



FINAL REPORT

A Pilot Study to Quantify Volatile Organic Compounds and Their Sources Inside and Outside Homes in Urban India

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Executive Summary

Over the past 30 years India has experienced rapid growth in GDP, urbanization and living standards along with a decline in its rural population. Indian cities currently have some of the poorest air quality globally and as the urban population has increased so has exposure to urban air pollution. Indoor exposure to volatile organic compounds (VOCs) and flame retardants (FRs) – many of which adversely affect health – and their indoor sources remain understudied in India. In this pilot study we quantified five different types of flame retardants in house dust (18 homes) and road dust (2 sites) and hundreds of VOCs inside and outside homes (26 homes) in Ahmedabad and Gandhinagar, Gujarat, India. The study conducted VOC sampling in May 2019 and VOC and FR sampling in January 2020. VOCs were sampled in the morning and afternoon/evening to capture temporal variability.

Total indoor VOCs were measured at higher concentrations in winter ($327.0 \pm 224.2 \text{ mg m}^{-3}$) than summer ($150.1 \pm 121.0 \text{ mg m}^{-3}$), and exceeded those measured outdoors. Using variable reduction techniques, we identified potential sources of compounds (cooking, plastics [with an emphasis on plasticizers], consumer products, siloxanes [as used in the production of consumer products], vehicles). Contributions differed by season and between homes. In May, when temperatures were high, plastics contributed substantially to indoor pollution (mean of 42% contribution to total VOCs) as compared to in January (mean of 4%). Indoor cooking and consumer products contributed on average 29% and 10% to all VOCs indoors in January and 16% and 4% in May. Cooking contributed substantially to outdoor VOCs (on average 18% in January and 11% in May) and vehicle-related sources accounted for up to 84% of VOCs in some outdoor samples.

Total FRs, sum of polybrominated biphenyls (PBB), polybrominated diphenyl ethers (BDE), novel brominated FRs (NBFRs), organophosphorus FRs (OPFRs) and hexabromocyclododecane (HBCDD were present in-house dust at all the homes sampled). Concentrations ranged from a minimum of 0.02 ppm to a maximum of 11.3 ppm. The types and concentrations of FRs varied widely from home to home. Four of the homes had total FR concentrations above 3 ppm. FRs at two of these homes were dominated by newer OPFRs, while FRs at the other two homes were dominated by older BDE FRs. The homes with predominately OPFRs characteristically contained large amounts of western style furniture.

Overall, the results indicate a strong seasonal dependence of indoor VOC concentrations and sources and the presence of FRs in house dust. The results underscore the need to better understand factors driving these health-harming pollutants inside homes to facilitate exposure reduction.

1.0 Introduction

Poor air quality in India has long been recognized as a threat to human health¹ and the environment.² Various measures have been taken to curb air pollution in India,^{3,4} yet Indian cities remain some of the most polluted in the world. It is estimated that in 2017 alone, approximately 1.24 million deaths, or 12.5% of all deaths in the country, were attributable to air pollution.⁵

In review papers, researchers have stressed the need for increased work in India to better characterize the air pollution problem, especially due to India's large population and high population density; with a population of this size, even minor changes in air quality may be devastating at the population level.^{6,7} Furthermore, pollutant composition and sources in India may differ from those in other highly polluted regions of the world (e.g., China) due to different cultural practices, infrastructure, and policies (e.g., emission standards, rules about vehicle use, zoning), and differences in the topography, geography and climate that can drive ambient concentrations. This further highlights the need for region-specific research. To date, studies of VOCs in India have tended to focus on specific sources (e.g., petrol stations, petroleum refineries, vehicle, or evaporative emissions).⁸⁻¹² A few studies have sought to characterize pollutants in indoor environments, but have targeted these efforts to kitchens,¹³⁻¹⁶ university campuses (e.g., in libraries, dormitories, campus shops),^{17,18} or public spaces (e.g., restaurants, shops, shrines, temples),¹⁹ or in other non-residential locations (i.e., a laboratory, a recently renovated central hall in a library, and a room with no apparent sources of VOCs)²⁰ or have characterized pollutants generated during specific events (e.g., ceremonies).^{21,22} A gap remains in identifying and quantifying VOCs in homes during normal daily activities, and especially in homes that do not rely on the combustion of biomass for cooking and heating. Additionally, little is known about the broad range of compounds that we might expect to encounter in these environments as much of the previous work has targeted a small subset of compounds or measured total VOCs.

Organic flame retardants (FRs) have been added to many home consumer products and construction materials over the past fifty years to meet flammability standards. These compounds have been shown to migrate from products and accumulate in the indoor and outdoor environment resulting in human exposure.²³ Over time different types of FRs have been shown to be toxic to humans and persist in the environment resulting in banning and or strict control of their use. For example, PBBs, PBDEs and HBCDD have been phased out as part of the UNEP Stockholm Convention and other multilateral legislation.²⁴ As these FRs have been phased out newer types of FRs have emerged to take their place including NBFRs and OPFRs. However, many of these alternate FRs have also been found to have potential health effects. House dust has been shown to contain significant concentrations of FRs and is an important FR exposure source through inhalation and ingestion. While there have been many house dust FR studies worldwide²⁵⁻³¹ the prevalence of legacy FRs or alternative NBFRs and OPFRs in Indian homes are underreported.²⁶ It's expected that a wide range of FRs are present in Indian homes, but at present few studies exist.

2.0 Approach

This study involved sample and data collection at 26 homes in Ahmedabad and Gandhinagar, Gujarat, India. We recruited participating households through the networks of our collaborators and local students working on the project and approached individuals from both cities to capture the diverse range of sources in this area. Homes with known smokers were excluded. Twenty homes were initially recruited for the study and sampled in May, and although we aimed to re-sample at these homes in January this was not feasible for all homes; 13 homes were re-sampled and six new homes were recruited for sampling in January 2020. House dust FR sampling was added to the project and took place in parallel to the VOC collection in January 2020. House dust samples were collected from 18 of the homes sampled for VOCs and two roadside sites in Ahmedabad.

We conducted sampling at homes between May 9-23, 2019 (temperature: 28–45°C), and between January 10-23, 2020 (temperature: ~7–30°C). There was no rain during either period. We collected 90-min integrated air samples on 2,4-dinitrophenylhydrazine (DNPH) (Sigma-Aldrich, Sternheim, Germany; flow rate 0.3 liters per min [LPM]) and Tenax cartridges (Tenax TA, SKC, Eighty Four, PA, USA; flow rate 0.2 LPM) at all homes using SKC AirChek XR5000 pumps and low-flow constant pressure controllers (SKC Inc., EightyFour, PA, USA). Samples were collected simultaneously indoors in the main room of the home or in a secondary room and outdoors on a balcony or on the front step of the home with the cartridges situated at approximately breathing height using tripods. We collected morning samples in all homes during both seasons and afternoon samples in all homes in January. In May, we collected afternoon samples in a subset of 12 homes selected based on project logistics and equipment and participant availability. House dust samples were collected for FR analysis using household vacuums fitted with Zeflon carpet and dust vacuum collection nozzles.

FR house dust samples were transported to the Wisconsin State Laboratory of Hygiene for sample preparation and analysis. Dust aliquots (~100 mg) were weighed and spiked with internal standards before extraction in 3:1 Hexane/Acetone (using a mixture of vortex and sonication) and separation by centrifugation (10 mins at 3800 RPM). The organic phase was evaporated to dryness and reconstituted into 1mL 3:1 Hexane/Acetone for SPE clean-up. The reconstituted sample was loaded dropwise on to a pre-conditioned florisil cartridge (conditioned with 6mL ethyl acetate and 6mL hexane) followed by fractionation with 6 mL of hexane, 8 mL of ethyl acetate and 4mL Methanol. The fractions were combined and blown down with nitrogen. The dried samples were reconstituted into 200uL of 3:1 Toluene/Methanol mixture and filtered through a 0.22 micron filter. FRs were determined by a combination of LC-MS/MS (Agilent 1260 HPLC system coupled with Sciex 4000 triple quad mass spec using scheduled multiple reaction monitoring) and GC MS (negative chemical ionization under SIM mode).

3.0 Findings

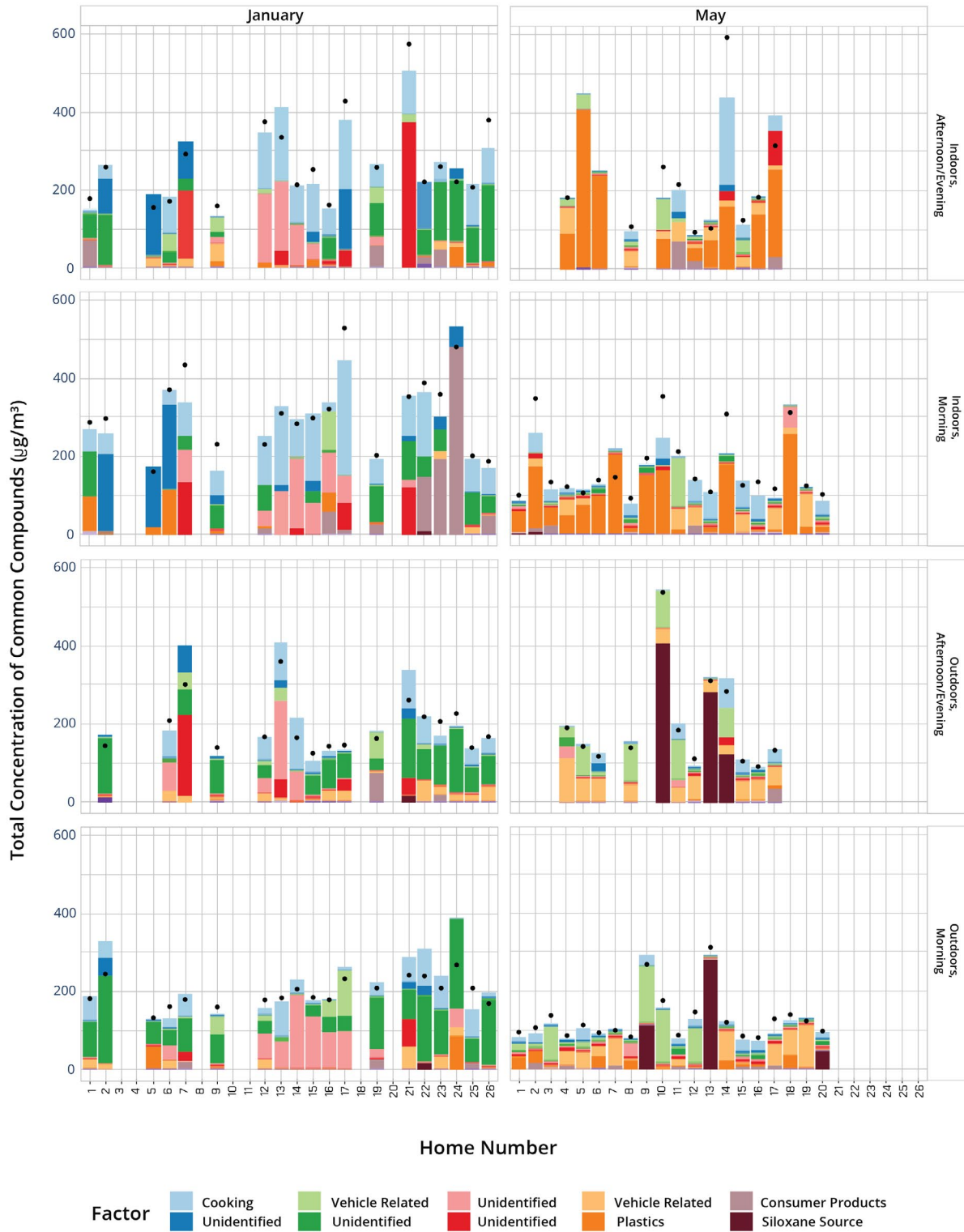


Figure 1: Estimated VOC contributions separated by season, sampling location, and time of day [2021].

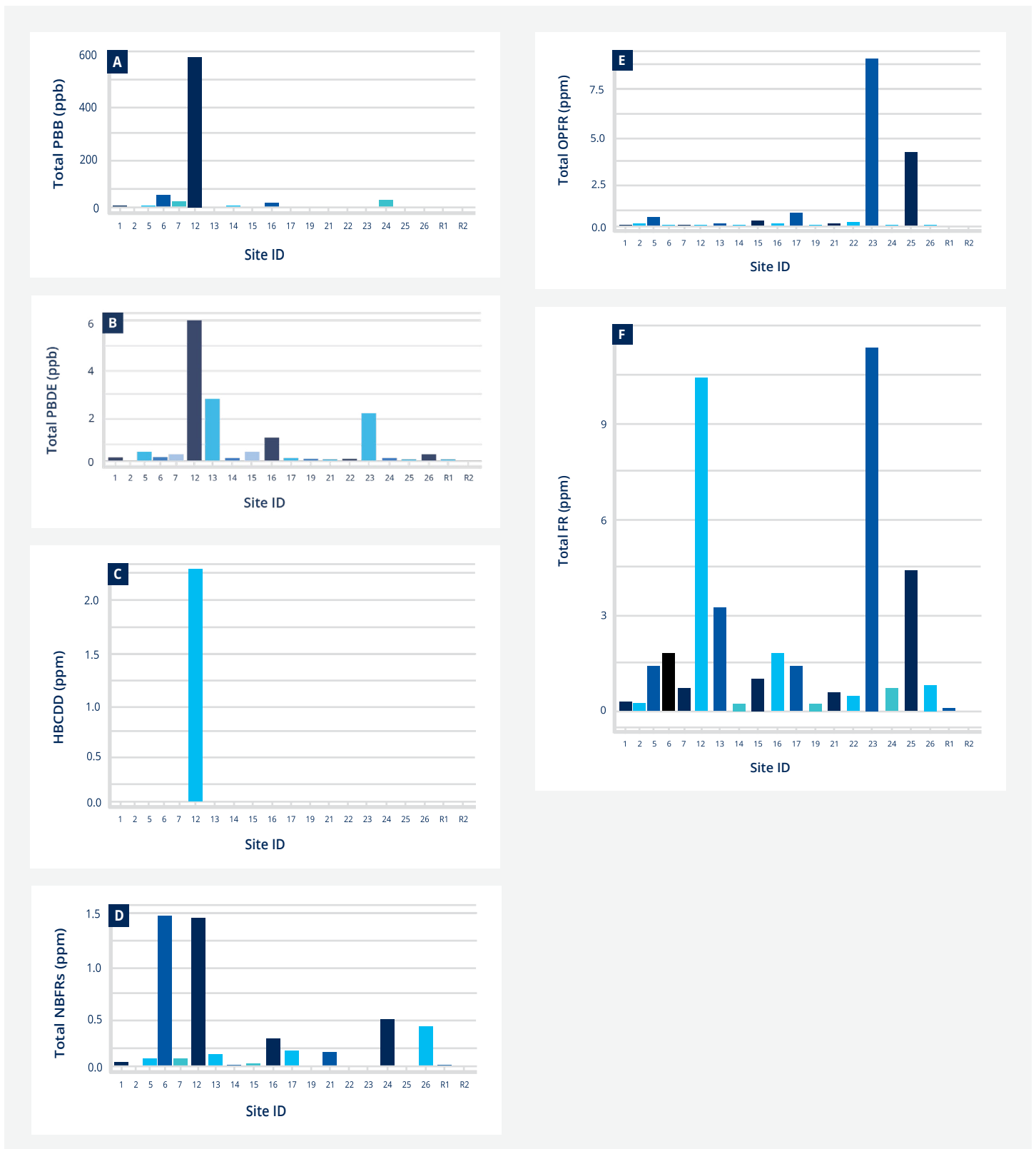


Figure 2: House dust flame retardants from homes in Ahmedabad and Gandhinagar, India. (a) Total PBBs sum of: PBB-3, PPB-15, PBB-18, PBB-52, PBB-101, PBB-153, PBB-180, PBB-194, PBB-206; (b) Total PBDEs sum of: PBDE-47, PBDE-49, PBDE-66, PBDE-71, PBDE-77, PBDE 85, PBDE-99, PBDE-100, PBDE-119, PBDE-126, PBDE-138, PBDE-156, PBDE-153, PBDE-191, PBDE-196, PBDE-197, PBDE-206, PBDE-207; (c) Hexabromocyclododecane; (d) Total novel brominated FRs sum of: EHTBB, BEHTPH, and BTBPE ; (e) Total organophosphorus FRs sum of: TCEP, TCIPP, TPP, ITP, TDBPP, TBPP, MPP, V6, 4tBPDP, EHDP, and TNBP; (f) Total FRs sum of all FR species.

Figure 1 shows the contribution of VOC sources to overall concentrations for households during the study. In general, total VOC concentrations were higher indoors than outdoors for both seasons, with indoor concentrations being highest during winter. There was large variability in the concentrations of VOCs measured across homes, although in general concentrations were higher in the later-day sampling sessions compared to the morning sessions in May, and higher indoors than outdoors in both seasons. Ten potential source groupings were identified for compounds detected at least five times, although for some of these groupings there was not a single clear underlying source or factor. Factors identified related to cooking, plastics, consumer products, siloxanes, and vehicles. Of note, plastic sources contributed substantially to indoor air quality in May but not January, pointing to potential impacts of heat on off-gassing. The large number of compounds quantified that have previously documented adverse associations with health highlights the importance of understanding where these compounds are coming from and how prevalent they are in the indoor environments where people spend most of their time. This work represents a first step towards quantifying indoor VOCs in Indian cities and their contribution to poor air quality and associated health impacts. House dust FR concentrations and composition determined by the project are shown in **Figures 2** and **Figure 3**. Total FRs ranged from 0.02 ppm to 11.31 ppm with a median of 0.86 ppm. The homes with the two highest FRs (sites 23 and 12) were composed of contrasting FR components. FRs at site 23 were comprised primarily of newer OPFRs. The home was in a multi-story apartment complex and contained an abundance of western style furniture and consumer goods. In contrast site 12 FRs were comprised of legacy FRs (PBBs, BDEs), NBFRs and HBCDD. Site 12 was on the ground floor off a dirt lane way. The site was undergoing extensive renovation, including the addition of a second concrete floor above the primary residence. The home had few items of western style furniture. This site was also the only home where HBCDD was detected. Other homes studied contained FRs varying in composition from legacy FRs to newer (for example sites 25 and 13). Road dust samples contained low total FR concentrations from 0.02 to 0.10 ppm. The highest total FRs found in the house dust were comparable to those found in the United States, Europe and China.²⁴⁻³¹ The study shows that the FR concentration and composition can vary widely from home to home in the study area and that a larger dataset is needed to gain insight into indoor sources and exposure. Chemical analysis data was aggregated into a master datafile that reported the identity and levels of chemicals detected in the indoor and outdoor air samples. Figure 3 shows indoor and outdoor TVOC levels of each home for both the 1-hour and 4-hour samples. The data demonstrate that the indoor TVOC and aldehyde levels are tens to over a hundred times higher relative to outdoors and that the sample duration of 1-hour vs. 4-hour results in a similar concentration.

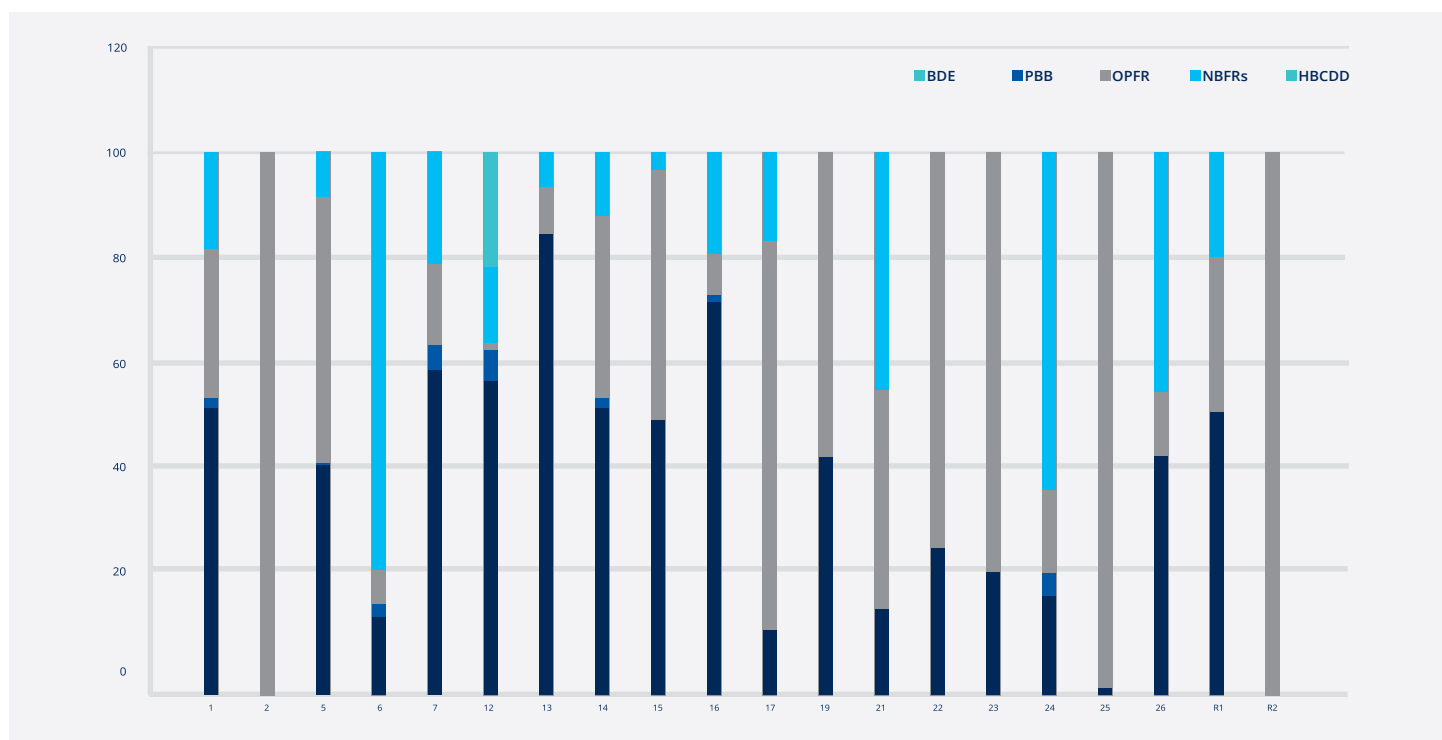


Figure 3: House dust Total FR percentage composition of total PBB, total BDEs, total OPFR, total NBFRs and HBCDD.

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