Environment International 130 (2019) 104921

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Reduction of hazardous chemicals in Swedish preschool dust through article substitution actions

Georgios Giovanoulis[a,*], Minh Anh Nguyen[a], Maria Arwidsson[b], Sarka Langer[a], Robin Vestergren[a], Anne Lagerqvist[b]

[a] IVL Swedish Environmental Research Institute, 100 31 Stockholm, Sweden
[b] City of Stockholm Environment and Health Administration, Environmental Analysis, 104 20 Stockholm, Sweden

ARTICLE INFO

Handling Editor: Heather Stapleton

Keywords:
Preschool
Dust
Plasticizers
Flame retardants
Bisphenols
PFAS

ABSTRACT

Consumer goods and building materials present in the preschool environment can be important sources of hazardous chemicals, such as plasticizers, bisphenols, organophosphorus and brominated flame retardants, poly- and perfluoroalkyl substances, which may pose a health risk to children. Even though exposure occurs via many different pathways, such as food intake, inhalation, dermal exposure, mouthing of toys etc., dust has been identified as a valuable indicator for indoor exposure. In the present study, we evaluate the efficiency of product substitution actions taken in 20 Swedish preschools from the Stockholm area to reduce the presence of hazardous substances in indoor environments. Dust samples were collected from elevated surfaces in rooms where children have their everyday activities, and the concentrations found were compared to the levels from a previous study conducted in 2015 at the same preschools. It was possible to lower levels of hazardous substances in dust, but their continued presence in the everyday environment of children was confirmed since bisphenol A, restricted phthalates and organophosphate esters were still detectable in all preschools. Also, an increase in the levels of some of the substitutes for the nowadays restricted substances was noted; some of the alternative plasticizers to phthalates, such as DEHA and DEHT, were found with increased concentrations. DINP was the dominant plasticizer in preschool dust with a median concentration of 389 μg/g, while its level was significantly ($p = 0.012$) higher at 716 μg/g in preschools with polyvinyl chloride (PVC) flooring. PBDEs were now less frequently detected in dust and their levels decreased 20% to 30%. This was one of the few times that PFAS were analyzed in preschool dust, where 6:2 diPAP was found to be most abundant with a median concentration of 1140 ng/g, followed by 6:2 PAP 151 ng/g, 8:2 diPAP 36 ng/g, N-Et-FOSAA 18 ng/g, PFOS 12 ng/g, PFOA 7.7 ng/g and PFNA 1.1 ng/g. In addition, fluorotelomer alcohols were detected in 65–90% of the samples. Children's exposure via dust ingestion was evaluated using intermediate and high daily intake rates of the targeted chemicals and established health limit values. In each case, the hazard quotients (HQs) were < 1, and the risk for children to have adverse health effects from the hazardous chemicals analyzed in this study via dust ingestion was even lower after the product substitution actions were taken in preschools.

1. Introduction

Ensuring the safety of children is a top priority for preschools. This includes physical as well as chemical safety. During a typical day in the preschool, children encounter a variety of items and products such as furniture and carpets, toys and creative materials (e.g. papers, pencils, pens, yarn, textiles, glues, paints etc.), kitchen utensils and food package materials, as well as cosmetic and chemical products, such as soaps and disinfectants. The frequent mouthing behavior of younger children entails the possibility of exposure to hazardous substances through direct contact with articles or ingestion of dust deposited on toys and other items or directly from the floor. Dust, being a reservoir for many hazardous chemicals released from items in the indoor environment, implies a risk to young children when ingested (Kademoglou et al., 2017; Larsson et al., 2018; Larsson et al., 2017; Winkens et al., 2018). Compared to adults, the frequent hand to mouth activity of young children results in higher dust ingestion rates for this age group (USEPA, 2011). In addition, young children are still under development and have a lower body weight, resulting in increased vulnerability to toxicity from chemical exposure.

* Corresponding author.
E-mail address: georgios.giovanoulis@ivl.se (G. Giovanoulis).

https://doi.org/10.1016/j.envint.2019.104921
Received 4 April 2019; Received in revised form 30 May 2019; Accepted 10 June 2019

There are numerous indoor contaminants originating from different sources. Phthalate esters are plastic additives extensively used in various consumer products, resulting in ubiquitous presence indoors, as they are not covalently bound to the polymeric materials, and are released fairly easily, mainly to air and dust (Bergh et al., 2011). Thus, phthalates are recognized as major indoor contaminants and their use is now restricted in many applications due to their adverse health effects, such as endocrine disruption, reproductive toxicity and increased risk of allergies and asthma in children (Bornehag et al., 2004; Braun et al., 2013; Jurewicz and Hanke, 2011; Kolarik et al., 2008; Rudel et al., 2003). As a consequence, alternative plasticizers to phthalates with lower human toxicity and leaching potential have been introduced to the market during the 2000s, such as acetyltributylcitrate (ATBC), di(2-ethylhexyl)adipate (DEHA), di(2-ethylhexyl)terephthalate (DEHT) and 1,2-cyclohexane dicarboxylic acid diisononyl ester (DINCH) (Bui et al., 2016). Hence, these are now found in indoor dust at comparable concentrations with phthalates (Giovanoulis et al., 2018; Kademoglou et al., 2018; Larsson et al., 2017).

Tetrabromobisphenol A (TTBPA) is a common flame retardant incorporated into electronic/electrical products (Liu et al., 2016), while bisphenol A (BPA) and its analogues (i.e. BPF, BPAF and BPS) are used in plastics, such as kitchen utensils, as well as in thermal papers (e.g. sales receipts) and epoxy resins (Liao and Kannan, 2011). All of them were detected in considerable amounts in dust from preschools, homes and several other microenvironments in Sweden and other countries (Larsson et al., 2017; Wang et al., 2015). Bisphenols exhibit endocrine disrupting effects, reproductive toxicity, dioxin-like effects, and neurotoxicity in in vitro assays and laboratory animal studies (Chen et al., 2016).

Furthermore, preschools, similar to most households and workplaces all over the world, possess furniture, electronics and construction materials, all of which may contain potentially toxic brominated or chlorinated flame retardants to prevent fire hazards (Allgood et al., 2017). For example, polybrominated diphenyl ethers (PBDEs) are persistent, bioaccumulative, and there is evidence for adverse health effects, including endocrine disruption and altered fetal development from these substances (Schreiber et al., 2010). Many PBDEs are listed under the Stockholm Convention on persistent organic pollutants (POPs) as substances for exclusion, and since 2004 their use in the EU is forbidden (UNEP, 2015). Hence, organophosphorus flame retardants have been introduced in many cases, as PBDE replacements in textiles and plastics. However, the elimination of PBDE containing articles, and disposal of these is still a challenge. Consequently, indoor air and dust are contaminated with PBDEs and organophosphate esters (OPEs) that are released from articles and materials (Larsson et al., 2018; Xu et al., 2016; Xu et al., 2017). Moreover, the presence of OPEs in house dust has been associated with adverse health effects, such as altered hormone levels and decreased semen quality in men (Meeker, 2012; Meeker and Stapleton, 2010). For that reason, some OPEs (i.e. TCEP, tris(2-chloroethyl) phosphate; TCPP, tris(2-chloropropyl) phosphate; and TDCPP, 1,3-dichloro-2-propanol phosphate) are regulated in children's toys through the EU Toy Safety Directive (2009/48/EC).

Poly- and perfluoroalkyl substances (PFAS) are used in a variety of articles and products such as textiles, kitchen utensils and lubricants, for their excellent water, oil and dirt repellent properties. PFAS have been measured and detected in indoor dust of various microenvironments, such as homes, offices and children's bedrooms (Moriwaki et al., 2003; Shoeib et al., 2011; Tian et al., 2016; Winkens et al., 2018), but the amount of studies on PFAS levels in preschools are limited. The levels found in some of these studies imply that children's intake of PFAS via dust ingestion could be a more important exposure pathway than from the diet which is the main exposure pathway for adults (Nadal and Domingo, 2014). The most abundant compounds in dust were perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), polyfluoroalkyl phosphoric acid esters (PAPs) and fluorotelomer alcohols (FTOHs) (Eriksson and Karrman, 2015; Karaskova et al., 2016; Padilla-Sanchez and Haug, 2016; Winkens et al., 2018; Yao et al., 2018).

The present study was part of the “chemical smart preschool” initiative, developed by the Environment and Health Administration at the City of Stockholm, focusing on the reduction of hazardous substances in preschools, thereby reducing the risk of children's exposure to such substances. Within the initiative, a guidance document for “chemical smart preschools” was developed, including actions such as discarding old polyvinyl chloride (PVC) items (e.g. toys), exchange of resting mattresses with new hazardous substance free alternatives, and phase-out of plastic kitchen utensils. Information on chemical analyses of old and new articles and materials from Stockholm's preschools and the procured preschool assortments, together with the guidance document is present at www.stockholm.se/kemikaliesmartforskola. In brief, the results from these analyses showed that old toys and mattresses collected at preschools often contain high concentrations of hazardous substances, which are now regulated within EU, while it is rare to find such substances in newly purchased articles from the procured assortments.

The main aim of this study was to evaluate the efficiency of the actions taken to reduce the presence of hazardous chemicals in the indoor environment of 20 preschools in Stockholm according to the guidance document associated with the “chemical smart preschool” initiative. The samples, collected in 2018, were analyzed for legacy, as well as emerging indoor contaminants (Table 1). The determined levels were compared with results obtained from a previous sampling occasion in 2015 at the same preschools (Larsson et al., 2018; Larsson et al., 2017) which took place before performing the “chemical smart preschool” actions. In addition, we evaluated children's exposure to targeted compounds via unintended dust ingestion and related the levels of substances in dust with features in the indoor environment, such as flooring material. Overall, this study will enhance the understanding of different exposure pathways to hazardous chemicals for children, and it illustrates the possibility to facilitate the achievement of a healthy preschool environment through targeted actions.

2. Materials & methods

2.1. Sample collection

Out of the 100 preschools which participated in a previous study during 2015 (Larsson et al., 2018; Larsson et al., 2017) 20 were selected for repeated dust analysis since they had done the chemical smart actions in the guidance document. The preschool staff had received training seminars concerning hazardous chemicals in products, articles and materials that aimed to provide a deeper understanding into the composition of different materials and choices in relation to the presence of hazardous substances in the preschool environment. Prior to the 2018 sampling, contact had been established and confirmation on performed actions within the chemical smart preschool was received. The preschools which confirmed that the staff had removed old articles and materials with high risk of hazardous substances content, and used lists of chemicals smart choices, provided by the Environment and Health Administration, when doing purchases for their units, were chosen for the follow up sampling occasion in 2018 (the lists and other materials are found at www.stockholm.se/kemikaliesmartforskola). Furthermore, close collaboration with the municipality inspectors, allowing an overview of how the work of hazardous substances reduction is functioning in the preschools provided another basis. Questionnaires were used both when the inspectors performed their usual visits to preschools and when they collected samples during 2015 and 2018. The questionnaires included inquiries regarding the indoor materials (type of floor, number and type of electronics, etc.), daily cleaning routines, floor polishing and ventilation function.

The dust collection for this follow up study was carried out during January to February 2018. The dust samples were delivered to IVL

Table 1
Name, abbreviation, CAS number and method limit of detection (μg/g or ng/g) for each studied compound.

Compound name	Abbreviation	CAS number	LOD
Phthalate & alternative plasticizers (μg/g)			
Dimethyl phthalate	DMP	131-11-3	0.01
Diethyl phthalate	DEP	84-66-2	0.004
Diisobutyl phthalate	DiBP	84-69-5	0.01
Di-n-butylphthalate	DnBP	84-74-2	0.02
Benzyl butyl phthalate	BzBP	85-68-7	0.02
Di(2-ethylhexyl)phthalate	DEHP	117-81-7	0.48
Diisononyl phthalate	DINP	28553-12-0	0.34
Diisodecyl phthalate	DIDP	26761-40-0	0.34
Di(2-propylheptyl)phthalate	DPHP	53306-54-0	0.03
Acetyltributylcitrate	ATBC	77-90-7	0.02
Di(2-ethylhexyl)adipate	DEHA	103-23-1	0.01
Di(2-ethylhexyl)terephthalate	DEHT	6422-86-2	0.01
1,2-Cyclohexane dicarboxylic acid diisononyl ester	DINCH	166412-78-8	0.17
Organophosphate esters (μg/g)			
Triisobutyl phosphate	TiBP	126-71-6	0.007
Tri-n-butyl phosphate	TnBP	126-73-8	0.007
Tris(2-chloroethyl) phosphate	TCEP	115-96-8	0.034
Tris(2-chloropropyl) phosphate	TCPP	13674-84-5	0.017
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	13674-87-8	0.017
Tris(2-butoxyethyl) phosphate	TBEP	78-51-3	0.34
Triphenyl phosphate	TPhP	115-86-6	0.017
2-Ethylhexyl diphenyl phosphate	EHDPP	1241-94-7	0.017
Tris(2-ethylhexyl) phosphate	TEHP	78-42-2	0.017
Tricresyl phosphate	TCrP	1330-78-5	0.034
Bisphenols (μg/g)			
Bisphenol A	BPA	80-05-7	0.11
Bisphenol F	BPF	620-92-8	0.017
Bisphenol AF	BPAF	1478-61-1	0.25
Bisphenol S	BPS	80-09-1	0.02
Tetrabromobisphenol A	TBBPA	79-94-7	0.02
Polybrominated diphenyl ethers (ng/g)			
2,4,4′-TriBDE,2,4,4′-Tribromodiphenyl ether	PBDE 28	41318-75-6	3.4
2,2′,4,4′-TetraBDE,2,2′,4,4′-Tetrabromodiphenyl ether	PBDE 47	5436-43-1	2.7
2,2′,3,4′,4-PentaBDE,2,2′,3,4′,4-Pentabromodiphenyl ether	PBDE 85	182346-21-0	3.4
1,2,4-Tribromo-5-(2,4-dibromophenoxy) benzene,2,2′,4,4′,5-PentaBDE, 2,2′,4,4′,5-Pentabromodiphenyl ether	PBDE 99	60348-60-9	4.1
2,2′,4,4′,6-PentaBDE,2,2′,4,4′,6-Pentabromodiphenyl ether solution	PBDE 100	189084-64-8	2.7
2,2′,4,4′,5,5′-HexaBDE,2,2′,4,4′,5,5′-Hexabromodiphenyl ether	PBDE 153	68631-49-2	5.4
2,2′,4,4′,5,6′-Hexabromodiphenyl ether	PBDE 154	207122-15-4	3.4
Decabromodiphenyl ether	PBDE 209	1163-19-5	166
Poly- & perfluoroalkyl substances (ng/g)			
Perfluorobutanoic acid	PFBA	375-22-4	0.5
Perfluoropentanoic acid	PFPeA	2706-90-3	0.5
Perfluorohexanoic acid	PFHxA	307-24-4	0.5
Perfluoroheptanoic acid	PFHpA	375-85-9	0.5
Perfluorooctanoic acid	PFOA	335-67-1	0.5
Perfluorononanoic acid	PFNA	375-95-1	0.5
Perfluorodecanoic acid	PFDA	335-76-2	1
Perfluoroundecanoic acid	PFUnDA	2058-94-8	0.5
Perfluorododecanoic acid	PFDoDA	307-55-1	0.5
Perfluorobutanesulfonic acid	PFBS	375-73-5	0.5
Perfluorohexanesulfonic acid	PFHxS	355-46-4	0.5
Perfluorooctanesulfonic acid	PFOS	1763-23-1	0.2
Perfluorodecanesulfonic acid	PFDS	335-77-3	1
Perfluorooctane sulfonamide	FOSA	754-91-6	0.3
6:2 fluorotelomer sulfonate	6:2 FTS	27619-97-2	1
Mono[2-(perfluorohexyl)ethyl] phosphate	6:2 PAP	57678-01-0	1
Mono[2-(perfluorooctyl)ethyl] phosphate	8:2 PAP	57678-03-2	1
Bis[2-(perfluorohexyl)ethyl] phosphate	6:2 diPAP	57677-95-9	1
Bis[2-(perfluorooctyl)ethyl] phosphate	8:2 diPAP	678-41-1	1
N-methylperfluorooctane sulfonamidoacetic acid	N-Me-FOSAA	2355-31-9	1
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-Et-FOSAA	2991-50-6	1
6:2 fluorotelomer alcohol	6:2 FTOH	647-42-7	0.06
8:2 fluorotelomer alcohol	8:2 FTOH	678-39-7	0.04
10:2 fluorotelomer alcohol	10:2 FTOH	865-86-1	0.02

Swedish Environmental Research Institute for analysis. One settled dust sample from elevated surfaces (50–250 cm above the floor) from different areas of a play room at each preschool was collected (the same room as in the study of 2015 was sampled), using the dust sampling method previously described in Papadopoulou et al. (2016). Briefly, each sample was collected using a cellulose filter pre-cleaned with methanol and fixed in a styrene acrylonitrile container. The container was inserted into a holder made of polypropylene (Krim. TekniskMateriel AB, Bålsta, Sweden) and mounted on the nozzle of a vacuum cleaner. The filter weight was noted before and after sampling, under identical conditions of room temperature and relative humidity. Field blank samples were also collected from the same room where the dust samples were taken, by attaching a holder with an unused filter to the nozzle of the vacuum cleaner, as when taking a sample but instantly starting and stopping the vacuum cleaner without touching any surface. The filter container was wrapped in aluminum foil and stored at −20 °C until analysis.

2.2. Chemical analysis

2.2.1. Plasticizers and organophosphate esters

Dust samples (approx. 50 mg each) were spiked with 200 ng deuterated internal standard (IS) mix for the phthalate and alternative plasticizers, consisting of DMP-d_4, DnBP-d_4 and DEHP-d_4, and 200 ng IS mix for the organophosphate esters, consisting of phosphoric acid tri-n-amyl ester (TAP) and TPhP-d_{15}. The samples were extracted with organic solvent (10 mL of acetone: n-hexane 2:1, v/v) and microwave-assisted extraction (Milestone Ethos UP, Sorisole, Italy) under controlled pressure and temperature program (15 min at 100 °C). The dust clean-up was performed with a Florisil solid phase extraction (SPE) cartridges (ISOLUTE FL 500 mg/3 mL from Biotage, Uppsala) pre-cleaned with 6 mL acetone, allowed to dry, and then conditioned with 3 mL n-hexane. Each sample extract was loaded onto the SPE and washed with 6 mL n-hexane. Plasticizers and OPEs were eluted with 6 mL acetone: n-hexane (1:1, v/v), concentrated by applying a gentle nitrogen (N_2) stream to approx. 1 mL, and then 100 ng biphenyl was added as volumetric pre-injection standard. The analyses were carried out, first for plasticizers and after for organophosphate esters, with a gas chromatography tandem mass spectrometry GC/MS/MS system (Agilent 7000; Agilent Technologies, Inc., Santa Clara, CA, USA) in electron impact ionization mode (EI) with DB-5 30 m, 0.25 mm, 0.25 μm column. The instrument was equipped with an auto injector (Agilent 7683B) and the injection was in pulsed splitless mode. Integration was made with MassHunter software version B.04.00 for quantitative analysis (Agilent Technologies, Inc. 2008).

2.2.2. Bisphenols

The dust extraction method for bisphenols using 200 ng BPA-d_{16} as IS was similar to plasticizers and OPEs with an extra derivatization step of the final extracts. Derivatization was performed with the use of *N*-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA; CAS 24589-78-4) (Fan et al., 2019). Dust sample extracts were concentrated to 0.2 mL and then 50 μL of MSTFA was added and the mixture vortexed for 30 s. Afterwards, the extracts were incubated at 60 °C for 30 min, and then diluted to 1 mL with n-hexane. The analyses were carried out with the same GC/MS/MS system in EI mode, as described above.

2.2.3. Polybrominated diphenyl ethers

Dust samples (approx. 50 mg each) were spiked with an internal standard mix containing 4.86 ng of each PBDE 166 and PBDE 190, and 14.69 ng of PBDE 119. The samples were extracted with 2 × 4 mL acetone and 2 × 4 mL n-hexane: methyl tert-butyl ether (9:1 v/v) in an ultrasonic bath for 20 min per cycle. The sample extracts were concentrated by a gentle N_2 stream to 0.5 mL. After, the dust extracts were treated with concentrated sulfuric acid and fractionated using an aluminum oxide column under controlled polarity. Fraction 1 was eluted with 15 mL pentane and was not used for analysis. Fraction 2, containing PBDE 28, 47, 85, 99, 100, 153 and 154, was eluted with 10 mL pentane: toluene (9:1 v/v). Fraction 3, containing BDE 209, was eluted with 10 mL pentane: toluene: diethyl ether (45:5:50 v/v). Finally, fractions 2 and 3 were concentrated by applying a gentle nitrogen (N_2) stream to approx. 0.5 mL and spiked with 9.83 ng octachloronaphtalene as volumetric standard. The analyses were carried out on GC-ECD Thermo Trace 1310 with CP-SIL8 CB 50 m, 0.25 mm, 0.25 µm column.

2.2.4. Poly- and perfluorinated substances

Dust samples (approx. 50 mg each) were spiked with 4.75 ng of an internal standard mix containing sodium perfluoro-1-(1,2,3,4-$^{13}C_4$)octane sulfonate ($^{13}C_4$-PFOS), perfluoro-n-(1,2,3,4-$^{13}C_4$)octanoic acid ($^{13}C_4$-PFOA) and sodium 1H, 1H, 2H, 2H-perfluoro-1-[1,2-$^{13}C_2$]octane sulfonate ($^{13}C_2$-6:2-FTS), and 50 ng 2-perfluorohexyl-(1,2-$^{13}C_2$)ethanol ($^{13}C_2$-8:2 FTOH). The samples were then extracted with 2 × 3 mL methanol in an ultrasonic bath and cleaned up by resuspension with the addition of 10 mg ENVI-Carb to the extracts. The sample extracts were concentrated by applying a gentle N_2 stream to approx. 0.5 mL and then 50 ng of 3,5-bis(trifluoromethyl)phenyl acetic acid (3,5-BTPA) was added as volumetric standard before the analyses. PFAS analyses were performed using high pressure liquid chromatography tandem mass spectrometry HPLC/MS/MS (API 4000™ system) in negative electron spray ionization (-ESI). The data were quantified using Analyst software (Analyst 1.63, AB SCIEX). After the PFAS LC analysis, the solvent was exchanged from methanol to ethyl acetate, and all samples were injected to GC/MS/MS (Agilent 7000; Agilent Technologies) in EI mode to determine the fluorotelomer alcohol (FTOH) levels.

2.3. Quality assurance and quality control

To avoid external contamination, laboratory glassware was rinsed with acetone, dried, covered with aluminum foil and heated at 400 °C overnight before use. All organic solvents were tested in advance for contamination, and no background levels were detected. The N_2 gas stream was filtered through glass Pasteur pipettes filled completely with activated charcoal powder and glass wool on the narrow point during the evaporation of sample extracts. Solvent and field blanks were analyzed together with the dust samples. The determined dust levels were blank subtracted, if needed, and the limit of detection (LOD) for each compound was defined as three times the standard deviation of the blanks (Table 1). If nothing was observed in the blanks, the LOD was based on a signal to noise ratio of three of a standard solution. The standard reference material (SRM) 2585 from National Institute of Standard and Technology (NIST, USA) was analyzed each time in replicate (n = 4) to evaluate the accuracy of the analytical method for the determination of the selected compounds (see Table S1). The accuracy ranged between 80 and 112% for OPEs, 89–114% PBDEs and 81–140% for PFAS compared to the available NIST certified values. In addition, the results for phthalates, OPEs, BPA and PFAS were in good agreement with previously reported values in literature (Ali et al., 2012; Bergh et al., 2012; Fan et al., 2019; Luongo and Ostman, 2016; Reiner et al., 2015; Sahlstrom et al., 2012; Tay et al., 2017; Winkens et al., 2018).

2.4. Data analysis

All chemical concentrations in the 20 dust samples were summarized by standard descriptive statistics. Also, detection frequencies (DFs) were reported for all measured compounds. Further, statistical analyses and exposure assessment were only performed for chemicals with DF > 50%. Values below the respective LOD were replaced with LOD/2. Most of the compounds failed the Shapiro-Wilk normality test ($p > 0.05$). Therefore, a non-parametric Wilcoxon matched-pairs signed rank test was applied to compare the determined dust levels of the different substances between 2015 and 2018 for each preschool. We assessed the median percentage change (%) per chemical compound between the two different sampling occasions using Eq. (1).

$$\text{Change (\%)} = \frac{C_{\text{dust 2018}} - C_{\text{dust 2015}}}{C_{\text{dust 2015}}} \times 100 \quad (1)$$

We evaluated the correlations between different chemicals in dust by Spearman correlation coefficient for non-normal distributed data. Furthermore, we performed the nonparametric unpaired Mann–Whitney U compare rank test to evaluate the correlations between different chemicals in dust and the floor material. Spearman rank test was also used to identify correlations between chemicals in dust and the number of electronics (i.e. computer, tv, radio, cd player, microwave, dishwasher, refrigerator etc.) present in the room from where the dust was collected. In each case, significant correlations and differences were considered if $p < 0.05$. All statistical analyses were performed using GraphPad Prism 8.

2.5. Exposure assessment

To estimate children's exposure via unintended dust ingestion (assuming 100% chemical absorption rate), the results from analyses of dust collected from elevated surfaces in the 20 preschools in 2018 were used and expressed in ng/kg bw/day for children of age 1 to < 6. Daily intake (DI_{dust}) was calculated using Eq. (2).

$$DI_{dust} = \frac{C_{dust} \times I_{dust}}{BW} \quad (2)$$

where C_{dust} is the concentration in the elevated surface dust (ng/mg_{dust}), I_{dust} the daily dust ingestion rate (mg_{dust}/day) for intermediate (30 mg) and high (50 mg) exposure scenario of children attending a preschool (duration of 8 h). BW is the average body weight (14.23 kg; calculated as the average of 11.3 kg for 1 to < 2 years, 13.6 kg for 2 to < 3 years and 17.8 kg for 3 to < 6 years) (USEPA, 2011).

Contribution from other exposure pathways related to indoor dust, such as exposure via dust adhered to the skin and inhalable dust, were not calculated because their contribution is considered to have a minor effect on the total intake (Beko et al., 2013; Giovanoulis et al., 2018; Guo and Kannan, 2011). For example, Guo and Kannan (2011) found that the total DI of phthalate esters through dust ingestion was 100–1000 times higher than that through dust dermal absorption.

To assess the health risk for children, we calculated the hazard quotient (HQ) according to Eq. (3), that is the ratio between the total daily intake estimated via dust ingestion and established health limit values, expressed as oral reference doses (RfDs) or tolerable daily intakes (TDIs) or derive no effect levels (DNELs) for each compound (Table S2).

$$HQ = \frac{DI_{dust}}{\text{RfD or TDI or DNEL}} \quad (3)$$

3. Results & discussion

3.1. Descriptive statistics

Data on phthalates, alternative plasticizers, bisphenols, OPEs, PBDEs and PFAS in dust samples from the 20 preschools in 2018 are presented in Table 2. Also, the dust levels found from a previous sampling occasion at the same preschools in 2015 (Larsson et al., 2018;

Table 2
Descriptive statistics (detection frequency, median value and 95% percentile) for compounds found in dust from Swedish preschools (n = 20) during the sampling occasions of 2015 and 2018.

	Compound name	DF %		Median		95% P	
		2015	2018	2015	2018	2015	2018
Phthalate & alternative plasticizers (μg/g)	DMP	80	95	0.095	0.045	10.8	0.247
	DEP	40	100	0.025	0.3	126	5.51
	DiBP	100	100	6.8	4.2	27.8	30.5
	DnBP	100	100	16.0	13.1	91.2	527
	BzBP	100	90	9.2	6.4	46.3	38.6
	DEHP	100	100	285	117	3420	329
	DINP	100	100	940	389	2550	2445
	DIDP	100	100	61	57	249	87.3
	DPHP	100	100	5.8	4.7	248	16.2
	ATBC	100	100	5.3	5.03	58	39.8
	DEHA	100	100	5.65	8.54	165	138
	DEHT	100	100	80	98.6	410	401
	DINCH	100	100	64.5	57.2	5095	2107
Organophosphate esters (μg/g)	TiBP	–	100	–	0.025	–	1.61
	TnBP	–	95	–	0.055	–	2.01
	TCEP	50	100	7.8	35.2	72.9	506
	TCPP	25	100	4.1	1.66	62.2	39.4
	TDCPP	100	100	1.5	2.79	9.5	358
	TBEP	75	100	38.2	256	1185	1913
	TPhP	100	100	0.8	0.535	9.32	10.4
	EHDPP	–	100	–	1.77	–	356
	TEHP	–	100	–	0.4	–	1.14
	TCrP	–	100	–	0.98	–	7.46
Bisphenols (μg/g)	BPA	100	100	1.65	0.778	5.17	6.1
	BPF	60	80	0.06	0.023	4.35	0.251
	BPAF	30	0	0.065	< LOD	0.17	< LOD
	BPS	80	95	0.255	0.626	0.991	0.971
	TBBPA	100	80	0.105	0.134	2.34	1.61
Polybrominated diphenyl ethers (ng/g)	PBDE 28	–	5	–	< LOD	–	4.27
	PBDE 47	100	75	6.7	5.52	590	314
	PBDE 85	–	0	–	< LOD	–	< LOD
	PBDE 99	95	65	8.2	6.72	424	231
	PBDE 100	60	45	1.48	< LOD	117	81.9
	PBDE 153	25	5	< LOD	< LOD	20.7	4.89
	PBDE 154	–	5	–	< LOD	–	4.95
	PBDE 209	100	60	295	189	3110	10,321
Poly- & perfluoroalkyl substances (ng/g)	PFBA	–	15	–	< LOD	–	18.4
	PFPeA	–	25	–	< LOD	–	7.61
	PFHxA	–	40	–	< LOD	–	15.2
	PFHpA	–	35	–	< LOD	–	8.894
	PFOA	–	95	–	7.71	–	35.1
	PFNA	–	55	–	1.09	–	56.0
	PFDA	–	0	–	< LOD	–	< LOD
	PFUnDA	–	5	–	< LOD	–	9.68
	PFDoDA	–	10	–	< LOD	–	8.03
	PFBS	–	0	–	< LOD	–	< LOD
	PFHxS	–	0	–	< LOD	–	< LOD
	PFOS	–	85	–	12.2	–	48.9
	PFDS	–	45	–	< LOD	–	209
	FOSA	–	20	–	< LOD	–	0.287
	6:2 FTS	–	0	–	< LOD	–	< LOD
	6:2 PAP	–	80	–	151	–	2728
	8:2 PAP	–	35	–	< LOD	–	423
	6:2 diPAP	–	100	–	1143	–	42,281
	8:2 diPAP	–	100	–	35.9	–	377
	N-Me-FOSAA	–	0	–	< LOD	–	< LOD
	N-Et-FOSAA	–	95	–	18.4	–	283
	6:2 FTOH	–	65	–	4.05	–	399
	8:2 FTOH	–	90	–	18.3	–	142
	10:2 FTOH	–	80	–	12.4	–	74.8

Larsson et al., 2017) are included in the table to make the comparison easier. In addition, box plots for all compounds with DF > 50% are shown in Fig. 1.

The levels of phthalates, alternative plasticizers, bisphenols and organophosphorus flame retardants were either always above the LOD_m or detected with high frequency (80–100% DF), except for BPAF that was not identified in any of the samples. The presence of PBDEs varied a lot and only PBDE 47, 99 and 209 were frequently detected (60–75% DF). Also, this was one of the few times that PFAS were analyzed in preschool dust, and out of the 21 fluorinated compounds included in the LC/MS/MS fraction, only PFOA, PFNA, PFOS, 6:2 PAP, 6:2 diPAP, 8:2 diPAP, N-et-FOSAA (55–100% DF) were regularly found. For FTOHs which were detected by GC/MS/MS, all three compounds including 6:2, 8:2, and 10:2 FTOHs were found at high detection frequencies (65–90% DF).

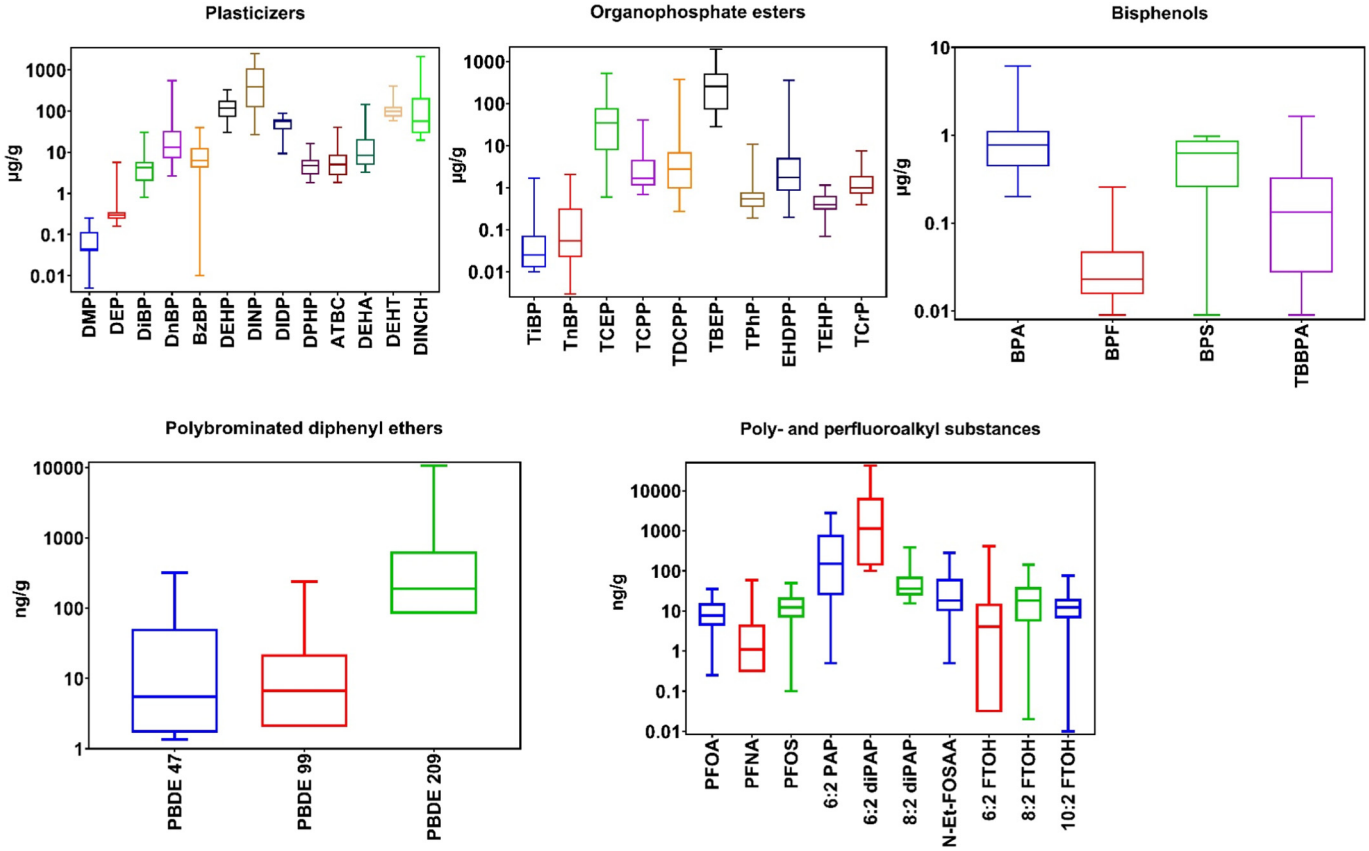

Fig. 1. Box-Whisker plots for the different chemical groups (µg/g or ng/g of dust). Boxes represent 25th, 50th (horizontal line) and 75th percentile. Whiskers above and below the boxes show the locations of the minimum and maximum. Y-axis is in log scale.

3.2. Levels in preschool dust before and after the article substitution actions, and comparison with other studies

The highest median level among the phthalates was observed for DINP (389 µg/g), followed by DEHP (117 µg/g) and DIDP (57 µg/g) and DnBP (13 µg/g), whereas DEHT (99 µg/g) and DINCH (57 µg/g) were the alternative non-phthalate plasticizers found at the highest median levels (Table 2). The levels of all phthalates found in preschool dust in 2015 were now decreased between 2% to 60%, after the "chemical smart" actions were taken, and some of them were significantly lower ($p < 0.05$; Fig. 2). The concentrations in dust for some of the alternative plasticizers were instead increased since 2015, although not significant; DEHA (median 5.7 µg/g) and DEHT increased by 34% and 36% respectively, while ATBC (median 5.3 µg/g) decreased by 26%. On the other hand, the content of DINCH in the dust was reduced by 39%, which may be due to discarding newer toys or mattresses with DINCH content by preschools during the sorting. It is rarely known when the items were bought and most often there is no label stating the year of production, which makes it difficult for the preschool staff to judge the age of these articles and some might be discarded although they are not that old. The median concentrations of phthalates found in the preschool dust in this study (Table 2) were much lower than vacuumed dust from French schools (DEHP 1430, DINP 1030, BzBP 105, DnBP 52.6, DiBP 38.2, DEP 52.6 and DMP 3.3, all in unit of µg/g) (Raffy et al., 2017), as well as lower than dust from Danish (DEHP 500, BzBP 17, DnBP 38, DiBP 23 and DEP 2.2, all in unit of µg/g) (Langer et al., 2010) and German (DINP 302, DEHP 888, DnBP 21, DiBP 20, DEP 1.4 and DMP 0.3, all in units of µg/g) (Fromme et al., 2013) daycare centers. Similarly, the alternative plasticizers in Swedish preschool dust from this study were lower than the levels found previously at German daycare centers (DINCH 302, DEHT 40, DEHA 49 and ATBC 24, all in units of µg/g), except for DEHA where the level was comparable but slightly higher (Fromme et al., 2016).

Regarding the bisphenols, the median levels of BPA (0.78 µg/g) and BPF (0.023 µg/g) significantly declined in the second dust sampling occasion by 49% and 78% respectively ($p < 0.05$). Also, BPAF was not detected at any of the dust samples similar with 2015 where it was poorly detected (30% DF). At the same time, BPS with a median concentration of 0.63 µg/g increased significantly by 93% ($p = 0.026$), which might be due to it being the main replacement for BPA applications. TBBPA, which is used in other applications than BPA, BPF and BPS (median 0.13 µg/g) was reduced to half of the concentration in 2015 (Fig. 2). However, although the sum of TBBPA, BPA and its analogues (median 1.56 µg/g) found in the preschool dust in 2018 was reduced by a quarter compared to 2015 (median 2.07 µg/g), it was still higher than the median level (0.61 µg/g) in house dust from 12 countries (Wang et al., 2015). This may be due to different bisphenol sources in preschools compare to households.

The presence of brominated and organophosphorus flame retardants in preschool dust was confirmed. Thus, there is a risk for children's exposure via ingestion, transdermal and inhalation exposure of these substances which has also been found in other studies that analyzed occupational and household dust samples (Abdallah et al., 2015; Xu et al., 2016). However, the median concentrations for PBDE 28, 85, 100, 153 and 154 were below the LOD, while for the rest of PBDEs the levels decreased 20% to 30% between 2015 and 2018 at the same preschools (see Fig. 2). This decrease was especially evident and found to be significant (−23%; $p < 0.05$) for PBDE 99 with a median concentration of 8.2 µg/g and 6.7 µg/g for 2015 and 2018, respectively. The reason might be that one of the actions in the guidance document is to remove electronic equipment from the playrooms and not to play with old electronics. We did not find any PBDEs or polybrominated

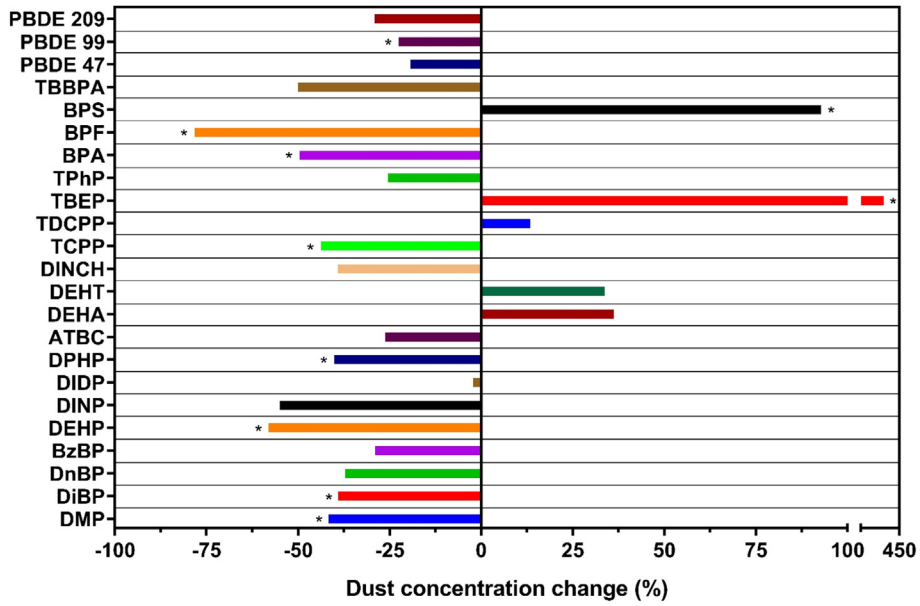

Fig. 2. Median percentage change (%) of chemicals found in preschool dust between years 2015 and 2018. Statistically significant difference shown here (* $p < 0.05$).

biphenyls in toys or furniture which we analyzed in another study (Pettersson et al., 2018). Moreover, TCPP which is another toxic flame retardant commonly used in polyurethane foam in consumer products, home insulation and electronics was now significantly reduced by 44% ($p = 0.006$) compared to the measurement in 2015 (Fig. 2). Tris(2-butoxyethyl) phosphate (TBEP) was detected at the highest concentration (median of 256 μg/g; max of 1966 μg/g) among all OPEs and its level was significantly increased ($p = 0.0003$) by 4 orders of magnitude compared to 2015 (Fig. 2). The large amount of TBEP found in dust can be explained from the fact that it is a primary plasticizer and a leveling agent in floor polishes (Mizouchi et al., 2015; Persson et al., 2018). It has also been identified as the most abundant OPE in handheld devices (e.g. cell phones, tablets and laptops) (Yang et al., 2019). Nevertheless, the determined median concentration of TBEP was approximately six times lower than the level previously found in Swedish daycare centers (median 1600 μg/g; max 4100 μg/g) (Bergh et al., 2011) and Japanese households (median 1570 μg/g; max 5890 μg/g) (Kanazawa et al., 2010), and similar with levels found in German daycare centers (median 225 μg/g, max 4711 μg/g) (Fromme et al., 2014) and elementary schools in Japan (median 270 μg/g; max 5500 μg/g) (Mizouchi et al., 2015). Still, it was much higher than the median in Danish daycare centers (median 26 μg/g; max 11,000 μg/g) (Langer et al., 2016), Norwegian classrooms (median 87.2 μg/g; max 163 μg/g) and households (median 8.2 μg/g; max 540 μg/g) (Xu et al., 2016). For the other OPEs, TPhP (median 0.53 μg/g) decreased by 25% and TDCPP (median 2.8 μg/g) increased by 13% but none of these findings were statistically significant ($p > 0.05$). TCEP was detected in all preschools (median 35 μg/g) with a comparable concentration with a previous study from Swedish daycare centers (median 30 μg/g) (Bergh et al., 2011). Yet, we avoided comparing it with the previous measurement in the same preschools in 2015 since the detection frequency for TCEP was low in those samples (median 7.8 μg/g; DF 50%). In general, the levels for OPEs in this study were comparable or less than other daycare centers in Sweden, Denmark, Germany and China (Bergh et al., 2011; Fromme et al., 2014; Langer et al., 2016; Wu et al., 2016).

PFAS were not analyzed in the previous sampling occasion in the same preschools in 2015, therefore it was impossible to know if the levels decreased after the “chemical smart” actions. However, comparisons have been made with other indoor dust studies and are discussed in detail. Perfluorinated carboxylic and sulfonic acid levels in this study were most of the times similar or lower than previous studies of dust in other indoor environments from Sweden and other countries. PFOA and PFOS, the most common PFAS reported in all environmental compartments were also detected most frequently in dust samples in this study. The level of PFOA in this study (median 7.7 ng/g; max 36 ng/g) was in similar range with a previous measurement in the dust of 39 child care facilities in USA (median 8 ng/g; max 235 ng/g) (Bradman et al., 2012), while it was five times lower compared with another study from 10 Swedish daycare centers (median 41 ng/g; max 110 ng/g) (Bjorklund et al., 2009) and much lower than 102 homes and 10 day care centers (median 142 ng/g; max 1960 ng/g) in USA (Strynar and Lindstrom, 2008). For PFOS, the result in this study (median 12 ng/g; max 49 ng/g) was slightly higher than in US child care centers (median 6.2 ng/g; max 67 ng/g) but lower than in dust from Swedish daycare centers (median 31 ng/g; max 65 ng/g) (Bjorklund et al., 2009; Bradman et al., 2012) and US homes and day care centers (median 201 ng/g; max 12,100 ng/g) (Strynar and Lindstrom, 2008). In a previous study by Goosey and Harrad (2011), where dust from daycare centers and classrooms was collected in UK during 2007–2008, the PFOA level (median 240 ng/g; max 1700 ng/g) and PFOS (median 840 ng/g, max 3700 ng/g) levels were 31 and 69 times higher respectively than the determined levels in this current study. In addition, PFNA (median 1.1 ng/g) concentration was lower than that of the US homes and daycare centers (8 ng/g) (Strynar and Lindstrom, 2008). Regarding PFAS precursors, the median levels (34.7 ng/g) observed in this study for the ΣFTOHs, including 6:2, 8:2 and 10:2 FTOH, were lower than in dust from 65 children's bedrooms in Finland (89.1 ng/g) (Winkens et al., 2018), and homes and daycare centers in USA (87 ng/g) (Strynar and Lindstrom, 2008). However, 6:2 diPAP (median 1143 ng/g), followed by 6:2 PAP (median 151 ng/g), and 8:2 diPAP (median 36 ng/g) in this study were higher compared to Winkens et al. (2018) with median dust concentrations of 54 ng/g, 15 ng/g and 3.5 ng/g, respectively. The median concentration of 6:2 diPAP in the 20 Swedish preschools was 2.5 times higher than residential dust from a study conducted in Canada (median 460 ng/g) (De Silva et al., 2012), whereas 8:2 diPAP was 15 times lower compared to the same study in Canada (median 535 ng/g). Professional floor polish solutions, other cleaning products and water-based paints could be important sources of diPAPs (De Silva et al., 2012). Considering that floor polish solutions

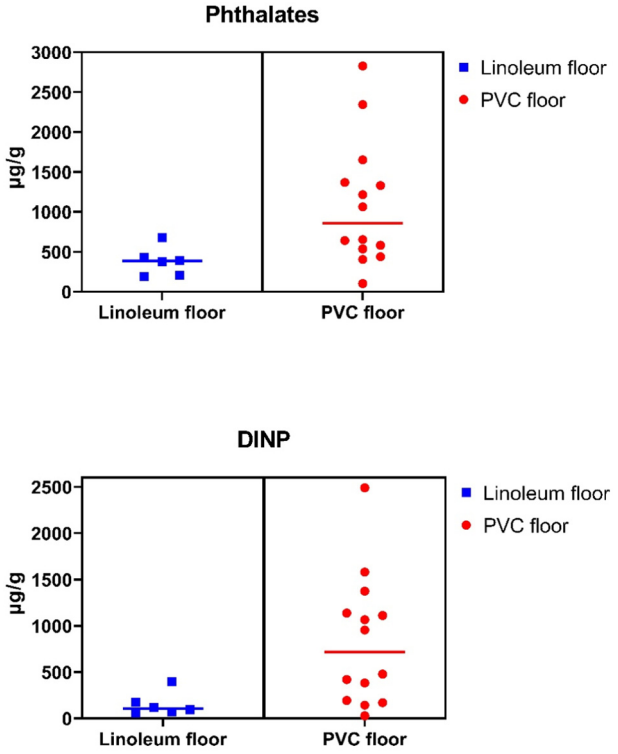

Fig. 3. Phthalates and DINP dust concentration (µg/g) plotted by floor material. The horizontal line indicates the overall median dust concentration from preschools with the same floor material. Differences in dust levels shown here were statistically significant ($p < 0.015$) based on unpaired Mann-Whitney U compare rank test between PVC vs linoleum floor.

are typically only used in public buildings this could potentially explain the relatively high concentrations of 6:2 diPAPs found in the Swedish preschools compared to residential buildings (Jensen et al., 2008; Moriwaki et al., 2003). The variation in concentrations of precursors in this study compared to other studies might have been affected by the sampling location and consumer products which were present in the room (De Silva et al., 2012; Winkens et al., 2018), but all the studies show an increasing trend in the use of short-chain C4-C6 PFAS, including PAPs, in consumer products (Daikin, 2007).

3.3. Correlation between the different hazardous chemicals in dust

Moderate ($r = 0.40–0.59$) and strong correlations ($r > 0.6$) were observed between the individual phthalates in preschool dust and many of them were significant (Fig. S1). This may reflect that phthalates derive from the same indoor sources of contamination, such as old PVC flooring, toys and mattresses, as well as in recycled materials in new PVC flooring and/or other indoor equipment (Christia et al., 2019; Pettersson et al., 2018). Strong positive and highly significant correlations were found between PFOA - PFNA ($r = 0.88$, $p < 0.001$), 6:2 PAP - 6:2 diPAP ($r = 0.92$, $p < 0.001$), 6:2 di PAP - 6:2 FTOH ($r = 0.57$, $p < 0.001$) and 6:2 PAP - 6:2 FTOH ($r = 0.68$, $p < 0.001$). Formation or degradation can occur from PAPs and diPAPs to FTOHs via hydrolysis and then to perfluorinated carboxylic acids (e.g. PFOA, PFNA) via oxidation during the telomerization process from perfluoroalkyl iodide, which might explain the correlations found for these substances (Buck et al., 2011). Also, a strong positive correlation existed between 8:2 FTOH and 10:2 FTOH ($r = 0.73$; $p < 0.001$) due to their common origin in the telomerization process (Wang et al., 2014a; Wang et al., 2014b). 6:2 FTOH showed a strong positive association with TBBPA ($r = 0.62$, $p < 0.005$), maybe due to newly bought electronics, furniture and carpets containing these compounds, while it had a moderate negative association with DEHT, DINP and PBDE 209 ($p < 0.05$). Furthermore, we found N-Et-FOSAA to have a positive correlation with PFOS ($r = 0.52$; $p < 0.02$), while it had negative associations with OPEs, bisphenols and phthalates (see Fig. S1). Many of the above mentioned intra-PFAS correlations in preschool dust were in agreement with Winkens et al. (2018) who indicated that a fraction of PFAS in indoor dust can originate from the same product applications as they pre-existed in mixtures during the electrochemical fluorination production. Apart from the intra-phthalate correlation described above, DINP was positively associated ($p < 0.03$) with some of the alternative plasticizers (i.e. DEHA and DEHT), OPEs (i.e. TDCPP, TEHP and TCrP) and PBDE 99. At the same time, DINP had moderate negative correlations ($p < 0.05$) with most of the PFAS (Fig. S1). DiBP and DEHP were positively correlated with BPA ($r = 0.61$ and 0.46 respectively, $p < 0.04$) which could suggest that this co-existence may derive from similar indoor sources. Most of the OPEs, had positive correlations with each other, especially for TCrP with TCPP, TDCPP, TPhP, EHDPP and TEHP ($r = 0.46–0.81$; $p < 0.015$). TCrP was also positively associated with DEHT ($r = 0.51$; $p < 0.001$). Finally, PDBE 49 and 99 were strongly positively correlated ($p < 0.001$), and we found some interesting significant positive correlations ($p < 0.05$) between the sum of PBDEs with the sum of phthalates and the sum of bisphenols. This correlation may indicate that these substances are all present in the same articles, for example electronic equipment where PBDEs provide flame retardancy, phthalate plasticizers are added for flexibility in the cables and bisphenols are present in the plastic casing.

3.4. Associations between dust and indoor parameters

The use of PVC flooring in Swedish preschools is extensive (Larsson et al., 2010). This type of floor can be an important source for phthalates in indoor dust. The presence of PVC flooring has been shown to be associated with asthma and allergy among children and related to increased urinary levels of phthalate metabolites in pregnant women (Shu et al., 2014; Shu et al., 2019). The content of phthalates in newly purchased PVC flooring material in China sometimes may exceed 20% and DnBP, BzBP, DEHP and DINP can be the dominant plasticizers used (Liang and Xu, 2014), while in the European PVC flooring production alternative plasticizers such as DINCH are mainly used. Both types of PVC floors can be found on the Swedish market, and the more common phthalate in imported PVC flooring materials nowadays is DINP (IVL, 2016).

In this study (see Fig. 3), the dust concentration of phthalates was more than two times higher in preschools with PVC flooring (median of 857 µg/g; $p = 0.015$) than preschools with linoleum floor material (median of 384 µg/g). In 2015, the PVC floors from the preschools included in this study were analyzed and high contents of DINP were reported (i.e. 7.5–41% w/w) (WSP, 2015). Therefore, it was reasonable to find that the difference in DINP level in dust was significant and seven times higher in preschools with PVC flooring (median of 716 µg/g, $p = 0.012$) compared to dust from preschools with linoleum floors (median of 105 µg/g). Also, the number of electronic devices present in the room, from where the dust was collected, was positively associated with the presence of BPA ($r = 0.5$; $p = 0.038$), PBDE 49 ($r = 0.5$; $p = 0.045$) and the sum of alternative plasticizers ($r = 0.46$; $p = 0.04$). Associations between the levels of hazardous substances found in dust and other potential sources of indoor contamination were either not significant ($p > 0.05$) or avoided, since items such as toys and textiles might be associated with high uncertainties as such items are easily moved around.

3.5. Assessment of children's exposure to hazardous chemicals via dust ingestion

Children's daily intakes of hazardous substances from ingestion of preschool dust were estimated based on the median and 95th percentile

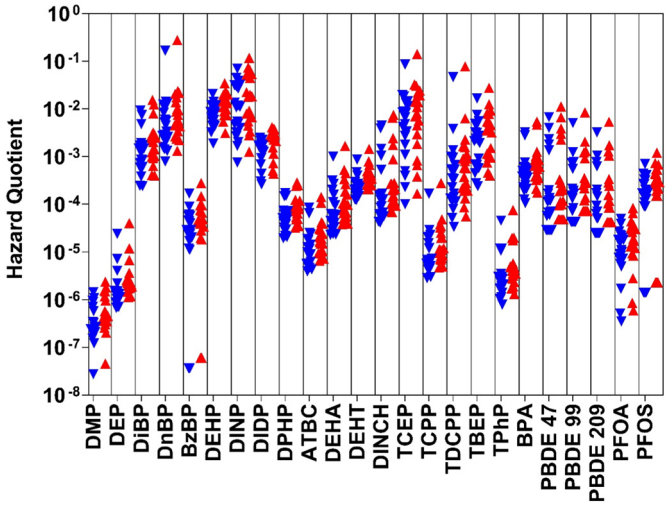

Fig. 4. Hazard quotients based on the estimated daily intakes via unintended dust ingestion at intermediate ▼ and high ▲ exposure scenario and established reference values.

levels at intermediate and high exposure scenarios (Table S3). After comparing these intakes with the available established health reference values (see Fig. 4), the HQs in all cases were < 1, indicating no risk for the children from dust ingestion, even for the worst-case scenario (i.e. all max values of the high exposure scenario < 1). Also, even when we compared the total daily intake for all PFAS with the sum of the two available reference values for PFOS and PFOA (1650 ng/kg/day; Table S2), the 95th percentile of the HQ for the high exposure scenario was only 0.09. The risk for children via dust ingestion was now even lower than 2015 in the same preschools, when we compare the risk assessment with the results from Larsson et al. (2017, 2018) for plasticizers, bisphenols, OPEs and PBDEs. However, it must be considered that other important exposure pathways such as diet, inhalation and dermal contact were not estimated in this study but would also contribute to the total daily intake of hazardous chemicals for children (Clark et al., 2011; Giovanoulis et al., 2018). Dust adhered to the skin and the inhalable dust, which may act as alternative exposure routes, have not been considered here and may also contribute, especially to certain hazardous substances such as low molecular weight phthalates (Kademoglou et al., 2018). Furthermore, many of the reference doses are calculated for adults, while for children the actual RfD or TDI or DNEL might be lower, due to physiological differences between children and adults. This, together with the continuous complexity of exposure to many different substances indicates that the risk, including that from dust ingestion, might be underestimated for children specifically.

4. Conclusions

The present study reported levels of phthalate and alternative plasticizers, OPEs, bisphenols, PBDEs and PFAS in preschool dust. While DINP, DEHP, DEHT and DINCH were still the most abundant chemicals in dust, there was a decrease in the levels compared to the previous sampling round in 2015, at the same preschools. The same was seen for BPA and BPF, as well as for TCPP which were significantly lower ($p < 0.05$) although BPS and TBEP levels increased. PFAS, which have been rarely analyzed in preschool dust prior to this study, were also found. This indicates that dust is a reservoir and potential indicator for hazardous chemicals in the preschool environment but that levels can be decreased by following the guidance document for "chemical smart preschools", and by this achieving an indoor environment with lower levels of hazardous chemicals for children attending the preschools. The type of flooring material in the preschool was identified as an important contributor to phthalate concentrations in preschool dust, especially for DINP. Children's estimated daily exposures to hazardous chemicals via dust ingestion were below the established health reference values, both when using the intermediate and high exposure scenarios. Still, the ingestion of dust is only one pathway of exposure, while diet, inhalation and transdermal exposure have major contribution to the overall exposure of children to hazardous chemicals. Also, RfDs or TDIs or DNELs are often developed for adults and do not take the exposure to complex mixtures into account. Due to this, it is hard to say if there is a risk for children when considering the total exposure to hazardous substances, in terms of hormonal effects and long-term disease development. Overall, the continuous presence of these substances in the everyday environment of children was confirmed and it is highly likely to originate from items in the indoor environment. Nevertheless, it was possible to drastically reduce hazardous substances at the preschools by following specific product substitution actions and removing items with risk of hazardous substances content. However, some alternative plasticizers, BPS and TBEP were increased by the product substitution actions which means that the contaminant profile has now started to change and the effect of this on human health is largely unknown. Hence, it is difficult to reduce the overall chemical exposure for children attending the preschools as some of the regulated hazardous substances have been replaced by alternatives occurring in the indoor environment. In total, this study shows that it is possible to change the exposure to hazardous substances in the indoor environment, and the chemical smart actions have the potential to drastically reduce the amounts of known hazardous substances and the connected human exposure. Although this yields a cost for the preschool now, it could reduce costs for healthcare later in life.

Declaration of Competing Interest

None.

Acknowledgement

This work was funded by the EU Interreg Baltic Sea project #R010 NonHazCity. The authors would like to thank the preschool managers and educators for their collaboration during the sampling period.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.104921.

References

Abdallah, M.A.E., Pawar, G., Harrad, S., 2015. Evaluation of in vitro vs. in vivo methods for assessment of dermal absorption of organic flame retardants: a review. Environ. Int. 74, 13–22.

Ali, N., Dirtu, A.C., Van den Eede, N., Goosey, E., Harrad, S., Neels, H., Mannetje, A., Coakley, J., Douwes, J., Covaci, A., 2012. Occurrence of alternative flame retardants in indoor dust from New Zealand: indoor sources and human exposure assessment. Chemosphere 88, 1276–1282.

Allgood, J.M., Jimah, T., McClaskey, C.M., La Guardia, M.J., Hammel, S.C., Zeineddine, M.M., Tang, I.W., Runnerstrom, M.G., Ogunseitan, O.A., 2017. Potential human exposure to halogenated flame-retardants in elevated surface dust and floor dust in an academic environment. Environ. Res. 153, 55–62.

Beko, G., Weschler, C.J., Langer, S., Callesen, M., Toftum, J., Clausen, G., 2013. Children's phthalate intakes and resultant cumulative exposures estimated from urine compared with estimates from dust ingestion, inhalation and dermal absorption in their homes and daycare centers. PLoS One 8.

Bergh, C., Torgrip, R., Emenius, G., Ostman, C., 2011. Organophosphate and phthalate esters in air and settled dust - a multi-location indoor study. Indoor Air 21, 67–76.

Bergh, C., Luongo, G., Wise, S., Ostman, C., 2012. Organophosphate and phthalate esters in standard reference material 2585 organic contaminants in house dust. Anal. Bioanal. Chem. 402, 51–59.

Bjorklund, J.A., Thuresson, K., De Wit, C.A., 2009. Perfluoroalkyl compounds (PFCs) in indoor dust: concentrations, human exposure estimates, and sources. Environmental Science & Technology 43, 2276–2281.

Bornehag, C.G., Sundell, J., Weschler, C.J., Sigsgaard, T., Lundgren, B., Hasselgren, M.,

Hagerhed-Engman, L., 2004. The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case-control study. Environ. Health Perspect. 112, 1393–1397.
Bradman, A., Gaspar, F., Castorina, R., Tong-Lin, E., Mckone, T., 2012. Environmental Exposures in Early Childhood Education Environments. Report for the California Air Resources Board. California Environmental Protection Agency.
Braun, J.M., Sathyanarayana, S., Hauser, R., 2013. Phthalate exposure and children's health. Curr. Opin. Pediatr. 25, 247–254.
Buck, R., Franklin, J., Berger, U., Conder, J., Cousins, I., de Voogt, P., Jensen, A., Kannan, K., Mabury, S., van Leeuwenkk, S., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integr. Environ. Assess. Manag. 513–541.
Bui, T.T., Giovanoulis, G., Cousins, A.P., Magner, J., Cousins, I.T., de Wit, C.A., 2016. Human exposure, hazard and risk of alternative plasticizers to phthalate esters. Sci. Total Environ. 541, 451–467.
Chen, D., Kannan, K., Tan, H.L., Zheng, Z.G., Feng, Y.L., Wu, Y., Widelka, M., 2016. Bisphenol analogues other than BPA: environmental occurrence, human exposure, and toxicity-a review. Environmental Science & Technology 50, 5438–5453.
Christia, C., Poma, G., Harrad, S., de Wit, C.A., Sjostrom, Y., Leonards, P., Lamoree, M., Covaci, A., 2019. Occurrence of legacy and alternative plasticizers in indoor dust from various EU countries and implications for human exposure via dust ingestion and dermal absorption. Environ. Res. 171, 204–212.
Clark, K.E., David, R.M., Guinn, R., Kramarz, K.W., Lampi, M.A., Staples, C.A., 2011. Modeling human exposure to phthalate esters: a comparison of indirect and biomonitoring estimation methods. Hum. Ecol. Risk. Assess. 17, 923–965.
Daikin, 2007. Elimination of PFOA in Fluorochemical Products. Press release. https://www.daikin.com/press/2007/071221/.
De Silva, A.O., Allard, C.N., Spencer, C., Webster, G.M., Shoeib, M., 2012. Phosphorus-containing fluorinated organics: polyfluoroalkyl phosphoric acid diesters (diPAPs), perfluorophosphonates (PFPAs), and perfluorophosphinates (PFPIAs) in residential indoor dust. Environmental Science & Technology 46, 12575–12582.
Directive, 2009/48/EC. of the European Parliament and of the Council of 18 June 2009 on the safety of toys; addition M3, Commission Directive 2014/79/EU of 20 June 2014 on the safety of toys, as regards TCEP, TCPP and TDCP, Official Journal of the European Union.
Eriksson, U., Karrman, A., 2015. World-wide indoor exposure to polyfluoroalkyl phosphate esters (PAPs) and other PFASs in household dust. Environmental Science & Technology 49, 14503–14511.
Fan, X.H., Kubwabo, C., Wu, F., Rasmussen, P.E., 2019. Analysis of bisphenol A, alkylphenols, and alkylphenol ethoxylates in NIST SRM 2585 and indoor house dust by gas chromatography-tandem mass spectrometry (GC/MS/MS). J. AOAC Int. 102, 246–254.
Fromme, H., Lahrz, T., Kraft, M., Fembacher, L., Dietrich, S., Sievering, S., Burghardt, R., Schuster, R., Bolte, G., Volkel, W., 2013. Phthalates in German daycare centers: occurrence in air and dust and the excretion of their metabolites by children (LUPE 3). Environ. Int. 61, 64–72.
Fromme, H., Lahrz, T., Kraft, M., Fembacher, L., Mach, C., Dietrich, S., Burkardt, R., Volkel, W., Goen, T., 2014. Organophosphate flame retardants and plasticizers in the air and dust in German daycare centers and human biomonitoring in visiting children (LUPE 3). Environ. Int. 71, 158–163.
Fromme, H., Schutze, A., Lahrz, T., Kraft, M., Fernbacher, L., Siewering, S., Burkardt, R., Dietrich, S., Koch, H.M., Volkel, W., 2016. Non-phthalate plasticizers in German daycare centers and human biomonitoring of DINCH metabolites in children attending the centers (LUPE 3). Int. J. Hyg. Environ. Health 219, 33–39.
Giovanoulis, G., Bui, T., Xu, F., Papadopoulou, E., Padilla-Sanchez, J.A., Covaci, A., Haug, L.S., Cousins, A.P., Magnér, J., Cousins, I.T., de Wit, C.A., 2018. Multi-pathway human exposure assessment of phthalate esters and DINCH. Environ. Int. 115–126.
Goosey, E., Harrad, S., 2011. Perfluoroalkyl compounds in dust from Asian, Australian, European, and North American homes and UK cars, classrooms, and offices. Environ. Int. 37, 86–92.
Guo, Y., Kannan, K., 2011. Comparative assessment of human exposure to phthalate esters from house dust in China and the United States. Environmental Science & Technology 45, 3788–3794.
IVL, 2016. Produktval av golv- och väggbeklädnader av PVC som innehåller DINP/DIDP. Report in Swedish. www.bastaonline.se/wp-content/uploads/2016/04/672eb12638ddf50bb4ac0fc1c8e863ca.pdf.
Jensen, A.A., Poulsen, P.B., Bossi, R., 2008. Survey and Environmental/Health Assessment of Fluorinated Substances in Impregnated Consumer Products and Impregnating Agents, Survey of Chemical Substances in Consumer Products, No. 99. Danish EPA, Copenhagen.
Jurewicz, J., Hanke, W., 2011. Exposure to phthalates: reproductive outcome and children health. A review of epidemiological studies. Int. J. Occup. Med. Environ. Health 24, 115–141.
Kademoglou, K., Xu, F.C., Padilla-Sanchez, J.A., Haug, L.S., Covaci, A., Collins, C.D., 2017. Legacy and alternative flame retardants in Norwegian and UK indoor environment: implications of human exposure via dust ingestion. Environ. Int. 102, 48–56.
Kademoglou, K., Giovanoulis, G., Palm-Cousins, A., Padilla-Sanchez, J.A., Magner, J., de Wit, C.A., Collin, C.D., 2018. In vitro inhalation bioaccessibility of phthalate esters and alternative plasticizers present in indoor dust using artificial lung fluids. Environmental Science & Technology Letters 5, 329–334.
Kanazawa, A., Saito, I., Araki, A., Takeda, M., Ma, M., Saijo, Y., Kishi, R., 2010. Association between indoor exposure to semi-volatile organic compounds and building-related symptoms among the occupants of residential dwellings. Indoor Air 20, 72–84.
Karaskova, P., Venier, M., Melymuk, L., Becanova, J., Vojta, S., Prokes, R., Diamond, M.L., Klanova, J., 2016. Perfluorinated alkyl substances (PFASs) in household dust in Central Europe and North America. Environ. Int. 94, 315–324.
Kolarik, B., Naydenov, K., Larsson, M., Bornehag, C.G., Sundell, J., 2008. The association between phthalates in dust and allergic diseases among Bulgarian children. Environ. Health Perspect. 116, 98–103.
Langer, S., Weschler, C.J., Fischer, A., Beko, G., Toftum, J., Clausen, G., 2010. Phthalate and PAH concentrations in dust collected from Danish homes and daycare centers. Atmos. Environ. 44, 2294–2301.
Langer, S., Fredricsson, M., Weschler, C.J., Beko, G., Strandberg, B., Remberger, M., Toftum, J., Clausen, G., 2016. Organophosphate esters in dust samples collected from Danish homes and daycare centers. Chemosphere 154, 559–566.
Larsson, K., Lindh, C.H., Jonsson, B.A.G., Giovanoulis, G., Bibi, M., Bottai, M., Bergstrom, A., Berglund, M., 2017. Phthalates, non-phthalate plasticizers and bisphenols in Swedish preschool dust in relation to children's exposure. Environ. Int. 102, 114–124.
Larsson, K., de Wit, C.A., Sellstrorm, U., Sahlstrom, L., Lindh, C.H., Berglund, M., 2018. Brominated flame retardants and organophosphate esters in preschool dust and children's hand wipes. Environmental Science & Technology 52, 4878–4888.
Larsson, M., Hagerhed-Engman, L., Kolarik, B., James, P., Lundin, F., Janson, S., Sundell, J., Bornehag, C.G., 2010. PVC - as flooring material - and its association with incident asthma in a Swedish child cohort study. Indoor Air 20, 494–501.
Liang, Y.R., Xu, Y., 2014. Emission of phthalates and phthalate alternatives from vinyl flooring and crib mattress covers: the influence of temperature. Environmental Science & Technology 48, 14228–14237.
Liao, C.Y., Kannan, K., 2011. Widespread occurrence of bisphenol a in paper and paper products: implications for human exposure. Environmental Science & Technology 45, 9372–9379.
Liu, K., Li, J., Yan, S.J., Zhang, W., Li, Y.J., Han, D., 2016. A review of status of tetrabromobisphenol A (TBBPA) in China. Chemosphere 148, 8–20.
Luongo, G., Ostman, C., 2016. Organophosphate and phthalate esters in settled dust from apartment buildings in Stockholm. Indoor Air 26, 414–425.
Meeker, J.D., 2012. Exposure to environmental endocrine disruptors and child development. Archives of Pediatrics & Adolescent Medicine 166, 952–958.
Meeker, J.D., Stapleton, H.M., 2010. House dust concentrations of organophosphate flame retardants in relation to hormone levels and semen quality parameters. Environ. Health Perspect. 118, 318–323.
Mizouchi, S., Ichiba, M., Takigami, H., Kajiwara, N., Takamuku, T., Miyajima, T., Kodama, H., Someya, T., Ueno, D., 2015. Exposure assessment of organophosphorus and organobromine flame retardants via indoor dust from elementary schools and domestic houses. Chemosphere 123, 17–25.
Moriwaki, H., Takata, Y., Arakawa, R., 2003. Concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in vacuum cleaner dust collected in Japanese homes. J. Environ. Monit. 5, 753–757.
Nadal, M., Domingo, J.L., 2014. Indoor dust levels of perfluoroalkyl substances (PFASs) and the role of ingestion as an exposure pathway: a review. Curr. Org. Chem. 18, 2200–2208.
Padilla-Sanchez, J.A., Haug, L.S., 2016. A fast and sensitive method for the simultaneous analysis of a wide range of per- and polyfluoroalkyl substances in indoor dust using on-line solid phase extraction-ultrahigh performance liquid chromatography-time-of-flight-mass spectrometry. J. Chromatogr. A 1445, 36–45.
Papadopoulou, E., Padila-Sanchez, J.A., Collins, C.D., Cousins, I.T., Covaci, A., de Wit, C.A., Leonards, P.E.G., Voorspoels, S., Thomsen, C., Harrad, S., Haug, L.S., 2016. Sampling strategy for estimating human exposure pathways to consumer chemicals. Emerging Contaminants 2 (1), 26–36 (March).
Persson, J., Wang, T., Hagberg, J., 2018. Organophosphate flame retardants and plasticizers in indoor dust, air and window wipes in newly built low-energy preschools. Sci. Total Environ. 628-629, 159–168.
Pettersson, M., Oldén, M., Lagerqvist, A., 2018. Hazardous Substances in Articles and Materials. Analysis of Phthalates and Alternative Plasticisers, Flame Retardants, Chlorinated Paraffins, Highly Fluorinated Substances and Formamide in Old and New Preschool Items. Report from the Chemicals Centre. Environment and Health Administration, City of Stockholm, Sweden. http://www.stockholm.se/kemikaliesmartforskola.
Raffy, G., Mercier, F., Blanchard, O., Derbez, M., Dassonville, C., Bonvallot, N., Glorennec, P., Le Bot, B., 2017. Semi-volatile organic compounds in the air and dust of 30 French schools: a pilot study. Indoor Air 27, 114–127.
Reiner, J.L., Blaine, A.C., Higgins, C.P., Huset, C., Jenkins, T.M., Kwadijk, C., Lange, C.C., Muir, D.C.G., Reagen, W.K., Rich, C., Small, J.M., Strynar, M.J., Washington, J.W., Yoo, H., Keller, J.M., 2015. Polyfluorinated substances in abiotic standard reference materials. Anal. Bioanal. Chem. 407, 2975–2983.
Rudel, R.A., Camann, D.E., Spengler, J.D., Korn, L.R., Brody, J.G., 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust. Environmental Science & Technology 37, 4543–4553.
Sahlstrom, L., Sellstrom, U., de Wit, C.A., 2012. Clean-up method for determination of established and emerging brominated flame retardants in dust. Anal. Bioanal. Chem. 404, 459–466.
Schreiber, T., Gassmann, K., Gotz, C., Hubenthal, U., Moors, M., Krause, G., Merk, H.F., Nguyen, N.H., Scanlan, T.S., Abel, J., Rose, C.R., Fritsche, E., 2010. Polybrominated diphenyl ethers induce developmental neurotoxicity in a human in vitro model: evidence for endocrine disruption. Environ. Health Perspect. 118, 572–578.
Shoeib, M., Harner, T., Webster, G.M., Lee, S.C., 2011. Indoor sources of poly- and perfluorinated compounds (PFCS) in Vancouver, Canada: implications for human exposure. Environmental Science & Technology 45, 7999–8005.
Shu, H., Jonsson, B.A., Larsson, M., Nanberg, E., Bornehag, C.G., 2014. PVC flooring at home and development of asthma among young children in Sweden, a 10-year follow-up. Indoor Air 24, 227–235.

Shu, H., Jonsson, B.A.G., Gennings, C., Lindh, C.H., Nanberg, E., Bornehag, C.G., 2019. PVC flooring at home and uptake of phthalates in pregnant women. Indoor Air 29, 43–54.
Strynar, M.J., Lindstrom, A.B., 2008. Perfluorinated compounds in house dust from Ohio and North Carolina, USA. Environmental Science & Technology 42, 3751–3756.
Tay, J.H., Sellstrom, U., Papadopoulou, E., Padilla-Sanchez, J.A., Haug, L.S., de Wit, C.A., 2017. Human exposure to legacy and emerging halogenated flame retardants via inhalation and dust ingestion in a Norwegian cohort. Environmental Science & Technology 51, 8176–8184.
Tian, Z., Kim, S.K., Shoeib, M., Oh, J.E., Park, J.E., 2016. Human exposure to per- and polyfluoroalkyl substances (PFASs) via house dust in Korea: implication to exposure pathway. Sci. Total Environ. 553, 266–275.
UNEP, 2015. Guidance for the Inventory of Polybrominated Diphenyl Ethers (PBDEs) Listed under the Stockholm Convention on Persistent Organic Pollutants, Stockholm Convention on Persistent Organic Pollutants. UNEP/POPS/COP.7/INF/27.
USEPA, 2011. U.S. Environmental Protection Agency - Exposure Factors Handbook. (Washington DC).
Wang, W., Abualnaja, K.O., Asimakopoulos, A.G., Covaci, A., Gevao, B., Johnson-Restrepo, B., Kumosani, T.A., Malarvannan, G., Minh, T.B., Moon, H.B., Nakata, H., Sinha, R.K., Kannan, K., 2015. A comparative assessment of human exposure to tetrabromobisphenol A and eight bisphenols including bisphenol A via indoor dust ingestion in twelve countries. Environ. Int. 83, 183–191.
Wang, Z., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbuhler, K., 2014a. Global emission inventories for C-4-C-14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, part II: the remaining pieces of the puzzle. Environ. Int. 69, 166–176.
Wang, Z.Y., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbuhler, K., 2014b. Global emission inventories for C-4-C-14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, part I: production and emissions from quantifiable sources. Environ. Int. 70, 62–75.
Winkens, K., Giovanoulis, G., Koponen, J., Vestergren, R., Berger, U., Karvonen, A.M., Pekkanen, J., Kiviranta, H., Cousins, I.T., 2018. Perfluoroalkyl acids and their precursors in floor dust of children's bedrooms - implications for indoor exposure. Environ. Int. 119, 493–502.
WSP, 2015. Ftalat-Inventering Av PVC-Mattor I 29 förskolor I Stockholm. Report in Swedish. https://www.wsp.com/sv-SE/.
Wu, M., Yu, G., Cao, Z.G., Wu, D.K., Liu, K., Deng, S.B., Huang, J., Wang, B., Wang, Y.J., 2016. Characterization and human exposure assessment of organophosphate flame retardants in indoor dust from several microenvironments of Beijing, China. Chemosphere 150, 465–471.
Xu, F.C., Giovanoulis, G., van Waes, S., Padilla-Sanchez, J.A., Papadopoulou, E., Magner, J., Haug, L.S., Neels, H., Covaci, A., 2016. Comprehensive study of human external exposure to organophosphate flame retardants via air, dust, and hand wipes: the importance of sampling and assessment strategy. Environmental Science & Technology 50, 7752–7760.
Xu, F.C., Tay, J.H., Covaci, A., Padilla-Sanchez, J.A., Papadopoulou, E., Haug, L.S., Neels, H., Sellstrom, U., de Wit, C.A., 2017. Assessment of dietary exposure to organohalogen contaminants, legacy and emerging flame retardants in a Norwegian cohort. Environ. Int. 102, 236–243.
Yang, C.Q., Harris, S.A., Jantunen, L.M., Siddique, S., Kubwabo, C., Tsirlin, D., Latifovic, L., Fraser, B., St-Jean, M., De La Campa, R., You, H.Y., Kulka, R., Diamond, M.L., 2019. Are cell phones an indicator of personal exposure to organophosphate flame retardants and plasticizers? Environ. Int. 122, 104–116.
Yao, Y.M., Zhao, Y.Y., Sun, H.W., Chang, S., Zhu, L.Y., Alder, A.C., Kannan, K., 2018. Per- and polyfluoroalkyl substances (PFASs) in indoor air and dust from homes and various microenvironments in China: implications for human exposure. Environmental Science & Technology 52, 3156–3166.