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Multiresidue analytical method for high production volume chemicals in dust samples, occurrence and human exposure assessment

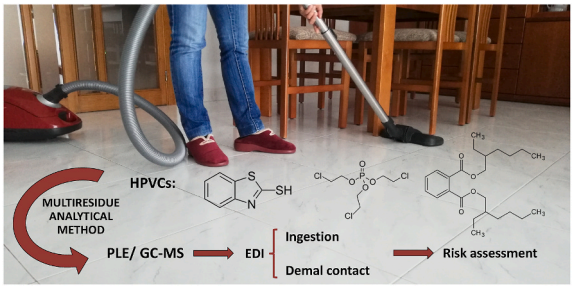
Mireia Núñez, Núria Fontanals, Francesc Borrull, Rosa Maria Marcé *

Universitat Rovira i Virgili, Department of Analytical Chemistry and Organic Chemistry, Sescelades Campus, Marcel·lí Domingo s/n, Building N4, Tarragona, 43007, Spain

HIGHLIGHTS

- New multiresidue method based on PLE/GC-MS to determine 22 HPVCs in indoor dust.
- Phthalate and organophosphate esters were the most abundant HPVCs.
- Two benzenesulfonamides were detected in dust for the first time.
- $EDI_{ingestion}$ and EDI_{dermal} were evaluated.
- Both non-carcinogenic and carcinogenic risk were assessed.

GRAPHICAL ABSTRACT



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ABSTRACT

A multiresidue analytical method based on pressurised liquid extraction and gas-chromatography mass spectrometry was developed to determine 22 compounds belonging to different chemical families in indoor dust.: Seven organophosphate esters, six phthalate esters, three benzotriazoles, five benzothiazoles and four benzenesulfonamides were included in the present study, all of them belonging to the category of high production volume chemicals (HPVCs). Apparent recoveries ranged between 45% and 123% and method quantification limits ranged from 0.03 μg/g to 3.8 μg/g. The occurrence of the selected HPVCs was evaluated in indoor dust from different locations in the Tarragona (Catalonia, Spain) region. Two benzenesulfonamides, ortho-toluenesulfonamide and para-toluenesulfonamide, were detected in dust samples for the first time. Phthalate esters and organophosphate esters were the most abundant compounds found, and di-(2-ethylhexyl) phthalate (DEHP) was determined at the highest concentrations. With the data obtained, human exposure was assessed by calculating the estimated daily intakes (EDI) via ingestion and dermal contact. Non-carcinogenic and carcinogenic risk assessments found no risks in any of the scenarios tested, which included two age classes (children and adults) and two possible exposure scenarios (median and worst-case scenario), except for the evaluation of carcinogen risk due to ingestion of DEHP in the worst-case scenario.

* Corresponding author.
E-mail address: rosamaria.marce@urv.cat (R.M. Marcé).

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1. Introduction

In today's world, many people spend much of their time in indoor environments such as homes and offices. The study of these environments has therefore gained attention as an important potential source of human exposure to environmental contaminants. Indoor dust is a complex matrix that consists of a heterogeneous mixture of organic and inorganic particles from different origins that vary in shape and size, but with a diameter not exceeding 500 μm (Velázquez-Gómez et al., 2018). Dust acts as a sink for different pollutants such as semi-volatile organic compounds (SVOCs) (Kurt-Karakus, 2012). Humans are exposed to dust and to the pollutants contained in it via inhalation, ingestion and dermal contact. This exposure is of special concern in children and toddlers who are even more exposed than adults due to common behaviours like crawling and making frequent hand-to mouth contact (García et al., 2007b; Mercier et al., 2014).

Some SVOC families belong to the category of high production volume chemicals (HPVCs), which are compounds that have been produced or imported at amounts exceeding 1000 tonnes per year in at least one member of the Organisation for Economic Cooperation and Development (OECD). Due to their widespread use, these compounds can easily reach different environmental compartments (Herrero et al., 2014). An elevated number of groups belong to this category, among which, five have been selected in the present study: benzotriazoles (BTRs), benzothiazoles (BTHs), benzenesulfonamides (BSAs), phthalate esters (PAEs) and organophosphate esters (OPEs).

BTRs can be added to metal compounds such as copper to form a stable coordinate compound with anticorrosive properties. This has resulted in their extensive use as corrosion inhibitors in fluids such as industrial cooling systems, antifreeze formulations, hydraulic fluids and dishwasher detergents (Herrero et al., 2014). Moreover, some derivatives have been employed in the pharmaceutical industry due to their specific chemical and biological properties. BTRs have been identified as potentially estrogenic, carcinogenic and mutagenic (Li et al., 2020) and some studies have reported their presence in indoor dust (Wang et al., 2013; Li et al., 2020).

BTHs are thermally stable compounds used in numerous applications. One of their main applications is as vulcanisation accelerators in the manufacture of rubber. They are also used as fungicides in paper and leather manufacturing, as photosensitisers in photography, corrosion inhibitors in antifreeze formulations and, in some cases, as precursors in pharmaceutical production (Herrero et al., 2014; Liao et al., 2018). They have been reported as dermal sensitisers and respiratory tract irritants. Some of them are cytotoxic, carcinogenic and genotoxic (Li et al., 2020), and some have been identified in indoor dust (Wang et al., 2013; Li et al., 2020).

BSAs are used in several applications. BSA is used in the synthesis of dyes, photochemical products and disinfectants. Ortho-toluenesulfonamide (o-TSA) is used in the synthesis of the artificial sweetener saccharin. Para-toluenesulfonamide (p-TSA) is employed as a plasticiser, as a medium for pesticides and drugs, and as a fungicide in paints and coatings (Richter et al., 2008; Herrero et al., 2014). This group of compounds has been less studied than those previously mentioned and, to the best of our knowledge, this is the first time they have been studied in indoor dust.

PAEs are a group of HPVCs that are ubiquitous contaminants in the indoor environment. They have different uses and properties depending on their molecular weight. Low-molecular-weight phthalates such as dimethyl phthalate (DMP), diethyl phthalate (DEP) and dibutyl phthalate (DBP) are widely used in personal care products, lacquers, coatings and varnishes. Meanwhile, high-molecular-weight phthalates such as di-(2-ethylhexyl) phthalate (DEHP), diisobutyl phthalate (DiBP), di-isononyl phthalate (DiNP), and di-n-octyl phthalate (DnOP) are generally used as plasticisers in buildings materials, furniture, and plastic toys (Li et al., 2016; Xu and Li, 2021). This study also includes the compound diethylhexyl adipate (DEHA) within this group of contaminants. DEHP is the most studied phthalate contaminant and has been found in the highest concentrations in the majority of studies because it represents 50% of total phthalate production (Xu and Li, 2021). Several studies have noted the potential adverse effects of phthalates on human health. Moreover, the International Agency for Research on Cancer (IARC) has identified DEHP as a possible carcinogen to humans (Hu et al., 2020). Due to their widespread use, phthalates have been determined in a wide range of environmental conditions, including indoor dust (Zhu et al., 2019; Xu and Li, 2021).

OPEs are used in a multitude of products such as textiles, plastics, electronics, building materials, lubricants, and furniture varnish, among others (Wang et al., 2020). As replacements for polybrominated diphenyl ethers, which were banned in early 2000, these compounds are increasingly produced and used (Velázquez-Gómez et al., 2019). Normally, chlorinated and brominated OPEs such as tris(2-chloroethyl) phosphate (TCEP) and tris(2-chloro-1-methylethyl) phosphate (TCPP) are mainly used as flame retardants, while non-halogenated OPEs such as triisobutyl phosphate (TiBP) and triphenyl phosphate (TPP) are used as plasticisers (Andresen and Bester, 2006; Wang et al., 2020). However, some of them have also been used as flame retardants, which is the case, for example, of TPP which has been employed in electronic devices (Andresen and Bester, 2006). OPEs have been reported to adversely affect human health. For example, some OPEs such as TCEP and TCPP have been identified as carcinogenic and neurotoxic (Hou et al., 2021). As phthalates, their presence has been reported in different environments including indoor dust (Cristale et al., 2016; de la Torre et al., 2020).

As mentioned, dust is a highly complex matrix. Studies of the contaminants it contains therefore require efficient extraction procedures and instrumental techniques. Liquid (LC) or gas chromatography (GC) coupled to mass spectrometry based detection provide high selectivity and sensitivity resulting in their effective identification and quantification in dust (Herrero et al., 2014; Wang et al., 2020). Different extraction techniques have been used to determine the selected compounds in solid matrices such as dust. The most common extraction procedure described in the literature involves simple agitation or ultrasonication or a combination of the two (Van den Eede et al., 2012; Wang et al., 2013; Li et al., 2016; Velázquez-Gómez et al., 2018; Christia et al., 2019; Li et al., 2020; Xu and Li, 2021). After this step, the extract is typically centrifuged. This is a simple extraction technique which does not require expensive equipment; however, the entire procedure involving extraction and centrifugation usually needs to be repeated two or three times to obtain suitable results, giving rise to long extraction times in some cases. Other procedures described in the literature include the conventional Soxhlet extraction technique (Hu et al., 2020), thermal desorption (Mercier et al., 2020), matrix solid-phase dispersion (García et al., 2007a), microwave assisted extraction (García et al., 2007b) and pressurised liquid extraction (PLE) (Mercier et al., 2014; Sánchez-Piñero et al., 2020). The latter was chosen for use in this study. Few studies have described the extraction of some HPVCs, mainly OPEs (Mercier et al., 2014; Sánchez-Piñero et al., 2020) and PAEs (Sánchez-Piñero et al., 2020), using PLE from dust. Although specific equipment is required, PLE is a semi-automated extraction process that consumes lower solvent volumes and is faster than other extraction techniques.

This work aimed to develop a multiresidue method based on pressurised liquid extraction and GC-MS to simultaneously quantify 24 HPVCs belonging to different groups in indoor dust. The proposed method was applied to indoor dust samples collected in the Tarragona area. Lastly, with the results obtained, we estimated the human exposure to the target compounds via dust ingestion and dermal absorption and the associated risk.

2. Materials and methods

2.1. Reagents and standards

All of the chemical standards used were purchased from Sigma Aldrich (St. Louis, USA). These were three benzotriazole derivates (BTRs): 1-H-benzotriazole (BTR), 5- methyl-1-H-benzotriazole (5TTR) and 5,6-dimethyl-1-H-benzotriazole (XTR); five benzothiazole derivates (BTHs): 1-H-benzothiazole (BTH), 2- hydroxybenzothiazole (OHBTH), 2-amino-1-H-benzothiazole (NH_2BTH), 2-chlorobenzothiazole (ClBTH), 2-(methylthio)-benzothiazole (MeSBTH); four benzenesulfonamides (BSAs): benzenesulfonamide (BSA), para-toluenesulfonamide (p-TSA), ortho-toluenesulfonamide (o-TSA), N-methyl-para-toluenesulfonamide (Me-p-TSA); seven organophosphate esters (OPEs): tributyl phosphate (TBP), triethyl phosphate (TEP), triisobutyl phosphate (TiBP), triphenyl phosphate (TPP), tris(2-ethylhexyl) phosphate (TEHP), 2-ethylhexyl diphenyl phosphate (EHDP), tris(2-chloroethyl) phosphate (TCEP); and six phthalate esters (PAEs): diethylhexyl adipate (DEHA), di-(2-ethylhexyl) phthalate (DEHP), diisobutyl phthalate (DiBP), dimethyl phthalate (DMP), di-n-octyl phthalate (DnOP) and diethyl phthalate (DEP). The internal standards (IS) used, d_4-BTH, d_{27}-TBP and d_4-DEHP, were also acquired from Sigma-Aldrich.

Stock solutions of individual standards at 1000 mg/L were prepared in ethyl acetate and stored at −20 °C. A mixture of 100 mg/L for each group of compounds was prepared in ethyl acetate. A mixture of 10 mg/L of all of the compounds was freshly prepared, also in ethyl acetate, and stored at 4 °C.

Acetone and ethyl acetate from J.T. Baker (Deventer, Netherlands) were of GC grade with purity exceeding 99.9%. Isopropanol employed for cleaning purposes was from Chem-Lab (Zedelgem, Belgium).

The cellulose filters and diatomaceous earth used for PLE were purchased from Thermo Scientific (Barcelona, Spain) and Florisil from Sigma Aldrich. The PTFE filters and syringes used to filter the extracts were purchased from Scharlab (Barcelona, Spain).

Nitrogen gas used for evaporation, nitrogen gas for PLE and helium gas at a purity of 99.999% used for GC analysis and nitrogen used for the MS system were sourced from Carburos Metálicos (Tarragona, Spain).

2.2. Sampling

Indoor dust samples were obtained from the floor of different private houses in the Tarragona region between September 2020 and February 2021. Samples were obtained from three locations that have different number of inhabitants; in particular, six samples were obtained from a city of 135400 inhabitants (Tarragona), seven samples from a town of 38900 (El Vendrell) and three samples from a village of 6700 inhabitants (Constantí). Fig. S1 shows the locations in the map. All of them were collected with conventional vacuum cleaners. Dust samples were ground and sieved (75 μm) as a way to homogenise the samples to achieve higher reproducibility (Velázquez-Gómez et al., 2018) and obtain higher surface area in order to favour the contact with the extraction solvent. Once sieved, the samples were stored at 4 °C until the analysis. Spiked samples were prepared by adding the stock mixture of standards to acetone (the required volume to wet and cover the dust), and the solvent was slowly evaporated at room temperature inside an extraction hood.

2.3. Pressurised liquid extraction

Extractions were performed on an ASE 350 accelerated solvent extractor system (Dionex, Sunnyvale, USA). A cellulose filter was placed at the bottom of 10 mL stainless steel extraction cell. It was then filled with 1 g of diatomaceous earth, 0.1 g of dust sample mixed with 1 g of diatomaceous earth. The void volume of the extraction cell was filled with diatomaceous earth and it was compacted and closed before extraction. Extraction was performed with 1 cycle of ethyl acetate at 70 °C and 1500 psi for 10 min. The preheating time was 5 min, flush volume was 80% of the cell volume and the purge time was 120 s.

The sample was evaporated to approximately 0.5 mL under a flow of nitrogen gas. The extract was then filtered through 0.22 μm PTFE filter. The internal standards were added and the extract was filled up to 1 mL with ethyl acetate prior being analysed by GC-MS.

2.4. GC-MS analysis

Chromatographic separation was performed using a GCMS-QP2010 ultra high-performance gas chromatography system, equipped with a split/splitless AOC-20i autoinjector coupled to a quadrupole MS detector by electron ionisation operating at 70 eV. The ion source temperature was set at 230 °C and the temperature of the GC-MS interface was 280 °C. The sample (2 μL) was injected using splitless mode and the injection temperature was set at 250 °C. The MS acquisition mode was set to ion monitoring (SIM). Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min.

A Zebron ZB-50 (50% phenyl, 50% dimethylsiloxane) capillary column (30 m × 0.25 mm i.d., and 0.25 μm film thickness) from Phenomenex (Torrance, USA) was used. The temperature program was as follows: initial column temperature was set at 80 °C, which was linearly increased at a rate of 5 °C/min until 210 °C (26 min), from 210 °C to 300 °C (30.5 min) at 20 °C/min and maintained at 300 °C for 5 min. The total run time was 35.5 min.

2.5. Quality assurance/quality control (QA/QC)

In order to ensure appropriate results, several precautions were taken throughout the method to minimise procedural contamination. Whenever possible, glass material carefully cleaned with isopropanol and with ethyl acetate was employed to avoid the use of any plastics. Blanks of the whole procedure (procedural blanks) were performed, which means that the extraction, evaporation and reconstitution were conducted without using dust and without adding the compounds of interest. Several compounds appeared into the procedural blanks, which were: DEP, DiBP, DEHP, TEHP and DEHA and they were in the range of 10–110 μg/L. The mean procedural blank signal of each target compound was subtracted from the values of the samples in order to avoid an overestimation of the compounds. In addition, standard controls and solvent blanks were analysed thought the GC-MS sequences and three sequential washing steps of the syringe were included before and after each injection in order to avoid carryover effects.

2.6. Human exposure health risk assessment

There are three main pathways of human exposure to contaminants present in indoor dust: direct ingestion of dust particles, intake through the mouth and nose by inhalation of suspended material, and intake via absorption from dust particles adhered to the skin, i.e., dermal contact (Li et al., 2018). The concentrations found in house dust were used to evaluate the estimated daily intake (EDI) via dust ingestion and dermal absorption. Since this study only focuses on settled dust and not suspended dust (exposure via inhalation), inhalation exposure was not evaluated. Two different age classes were considered: children (from 1 to 11 years of age) and adults (18–70 years of age) (Li et al., 2018). This distinction was made because the behaviour of children potentially increases their exposure to the contaminants present in dust by means of indirect ingestion by way hand-mouth activities, touching and climbing on dust-contaminated objects and their lower body weight (Kurt-Karakus, 2012; Li et al., 2018). For EDI calculations, two scenarios were considered: median concentrations and the 95th percentile concentrations, which represent the median and the worst-case scenario, respectively. EDI, expressed in μg/kg/day, via dust ingestion and dermal absorption were calculated according to the following equations (Li et al., 2018):

$$EDI_{ingestion} = C_{dust} \times IngR \times EF \times ED \times CF/(BW \times AT)$$

Table 1
Validation results for PLE/GC-MS method.

Compound	MDL (μg/g)	MQL (μg/g)	Recovery (%)[a] (%)	Intra-day precision[b] (%RSD, n = 5)	Inter-day precision[c] (%RSD, n = 5)
TEP	0,11	0,22	45	15	16
BTH	0,08	0,17	59	18	17
ClBTH	0,02	0,03	64	24	17
TiBT	0,01	0,03	71	5	8
DMP	0,01	0,03	72	18	21
TBP	0,01	0,03	79	4	15
DEP	0,4	1,3	74	16	27
MeSBTH	0,06	0,12	82	18	22
5TTR	1,6	2,1	121	7	8
BSA	0,62	1,2	81	2	13
NH2BTH	1,5	3,8	65	5	8
O-TSA	0,14	0,35	72	11	17
OHBTH	1,7	2,2	115	12	4
Me-p-TSA	0,06	0,30	83	11	14
P-TSA	0,59	1,2	85	15	13
XTR	1,6	2,0	123	10	8
DiBP	0,4	1,3	77	21	12
TCEP	0,12	0,30	83	12	23
DEHA	0,01	0,05	104	16	18
TEHP	0,02	0,06	88	15	14
EHDP	0,01	0,05	110	8	16
DEHP	0,60	1,5	80	11[d]	13[d]
TPP	0,02	0,06	86	8	16
DnOP	0,05	0,10	97	8	15

[a] Recoveries calculated by a 20 μg/g spiked dust.
[b] Intra-day precision calculated as %RSD by a 5 μg/g spiked dust.
[c] Inter-day, day to day, calculated as %RSD by a 5 μg/g spiked dust.
[d] Values calculated at 20 μg/g.

Table 2
Concentrations found in the 16 dust samples analysed, expressed in μg/g.

Compound	Mean	Median	95th percentile	Concentration Range	DF[a]
BTHs					
BTH	0,70	0,47	1,67	< MQL- 3,23	100
BSAs					
O-TSA	0,26	0,18	0,59	< MDL- 0,9	69
P-TSA	0,82	0,30	2,12	< MDL- 3,03	44
PAEs					
DEHA	7,24	4,08	18,56	2,48- 47,2	100
DEHP	255,59	78,87	987,27	46,2- 2197,5	100
DiBP	6,63	5,36	13,72	0,48- 14,1	100
DMP	0,30	0,31	0,56	0,04- 0,58	100
DEP	7,53	0,07	39,68	< MDL- 44,2	44
OPEs					
TBP	0,06	0,01	0,23	< MDL- 0,27	25
TEP	0,72	0,08	2,65	< MDL- 2,67	50
TPP	6,92	1,27	24,51	0,65- 89,0	100
TEHP	0,40	0,19	1,30	< MDL- 2,20	63
EHDP	0,61	0,32	1,66	0,2- 2,6	100
TCEP	1,48	0,74	5,30	< MQL- 7,81	100

[a] Detection frequency (DF) expressed in %.

$$EDI_{dermal} = C_{dust} \times SA \times ABS \times AF \times EF \times ED \times CF/(BW \times AT)$$

where C_{dust} corresponds to the concentration of the compound quantified in dust, expressed in μg/g; IngR is the daily ingestion rate of dust (30 mg/day for adults and 60 mg/day for children); EF is the exposure frequency over one year (180 days/year for adults and 185 days/year for children); ED is the lifetime exposure duration (53 years for adults and 10 years for children); CF is the conversion factor (0.001 g/mg); BW is the body weight (70 kg for adults and 24 kg for children); AT is the average time, expressed in days, for carcinogen compounds: TBP, DEHP, DEHA, TCEP and TEHP (Li et al., 2018; Maceira et al., 2020), AT is 25,

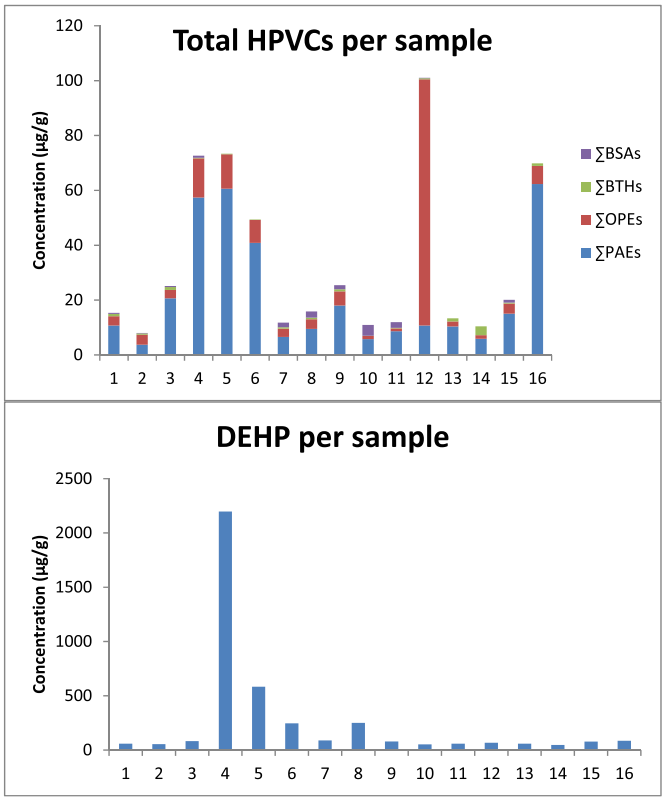

Fig. 1. Concentrations (μg/g) of the different groups of HPVCs found in each sample analysed.

500 days and for non-carcinogens, AT is equal to ED, expressed in days; SA is the exposed body surface area (5700 cm^2/day for adults and 2800 cm^2/day for children); AF is the dust added to skin (0.07 mg/cm^2 for adults and 0.2 mg/cm^2 for children); ABS is the fraction of the compound absorbed by the skin. For compounds whose value was available in the literature, the published values were used, such as DMP 0.00048, DEP 0.01025, DiBP 0.0006, DEHP 0.000053 (Christia et al., 2019); BTH 0.14 (Li et al., 2020); TBP, TPP, EHDP 0.17 (de la Torre et al., 2020); TEHP 0.219 and TCEP 0.283 (Christia et al., 2018), whereas for the compounds whose value was not available, the value of 0.1 for semi-volatile compounds was used, in accordance with the USEPA (USEPA, 2017). The non-cancer assessment was based on the hazard index (HI) and the hazard quotient (HQ). These parameters were calculated according the following equations:

$$HQ_{ingestion} = EDI_{ingestion}/RfD$$

$$HQ_{dermal} = EDI_{dermal}/RfD \times GIABS$$

$$HI = HQ_{ingestion} + HQ_{dermal}$$

GIABS is the gastrointestinal absorption factor, which was 1 (USEPA, 2017; Li et al., 2018). Similar to the compounds reported in the literature, DEHA value was also considered 1 in this study.

RfD is the oral reference dose for each compound, expressed in μg/kg/day; these values were derived from the literature when they were available, when the RfD was not available in the literature it was calculated according the following equation:

$$RfD = NOAEL/UF$$

where NOAEL is the no-observed-adverse-effect level, expressed in μg/Kg/day, which was obtained from the literature, and UF is the uncertainty factor (1000) (Ali et al., 2012).

The risk assessment of carcinogenic effects (CR) was estimated using

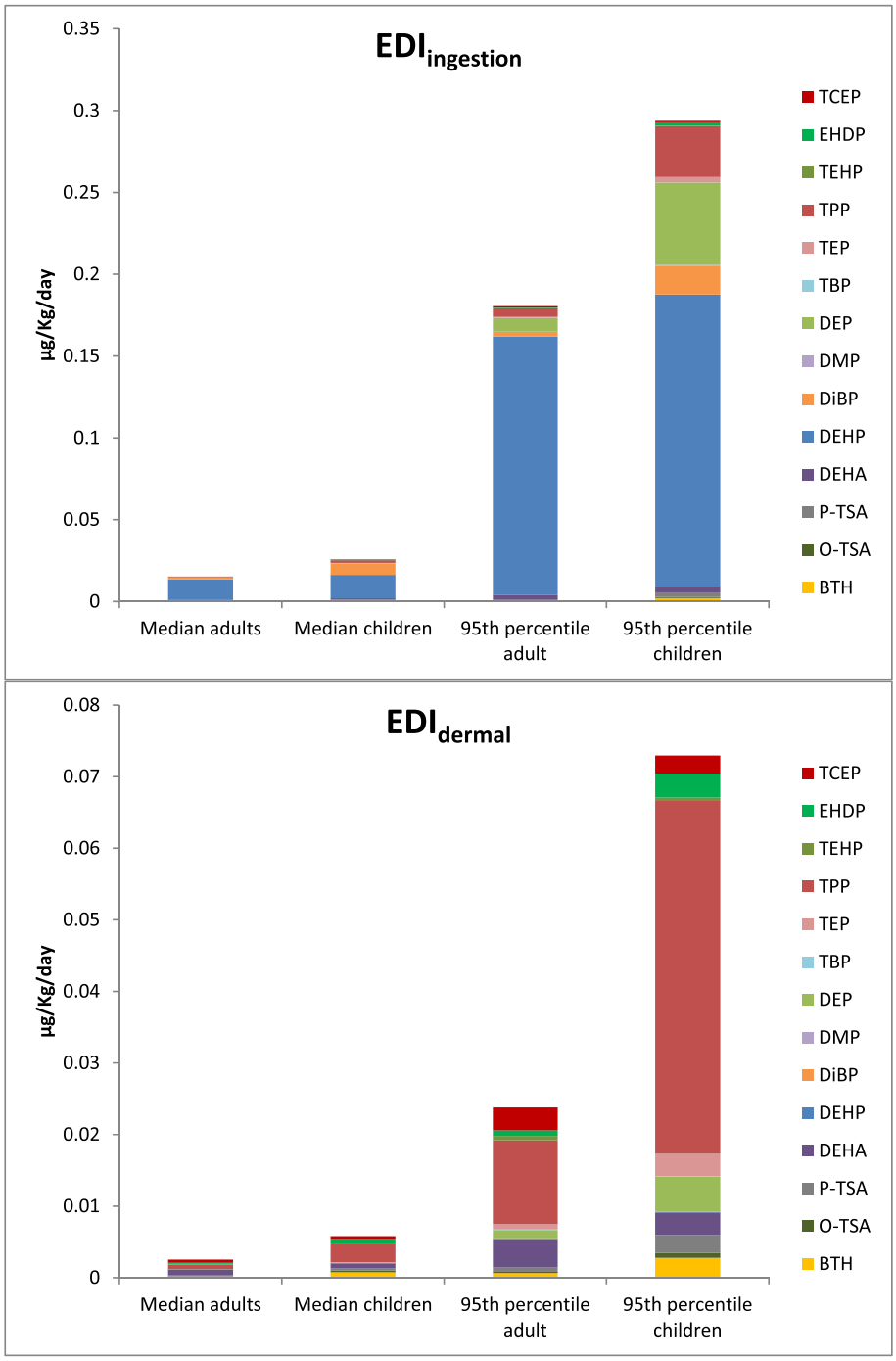

Fig. 2. EDI via ingestion and dermal contact.

the following equations:

$CR_{ingestion} = EDI_{ingestion}$ x SFO

$CR_{dermal} = EDI_{dermal}$ x SFO/GIABS

$CR = CR_{ingestion} + CR_{dermal}$

where SFO is the oral cancer slope factor, expressed in $(\mu g/kg/day)^{-1}$ and its values were extracted from the literature. The compounds studied were TBP, TEHP, TCEP, DEHP and DEHA, whose SFO values were 9×10^{-6}, 3.2×10^{-6}, 2×10^{-5}, 1.4×10^{-5} and 1.2×10^{-6}, respectively (Li et al., 2018; Maceira et al., 2020).

Tables S2 and S3 provide a summary of all the values and considerations used to perform the calculations.

3. Results and discussion

3.1. GC-MS method

The chromatographic separation process used was adapted from the study of Maceira et al. (2020), in which the same compounds were determined in particulate matter from air samples. Table S1 summarises the optimised MS conditions. For each compound, its retention time and three or four ions were selected in SIM mode. The most abundant *m/z* was used for quantification to increase sensitivity and the others for confirmation purposes. The relative abundances between the quantification ion and the confirmation ions are also detailed in Table S1. Three IS were employed to successfully quantify the selected compounds,

Table 3
Hazard index (HI) for children and adults in two scenarios.

Compound	HI			
	Adult		Children	
	Median	95th percentile	Median	95th percentile
BTH	5,67E-05	2,02E-04	2,74E-04	9,75E-04
O-TSA	2,65E-07	8,96E-07	1,32E-06	4,46E-06
P-TSA	2,23E-06	1,61E-05	1,11E-05	8,01E-05
DEHA	2,54E-06	1,15E-05	2,38E-06	1,08E-05
DEHP	6,32E-04	7,90E-03	7,14E-04	8,94E-03
DiBP	5,71E-06	1,46E-05	3,41E-05	8,74E-05
DMP	1,76E-07	3,20E-07	1,05E-06	1,91E-06
DEP	2,10E-07	1,19E-04	1,21E-06	6,89E-04
TBP	1,09E-07	5,09E-06	9,75E-08	4,57E-06
TEP	3,25E-07	1,05E-05	1,62E-06	5,20E-05
TPP	1,25E-05	2,41E-04	5,94E-05	1,15E-03
TEHP	1,22E-06	8,13E-06	1,07E-06	7,16E-06
EHDP	3,73E-05	1,91E-04	1,77E-04	9,08E-04
TCEP	2,58E-05	1,84E-04	2,23E-05	1,59E-04
$\sum$ PAEs	6,40E-04	8,05E-03	7,53E-04	9,73E-03
$\sum$ OPEs	7,72E-05	6,39E-04	2,62E-04	2,28E-03
$\sum$ BTHs	5,67E-05	2,02E-04	2,74E-04	9,75E-04
$\sum$ BSAs	2,50E-06	1,70E-05	1,24E-05	8,45E-05

which were d_4-BTH, d_{27}-TBP and d_4-DEHP. Their ions and retention times are also detailed in Table S1.

Some compounds exhibited co-elution, but their differences in MS spectra allowed them to be successfully quantified. This was the case of BTH and the IS d_4-BTH and of EHDP, DEHP and the IS d_4-DEHP. BTR was initially included in the method; however, it was eliminated due to the low sensitivity shown.

Good linearity was achieved between the instrumental limit of quantification (LOQ) and 5 mg/L for most of the compounds, except for 5TTR, OHBTH, XTR and EHDP, which was up to 3.5 mg/L. In order to properly quantify the compounds, in some cases two calibration curves were conducted (lower and higher level). Instrumental limits of quantification (LOQs) were considered the lowest concentration of the calibration curve which also achieved an S/N $\geq$ 10. LOQs were between 2 and 10 μg/L for most of the compounds, 25 μg/L for o-TSA, Me-p-TSA and TCEP and between 100 and 250 μg/L for BSA, NH_2BTH, OHBTH, p-TSA, XTR and 5TTR. Instrumental limits of detection (LODs) were calculated as S/N $\geq$ 3. In general, they were in the range of 0.5–5 μg/L for most of the compounds, but between 10 and 100 μg/L for BSA, o-TSA, TCEP, p-TSA, NH_2BTH and 200 μg/L for 5TTR, XTR and OHBTH.

3.2. Pressurised liquid extraction

To effectively obtain an extraction from a solid sample like dust by means of pressurised liquid extraction, several operational parameters have to be optimised. The initial extraction conditions were obtained from Maceira et al. (2020), in which the same group of compounds was extracted from PM_{10} filters.

The extraction solvent selected was ethyl acetate. Other extraction conditions established as initial conditions in this study were a temperature of 70 °C and one 5 min-cycle of static time (Maceira et al., 2020). The other parameters are detailed in Section 2.3.

To assess extraction conditions, 0.1 g of dust sample (Velázquez-Gómez et al., 2018; Zhu et al., 2019) was spiked at 20 μg/g. In addition, non-spiked dust samples were also analysed in order to subtract the signal of the compounds present in the sample. With the above-mentioned initial conditions, extractions were performed and apparent recoveries were calculated by interpolation with an internal standard calibration curve. They ranged from 35% to 110%. EHDP, TEP and DiBP were the compounds with the lowest apparent recoveries. Some of the parameters affecting extraction were modified in an attempt to increase the lowest apparent recoveries.

In addition to the solvent, another important parameter is temperature. We evaluated the effect of increasing this parameter and found that with an extraction temperature of 90 °C most OPEs and PAEs yielded similar apparent recoveries. However, a decrease in apparent recoveries ranging from 7% to over 30% was observed for all BTHs and BSAs. TEP and TEHP also decreased by 10% and 18%, respectively. For this reason, the temperature was set at that used in the initial conditions, 70 °C.

Static time and the number of cycles were also evaluated. Extraction time was increased to 10 and 15 min. For BTRs and BSAs, when the extraction time was set at 10 min, all recoveries increased with the exception of BSA (20% decrease). When the time was increased to 15 min, apparent recoveries of BSA and p-TSA decreased, achieving values of 30%. Within the BTHs, only OHBTH increased at 10 min, while the other compounds had similar apparent recoveries, but for most of them recoveries decreased at 15 min. Similar apparent recoveries were obtained for OPEs at 10 min with the exception of TEHP and EHDP (>30% increase); TEP showed a reduction at 15 min while similar apparent recoveries or slightly lower ones were obtained for the remainder of the compounds. For PAEs, at 10 min, while recoveries of DEP and DMP decreased, DiBP, DEHA and DnOP increased their apparent recoveries between 20% and 35%, and similar values were obtained at 15 min. Based on these results, 10 min was selected as the final extraction time.

Because the introduction of fresh solvent into the extraction cell can increase extraction efficiency, we decided to increase the number of cycles as well. However, adding a second cycle did not result in any increases in apparent recoveries (data not shown). For this reason, this parameter was kept at the initial conditions, with just one cycle. Other parameters considered of minor importance were also maintained at the initial conditions (Section 2.3).

As mentioned previously, because dust is a complex matrix, we also tested performing an in-cell clean-up with the aim of obtaining a cleaner extract. Florisil was tested for this purpose as this sorbent had been used for clean-up in SPE cartridges when PAEs and OPEs, among other compounds, were studied in indoor dust (Velázquez-Gómez et al., 2018; Christia et al., 2019). The extraction cell was assembled as follows: 1 g of Florisil was placed at the bottom of the extraction cell, then 0.1 g of dust sample previously mixed with diatomaceous earth was added, and finally the void volume was filled with diatomaceous earth. No cleaner extract was obtained and we observed a decrease in the apparent recoveries for some of the compounds, such as o-TSA, Me-p-TSA, p-TSA, DiBP and TEHP, probably because they were retained by the sorbent. For this reason, this step was rejected and no in-cell clean-up was performed.

Table 4
Cancer risk (CR) due to ingestion and dermal absorption.

Compound	$CR_{ingestion}$				CR_{dermal}			
	Adult		Children		Adult		Children	
	Median	95th percentile	Median	95th percentile	Median	95th percentile	Median	95th percentile
DEHA	7,83E-10	3,56E-09	8,86E-10	4,03E-09	1,04E-09	4,74E-09	8,27E-10	3,76E-09
DEHP	1,77E-07	2,21E-06	2,00E-07	2,50E-06	1,25E-10	1,56E-09	9,89E-11	1,24E-09
TBP	7,20E-12	3,37E-10	8,15E-12	3,82E-10	1,63E-11	7,63E-10	1,29E-11	6,05E-10
TEHP	9,94E-11	6,65E-10	1,12E-10	7,53E-10	2,90E-10	1,94E-09	2,30E-10	1,54E-09
TCEP	2,38E-09	1,70E-08	2,69E-09	1,92E-08	8,96E-09	6,38E-08	7,12E-09	5,07E-08

3.3. Method validation

The method validation process involved evaluating apparent recoveries, method quantification limits (MQLs) and method detection limits (MDLs), intra-day precision and inter-day precision. All of the results are shown in Table 1.

Apparent recoveries were calculated at two different spiked concentration levels, 20 μg/g and 5 μg/g, as described in section 3.2. Table 1 shows the results obtained at 20 μg/g and shows that apparent recoveries were over 71% for all of the compounds with the exception of TEP, BTH, ClBTH and NH_2BTH. It is important to mention that the recovery value for the compound DEHP could not be calculated at 5 μg/g due to its high concentration in the sample before the spike.

MQLs and MDLs were estimated taking into account the instrumental LOQs and LODs, previously calculated as in Section 3.1, and applying the recovery values. The concentrations of the compounds that appeared in the procedural blank were also taken into account in the estimation of MQLs and MDLs. Notably, the compounds exhibiting higher MQLs and MDLs, such as OHBTH, 5TTR and XTR and other compounds belonging to the BTHs and BTRs groups, have rarely been studied in dust samples (Wang et al., 2013; Li et al., 2020), and had been previously analysed by means of LC-MS/MS. According to Herrero et al. (2014), these groups of compounds as well as BSAs are preferably analysed by means of LC instead of GC due to their low volatility, which makes LC a better option that yields better results. However, we included them in this study in order to develop a multiresidue method for determining HPVCs.

Intra-day precision and inter-day precision were calculated with five replicates at two spiked concentration levels (20 μg/g and 5 μg/g) and they are expressed as % relative standard deviation (%RSD). Table 1 shows the results obtained at the lower concentration level of 5 μg/g. The results were considered acceptable, as intra-day precision values ranged from 2 to 24% and inter-day precision from 4 to 27%.

3.4. Occurrence of HPVCs in dust samples

Once the method was validated, it was applied to 16 samples taken from different houses in the Tarragona area. This was the first time that the selected compounds were studied in dust from the Tarragona region. Each sample was analysed in triplicate. The extract was diluted for compounds that exhibited concentrations higher than the upper limit of the linear range.

Fourteen target compounds were found in one or more of the analysed samples. Table 2 shows the mean, median, 95th percentile, the concentration range for each compound and its detection frequency. In order to perform the calculations for the compounds that were present in concentrations less than the MDL or less than the MQL, their values were considered MDL/2 and MQL/2, respectively (Núñez et al., 2020). The group of PAEs and OPEs were found in most samples. None of the selected BTRs was found in any of the samples and two BSAs and one BTH were detected. Fig. 1 shows the contribution of each group of compounds in each sample (house) studied. DEHP is represented separately due to its higher concentration. As the figure indicates, PAEs were the predominant contaminants found and, in some cases, OPEs were also considerably frequent.

Five PAEs were detected (DEHP, DEHA, DiBP, DMP and DEP) and, with the exception of DEP, they were found in all the analysed samples. A wide range of concentrations of phthalates has been reported in the literature; according to Xu and Li (2021), this wide range of concentrations is indicative of a great diversity of phthalate usage depending on the country or region under study. In the present study, DEHP was the compound determined at the highest concentration, ranging from 46.2 μg/g to 2197.5 μg/g, although most of the samples were in the range 46.2 and 583.3 μg/g As an example of the wide range of concentrations of phthalates in house dust samples, in a study conducted in France, Mercier et al. (2014) reported concentrations of DEHP from 138 to 785 μg/g, while Zhu et al. (2019) found concentrations ranging from 0.503 to 1550 μg/g in a study conducted throughout different regions of China. Moreover, other studies have reported even higher levels of DEHP, such as Xu and Li (2021), who reported concentrations between 235 and 2838.5 μg/g. In a study of Denmark schools, levels of DEHP were detected measuring up to 3214 μg/g (Clausen et al., 2003). The concentrations and frequencies reported in the literature, which are in agreement with those found in this study, make DEHP the most frequently detected and dominant PAE in indoor dust (Velázquez-Gómez et al., 2019). Concentrations of DMP, DiBP, DEP found in the present study were in the range of those found by Velázquez-Gómez et al. (2019) and Mercier et al. (2014), although the concentrations of DiBP reported in Mercier's study were higher (9340–574000 ng/g) than those found here. Other studies have also reported higher values for DMP and DiBP (Zhu et al., 2019; Xu and Li, 2021). For DEHA, the range of concentrations of this compound was between 2.48 and 47.2 μg/g being most of the samples in the range of 2.48 and 9.27 μg/g. These results agree with those reported by Christia et al. (2019), in a study of plasticisers in home dust from different European countries which reported a mean value of 19 μg/g in Belgium, 4.7 μg/g in the Netherlands and 3 μg/g in Ireland. The phthalate DnOP, which was not detected in this study, has been reported by other authors at a maximum concentration of 6.81 μg/g (Zhu et al., 2019; Xu and Li, 2021). The levels encountered and their detection rates indicate that PAEs are widely used consumer products and humans are exposed to them through house dust (Xu and Li, 2021).

Six OPE compounds (TBP, TEP, TPP, TEHP, EHDP and TCEP) were found in the analysed samples. TPP, EHDP and TCEP were present in all the samples analysed, while TBP and TEP were present in only a few of them, with maximum concentrations of 0.27 μg/g and 2.67 μg/g, respectively. Regarding TPP, concentrations were between 0.65 μg/g and 3.01 μg/g in all the samples with the exception of one sample in which the concentration was 89.03 μg/g. As regards EHDP, the concentration range was between 0.2 μg/g and 2.6 μg/g, and for TCEP, from <MQL and 7.81 μg/g.

For this group of compounds, a wide range of concentrations has been reported in the literature, from ng/g up to μg/g. According to de la Torre et al. (de la Torre et al., 2020), these concentrations vary broadly by country due to diversified lifestyles, buildings and decorating characteristics, habits, consumer products, and the economic status of the region. In a study conducted in Barcelona, Cristale et al. (2016) reported concentrations of OPEs in house dust of 156–719 ng/g for TEHP, 449–2271 ng/g for EHDP, 580–2633 ng/g for TPP, 134–13200 ng/g for TCEP, and 93.7–131 ng/g for TBP, which are consistent with the values determined in this study. De la Torre et al. (de la Torre et al., 2020) also reported higher concentrations: up to 34,1208 ng/g for TCEP, 23,770 ng/g for TPP, 72,856 ng/g for TBP and 15,595 ng/g for EHDP. The concentrations found in the present study were also in the range of those reported by other authors (García et al. 2007a, 2007b; Velázquez-Gómez et al., 2019). The OPE TiBP was not detected, although it has been reported in other studies in concentrations ranging from <MQL to 0.58 μg/g (García et al., 2007a, 2007b; Cristale et al., 2016).

Of the other HPVCs studied, just one BTH (BTH), which has been reported as having the largest production volume of all BTHs (Wang et al., 2013), and two BSAs (o-TSA and p-TSA) were determined in some samples. The BTH group of compounds has not been the focus of much research in indoor samples, and only two studies are available in the literature (Wang et al., 2013; Li et al., 2020). In this study, BTH was present in all the analysed samples with a maximum concentration of 3.23 μg/g. Similar to our results, up to 2780 ng/g were reported in house

dust by Wang et al. (2013) and from <MDLup to 1560 ng/g in urban residential houses by Li et al. (2020). However, in their studies, other BTHs such as OHBTH, NH_2BTH and MeSBTH and BTRs such as BTR, XTR and TTR (a mixture of isomers of 5TTR and 4TTR) were also found (Wang et al., 2013; Li et al., 2020). In the present study, the BSAs were only detected in some samples, but they could be quantified in a few of them at the maximum concentration of 3.03 μg/g for p-TSA. To the best of our knowledge, this is the first time that BSAs have been studied in dust samples, and two of them were detected in some samples.

3.5. Human exposure via dust ingestion and dermal absorption

In order to estimate human exposure to these compounds, we calculated the EDI through dust ingestion and dermal absorption for adults and children under median and high exposure scenarios. We used the median and 95th percentile concentration values detailed in Table 2. Fig. 2 shows the values obtained in the evaluation. As shown, $EDI_{ingestion}$ makes a much greater contribution to exposure than EDI_{dermal}. This greater contribution has been repeatedly reported in the literature (Christia et al., 2019; Zhu et al., 2019; de la Torre et al., 2020).

The compound that contributes the most to $EDI_{ingestion}$ is DEHP, but other compounds such as DEP and TPP also played an important role in the worst-case scenario. However, the compound that contributes the most to EDI_{dermal} is TPP. Moreover, children are more affected than adults, as expected. Similarly, Christia et al. (2019) also calculated the EDI via ingestion and dermal contact for several phthalates in samples from different European countries. Although the variability found by those authors differed between countries by several orders of magnitude, the results found in the present study are comprised within that variability. De la Torre et al. (de la Torre et al., 2020) also calculated the EDI via ingestion and dermal contact for OPEs and reported higher values than those determined in this study.

To assess the cumulative non-carcinogenic risk, HI was calculated as the sum of $HQ_{ingestion}$ and HQ_{dermal} for each compound, as detailed in Section 2.6. Table 3 shows the HI values for adults and children in the two scenarios studied (median and worst-case scenario). A >1 HI value indicates that there is a chance that non-carcinogenic effects may occur, while <1 HI values indicate that no significant risk for non-carcinogenic effects is expected (Kurt-Karakus, 2012; Li et al., 2018). As the Table 3 shows, none of the calculated HIs was higher than one, even when the worst-case exposure scenario was considered, indicating an unlikely health risk via dust ingestion or dermal contact. The HI values ranged from 9.75×10^{-8} to 8.94×10^{-3}.The sum HI for each group of compounds was always also lower than one, even in the worst-case scenario. The big difference among the HI values are not only due to the different concentrations of each compound in the samples but also the different values of the parameters that are considered in the calculation of HQ, as can be seen in Table S2. In a study conducted by Xu and Li (2021), the cumulative risk of exposure (HI) was also calculated considering HI as the sum of HQ due to ingestion of the most abundant phthalates encountered in their study (DBP, DiBP and DEHP), and the risk posed by dermal absorption was not evaluated. As in this study, they also found no non-carcinogenic risk posed by phthalates. In another study, the non-carcinogenic risk of plasticisers was evaluated by means of HQ; as in our study, none of the HQ values exceeded one, indicating an unlikely risk via dust ingestion (Christia et al., 2019).

The risk of carcinogenic effects from $EDI_{ingestion}$ and EDI_{dermal} was calculated for DEHA, DEHP, TBP, TEHP and TCEP using the equations described in Section 2.6. Values that exceed the threshold of $CR = 1 \times 10^{-6}$ indicate a potential adverse effect (Li et al., 2018). Table 4 shows the results of the calculation, which indicate that all of the compounds exhibit CR values lower than the above-mentioned threshold, with the exception of DEHP for ingestion in the worst-case scenario (95th percentile) for children and adults, with values of 2.50×10^{-6} and 2.21×10^{-6}, respectively. In a study conducted by Xu and Li (2021) which evaluated the CR for DEHP in dormitories and in houses in China, the CR values for DEHP due to ingestion obtained in dormitories were between 2.2×10^{-6} and 1.3×10^{-7}, which are in the same range as the values found in the present study. However, higher levels were encountered in houses, and the authors suggest potential risk due to DEHP, although their threshold for considering risk was 1×10^{-5}. Li et al. (2016) also evaluated the carcinogenic risk of DEHP due to ingestion and reported a median value for CR of 1.32×10^{-6} for adults in houses; in this case, the threshold for considering potential adverse effects was also 1×10^{-5}.

Therefore, no significant risk due to the presence of HPVCs was found in the dust samples from the Tarragona region. In a previous study which evaluated ambient inhalation risk for the same compounds (Maceira et al., 2020) from PM_{10} samples from the same region, no immediate health risk was found either. However, it would be of interest to study all three exposure routes as well as other possible risks like dietary exposure in future research to establish an exhaustive study of exposure to HPVCs in the region.

4. Conclusions

A new multiresidue method to determine 22 HPVCs belonging to different groups based on PLE and GC-MS was successfully developed and validated. The method was applied to evaluate the occurrence of the selected compounds in different dust samples from the Tarragona region. Among the groups studied, PAEs and OPEs were the most detected compounds. DEHP was the compound present at the highest concentrations, ranging from 46.2 μg/g up to 2197.5 μg/g. Two BSAs, o-TSA and p-TSA, were determined for the first time in dust samples. With the results obtained, EDI via ingestion and dermal contact were estimated for children and adults in two scenarios, employing median concentrations and 95th percentile concentrations. The non-cancer assessment produced by ingestion and dermal contact was evaluated by means of HI. From the HI results obtained, no estimated risk to the population is expected. Most of the compounds did not pose a carcinogenic risk, and only DEHP in the worst-case scenario (95th percentile) slightly exceeded the threshold ($CR = 1 \times 10^{-6}$).

Credit author statement

Mireia Núñez: Conceptualisation, Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing. Núria Fontanals: Conceptualisation, Methodology, Validation, Investigation, Resources, Writing – review & editing, Supervision. Rosa Maria Marcé; : Conceptualisation, Investigation, Resources, Writing – review & editing, Supervision, Project administration. Francesc Borrull: Conceptualisation, Resources, Writing – review & editing, Supervision, Project administration, Founding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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