifts of FR composition. Additional use of hexabromobenzene, 2,3,4,5,6-pentabromotoluene and removal of BDE-209 would make total human exposure to the modelled FR mixture increase after the restriction of penta- and octa-BDE, but decrease after deca-BDE was banned. Better knowledge of toxicity of substitutes is needed for a complete understanding of the health implications of such changes. Toddlers may be more affected by use changes than adults. Such studies are supportive to the management of FR use.

Keywords: Flame retardants, indoor contamination, indoor chemical exposure model, chemical use policy, decoration

Synopsis: Predictions using an indoor exposure model explored the influence of policy and decoration to indoor human exposure to flame retardants under different scenarios.

Introduction

Flame retardants (FRs) are extensively added to consumer products and building materials, e.g. electronics, plastics, furniture, textiles and decoration materials etc., to meet flammability standards.[1, 2] However, evidences indicate doubtful fire safety benefits from FRs used in many consumer products.[3] Meanwhile, many FRs are of increasing concern, as they are released from product materials due to the non-chemical bond to base materials, whilst some of them are highly persistent, bioaccumulative and toxic, such as polybrominated diphenyl ethers (PBDEs).[4-6] PBDE exposures have been linked to neurodevelopmental disorders (e.g. IQ loss) and other effects in humans.[7] Considering the adverse effects to both humans and the environment, penta- and octa-BDE technical mixtures were phased out in the EU and the US in 2004, and added to the Stockholm Convention with recycling exemptions in 2009.[8-10] Deca-BDE (BDE-209) was phased out in the US in 2009 and eventually added to the Stockholm Convention without recycling exemptions in 2017.[8] Following the Stockholm Convention, the ban of penta- and octa-BDE was announced in China in 2014, but without any statements on recycling of materials containing the two mixtures.[11] Commercial deca-BDE has not been regulated in China yet, but may be in the future.

In spite of the bans and phase-outs, old products and materials in use or reuse will release the regulated PBDEs in the future. Meanwhile, the production and use of popular alternative FRs, such as organophosphate esters (OPEs) and novel brominated flame retardants (NBFRs), has increased sharply in recent decades,[1, 12] which results in their ubiquitous existence in the environment and human tissues worldwide - including China.[13, 14] Scientists have questioned whether these substitutes are any safer.[15] For example, some OPEs have been shown to be potentially carcinogenic or cardiotoxic.[12, 16] Certain NBFRs can trigger adverse health effects and possibly possess POPs-like characteristics.[17]

Special attention needs to be paid to these FRs in indoor environments in China for the following reasons: (1) the majority of people spend >90% of their time indoors.[18, 19] (2) China has been a large consumer of legacy and novel FRs as a consequence of rapid urbanization;[20] the emission and exposure to FRs could be substantial, particularly in megacities such as Beijing. (3) China may possess distinct FR components and shifting patterns from PBDEs to novel FRs such as OPEs and NBFRs in indoor environments, compared with European and North American

countries/regions, where PBDEs were regulated much earlier. Although China lags behind in PBDE regulations, alternative FRs can enter the Chinese market quickly, driven by the international market. Meanwhile, new buildings arising from urban expansion and preference for new furniture and home appliances over used ones by most Chinese (80-90%) is common in China.[21] Increasing household income in China accompanied by popularity of indoor redecoration/renovation may accelerate the introduction of alternative FRs in indoor environments.[22, 23] Such a shift has been observed by measurements.[24] Therefore, it is interesting to understand how indoor FR occurrence and components may alter over time under the effect of a restriction policy.

Numerous studies have examined the components, exposure levels and fate of FRs in different indoor environments in China. However, most of them relied on measurements, which cannot confirm major sources and hardly reflect long-term patterns of FR occurrence indoors. A research gap exists between possible effects of restriction policies and FR occurrence. This study therefore uses a bottom-up modelling approach to predict FR concentrations in different typical indoor environments selected in Beijing to examine the major emission sources of FRs indoors. We also explore the potential combined effect of policy restrictions and decoration on indoor exposure to FRs under reasonable/realistic scenarios. Such results can provide insights on current uses of FRs and support the further management of PBDEs and novel FRs, such as OPEs and NBFRs, as alternatives in China.

Methods

Chemical selection

Five PBDEs (BDE-47, -99, -153, -183 and -209) were selected, because they are: major components of commercial penta-, octa- and deca-BDE[25]; ubiquitous in the environment; and data are available related to indoor emission estimates. Six NBFRs were selected, namely: hexabromobenzene (HBB) and 2,3,4,5,6-Pentabromotoluene (PBT) as replacements of penta-BDE and octa-BDE commercial mixtures in electronics, unsaturated polyesters and polymeric materials;[1, 13, 26-28] 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), frequently used in acrylonitrile butadiene styrene (ABS), high-impact polystyrene (HIPS), thermoplastics, thermoset resins, polycarbonate, and coatings as an alternative to octa-BDE;[13] decabromodiphenyl ethane (DBDPE), used as an alternative to deca-BDE in polymeric materials and textiles;[13] EH-TBB and

BEH-TEBP, the main brominated components of Firemaster 550 (FM 550) technical mixture, used as substitutes for technical penta-BDE in flexible polyurethane foam (PUF) in furniture, carpet, bedding and textiles.[29] Additionally, seven OPEs were selected: resorcinol bis(diphenyl phosphate) (RDP), tris(2-chloroisopropyl)phosphate (TCIPP), tris(1,3-dichloro-2-propyl)phosphate (TDCIPP), tris(2-butoxyethyl) phosphate (TBOEP), triphenyl phosphate (TPHP), 2-Ethylhexyl diphenyl phosphate (EHDPP) and tris(2-ethylhexyl) phosphate (TEHP). They were chosen because of (1) their extensive use and detection in indoor environments, (2) human health effects on female reproduction and fetal development, (3) potential application as substitutes of banned PBDEs and (4) data availability associated to indoor emission estimates and model evaluation.[13, 30-33] Detailed information and physicochemical properties of these FRs are given in Supporting Information (SI) Table S1.

Estimation of FR emissions indoors

In order to compare levels of PBDEs, NBFRs and OPEs in different typical indoor environments, one activity room (AR), one dormitory (D), three homes (H1, H2, and H3) and four offices (O1, O2, O3, O4) in Beijing were considered in this study. They were all located in or close to large residential districts or universities/research institutes, and none were close to any known FR manufacturers, major users or releasing hotspots such as E-waste recyclers. Additional information on the site of these indoor environments can be found in the study by Wang et al. (2019).[34] Such indoor environments are assumed to represent most typical indoor environments in urban China based on observation of the authors in past decades and the literature, although all located in Beijing. For example, the homes investigated are typical of apartments for >70% of urban residents with an average annual income of 25 – 85 thousand Chinese yuan (CNY).[22] The four offices cover typical office environments, including two large cubicle offices in companies with and without carpet, respectively, and two smaller offices in a university and a research institute. A brief introduction to these indoor environments and the representativeness is given in section S2 and Table S2 in the SI. Emissions of the selected FRs were estimated using equations 1 and 2 (Eqs. 1-2). The Eq. 1 was recommended by the EU and applied widely on this type of substances previously.[5, 35, 36]

$$\text{Percentage loss (\%)} = (1.1 \times 10^6) \times Vp \times N \quad (1)$$

$$\text{Emission rate (ng/h)} = \Sigma\,(\text{Percentage loss}/100/N \times C_i \times m_i \times 1000/365/24) \quad (2)$$

where Vp indicates vapor pressures (mmHg) of individual FRs at 25°C (given in Table S1). EU sources adopted Vp at 20 or 21°C, which might have been considered as comfortable room temperatures. However, 25°C was adopted in the indoor chemical exposure model, to be introduced below, as the standard ambient temperature recommended by the International Union of Pure and Applied Chemistry. It was therefore applied in this study so that the modelling approach gave a conservative assessment. Theoretically, the estimate should be a little higher than that under the EU settings, although the difference is minimal for most FRs. N is the service life (year) of flame retarded products; C_i (ng/g) is the inclusion rate of FRs in the indoor item i, which was taken from the literature (Table S3). Zero was assigned to C_i when there is no evidence for inclusion of a compound in a material (Table S3). m_i (kg) is the mass of indoor item i, estimated in terms of previously recorded item types and count (Tables S5-S6).[34] It should be noted that some OPEs may be added as plasticizers as well, rather than just FRs, such as EHDPP. The methods above actually considered both usages without differentiation, as the additive compounds as plasticizers can be released easily as well. TPHP in electronics (Table S3) was probably not added intentionally, but was converted from RDP.[37]

Model description, validation and uncertainty analysis

With estimated emissions as the input, the Indoor Chemical Exposure Classification/Ranking Model (ICECRM) previously developed by Zhang et al. [38, 39] was applied to simulate concentrations of the targeted FRs in indoor air and dust in this study. The model is a steady-state indoor multimedia chemical fate model, which is used to predict concentrations in indoor air, PUF, carpets, vinyl flooring and dust. A module predicting exposure for the human body is also imbedded in the ICECRM model, although it was not adopted in this study. The physicochemical properties and key environmental parameters are given in Tables S1-S2, including air exchange rates, geometric dimensions of rooms and areas of indoor hard surfaces. Average outdoor atmospheric concentrations of individual FRs in Beijing measured by Zhang et al. (samples collected in 2016-2017) were used as outdoor air advective inputs (Table S7).[40] To validate the model, model predictions were evaluated against measurements in $PM_{2.5}$ and dust in the individual indoor environments by Wang et al. (samples collected in 2016-2017).[34, 41] The concentrations of particles in different sizes as model inputs are given in Table S8.

Given the incomplete information on addition of FRs in products, attempts were made to apply different inclusion rates of several FRs, to consider the uncertainty of emission estimates. Inclusion rates (C_i) of OPEs in Table S3 were mostly from measurements in China and Japan.[42, 43] By contrast, higher C_i values for several OPEs in PUF, cloth and textile have been reported in the US and Belgium as shown in Table S4.[44, 45] This probably represents a usage scenario in the US and Europe, where the PBDE restriction was enforced earlier. Values in Table S4 were therefore also used to explore which set of inclusion rates of OPEs would fit better in China. Monte Carlo simulation was conducted to evaluate the model uncertainty induced by the variability of the input parameters, including chemical emission rates, environmental conditions such as indoor/outdoor air exchange rates and area of rooms, PUF, vinyl flooring, carpets, and hard surfaces. Log-normal distributions were assumed for air exchange rates, emission rates, concentrations of target FRs and particles in outdoor air.[46] Uniform distributions were assumed for the area of rooms, PUF, vinyl flooring, carpets, and hard surfaces, as various size is possibly present randomly. Measurements by Wang et al.[34, 41] and data collated from the literature were applied to calculate the mean, standard deviation and range of parameters, to generate the random datasets required for the Monte Carlo simulation (Table S9). Nationwide climatic and seasonal variations of air exchange rates were considered to ensure representativeness of the analysis (Table S9). One thousand runs were performed for the analysis.

Indoor exposure scenarios during 2010-2030

Five scenarios with different FR restriction policies, enforcement years and replacement strategies during 2010-2030 were modeled, to explore combined effects of policy and decoration on overall indoor exposure levels of FRs and their temporal trends. As FRs would normally reach steady-state concentrations indoors in a few days,[47] ICECRM was reasonably applied to predict annual indoor concentrations for 2010-2030. A representative office (O4) and home (H1) were selected for this practice. OPEs were extensively used in the Chinese market prior to the restriction of PBDEs in China, because of (1) their long history of production and existence in global markets and (2) the large use as plasticizers.[13, 48] Some of them have been restricted in some developed regions (e.g. TDCPP in California).[15] Therefore, substantial growth of the use of most OPEs as substitutes for PBDEs is not expected in China. RDP and NBFRs were considered as potential replacements in the scenarios in this study, based upon information found in the literature.

Table 1. Summary of the three scenarios during 2010-2030

	Scenario 1	Scenario 2	Scenario 3
Period	2010-2030	2010-2030	2010-2030
Renovation year	2010	2010; 2017; 2024	2010; 2017; 2024
Phase-out	None	**2014**: Penta-BDE and Octa-BDE	**2014**: Penta-BDE and Octa-BDE **2022**: Deca-BDE
Replacement	None	**2014**: PBT replaces BDE-47, -99 in electronics; EH-TBB and BEH-TEBP replace BDE-47, -99 in PUF; BTBPE replaces BDE-153, -183 in electronics; HBB replaces BDE-153, -183 in building, decorating and wooden materials.	**2014**: PBT replaces BDE-47, -99 in electronics; EH-TBB and BEH-TEBP replace BDE-47, -99 in PUF; BTBPE replaces BDE-153, -183 in electronics; HBB replaces BDE-153, -183 in building, decorating and wooden materials. **2022**: RDP replaces BDE-209 in electronics; DBDPE replaces BDE-209 in decorating materials and electronics.

Notes: The years in bold are the initial years for enforcement of the policy and replacement.

New furnishings were assumed for the initial year 2010 in the two indoor environments under all scenarios (see Table 1). Scenario 1 (Sc1) was viewed as a baseline scenario, in which there are no regulations on the use of PBDEs, and no redecoration or replacement of indoor items during 2010-2030. Scenario 2 (Sc2) represented a situation with existing FR regulation which restricted commercial penta- and octa-BDE in the Chinese market from 2014. In Sc2, penta-BDE (BDE-47 and -99) was assumed to be replaced by EH-TBB and BEH-TEBP in PUF[29] and by PBT in electronics.[1] Meanwhile, octa-BDE was replaced by BTBPE in electronics,[26] and by HBB in building, decorating and wooden materials.[1] Under Scenario 3 (Sc3), in addition to the regulation in Sc2, deca-BDE (BDE-209) was assumed to be banned in 2022, by assuming the five-year lag in enforcement of the ban for penta- and octa-BDE in China, compared to the Stockholm Convention. Sc3 assumed that Deca-BDE would be replaced by RDP and DBDPE in electronics and by DBDPE in decorating materials.[26, 33] The ratios of 1:1 and 1:2 (PBDEs : alternative FRs) were applied as two replacement strategies in both Sc2 and Sc3, to acquire a range of changes, considering uncertainties due to the absence of firm data on addition amounts of substitutes in China. Thus, there are two sub-scenarios under Sc2 and Sc3 respectively. When there was more than one substitute for a banned PBDE, equal addition amounts were assumed. O4 and H1 were assumed to be renovated every 7

years (i.e. in 2017 and 2024), under Scs2 and 3, without any recycled materials/products being used. All these conditions are summarized in Table 1. Human exposure was assessed following the modelled scenarios. The method is described in the SI and relevant parameters are provided in Tables S10-S12.

Results and discussions

Estimated emission rates of individual FRs

Based on the inclusion rate of FRs in indoor materials listed in Table S3, the emissions of the 18 representative OPEs, NBFRs and PBDEs into indoor air were estimated. Emission rates of individual FRs are given in Table S13. The total emission rates of all target FRs (Σ_{18}FRs) were 3.9×10^{2} - 1.8×10^{3} ng/h across all the modelled indoor environments. Σ_{7}OPEs contributed 75 - >99% of the total emission (Figures 1 and S1 and Table S13). The average emission rate was estimated to be 7.7×10^{2} ng/h (range, 3.2×10^{2}-1.7×10^{3} ng/h), 88 ng/h (0.4-156 ng/h) and 14 ng/h (6.3-51 ng/h) for Σ_{7}OPEs, Σ_{6}NBFRs and Σ_{5}PBDEs, respectively, in all indoor environments. The estimated emission rates of individual OPEs were significantly higher than those of other FRs (Figure 1B, Tukey HSD test, $p < 0.05$), between 1-6 orders of magnitude higher. The difference in emission rates of individual compounds between the NBFR and PBDE groups was insignificant.

TCIPP showed the highest emission rate, with an average of 524 ng/h (range, 2.6×10^{2}-1.1×10^{3} ng/h), followed by RDP (mean, 1.2×10^{2} ng/h; range, 0-316 ng/h), EH-TBB (85 ng/h; 3.2×10^{-4}-154 ng/h) and TPHP (76 ng/h; 28-174 ng/h) in all the indoor environments (Figure S2). This results from combined effects of higher vapor pressures and greater inclusion rates in primary indoor materials for the four FRs, compared to the other FRs. The vapor pressure is the key influential factor. Several less volatile FRs - BTBPE (2.8×10^{-3}-6.1×10^{-2} ng/h), BDE-153 (4.0×10^{-3}-8.7×10^{-2} ng/h), BDE-99 (3.0×10^{-2}-1.2×10^{-1} ng/h) and BDE-183 (2.0×10^{-2}-2.5×10^{-1} ng/h) - exhibited minimal emission rates. The vapor pressure of DBDPE is also very low (3.5×10^{-10} mm Hg), although it had a moderate emission rate at ~1 ng/h due to its high inclusion rates in product materials (Table S3). As for PBDEs, BDE-209 had emission rates over an order of magnitude higher than other BDE congeners, because of its much greater addition to indoor and building materials (Table S3). The estimated emission rate of Σ_{18}FRs was higher in AR (1.3×10^{3} ng/h) and O1 (1.8×10^{3} ng/h) than in other indoor environments, and was lowest in D (386 ng/h). For individual FRs, emission rates were significantly

higher in O1 than in most other indoor environments (except O2 and H3), and were significantly lower in D than in other indoor environments (except AR and O2). The difference between indoor environments was insignificant, except for AR-O1, AR-O2, H1-H2 and O3-O4 (paired t-test $p < 0.05$, Figure 1).

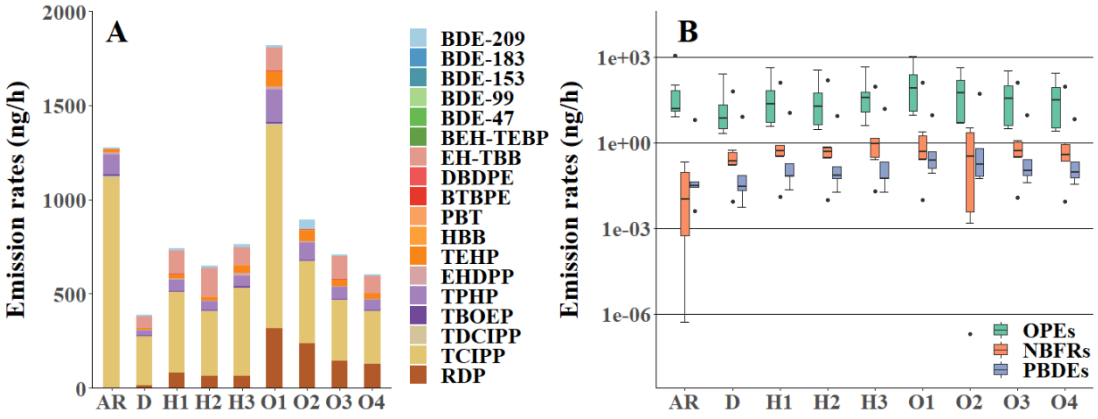


Figure 1. (A) Emission rates of FRs and composition in different indoor environments; (B) Boxplot of estimated emission rates (log transformed) of individual FRs; the dots indicate extreme values, lying 1.5 times out of the interquartile range.

Estimated concentrations and sources of FRs in indoor air and dust

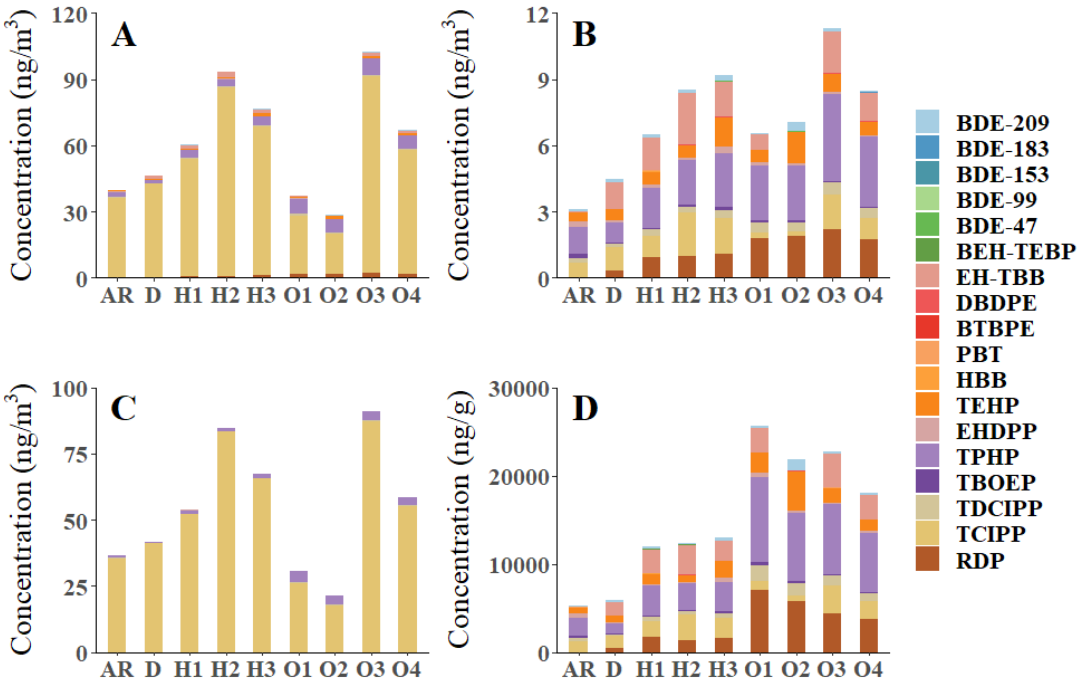
Using the above emission rates, the predicted concentrations of the individual FRs in indoor air (gaseous and particulate phases) and dust were derived (see Table S14). The estimated average concentration of Σ_{18}FRs in air was 61±26 ng/m^3 with a range of 28 - 102 ng/m^3. Σ_7OPEs contributed over 97% of Σ_{18}FRs. TCIPP was the dominant compound in air with an average concentration of 53 ng/m^3 (range, 18-89 ng/m^3), which contributed 63 - 91% of Σ_{18}FRs in air in the modelled indoor environments. TPHP was the second most abundant FR in air, accounting for 3.1-21% of Σ_{18}FRs concentrations, and was followed by RDP and EH-TBB. BTBPE, BEH-TEBP, BDE-47, -99, -153 and -183 exhibited extremely low concentrations and proportions in air. This matched the composition pattern of emissions. With high vapor pressures (10^{-5}-10^{-6}) and low octanol-air partition coefficients (K_{OA}, 10^8-10^9), most TCIPP (> 97%) and PBT (> 66%) were estimated to distribute in the gas phase in indoor air. In contrast, >99% of RDP, BTBPE, DBDPE, TBOEP, TEHP, EH-TBB, BEH-TEBP, BDE-153, -183 and -209 were estimated to be associated with total particles (Table S15), as a result of their high K_{OA} (10^{13}-10^{16}, Table S1). $PM_{2.5}$-bound concentrations of the ten individual FRs made up >69% of their concentrations in indoor air (Table S16). Besides these FRs,

TDCIPP, EHDPP, TPHP, BDE-47 and -99 were estimated to mostly distribute to particles, with the proportion ranging from ~50% to 97% (Table S15). With a relatively high total concentration in air, TPHP was predicted to be the dominant compound in the particulate phase, with an average contribution of 31% to the particle-bound FRs, followed by RDP, EH-TBB, TCIPP and TEHP (Figure 2B).

The average estimated concentration of Σ_{18}FRs in dust was 1.5×10^4 ng/g, with a range of 5.3×10^3-2.6×10^4 ng/g (Table S14). ΣOPEs contributed 69-96% of Σ_{18}FRs in dust. TPHP was dominant, contributing 31% on average, followed by RDP, TCIPP, EH-TBB and TEHP (Figure 2D). There were contrasts between emissions and concentrations in both chemical composition and indoor environments in different compartments. The FR composition of air particles generally matched that of dust, with the same dominant compounds as described above, but differed from the composition in emissions and the gaseous phase (Figure 2). There are large variations in the chemical properties of the 18 FRs, notably their vapor pressures and K_{OA}, which determines the gas-particle partitioning for different chemicals. Chemicals with low vapor pressures and high K_{OA} preferentially distribute to particles after direct emission to indoor air, and those with high vapor pressures and low K_{OA} were more prevalent in the gas phase. Dust was mainly derived from deposition of air particles following the model estimates, and therefore exhibited an identical composition to the particulate phase. The emission rate of Σ_{18}FRs was highest in O1, followed by AR and O2. In contrast, the estimated concentrations in O1, O2 and AR were the lowest in air. However, estimated concentrations in dust of offices 1-4 were high. This might be a result of high net flux f Σ_{18}FRs from air to floor in offices 1-4, especially for TPHP and RDP, which were major components of FRs in dust, particles and FR fluxes from air to the floor (Figures 2D and S3B).

Based on our estimates, generally electronics and building materials were important sources of most FRs, especially OPEs, BDE-153 and -183, in all the indoor environments, but particularly in offices due to the installation of computers. However, major sources actually varied for different FRs among various indoor environments (Figure S4). In contrast to OPEs and the two PBDEs, EH-TBB and BEH-TEBP were mainly emitted from PUF, with an exception in AR and O2 without PUF. BTBPE, DBDPE, HBB and PBT were mainly released from decorating materials and/or electronics. Building materials were the main sources of PBDEs in AR. Decorating materials were important

sources of BDE-47 and even the major sources of BDE-209. Except decorating materials, the other three materials were all important sources of BDE-209 (except for AR and O2).



Model evaluation and comparisons with use patterns in Europe and the US

Figure 3 illustrates generally good agreement between predictions and measurements for both $PM_{2.5}$- and dust-bound FRs in all indoor environments. Many points clustered around the 1:1 line and most fell within the 1:10 line, which agreed with the accuracy of such models for indoor concentration and exposure predictions.[49, 50] Only two points representing TBOEP in dust (Figure 3B) in O3 and O4 fell slightly below the lower 1:100 line. The clusters shown in Figure 3 represent either an individual compound or compound groups. Specifically, TPHP was slightly over-estimated in both $PM_{2.5}$ and dust, while TCIPP in $PM_{2.5}$ and TBOEP in dust were underestimated by 1-2 orders of magnitude. This made TPHP predominant, as described above, contrary to measurements with the predominance of TCIPP and TBOEP in $PM_{2.5}$ and dust, respectively.[34, 41] Predictions of the other compounds were closer to measurements, falling closer to the 1:1 line, depending on the indoor environments.

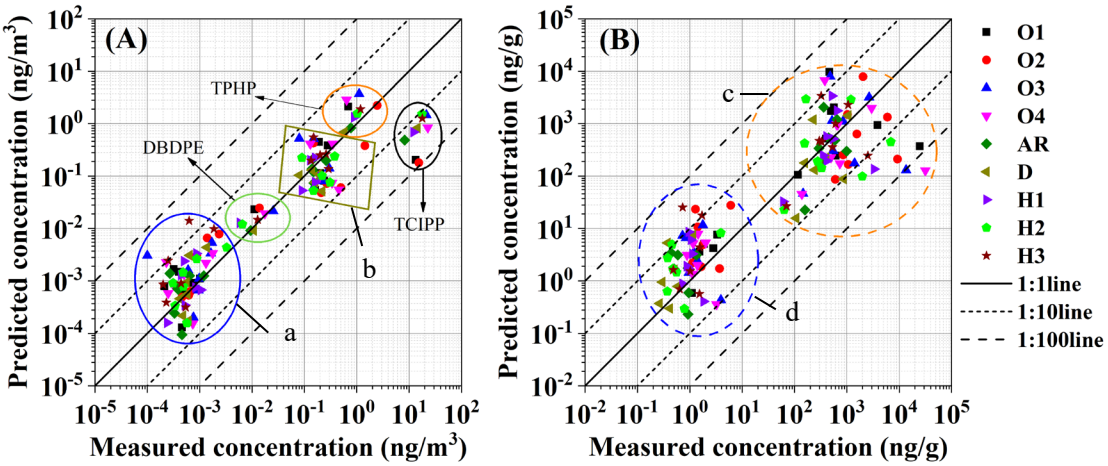


Figure 3. Point-to-point comparison of predicted and measured concentrations of flame retardants in (A) $PM_{2.5}$ and (B) dust in the nine indoor environments. (a) HBB, PBT, BTBPE, BDE-47, -99, -153, -183; (b) TDCIPP, TBOEP, EHDPP, TEHP, BDE-209; (c) TCIPP, TDCIPP, TBOEP, TPHP, EHDPP, TEHP, DBDPE, BDE-209; (d) HBB, PBT, BTBPE, BDE-47, -99, -153, -183. The measurement for comparison is from the study by Wang et al. (2019).[34, 41]

Disparities between estimates and measurements may occur due to: (1) limited data on inclusion rates of FRs in indoor materials in the Chinese market and the challenge of accurately estimating FR contents in all indoor products based on roughly predicted material mass; (2) inherent uncertainty in the method of estimating emission rates; (3) uncertainties in variables of indoor environmental conditions, such as air exchange rates, temperatures and surface area.[51-53] For example, as previously mentioned, TPHP is probably a converted product of RDP in electronics. Given the limited data in the literature, the adopted inclusion rate of TPHP has large uncertainty. TCIPP and TBOEP are widely used as plasticizers,[54] unidentified sources probably resulted in their underestimation. Nevertheless, the generally good agreement between measurements and modelling indicates the robust performance of the model.

Contrary to Figure 3, Figure S5 illustrates greater discrepancy between predictions and measurements for OPEs (except RDP, for which there are no measurements), when inclusion rates from possible use patterns of OPEs in Europe and the US were used to replace those in Table S3 (see Table S4). OPE concentrations were then overestimated by more than two orders of magnitude. This suggests that possibly lower levels of the selected OPEs have been added into materials such as PUF, clothing and textiles, in China compared to the US and Europe. Some other studies also suggested this. For example, a recent study suggested that measured OPE concentrations in play

mats from China were several orders of magnitude lower than those in similar children's mats, PUF samples widely used in baby products and toys from the US or Belgium.[55] A study on indoor dust from 12 countries found 1–2 orders of magnitude higher dust concentrations of ΣOPEs in the US than in China.[56] The different timing of bans between countries/regions has resulted in different histories of use of FRs in different countries. For instance, some OPEs have been added to products prior to the restriction of penta- and octa-BDE in the US.[27] The later ban of PBDEs in China probably resulted in substitutes other than OPEs being used.[27, 57] Direct evidence may be needed to confirm the lower use of OPEs in China. Varying fire safety regulations could also drive diverse use patterns of FRs across countries/regions. Results of the uncertainty analysis are shown in Figure S6 in the SI. Generally, concentrations of NBFRs, especially EH-TBB and BEH-TEBP, presented higher uncertainties than those of other FRs, possibly due to a wider range of emission rates of these substances. Emission rates are usually considered as one of the most influential parameters to predictions.[58]

Exposure under the modelled scenarios and influence of policy and decoration

As a baseline scenario, Sc1 suggested that FR concentrations would continuously decline in indoor air and dust if there is no redecoration and new products introduced during the 20 years, as a result of the continuing loss of FRs from indoor materials (Figures 4 and S7). This matched the conclusion from the previous study that tested emission rates of FRs in emission chambers.[59] Concentrations of Σ_7OPEs declined substantially in home and office air, by 77% and 71% respectively, over the first ten years. The decline decelerated over the later ten years, and was only 31% and 24% in the home and office, respectively. Dust concentrations decreased more slowly than air concentrations, with a reduction of 21% and 16% in the home and office, respectively, during the 20 years; indoor dust is a reservoir of these contaminants.[60] Relatively rapid loss of TCIPP was a big contribution to the reduction of OPEs, whilst concentrations of other compounds were steadier over time (Figure S8). NBFRs and PBDEs did not decrease much over the 20 years (< 2%) in both air and dust. The FR composition therefore changed in the indoor environments, especially in air. The predominant compound in air was TCIPP at the beginning (77% and 71% in the home and office, respectively, the same below), but became EH-TBB (35% and 27%), RDP (23% and 36%) and TPHP (around 17%) by 2030. The proportion of compounds did not vary so much in dust.

Redecoration of the indoor environments would introduce high indoor concentration of FRs. For instance, the air concentration of Σ_7OPEs after every decoration (in 2017 and 2024) would be 2.5 (office) and 2.9 (home) times that before decoration, and approximately 1.1 times (for both office and home) that before decoration in dust in Sc2 (Figures 4 and S7). Such results are consistent with previous research that illustrated significantly elevated indoor concentrations of FRs after installation of new electronics and furniture etc.[44, 61-63] This reflects the significant influence of resident preference and behaviors on the indoor exposure to these chemicals. Theoretically, maintaining original or old decoration, furnishings and other indoor items will possibly result in less cumulative exposure to FRs for residents, compared to the scenario that new materials or items are introduced into the indoor environment.

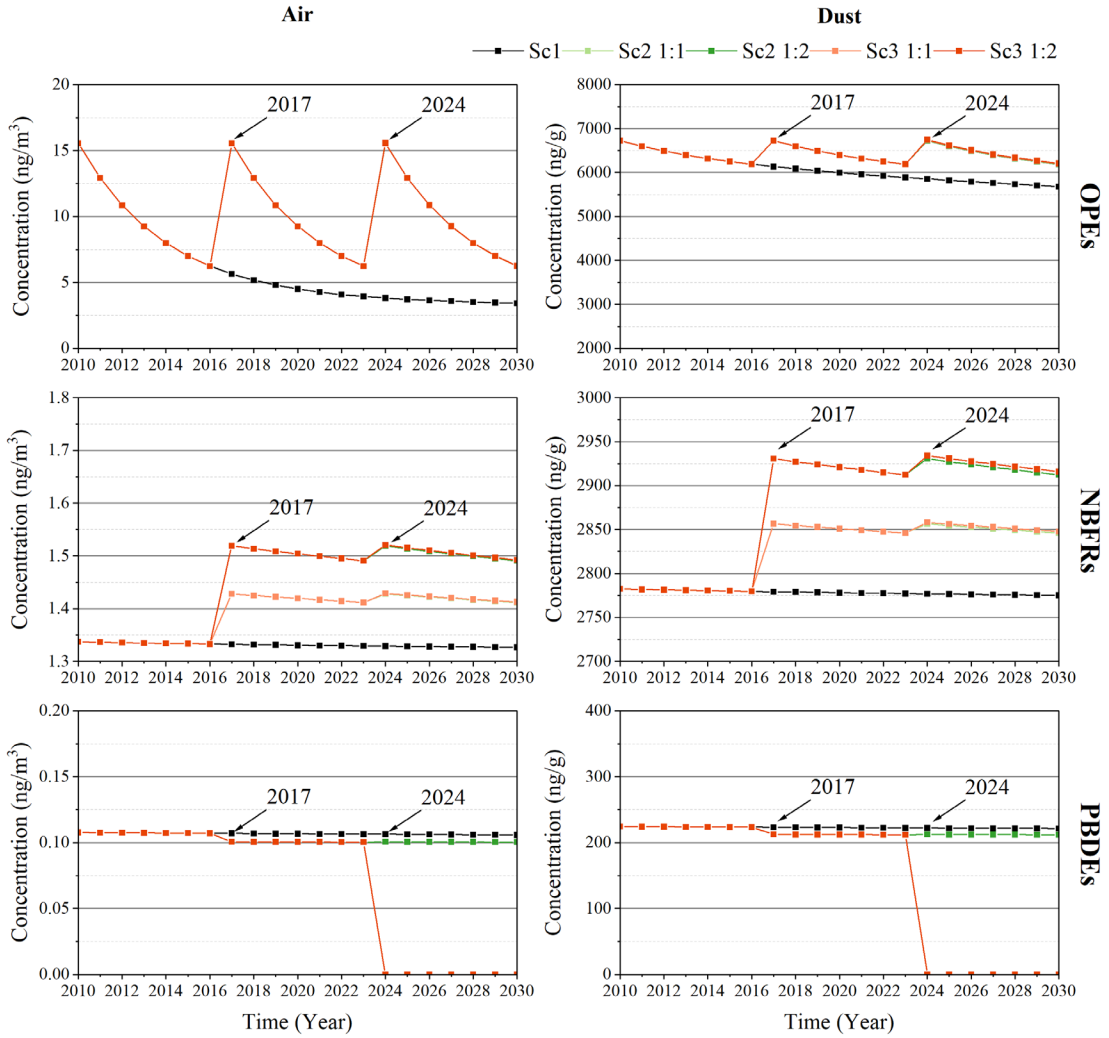


Figure 4. Estimated temporal variations of total concentrations of FRs in air and dust from the office under different scenarios.

Policy effects may be only reflected after interior redecoration/renovation, which will

368 introduce new materials containing alternative FRs. Comparison of FRs among the three decoration
369 years (2010, 2017 and 2024) in Sc3 indicated a clear increase of Σ_6NBFRs in 2017 and 2024, and a
370 slight decrease of Σ_5PBDEs in 2017 and final removal in 2024 after the ban of deca-BDE (Figure 4
371 and S7). Of the seven OPEs, only RDP was assumed a replacement of BDE-209 in electronics after
372 2022, so minimal increase of Σ_7OPEs only occurred in 2024. The release of HBB and PBT after
373 their addition as substitutes surpassed the removal of penta- and octa-BDE in 2017, and removal of
374 BDE-209 would largely surpass the release of RDP and DBDPE as the replacement (Figure S9).
375 Therefore, the total human exposure to the selected FR mixture would possibly increase in 2017 but
376 decrease in 2024 compared to 2010 (Figure S9). However, as the composition altered, any health
377 risk would rely on the toxicity of substitutes. Similar to Sc1, TCIPP was dominant in air in the
378 redecoration year (ca. 76% and 70% in the home and office, respectively, the same below), but its
379 proportion would decline rapidly afterwards until approximately 44% (home) and 37% (office) in
380 the 7th year (e.g. 2023 and 2030). Proportions of EH-TBB (20% and 17%), TPHP (12% and 13%)
381 and RDP (13% and 23%) would increase twofold after seven years compared to the initial decoration
382 year. The difference between Sc 1:1 and 1:2 replacement strategies was minimal. Compared to
383 effects of redecoration/renovation, effects of restriction policy on FR concentrations were minimal
384 and mainly responsible for composition shift.

385 Between different scenarios 2-3, the change of total concentrations was <3% in air and <5% in
386 dust over 2017-2030. The change in air was negligible considering the low air concentrations
387 (Figure 4 and S7). The reduction was more significant in Sc3 1:1 than in Sc3 1:2. The office and
388 home exhibited a similar alteration pattern, but a slightly greater variation in both total
389 concentrations and compositions between scenarios was found in the home than in the office. A
390 notable change in composition was the absence of penta- and octa-BDE after 2017 and deca-BDE
391 after 2024, following the use policy in the target indoor environments in Sc3. Similar effects of
392 restriction policy have been observed in house dust in California, where PBDEs in sampled dust
393 decreased from 2006 to 2011, especially for houses with remodeling or acquiring new furniture
394 during the six years.[64] However, the variation relied on the physico-chemical properties of the
395 individual substitutes in scenarios, e.g. vapor pressures, and the addition amount of substitutes
396 compared to the banned PBDEs. For example, if there is no re-decoration, PBT decreased markedly

in air and dust, while most other compounds (e.g. HBB and BTBPE) did not change much over time (Figures S10-S13). The difference of concentrations between the 1:1 and 1:2 replacement strategies was 91%, 48% and 17% for HBB, PBT and BTBPE (Figures S10-S12), but was minor for the other FRs, e.g. RDP (Figure S13).

Implications for potential effects on human exposure

The estimate of total daily intake (TDI) of FRs through inhalation, dust ingestion and dermal contact for adults and toddlers was described in the SI. The TDI was approx. 9.3 ng/(kg·bw·day) and 54 ng/(kg·bw·day) for adults and toddlers, respectively, in the three years with re-decoration in Sc3, and the difference was minimal among different years. The 1:2 replacement strategy will not result in obvious differences in TDI compared to the 1:1 strategy. However, there will be reduced or no human exposure to PBDEs after 2017 due to the ban in Sc3. A decline of human exposure to PBDEs due to the change in use policy has been observed in Northern California pregnant women.[65] A subsequent reduction of health risks is anticipated, such as the reduced probability of IQ loss induced by exposure to PBDEs.[66] Dust ingestion made up an average 34% (7-67%) and 49% (23-88%) of TDI for adults and toddlers, respectively. It was a more important exposure pathway for toddlers than adults for most FRs, due to a higher dust ingestion rate of toddlers (Figure S14), which matched the finding by some empirical research.[67, 68] Considering the obvious variation in dust concentrations during 2024-2030 between scenarios 2-3, toddlers were likely affected more by use changes assumed in this study than adults.

The TDI of most individual FRs via the three intake routes was lower than the reference dose values (RfD, given in Table S12) available from the literature (Figure S15). This means that health effects induced by exposure to these FRs through the three exposure pathways are possibly negligible in the typical indoor environments. Nevertheless, if OPEs were largely adopted as alternatives to the PBDEs, the indoor total concentrations of FRs would likely increase given the higher vapor pressures of many OPEs. Available evidence suggests potential health concerns of OPEs.[15] From this aspect, OPEs might not be an ideal replacement of banned PBDEs. However, the ultimate health effects of the use policy depend on the largely unknown toxicity of many novel FRs used as substitutes and their mixtures.[60] Investigation of toxicity of these FRs is urgently required.

Limitations and perspectives

Although the model prediction has been generally well validated against measurements, uncertainties of the current methodology should be noted. First, as mentioned previously, there is uncertainty in emission estimates because of the general lack of accurate inclusion rates of FRs in indoor products and materials for China. Data in Japan and Europe were adopted for some materials, which might cause uncertainties. Zero was assumed to be inclusion rates of some OPEs in PUF, but more reliable data for China are needed. Those inclusion rates in the ng/g range need be evaluated in further research, as they are probably inadequate to impart flame retardancy.[55] Identical inclusion rates were adopted for the same type of materials in different indoor environments, however, varying flame-retardant standards for materials are actually required in various indoor environments in China.[69] It is difficult to acquire such data currently. Second, materials with minimal information on usage and chemical content, such as insulation and those containing FRs as plasticizers, likely exist in indoor environments. To identify and estimate these sources are challenges to an accurate estimate of emissions. In addition, the exclusion of releases by abrasion, due to the lack of reliable methods and data would possibly cause underestimation, especially for FRs with high K_{OW}. Finally, the selection of substitutes was based on widely adopted replacement in a few references for developed regions. Although this is a reasonable assumption, other possibilities might be present in China. More complete information concerning these factors in China is needed.

Additionally, the indoor environments targeted are only applicable to around 70% of urban residents in China. Rural residents (approx. 40% in China in 2018) and urban people with extremely low or high annual income are probably mainly exposed in different indoor environments to those considered in this study and are not applicable to conclusions in this study.[70] Another limitation is that the scenario study initiated with inclusion rates in Table S3. Considering the low level of penta- and octa-BDEs in materials in Table S3, the alteration has probably already occurred. So, if inclusion rates prior to alteration in China can be acquired, the change and effect after the ban would probably be more obvious. In terms of effects on human exposure and health, the exposure scenario was simplified in this study as described in the SI. Exposure outside of the indoor environments explicitly analyzed were not considered, such as the exposure in transit and other indoor locations other than home and offices, dietary exposure, exposure from personal care products and

occupational exposure etc. Meanwhile, physiological parameters, such as respiration rates and ingestion rates etc., can vary individually across the population or during different human activities in various indoor environments. This was not taken into account, as it is not the focus of this study. However, these may introduce uncertainties in assessing policy effects on human health, and improvements should be accomplished in the future research.

This study offers an effective and efficient methodology to explore the policy effects of indoor FR changes and ultimate health effects. It focuses on China and – as such - the result is not generalizable to other countries owing to varied fire safety regulations and thus distinct FR use patterns in different countries. However, the established framework and methodology is adaptable to other countries or regions. Exposure in transit and other types of indoor environments with diverse or extreme indoor conditions can also be assessed by this method in the future, which may exhibit different FR changes under effects of policies. The initial attempt to explore such effects quantitatively in this study can support policy makers for management of FR use. Given the large number of other novel FRs in use and the value of assessing their effects on human health, further research is needed (1) to acquire a full list of novel FRs in use, characterize their manufacture, inclusion rates in and release from indoor materials/products; and (2) to pursue a more comprehensive assessment of human exposure and health effects, considering the variability of human physiological parameters and activity patterns in different scenarios. Such studies could help complete a more accurate and thorough assessment for decision-making.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/journal/esthag

Basic information of the target FRs; explanation of the estimation methods for emission and concentration of FRs indoors; methods for human exposure assessment; Figures and tables of estimated emission rates and concentrations

Acknowledgements

This research was supported by the National Natural Science Foundation of China (41977359 and 91743206), the National Key Research and Development Program of China (2017YFC1600301, 2018YFC0830802) and the Eco-environmental Excellent Innovation projects of Research Center

for Eco-Environmental Sciences (RCEES-EEI-2019-01).

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