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Analysis of industrial contaminants in indoor air. Part 2. Emergent contaminants and pesticides

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Abstract

This article reviews recent literature on the analysis of several contaminants related to the industrial development in indoor air in the framework of the REACH project. In this second part, the attention is focused on emergent contaminants and biocides. Among these chemicals, phthalates, polybrominated and phosphate flame retardants, fragrances, pesticides, as well as other emerging pollutants, are increasing their environmental and health concern and are extensively found in indoor air. Some of them are suspected to behave as priority organic pollutants (POPs) and/or endocrine disrupting compounds (EDC), and can be found both in air and associated to the suspended particulate matter (PM) and settled dust. Main literature considered for this review is from the last ten years, reporting analytical developments and applications regarding the considered contaminants in the indoor environment. Sample collection and pretreatment, analyte extraction or desorption, clean-up procedures, determination techniques, and performance results are summarized and discussed.

Keywords

Indoor air; dust; emergent contaminants; phthalates; flame retardants; synthetic musks; pesticides; review

Contents

1. Introduction

People in developed countries spend up to 90% of their time indoors [1, 2]. Many indoor environments can act as concentrators of emissions from plastics, paints, and other building materials. Inadequate ventilation coupled with the slow indoor degradation processes may increase indoor pollution levels. High temperature and humidity levels can also increase concentrations of some pollutants. Besides, the high comfort achieved in developed countries, increased the demand and the widespread consumption of biocides and fragranced household products. Hence, inhalation of indoor air is potentially the most important exposure pathway to many pollutants [2]. The Registration, Evaluation and Authorisation of CHemicals (REACH) system was created in the European Union (EU) in response to the ever-increasing concern about the production and use of many chemical substances lacking information on their environmental and health effects. REACH applies to all chemicals, not only those used in industrial processes but also those used in the day-to-day life, for example in cleaning products, paints, as well as in articles such as furnitures, clothes or electrical appliances [3]. The chemicals that are extensively found in indoor environments include compounds that are suspected to behave as POPs and endocrine disrupting compounds (EDC) such as phthalate esters, polybrominated and phosphate flame retardants, fragrances, pesticides, biocides, and other compounds (organotin and perfluorinated alkyl compounds) that are of increasing concern as indoor pollutants. An overview of the relative importance of all these compounds as environmental pollutants is presented in the corresponding sections of this review as well as the recent developments and applications of methodology for their analysis in indoor air including the concentration levels found indoors. Sample collection and pretreatment, analyte extraction or desorption, clean-up, determination techniques, and performance results are summarized and discussed.

Research literature from the latest ten years has generally been considered. The review focuses on indoor air analysis and hence, methodology developed or applied to atmospheric or ambient air analysis has been excluded. At this point, a recent and useful review by Xie and Ebinghaus [4] considers the determination of emergent pollutants focused on the atmosphere. However, in the present review only procedures that have been developed for indoor analysis, or those that can indistinctly be applied for both indoor and outdoor analysis, have been taken into consideration. Main attention has been paid to the analysis of the gas phase indoors. In addition, the importance of domestic dust and suspended PM as vehicles of these indoor pollutants is highlighted and thus, their occurrence and analysis in these solid matrices has been considered.

2. Phthalate esters

Phthalate esters are extensively used as softeners in the production of polymeric materials such as polyvynylchloride (PVC). Since phthalate esters are not chemically bound to the polymer, they can be easily released into the environment. PVC and other polymers are widely produced for building materials and thus, the surrounding environment can be polluted by phthalates. Due to their high volume production and their widespread use, phthalates, as well as some other chemicals present in the domestic environment, are potentially important indoor contaminants. In addition, people working in industrial plants producing plasticizers or living near such plants may be exposed, via indoor air inhalation, to levels of these pollutants that could constitute a significant contribution to the total daily intake [5].

Due to their ubiquity, phthalates can be found everywhere, including common laboratory equipment and reagents. In consequence, the main problem in phthalate analysis is external contamination coming from the sampling and sample preparation procedure and even the chromatographic analysis. This problem has been extensively studied by Frankhauser and Grob [6]. The analysis of blanks is of great importance, as are all the precautions in the treatment of the material and reagents used in any step of the analytical process. To minimize contamination [7,8], the use of plastic materials should be avoided, the sample preparation procedure should be as simple as possible with minimal extraction steps, and minimal glassware used. Glassware should be properly cleaned by solvent rinsing and thermal treatment at 400ºC. Prior to use, the it should be rinsed with blank tested organic solvent (cyclohexane or isooctane) to deactivate the surface. Organic solvents and laboratory grade water usually contain traces of phthalates, even the ones commonly available for trace analysis, and these must be checked to establish background levels. Also, reagents need to be checked. Additional contamination of material, water solvents, and reagents can occur due to the laboratory air. The material should be stored in a closed container or wrapped in aluminium foil to avoid adsorption of phthalates from the air. As previously commented, phthalates can be present in the chromatographic system and the most important contamination source is located in the inlet and gas supply system, inlet septa, liners and o-rings. Since the caps for autosampler vials also contain phthalates, as general precaution, only one injection should be made from each vial [9].

2.1. Sampling

In Table 1, details on the analysis of phthalate esters in indoor air samples are illustrated [5,10,11,17]. Sample volumes of 1 to 10 m^3 of air are usually enough [5,10], although procedures working with only 15 L of indoor air samples have also been reported achieving detection limits in the low ng m^{-3} [15]. The analysis of atmospheric levels of phthalates would however require higher sample volumes of up to 1000 m^3 [18]. The devices currently employed to retain the target compounds are cartridges filled with the sorbent material retained by glass wool. Such material can be polyurethane foam (PUF), Tenax GR, polydimethylsiloxane (PDMS) on Chromosorb, octadecylsilica, charcoal, or combinations of various sorbents like PUF and XAD resin. To prevent possible contamination, sorbent materials are usually preextracted by Soxhlet using different solvents or solvent mixtures [10] Breakthrough air volumes for each analyte need to be previously determined to select the maximum sample volume that can be concentrated [6]. In some studies, phthalates in PM are also the object of analysis. Collection of suspended solid particles can be accomplished by placing a particle quartz fiber filter (QFF) in front of the sorbent [10,11, 14].

2.2. Sample treatment

Desorption of phthalate esters from cartridges can be performed by extraction with organic solvents or by thermal desorption (TD). Solvent extraction (SE) methods using direct elution [16], Soxhlet extraction [10,11,18,19], pressurized solvent extraction (PSE) [12] or extraction assisted by ultrasounds (US) [5,20] have been reported.
In their pioneer study on the presence of phthalate esters in the Swedish atmosphere, Thuren and Larsson used polyurethane filters connected in series [20]. Compounds adsorbed to the PUF filters were extracted with acetone-hexane in an ultrasonic bath. More recently, Otake *et al* [5] extracted the charcoal tubes with the adsorbed phthalates by sonication with 1 ml of toluene for 10 min. These authors proved that longer sonication times did not improve the efficiency of the extraction (97.5 to 115%). Fromme *et al* [12] determined phthalate esters and musk compounds in indoor air using a procedure implying PSE (5% DCM in hexane) of PUF sampling cartridges (2 m^3 air collected) and gas chromatography-mass spectrometry (GC/MS) of the concentrated extracts with determination limits of 10 ng m^{-3}. Rudel *et al* [10,11] performed an extraction of QFF-PUF-XAD sampling cartridges in a Soxhlet apparatus using 200 mL of 6% ether in hexane for 16 h. Prior to the extraction, p-terpenyl-d_{14} was added as a surrogate standard. With this procedure recovery of the target phthalates ranged from 40

to 220% (%RSD= 15-25) and detection limits (LODs) of 2-75 ng m^{-3} have been achieved [11].

Extracts are usually concentrated to achieve sufficient overall method sensitivity or for solvent exchanging for further analysis. Before concentration, the addition of anhydrous sodium sulphate avoids the presence of residual water traces in the organic extracts. Either a gentle stream of nitrogen or Kuderna–Danish (K-D) can be used for the concentration of the extracts [17]. Cleanup procedures including the use of fuming concentrated sulphuric acid [20] or silica gel columns [17,18] have been reported. Thermal desorption of the sampling cartridges presents some advantages over the solvent-based extraction methods, much of them derived of the absence of solvent manipulation. In addition, since all the retained compounds are thermally desorbed into the GC, high sensitivity can be achieved. Nevertheless, some limitations deal with the high temperatures needed for quantitative desorption of the less volatile phthalates from typical sorbents, such as Tenax or carbon materials. An alternative to these sorbents could be the use of silicones as sorptive material. A procedure based on the use of this adsorbent for enrichment, thermal desorption-GC-MS was described by David *et al* [8]. An estimation of the LODs achieved sampling 15 L air ranged between 1 and 10 ng m^{-3}.

2.3. Determination

Phthalate diesters are sufficiently volatile and thermally stable to be analyzed by GC [21]. Although several detector types have been applied to phthalate GC analysis in environmental samples, most of the recently proposed methods involve the use of MSD working in the electron ionization (EI) mode [9]. Most phthalates fragmentize with characteristic ions, such as m/z 149. This is the case of diethyl phthalate (DEP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), bis-(2-ethylhexyl) phthalate (DEHP), and diisobutyl phthalate DIBP). Dimethyl phthalate (DMP) fragmetinze with m/z 163, and diisononyl and diisodecyl phthalates (DINP, DIDP) with m/z 307. These fragmentation patterns allow a very sensitive and selective detection, particularly when operating in the selected ion monitoring (SIM) mode [5,10,11,12,16]. Separation columns are usually 25 to 30 m x 0.25 to 0.32 mm I.D. coated with phenyl methylpolysiloxane or dimethylpolysiloxane stationary phases, which allow programming separations in a wide range of temperatures (typically, from about 50 to 300ºC at 10 ºC min^{-1}) with low bleeding. As commented above, the ubiquity of phthalate esters constitutes a very real problem through the analysis process, requiring a

careful check for blank concentrations for which values of >100 ng m^{-3} have been reported [5,16].

2.4.Concentration in indoor air

Phthalate indoors concentrations highly depend on the building materials and the type of furniture at each sampling emplacement. Hence, a broad range of values have been reported for the analyzed compounds (see Table 2). Sheldon *et al* [22], reported the results on 24 h phthalate monitorization in 125 homes in California (USA) showing a clear predominance of DBP and DEP in indoor air, with mean values of 410 and 350 ng m^{-3}, respectively. They also found DEHP (110 ng m^{-3}) and BBP (35 ng m^{-3}). Higher concentrations of total phthalates (>1000 ng m^{-3}) have been quantified in apartments and homes, as reported in other studies [5,12,16], which demonstrate that DBP predominates in the gas phase of domestic indoor environments. Fromme *et al* [12] extended the study of indoor occurrence of phthalates and musk compounds to kindergartens, finding mainly DMP and DBP at similar mean concentrations (1100-1200 ng m^{-3}). DBP and DEHP have also been quantified in office rooms by Toda *et al* [16], at concentrations in the broad range found in homes. In a very interesting study on the indoor exposure to EDCs, Rudel *et al* [11] found that phthalates were the most abundant among 89 organic chemicals considered in the 120 homes surveyed. Total concentrations of DEP, DBP; DEHP and BBP ranged from <90 to 7000 ng m^{-3}, indicating that the sources of these chemicals must be located indoors and highlighting the importance of indoor environments in the total exposure to chemicals.

3. Brominated flame retardants

Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol-A (TBBPA) and polybrominated biphenyls (PBBs), are among the most used brominated flame retardants (BFRs) and have attracted enormous attention over the past decade [23]. Other less known BFRs like bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DeBDethane) have an increasing interest due to their emerging use as substitutes of octaBDE and decaBDE commercial mixtures, respectively [24]. Similarly to other persistent organic pollutants (POPs), all these BFRs, with the exception of TBBPA, appear to be lipophilic and bioaccumulate in biota and humans [25]. Their widespread production and use, together with the increasing contamination of the environment, wildlife and people, highlights

the importance of identifying emerging issues associated with the use of BFRs, especially in indoor environments.

PBDEs are used in building materials, electronic equipment, lighting, electric wiring, textiles, furniture, industrial paints, and in many other common products. Due to their persistent and bioaccumulative nature, penta- and octabrominated commercial mixtures have been banned within the European Union and their use in North America has recently begun to be phased out [26]. However, vast reservoirs of PBDEs remain in existing consumer products, potentially contributing to environmental and human burdens of PBDEs for decades [27]. PBDEs are incorporated into materials as additives and thus may be released into air through volatilization during the product lifetime, and as a consequence levels are expected to be elevated in indoor air.

Sources of human exposure to PBDEs remain poorly characterised and, although intake through food consumption is undoubtedly important, the potential for exposure to PBDEs in the indoor environments is also real. In this way, inhalation and inadvertent ingestion of contaminated dust have been recently reported to be the largest contributors of PBDEs exposure of toddlers through to adults [28]. In addition, and because of higher concentrations, indoor air likely represents a significant source to outdoor air [29].

The analysis of some BFRs, such as TBBPA, HBCDs and the higher brominated PBDEs, is a relatively new challenge for most analytical laboratories. Special emphasis must be given to the need of an adequate QA/QC protocol, which is necessary for the reliable analysis of these environmental contaminants at trace levels [30].

Covaci et al [31] reviewed recent literature on the analysis of BFRs in different matrices, paying special attention to new analytical developments and quality assurance requirements.

PBDEs can be expected in any laboratory environment equipped with computers and other electronic devices. Significant concentrations of BDE47 and BDE99 have been identified in laboratory air by Thomsem et al [32]. Thus, in order to avoid a high content of BFRs in the procedural blanks it is important that all materials involved in the sample preparation are properly cleaned, and that direct exposure of the sample to the laboratory air is minimized. A proper glassware cleaning implies a thermal treatment at 450 ºC and solvent rinsing before used. PUF sorbents are usually precleaned by Soxhlet extraction with different solvents prior to sampling step. Moreover, the use of plastics should be reduced as possible in the determination of BFRs, since they can contain a wide range of these compounds. For the same reason,

unnecessary electric appliances and upholstered furniture should be avoided as well as unpackaging of goods in the laboratory where extraction and clean-up take place.
Of special interest and concern is BDE209, the primary component in the decaBDE commercial mixture—actually the most important PBDE mix in production. This compound as well as other highly brominated congeners are photosensitive, so direct exposure to UV light should be avoided. Thus, incoming sunlight into the laboratory as well as possible UV light from fluorescent tubes should be blocked by means of UV filters. Herrmann et al [33] reported up to 70% descomposition of BDE209 when stored for 24 h under light conditions. Wrapping glassware with aluminum foil during sample treatment and using amber glassware are simpler preventive measures to minimize UV-degradation of the analytes. Additional recommendations regarding this issue can be found in de Boer and Wells [34].

3.1. Sampling

Sampling of BFRs in indoor air and PM usually implies an active procedure, (see Table 3). In general, sample volumes ranging from a few hundreds of litres to less than 30 m^3 are enough to reach indoor LODs in the low ng m^{-3} level for most compounds. However, lower limits have been reported for sample volumes between 100 and 385 m^3 [38,45,48].
Active sampling devices commonly consist of a glass fiber filter (GFF) or a QFF to retain the airborne PM followed by a suitable sorbent to collect the compounds in the gaseous phase. PUF is the most used sorbent for sampling BFRs in indoor air [35,38,43,45,46,48,49,51], although XAD-2 resin has also been employed [24,36,44]. Rudel *et al*. [11] used this resin sandwiched between two PUF plugs for sampling volumes from 10 to 14 m^3 at flow rates between 8-9 L min^{-1}.
Other active systems for indoor sampling are based on the use of solid-phase extraction (SPE) disk or cartridges [32,42]. Thomsen *et al* [32] used styrene-divinylbenzene SPE cartridges with the aim of studying the influence of laboratory air on procedural blanks in the analysis of BFRs.
PUF disk passive air samplers are increasingly being employed for sampling of brominated compounds in indoor air [39-41,47,50]. They are considered particularly attractive because of their facility to obtain time-integrated samples in indoor locations, where active samplers would not be practical over such time periods due to the excessive noise, cost and equipment size. Conversion of contaminant masses per sample into concentrations in air requires knowledge of the air uptake rate of the PUF disk samplers and their deployment time. Wilford *et al* [39] estimated an average uptake rate

of 2.5 m^3 per day for tri- to hexaBDES. Sampling time usually ranges between 20 and 50 days, which approximately yields air volumes from 50 to 100 m^3.

Butt *et al* [37] used organic films from window surfaces as a time-integrated passive sampler for determining air concentrations of PBDEs. These organic films are formed by condensation of gas phase species and organic aerosols as well as by deposition of particulate-associated compounds. With knowledge of the uptake rate and film-air partition coefficient (K_{FA}), it is possible to estimate gas-phase air concentrations assuming that compounds in film and the gas-phase in air are at equilibrium.

3.2. Sample treatment

BFRs are commonly extracted from sorbents by Soxhlet extraction (Table 3). Despite its drawbacks, i.e. long extraction times and large solvent consumption, it is still widely used due to its general robustness and high extraction efficiency. Typical solvents include n-hexane, DCM, acetone, toluene and mixtures of them. Shoeib *et al* [45] reported recoveries higher than 98 % for tetra- to heptaBDEs after Soxhlet extraction with DCM and petroleum ether (PE)-acetone (1:1) for 18-24 h.

US-assisted extraction has also been used for the extraction of PBDEs and other brominated compounds [35,42,46,49,51]. This extraction technique allows a higher throughput of the analysis because of shorter extraction times, although lower extraction recoveries than with the Soxhlet extraction are, in general, obtained. Saito *et al* [42] extracted a number of BFRs by ultrasonication with 10 mL acetone achieving recoveries between 81 and 91 %. US-assisted extraction was also carried out by Tollback *et al* [49] to extract TBBPA with 5 mL acetonitrile (ACN) for 20 min (twice). Recoveries ranging from 75 to 107 % and RSD values lower than 7 % were reported.

Very recently, a PSE-based procedure was applied by Allen *et al* [43] for the analysis of tri- to decaBDE in residential indoor air. GFFs and PUF plugs were extracted separately with DCM and petroleum ether respectively. Extractions were performed at 100 ºC and 1500 psi for 5 min, and were completed after three cycles. Although higher costs are involved compared with Soxhlet extraction, this technique has the advantages of reduced extraction time and lower solvent consumption, which decreases the long-term cost and makes the procedures more environmentally friendly.

Most of the available methodologies imply one or several concentration steps and solvent exchanges aiming to improve the sensitivity for further analysis. Treatment with concentrated sulphuric acid [38,40,47] and a variety of clean-up procedures on silica gel, alumina, florisil or combinations of these sorbents are commonly used. Karlsson *et al*

[24] pre-cleaned Soxhlet extracts on a KOH/H_2SO_4-treated silica column followed by a clean-up on a gel permeation chromatography (GPC) system before analysis with GC/MS. Recoveries, evaluated by addition of ^{13}C-labeled surrogate standards, were in the range from 12 to 97% for tri- to decaBDE with LODs lower than 0.2 ng m^{-3}.

3.3. Determination

Separation of BFRs is generally performed by means of GC/MS. Nevertheless, thermal degradation during the chromatographic separation has been reported for highly substituted PBDEs, mainly BDE-209, which leads to a low repeatability in their analysis [52]. Therefore, special attencion should be paid to these compounds to ensure a proper analysis. Residence time in the column has been shown to be a critical factor in the GC analysis of this kind of compounds. If the residence time is too long, thermal degradation of highly substituted congeners, especially BDE-209, is substantial. Shorter standard columns were initially used for analysis of decaBDE, so use of two columns of different length was required for determination of low and high-brominated PBDEs. The development of narrow bore columns has allowed a proper determination of all congeners with only one column [53]. Narrow bore columns, with maximum length 8–10 m, small internal diameter (0.10 mm), and coated with a thin film (0.10 μm), can achieve the same resolution as standard columns in shorter analysis times [53, 54]. Bjorklund *et al* [55] reported a comprehensive study on the influence of main GC parameters on the determination of decaBDE. According to these authors, the on-column injector is the most suitable injector for clean samples analysis, whereas programmable temperature vaporizing (PTV) injector provides a good compromise between robustness and yield for more complex samples.

Regueiro et al [56] have recently described a further optimization of GC analysis of the highly substituted PBDEs including not only decaBDE but also the octa- and nona-brominated ethers. Satisfactory results in terms of yield, accuracy and precision were achieved using a narrow bore column and a split/splitless injector operated at a temperature of 320 ºC.

MS operating in negative chemical ionization (NCI) is the most widely used determination system for analyzing BFRs in indoor air samples [24,32,35,36,39,41,43,44,46,48,50,51]. This technique provides a very high sensitivity and selectivity for brominated compounds, especially with selected ion monitoring of the most abundant fragment, Br^- (m/z= 79/81). However, there may be problems with identification and coelution of other brominated compounds and it is not possible the

use of ^{13}C-labeled compounds as internal surrogate standards (SSs) [49]. Using GC/NCI-MS, Gevao *et al* [41] determined tri- to heptaBDEs in indoor air reaching LODs from 0.2 to 0.5 pg m^{-3}.

MS in the EI (SIM) mode has also been employed for quantification of this kind of compounds in indoor air [11,37,38,40,45,47], reporting LODs in the range 0.3-20 pg m^{-3} for the analysis of tetra- to hexaBDEs [45]. Determination of BFRs in indoor air has recently been performed by means of GC with an atomic emission detector (AED) [42]. A wavelength of 827 nm was selected for Br detection and LOD in the low ng m^{-3} were obtained for most of compounds.

Analysis of TBBPA and 2,4,6-tribromophenol (2,4,6-TBPh, another BFR and also the major breakdown product of TBBPA) by GC requires a previous derivatization step, to usually obtain the acetylated derivatives. In this way, acetylation was carried out with diazomethane [32,35]. The use of LC/MS in the determination of TBBPA is another possibility that provides several different detection modes and eliminates the need of derivatization. For the determination of TBBPA in air, Tollback *et al*. [49] developed a LC/MS method using electrospray ionization (ESI) in the negative ionisation mode with SIM. This kind of ionization was compared to atmospheric pressure ionization (APCI), achieving LODs between 30-fold and 40-fold lower.

3.4. Concentration in indoor air

Several studies have reported concentration levels of BFRs in air from electronics recycling facilities [11,35]. Sjodin *et al*. [35] investigated the presence of several BFRs in an electronics recycling plant and other indoor work environments in Sweden. The highest concentrations of all the identified BFRs were found in the recycling facility. For the rest of sampling sites, the corresponding concentrations in air were, in general, several orders of magnitude lower. Most abundant BFRs in the recycling plant were BDE183, BDE209, BTBPE, and TBBPA with mean values in the range 19-36 ng m^{-3}. On the other hand, BDE-47 was the most abundant PBDE congener in a computer teaching hall and a circuit board assembly plant with a mean concentration of 0.76 and 0.35 ng m^{-3}, respectively (see Table 2).

Harrad *et al* [38] reported levels of tetra- to hexaBDEs in outdoor and indoor air from different microenvironments (offices and homes). Concentrations of the tetra- and pentaBDEs in indoor air were always higher than those detected in outdoor air. Values for all studied compounds ranged from <1 pg m^{-3} to 1330 pg m^{-3}.

Wilford *et al* [39] measured indoor air concentrations of tri- to hexaBDEs from homes in Canada, detecting up to 1600 pg m^{-3}. These values were higher than those reported by Gevao *et al* [41] in indoor air in Kuwait with an average concentration in homes of 15 pg m^{-3}. Shoeib *et al* [45] determined concentrations in homes ranging between 76 pg m^{-3} and 2088 pg m^{-3} for tri- to heptaBDEs, whereas those reported by Chen *et al* [48] were in the range 0.3-1710 pg m^{-3}.

Indoor air concentrations of BFRs were generally higher in offices than in homes [38, 40-42]. A correlation between the concentration of several PBDEs and the number of electrical appliances and PUF-containing chairs in sampled rooms was observed [38]. Several studies have also conducted the analysis of air from a laboratory [32,45], showing the presence of PBDEs in the pg m^{-3} level. All these studies point out the ubiquity of these types of contaminants.

4. Organophosphate esters

Organophosphate esters (OPs) are manufactured on a large scale to be used as flame retarding agents and/or plasticizers in a variety of products such as electronic equipment, lubricants, plastics, glues, varnishes and furnishing fabrics. Several studies demonstrated the potential of these materials to emit phosphate flame retardants as well as their degradation products [42,57]. As additives, they may diffuse out at rates depending on their vapour pressures and the ambient temperature, and are thus emitted to the surrounding air [58]. Consequently, there are abundant sources of OPs in both public and domestic buildings, including diverse building materials and consumer products. Indoor environment represents the main source of human exposure to these pollutants through inhalation of air and inadvertent ingestion of dust. The most volatile OPs are found in the gas phase, whereas the OPs with higher molecular mass are mainly associated to the suspended PM and dust [35,58]. Several toxicological effects of organophosphate triesters have been reported, although very little is known about their health impact on humans. However, some reviews indicate that a number of these compounds, for instance tri-n-butyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP) and tris(2-chloropropyl) phosphate (TCPP), may negatively affect human health [59,60].

4.1. Sampling

Organophosphate flame retardants have been mainly collected from indoor air and PM by active sampling (see Table 4). Sample volumes between 1 and 14 m^3 are usually

employed at flow rates ranging from 1 to 10 L min^{-1}. Most of sampling devices consist on a GFF or QFF for collecting the PM and one or several PUF plugs for the gas phase [35, 57,61]. Saito *et al*. [42] and Yoshida *et al* [68] described active sampling methods for organophosphate compounds in air using a QFF disk followed by a C18 SPE disk. The main advantage of this disk-type configuration is the lower restriction of the flow rate. The use of aminopropyl silica SPE cartridges has also been proposed as a simple alternative for collecting both the gas phase and the PM [65,69].

Air sampling using solid-phase microextraction (SPME) has mostly been applied to more volatile compounds than organophosphate flame retardants. As known, semi-volatile compounds diffuse more slowly than VOCs, and thus require longer sampling periods to reach their air/fibre partition equilibrium. However, a dynamic air sampling method based on SPME was developed by Isetun *et al* [63,64,66], in which a controlled linear air flow is generated over the fibre in order to increase agitation and thus minimize the static layer surrounding the fibre. As a result, an increase in the extraction rate is produced and consequently the equilibration time is shortened. Extracted compounds are almost entirely from the gaseous phase, so no information about contribution of airborne PM is obtained.

The organophosphates are present primarily in the particle-associated phase rather than in the gaseous phase. Carlsson *et al* [61] observed that OP esters were mainly recovered from the GFF while the part passing into the PUF plugs was less than 1%.

4.2. Sample treatment

Ultrasound-assisted extraction (USAE) is the most widely used technique for recovering OP compounds from filters and sorbents. Sjodin *et al*. [35] carried out the extraction with 5 mL DCM for 20 min in an ultrasonic bath (power 50 W, frequency 48 KHz). The extraction procedure was repeated once using fresh solvent and recoveries higher than 95 % were obtained after concentration to 0.1 mL. Soxhlet extraction has also been applied by Ingerowski *et al* [62] with n-hexane/Acetone (4:1) for 8 h. In the case of sampling with SPE cartridges [65,69], extraction can be performed by elution or fractionation with a suitable solvent. Staaf *et al* [69] extracted organophosphate triesters from aminopropyl silica cartridges by using 5 mL methyl tert-buthyl ether (MTBE) reaching quantitative recoveries.

The use of very selective and sensitive detectors such as nitrogen phosphorus detector (NPD), allows a simple extract preparation, which usually consists on a filtration step followed by concentration to a small extract volume prior to the analysis by GC

[57,61,65]. In spite of it, LODs in the level of low ng m^{-3} are achieved for most of reported methods.

4.3. Determination

Organophosphate flame retardants in indoor air and PM have been mainly determined by GC. In most of cases, NPD is the selected technique for their quantification due to its high selectivity and sensitivity for this kind of compounds. Carlsson *et al* [57,61] achieved LODs lower than 0.1 ng m^{-3} with no further extract preparation than filtration through glass wool followed by volume concentration. However, NPD does not offer the possibility for positive identification, so MS is sometimes required for confirmation [35,57,61,65]. Furthermore, MS in the EI mode with SIM has also been employed [58,62,68] for quantification. Hartmann *et al* [58] determined OP flame retardants and plasticizers in indoor air obtaining LODs from 0.073 to 0.41 ng m^{-3}.

Positive chemical ionization (PCI)-tandem mass spectrometry (MS/MS) in the selected-reaction monitoring (SRM) mode has been applied by Bjorklund *et al* [67] in indoor air samples. A comparative study was performed between EI-MS and PCI-MS/MS under identical sampling and extraction conditions. LODs utilizing GC/PCI-MS/MS were found to be in the range 0.1-1.4 ng m^{-3}, which is about 50-fold lower than those obtained with GC/EI-SIM.

Recently, Saito *et al* [42] have used a flame photometric detector (FPD) for determination of organophosphate flame retardants indoors. This detector presents some of the advantages of the NPD such as high selectivity for phosphorous compounds. LODs between 0.24 and 3.5 ng m^{-3} were achieved with this detection technique.

The selection of suitable surrogate and internal standards (ISs) is conditioned by the extensive use of NPD and the impossibility of using isotopically labeled compounds with this detector. Several compounds such as tripropyl phosphate (TPP) and tripentyl phosphate (TPeP) are among the most frequently used ISs.

4.4. Concentration in indoor air

Organophosphate flame retardants have been found in indoor air in a number of homes [42,64,65,67] with concentrations ranging from less than 1 ng m^{-3} up to several μg m^{-3} (see Table 2). Marklund *et al* [65] reported the presence of these compounds in different indoor environments such as homes, offices, public buildings and domestic establishments. The chlorinated OPs, TCEP and TCPP, were the most abundant and

were present in all the sampled environments at concentrations up to 730 ng m^{-3} and 570 ng m^{-3}, respectively.

Levels of OPs were measured in schools and an office building by Carlsson *et al* [61]. TCEP was detected in the range 11-250 ng m^{-3}, whereas TBP was present at concentrations from 17 ng m^{-3} to 35 ng m^{-3}. Concentrations of triphenyl phosphate (TPhP) were lower with values up to 0.7 ng m^{-3}, which may be attributed to a lower migration rate because of its lower volatility.

Hartman *et al* [58] determined OPs in several workplaces, e.g. public buildings and cars at concentrations and up to 56 ng m^{-3} (for TCEP) and 29 ng m^{-3} (for TBP), TPhP levels were generally lower than 1 ng m^{-3}, which was consistent with the results reported by Carlsson *et al* [61].

5. Synthetic musk fragrances

Synthetic musk fragrances are added in large amounts to toiletries, cosmetics, household products, and a wide variety of other consumer products. In addition, synthetic fragrances such as air fresheners are used in products to scent the environment. They have been measured in workplaces and other crowded indoor environments, although there is an important lack of information about their concentration levels in domestic indoor air (Table 2). Owing to their chemical structures, synthetic musks can roughly be classified in two main categories: nitromusks and polycyclic musks. Among them, the polycyclic musks Galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(g) 2- benzopyrane, HHCB) and Tonalide (7-acetyl-1,1,3,4,4,6-hexamethyl-tetraline, AHTN) are used in the highest quantities, being the latter included in the United States Environmental Protection Agency (US EPA) high production volume (HPV) chemical list [73]. In 1997, the nitromusks musk xylene (1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, MX) and musk ketone (4-tert-butyl-3,5-dinitro-2,6-dimethylacetophenone, MK) were added to the list of chemicals for priority action of the EU and in 1998 MX was added to the corresponding list of the Oslo and Paris Commission (OSPARCOM) [74].

Although created to replace the more expensive and rare natural musks, polycyclic and nitromusks are not structurally or chemically similar to their natural counterparts. Their physical-chemical properties have more in common with hydrophobic and semivolatile organic pollutants that are known to biomagnify through the food chain [75].

Considering the tremendous use and exposure, there is limited information available related to health effects of synthetic musks. Nevertheless, fragrances can impact indoor

air quality and there is suggestive evidence that may play an important role in respiratory diseases and long-term impact [77]. In addition, there are environmental concerns, as synthetic musks contribute to both air and water pollution [74]. Hence, synthetic musks present enough properties which make them worth considering as a group of indoor air pollutants.

5.1. Sampling

Few studies have reported the analysis of musk compounds in indoor air and PM, as can be seen in Table 5. In all of them, synthetic musk have been collected by active sampling, using sample volumes ranging from 2 to 100 m^3 and, in general, reduced flow rates [12,70,71]. In a similar way to phthalates, special care should be taken to reduce the risk of contamination during the analysis due to the extensive presence of musk fragrances in soaps, perfumes and cosmetics [71]. Polyurethane foam is the most typical sorbent for sampling this kind of compounds in the gas phase, whereas a glass fibre filter is usually used to collect the airborne PM [70-72]. Chen *et al* [72] studied the distribution of musk fragrances between gas phase and PM for an indoor air sample from a cosmetic plant. Since the percentage of musks in the gas phase to the total was higher than 97 %, the authors point out the low affinity of these compounds towards the PM.

5.2. Sample treatment

Extraction of musk compounds from sorbents is typically carried out by Soxhlet using different solvent mixtures. Kallenborn *et al* [70,71] used this extraction technique with 300 mL n-hexane/diethyl ether (9:1) for 8 h followed by volume concentration under a gentle stream of nitrogen. Chen *et al* [72] extracted musks from PUF plugs with DCM for 72 h, showing recoveries ranging from 57 to 107 %. PSE has also been used for extraction of musk fragrances from sorbents with satisfactory yields. In this way, Fromme *et al* [12] extracted PUF with n-hexane/diethyl ether (19:1), which gave recovery rates between 91 and 100 %. Very recently, Regueiro et al. [76] have applied for the first time the SPME as an alternative to solvent extraction in the analysis of synthetic musks in air including polycyclic and nitro musks. By active sampling, musk compounds are adsorbed onto an amount of only 25 mg Tenax located in a glass SPE device. After addition of 100 µL acetone to the sorbent to favour the desorption, analytes are transferred to a DVB/CAR/PDMS fiber in the headspace (HS) mode.

Detection limits in the pg m^{-3} level were achieved for a sample volume of 5 m^3 using a GC/MS system operated in the full scan mode.

Regarding the clean-up procedure, most of authors have employed column chromatography on silica gel [70,71] or a combination of silica gel and alumina [72]. Kallenborn *et al*. [70,71] developed an extract fractionation on a silica column for selective elution of musk fragrances with 50 mL n-hexane/ethyl acetate (9:1) and further concentration under a stream of nitrogen. On the other side, no purification steps of the PSE extracts were performed by Fromme *et al* [12], but higher LODs, in the level of ng m^{-3}, were obtained.

5.3. Determination

Determination of synthetic musk fragrances is usually performed by GC using conventional capillary columns (30 m x 0.25 mm I.D., 0.25 µm film thickness) with common stationary phases, including 5 % phenyl substituted methylpolysiloxane and dimethylpolysiloxane. MS is the most extended detection technique for musk compounds and it is commonly operated in the EI mode with SIM [12,70,71], which leads to LODs in the pg m^{-3} level. However, nitromusk compounds have also been analyzed in the NCI mode [70,71] achieving LODs between 100-fold and 60-fold lower with regards to EI mode.

Deuterated musk xylene and AHTN standards are commercially available for use as surrogate and ISs. Nevertheless, deuterated AHTN has been reported to undergo partial deuterium to hydrogen exchange during analysis which may result in a inaccurate surrogate recovery [78]. A variety of other surrogate and ISs have also been used in different environmental matrices such as deuterated polycyclic aromatic hydrocarbons, pentachloronitrobenzene, hexamethylbenzene and various labeled and unlabeled polychlorinated byphenyls (PCBs). LODs, repeatabilities and recoveries reported in the analysis of musk compounds in air and PM are summarized in Table 5.

5.4. Concentration in indoor air

Kallenborn *et al*. [71] reported atmospheric concentrations of nitromusk and polycyclic musk in Norwegian air samples, not only in urban areas but also in remote areas. In one indoor laboratory air sample analyzed during the same sampling campaign, concentrations up to 2.5 ng m^{-3} of HHCB were measured, i.e. 10-fold higher than detected in outdoor air, which raise the suspicion that air as a transport and transfer medium for synthetic musk is still underestimated.

Musk compounds were further studied in several indoor workplace environments [70]. Highest values were found in a hairdresser facility with 44 ng m^{-3} HHCB, although a coffee bar contained also high synthetic musk burden with 35 ng m^{-3} HHCB and 12 ng m^{-3} AHTN, respectively. The presence of synthetic musk fragrances was also evaluated in indoor air samples from kindergartens in Berlin [12]. HHCB gave the highest levels ranging from 15 to 299 ng m^{-3}, whereas AHTN and Phantolide (6-acetyl-1,1,2,3,3,5-hexamethyl-indane, AHMI) where found at average concentrations of 47 and 22 ng m^{-3}, respectively. Chen *et al*. [72] measured polycyclic musk fragrances in a typical cosmetic plant and surroundings. Concentrations in the gaseous phase of the workshop were found to range from 32 to 4505 ng m^{-3}. Synthethic musks have been recently determined by Regueiro et al [76] in indoor air samples from homes of North-western Spain. Measured concentrations of HHCB and AHTN were in the range from 143 to 1129 ng m^{-3} and from 21 to 77 ng m^{-3}, respectively. Celestolide (4-acetyl-1,1-dimethyl-6-tert. –butylindane, ADBI) and AHMI were also found in one sample at concentrations of 2.6 and 8.5 ng m^{-3}, respectively, while Cashmeran (6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)indanone, DPMI), Traseolide (5-acetyl-1,1,2,6-tetramethyl-3-iso-propyldihydroindane, ATII), and musk moskene (4,6-dinitro-1,1,3,3,5-pentamethylindane, MM), were not found in any of the samples. These concentrations were higher than those measured by Kallenborn et al [71], but in the order of those reported by Fromme et al [12] in air of German kindergartens.

6. Pesticides

The extensive use of pesticides to improve agricultural productivity played an important role during the last century [79]. Although some of them have been banned and clasified by the United Nations (UN) as POPs, they or their metabolites are still present in the environment because of their persistence and lipophilic properties. Inhalation is an important route of exposure for humans, especially just after spraying application in domestic indoors or agricultural close areas. Table 6 summarizes recent publications where pesticides have been determined in indoor or workplace air.

6.1. Sampling

US EPA Methods TO-4A and TO-10A determined pesticides in air [104]. These methodologies have already been commented within the chapter dedicated to PCBs. Pesticide sampling usually consists of collecting known volumes of contaminated air using sampling cartridges filled with one or more adsorbents where the compounds are

retained. PUF [87, 89-92,95, 98,105], XAD-2 resin [80,82, 90,106], mixtures of both adsorbents [11,90,107], Tenax [85, 96, 99-101,108], Florisil [86,109-111], Supelpak [84], Empore disks [68], octadecyl silica bonded (C_{18}) [84], or silica gel [102] are adsorbents used to retain certain pesticides in indoor or workplace air. NIOSH methods 5600 and 5601 collect organophosphorus and organotitrogen pesticides, respectively in OVS-2 tubes [112]. These tubes contain a QFF and XAD-2 resin (270 mg /140 mg). Dobson *et al*. compared the efficiencies of PUF, XAD-2, XAD-4, and two different sandwich combinations; PUF/XAD-2/PUF and PUF/XAD-4/PUF at trapping currently used pesticides in the gaseous phase using high volume (hi-vol) samplers [113]. The sandwiches were only slightly more efficient than XAD-2 and XAD-4 resins, followed by PUFs. Therefore, and taking into account that losses of pumping efficiency were found using the sandwich designs, XAD-2 is the adsorbent recommended. Tsiropoulos *et al*. investigated the trapping efficiency of XAD-2, XAD-4, Supelpak-2, Florisil and C_{18} for five pesticides [84]. No breakthrough was observed at least when 480 L air was pumped. Supelpak-2 or C_{18} were selected as the best adsorbents, based on their performance characteristics, such as sufficient trapping efficiency, no dependence on the relative humidity, extended range of concentration levels, good recoveries and storage stability. Yoshida *et al*. tried to determine 92 SVOCs, including insecticides, synergists and fungicides, using QFFs and Empore disks [68]. Nevertheless, 20 pesticides, i.g. fenthion, piperonyl butoxide, allethrin or tetramethrin, could not be sufficiently collected by the disks, obtaining low retention efficiencies. A possible explanation is that some compounds may be decomposed by daylight during air sampling. Therefore, other adsorbents may be necessary for their collection. Other 13 pesticides, such as fenitrothion, pentachlorophenol or deltamethrin could not be quantified accurately as their calibration curves were not linear. Elflein *et al*. also underlined recovery problems when sampling 17 household insecticides by means of a GFFs and two PUFs [91]. They assumed a decomposition mechanism for four pyrethroids on the filter during the spiking experiment. In addition, they sentenced that PUF contributes to the “matrix-induced chromatographic response enhancement”. When adsorbents are used, calibration is usually performed by direct spiking of adsorbents with solutions of target analytes at known concentrations. Nevertheless, Cessna and Kerr introduced another procedure to calibrate trifluralin and triallate [114]. A polytetrafluoroethylene (PTFE) U-tube was fortified with a solution of pesticides in hexane and immersed in a water bath at 50 ºC. Then, air was continuously drawn through a U-tube (0.1 L min^{-1}) and subsequently through two mini-tubes packed with

Tenax TA arranged in series. In this way, an easy and realistic calibration was feasible, simulating different concentrations of air samples.

Regarding outdoor air, some papers should be emphasized due to their possible workplace implications. Cartridges with Florisil were used to estimate the leaf-air transfer of pesticides in vegetables [109,110] or to measure atrazine and alachlor concentrations in agricultural areas [111]. Egea Gonzalez and co-workers developed a screening method to analyze more than 70 pesticides in air of urban locations surrounded by greenhouses [115]. Three different adsorbents (Tenax TA, Chromosorb 106 and Supelpak) were tested obtaining the poorest recoveries with Supelpak. Several authors have reviewed the ambient air passive sampling of pesticides, among other organic pollutants [116-118]. Nevertheless, passive sampling studies for collecting pesticides in indoor air are scarce. Esteve-Turrillas and co-workers sampled pyrethroid insecticides with SPMDs [83]. The membranes were suspended about 2 m height for a total time of 48 h in a dark and closed room treated with different insecticide sprays. Dai *et al*. sampled chlorpyrifos (a termiticide) for one month in indoor air in houses using a passive sampler consisting of a porous PTFE tube filled with 0.75 g of Supelpak adsorbent resins [93]. Ramesh and Vijayalakshmi collected three pyrethroids in air of rooms treated with insecticides using an airtight syringe and then dissolved them in acetone [94].

An alternative for sampling pesticides in indoor air is by exposing a SPME fiber to the contaminated atmosphere. Ferrari *et al*. published a multiresidue method using SPME for the determination of 11 pesticides selected from different chemical families with a large range of saturated vapour pressures in confined atmospheres [88]. A PDMS fiber was immersed for 40 min in a 250-mL flask through which air samples were dynamically pumped from the analysed atmosphere. As a field application, the proposed method was applied for the determination of procymidone concentrations as a function of time in a greenhouse. This method completely avoids the use of solvents and can be applied to determine pesticide concentrations in workplace environments, like in the breathing zone of workers in greenhouses. Besides, Paschke *et al*. compared the applicability of SPME and SPMDs for semi-volatile chlorinated organic compounds in a landfill, where large amounts of lindane by-products were deposited in the past, together with other hazardous chemical residues [119]. Both samplers yielded comparable time-weighted average (TWA) air concentrations of lindane and its isomers and of dichloro-diphenyl-trichloroethane (DDT) with its metabolites. Cisper and Hemberger developed another method for the on-line detection of SVOCs, including pesticides, using membrane introduction mass spectrometry (MIMS) [120], clearly

expanding the practical limits of MIMS analysis. The method used a composite membrane made by plasma deposition of a thin PDMS layer on a microporous polypropylene support fiber. Sample air flowed over the outside of the fibres countercurrent to the helium flow. Concentrations were found in the pptv range.

6.2. Sample treatment

Once the analytes are retained on the adsorbent, an appropriate solvent is required, usually at high volumes, to quantitatively elute them. This, in turns, leads to time-consuming steps for concentration and clean up of the organic extracts, with the risk of analyte losses. An additional problem could arise from the possible photodecomposition of some of the pesticides, which has been reported in some multi-pesticide studies [68,91,102], showing that determination of some pesticides in air might require performing a rapid and careful trapping-extraction process. Classical extraction processes include Soxhlet with large volumes of solvents [11,80,81,90,92,95,98,107] or solvent extraction with acetone [84,99,100], methanol [111,121], acetonitrile [106], ethyl acetate [84,103], hexane and dichloromethane (DCM) [87], toluene [93], or mixtures of solvents [89], normally accompanied by shaking for several minutes. Deriving of the large volumes of solvents used for the extraction, a further concentration step is required. In addition, long and tedious drying with anhydrous sodium sulphate [109], filtration through silanized glass wool [97,100], HPLC fractionation [103], or cleaning procedures are generally needed, such as liquid-liquid extraction, SPE with Florisil [80,107], silica gel [87,98,109], alumina [83] , or C_{18} [83].

Besides the conventional solvent extraction procedures, other techniques have been proposed for the extraction of pesticides from the trapping sorbents. In a large number of papers, extraction of analytes is helped by sonication over a period of 2-15 minutes [68,82,85,91,97,105,110,115]. Using only 25 mg Tenax as trapping sorbent allowed Barro *et al* developing a method to determine several pesticides in indoor air based on US-assisted solvent extraction with a volume of ethyl acetate as low as 1 mL [85]. Detection limits for this simple and fast method ranged from 0.03 to 4.1 ng m^{-3} (1 m^3), with no need of concentration or further treatment of the extracts. Esteve-Turrillas *et al*. extracted insecticides from SPMDs by solvent re-extractions with 30 mL of a mixture of hexane-acetone and microwave extraction for 20 min [83]. Concentration, reconstitution of the extracts, as well as different clean up stages derived from the matrix effect of SPMDs were required to achieve good recoveries. A great reduction of solvent consumption (from 400 to 60 mL) and analysis time (from 48 to 1 h) was achieved

using the proposed method compared to the dialysis reference method. Detection limits ranged from 0.3 to 0.9 ng per membrane.

When a thermally desorbable adsorbent such as Tenax is used, thermal desorption is another alternative. Some authors extracted chlordanes [101], two herbicides (trifluralin and triallate) [114], or 10 pesticides including triazines, carbamates and organochlorides from Tenax by thermal desorption [122]. Baroja *et al*. determined fenothrion and its main metabolites in forestry air by sampling on Tenax and extracting using a thermal desorption cold trap (TCT) [123]. The use of HS-SPME has been proposed as an alternative to solvent and thermal desorption, enhancing the selectivity and the sensitivity of the analysis. In this way, Barro *et al*. collected 10 pesticides in indoor air using 25 mg of Florisil [86], and after addition of 100 µL acetone to the adsorbent, the SPME was carried out by exposing a polyacrilate fiber to the HS of the vial. Thus, the fiber was thermally desorbed in the injection port of a gas chromatograph. Method detection limits as low as 0.001 ng m^{-3} (1 m^3 air) were achieved for several insecticides when µECD detection was utilised.

6.3. Determination

GC/ECD [81,85,86,90,94,97,99,103,107,109,110,114] and GC/MS [80,89-92, 98,100,101,105,107,111,123] are the techniques of choice for the determination of pesticides in air. Although less common, other detectors such as thermoionic specific detector (TSD) [81], or NPD [84,99] may be used with GC. When higher sensitivity is required, GC/MS/MS [95] can also be used. Egea Gonzalez *et al*. determined 70 pesticides in a multiresidue method by GC/MS/MS using a large volume injection technique [115]. Injecting a higher volume of sample extract (10 µL) increases the sensitivity, achieving limits of quantification ranging from 0.2 for chlorothalonil to 27 ng m^{-3} for cypermethrin, based on a 1.44 m^3 air sampled.

However, the use of HPLC-UV [81,84,97,106] has also been reported. Vincent *et al*. determined quaternary ammonium compounds by cationic preconcentration column by ion chromatography (IC) or LC/MS/MS [82]. In this particular case, IC appears to be a good alternative because it is not expensive and its use is very simple compared to LC/MS/MS. Moreover, the limit of detection could be reduced by a factor of 100 with an injection volume of 50 µL.

6.4. Concentration in indoor air

Pesticide control indoors is getting increasing attention. Concentrations found in several indoor environments are summarized in Table 2. Concentrations of common household

pesticides are generally higher indoors than outdoors [124]. Class and Kintrup determined household insecticides in commercial formulations, residues, surfaces, and in air during and after indoor application [102]. The concentrations of insecticides in air and their deposits on surfaces (up to 1000 µg m^{-3}) revealed possible exposure of humans by inhalation or by skin adsorption. Electrically heated evaporators cause allethrin concentrations in air of 2-5 µg m^{-3} during application; much higher concentrations (up to 300 µg m^{-3} and more) were observed when pyrethroids and other insecticides were sprayed as aerosols into a room. The insecticides laid on surfaces and some readily formed transformation products persisted for 60 h or longer. Berger-Preiss *et al*. monitored the concentrations of two pyrethroids, pyrethrum and the synergist piperonyl butoxide in a model house over a period of two years after simulated pest control against cockroaches [97]. Only the pyrethrins decreased rapidly, mainly by photodecomposition. Deltamethrin and permethrin levels in the gas phase were 1.5 and 8 ng m^{-3} respectively, when a normal dose was applied. Roinestad *et al*. identified 34 pesticides in household air ranging from 5.7 to 254.7 ng m^{-3} [100]. Comparison of dichlorvos, o-phenylphenol and propoxur levels in a home were also carried out immediately after spraying (354.7, 63.0 and 434.3 ng m^{-3} respectively) and 8 weeks after application (not detected, 35.8 and 5.8 ng m^{-3}). In other study, concentrations of aldrin, dieldrin, four chlordanes, pentachloroanisole and hexachlorocyclohexanes were measured in the living area of a home and outdoors [98]. All compounds except the hexachlorocyclohexanes had higher indoor than outdoor air concentrations, implying that their sources were in the home. Ramesh and Vijayalakshmi deployed two different mosquito coils, an aerosol sample, and two different mosquito mats containing pyrethroids in a close room [94]. Air samples were collected at different intervals ranging from 15 min to 8 h from three different positions in the room (top, middle and bottom). The concentrations of pyrethroids were initially high at the top of the room, followed by a steady decline on moving towards the floor. At the end of a 6 h period, most of the residues were below 0.1 ppb. Rudel and co-workers determined pesticides, among other EDCs in 120 homes [11]. The 90th percentile concentrations for pesticides ranged from 10 to 19 ng m^{-3} in air. The indoor prevalence of pesticides that have been banned or restricted for many years, such as DDT, chlordane, heptachlor, methoxychlor, dieldrin and pentachlorophenol, suggested that indoor degradation is negligible. Whyatt *et al*. measured 8 pesticides in 48-h breathed out air samples collected from more than 200 mothers during pregnancy [92]. A significant correlation was seen between the levels of chlorpyrifos, diazinon and propoxur in the breathed out air and the levels of these insecticides or their metabolites in plasma samples (maternal and/or cord). The

fungicide o-phenylphenol was also detected in all the air samples, but it was not measured in plasma. Other studies measured pesticides in indoor air of homes, i.e. chlordanes [87], chlorpyrifos [90,93], phenols [80], or organophosphorus pesticides [89]. Moreover, biocides as DDT, lindane, methoxychlor, among others were identified in different locations of museums [108].

Gil and Sinfort reviewed the measurement techniques and simulation studies for pesticide emission to the air while spraying on crops [125]. The inhalational exposure to pesticides in greenhouses is considered as more critical than outdoors, because greenhouse walls restrict their rapid distribution and dilution via airflow [99]. Cruz Márquez and co-workers developed a method for assessing both likelihood and exposure of farmers to spray applications of malathion in greenhouses [95]. The malathion concentration in the breathing area during the application was found between 69.4-85.9 µg m^{-3}. Insecticides and fungicides were monitored in greenhouses for 3-4 days after application of plant protection products by manual sprayers on different types of crops (flowers and vegetables) [99]. The maximum concentration found was 28 µg m^{-3} for parathion, and after a dissipation period of several hours, the levels were greatly influenced by ventilation and temperature. The objective of Bouvier *et al* [81] was to assess the residential pesticide exposure of non-occupationally exposed adults, and to compare it with occupational exposure of subjects working indoors. The study involved 20 exposed persons, 38 insecticides, and the sampling of 19 residences, two greenhouses, three florist shops and three veterinary departments. Indoor air concentrations were often low, but could reach in residences 200-300 ng m^{-3} for atrazine and propoxur. As expected, gardeners were exposed to pesticides sprayed in greenhouses, although florists and veterinary workers were also indirectly exposed due to the former pest control operations. Pesticide measurements were up to 220 ng m^{-3} for methidathion in greenhouses, 28.6 ng m^{-3} for lindane in florist shops, and 52.9 ng m^{-3} for diazinon in veterinary departments. Other authors monitored the concentrations of widely used plant protecting agents during and after application, as well as their spatial and temporal distribution in agricultural areas [96,107,122,126,127].

7. Other organic contaminants

Perfluorinated alkyl compounds (PFAs) are a group of organic chemicals used in a variety of consumer products for water and oil resistance including surface treatments for fabric, upholstery, carpet, paper, and leather, in fire-fighting foams, and as insecticides [128]. Many of them combine bioaccumulative potential, toxic effects and

extreme persistence; thus, they are considered as candidates for the Stockholm Convention list of persistent organic pollutants (POPs) and are regarded as a new and emerging class of environmental contaminants. Perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA) and related compounds such as perfluoralkyl sulfonamides (PFASs) and fluorotelomer alcohols (FTOHs) figure among the most widespread PFAs [129,130].

Organotin compounds are widely employed as stabilizers of polyvinyl chloride (PVC) polymers and as industrial catalysts for polyurethane and silicone elastomers. Hence, they are present in water pipes, food packing materials, polyurethane foams and many other consumer products [131]. The prominent toxicological feature of the organotins is their immunotoxicity, an effect produced by di- and trialkyltins as well as triphenyltins. Furthermore, the importance of organotins as environmental endocrine disrupters and their potential to adversely affect human health, has prompted the European Commission to identify tributyl tin (TBT) as a priority hazardous substance [132].

7.1. Sampling, sample treatment and determination

Perfluoroalkyl sulfonamides have been collected in indoor air by both active and passive procedures (see Table 7). Active sampling has been carried out using SPE cartridges [130] or a GFF followed by PUF plugs [133], and air volumes between 20 an 200 m^3. These compounds have also been collected by means of PUF disk passive air samplers [129]. Very recently, Shoeib *et al* [134] have developed a novel type of PUF disk impregnated with XAD-4 powder, which provides a higher sorptive capacity for organic and polar chemicals, such as the FTOHs and PFASs. Uptake rates for this sorbent-impregnated PUF (SIP) disks from 1.4 to 4.6 m^3 day^{-1} were estimated for the studied compounds.

Extraction of fluorinated compounds has been mainly performed by Soxhlet [129,133,134] with no further clean-up after volume concentration. Analysis is usually carried out by GC/MS operated in the EI mode with SIM [129,133] or in the PCI mode [130,134]. Separation of PFASs can be performed with common stationary phases 5 % phenyl substituted methylpolysiloxane [129,133], although more polar capillary columns are required for FTOHs [130,134]. Shoeib *et al* [129] determined PFAS in indoor air with recoveries ranging from 64 to 89 %, RSD values lower than 8 % and LODs between 0.01 and 7.1 pg m^{-3}.

Organotin compounds have been collected from indoor air by active sampling through QFFs and an activated carbon-fibre filter [131]. A flow rate of 5 L min^{-1} was employed

for 24 h periods, which yields air volumes of approximately 7 m^3. Extraction was performed by ultrasonication twice with 10 mL 1M HCl in MeOH for 10 min and then twice with 2.5 mL benzene for 10 min. After derivatization with propyl magnesium and several clean-up steps, organotin compounds were analyzed by GC with FPD. Recoveries higher than 95 % and LOD in the range 0.2-0.4 ng m^{-3} were obtained.

7.2. Concentration in indoor air

Shoeib *et al* [133] determined concentrations of PFAS in indoor air from homes and laboratories. N-methyl perfluorooctane sulfonamidoethanol (MeFOSE), widely used as a stain repellent on carpets, was the most abundant in both indoor and outdoor air, followed by N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE) (see Table 2). Mean indoor concentrations of MeFOSE and EtFOSE were 2589 and 772 pg m^{-3}, respectively. These concentrations were approximately 100 times higher than outdoor values, establishing indoor air as an important source to the outside environment. Levels of PFAs in indoor air from office were evaluated by Jahnke *et al.* [130], obtaining values for MeFOSE and EtFOSE of 727 and 305 pg m^{-3}, respectively.
Regarding the orgatin compounds, Kawata *et al* [131] measured concentrations of several organotin chlorides in indoor air. Among studied compounds, only triphenyltin chloride (TPTC) was detected at concentrations ranging between 0.4 ng m^{-3} and 0.6 ng m^{-3}.

8. Analysis of contaminants in indoor dust and suspended particulate matter (PM)

According to the US EPA [135] house dust is a complex mixture of biologically-derived material, PM deposited from the indoor aerosol, and soil particles brought in by foot traffic. Many contaminants adsorb to PM suspended in indoor air that later settles out as house dust. Furthermore, these compounds have the potential to persist and accumulate in indoor dust, as they are not subjected to the same degradation processes that occur outdoors [136].
Equilibrium concentrations on dust particles generally far exceed those in the gaseous portion of indoor air; hence, dust and its associated fine PM tends to become a sink for semivolatile organic compounds (SVOCs) [137].
Inhalation, dermal adsorption and inadvertent ingestion of indoor dust have been recognized as important exposure pathways for organic contaminants [137], especially in the case of crawling children exhibiting hand-to-mouth behaviour [138]. Hence,

analysis of organic contaminants in house dust should be performed in an effort to characterize human exposure in the indoor environment.

In most of the reported methods for the analysis of organic contaminants in indoor dust, samples are collected from conventional vacuum cleaners equipped with paper dust bags. The content of bags is passed through a suitable sieve to remove large pieces and obtain a high degree of homogeneity. Dust samples are then weighed and solvent extracted using the extraction techniques summarized in Table 8 and the target compounds determined usually by GC/MS. Recently, a standard reference material has been developed for the determination of organic compounds in house dust. The SRM 2585 is intended for use in validation of methods for the analysis of PAHs, PCBs, chlorinated pesticides, and PBDEs [162]. Concentrations of pollutants found in indoor dust and air suspended PM are summarized in Table 9.

8.1. Phthalates

Phthalates have been extracted from dust using the Soxhlet extractor [9,10], simple agitation with hexane [140] or DCM [139] and PSE with a mixture of hexane and diethyl ether (95:5) [12]. Determination is usually performed by GC/MS. A typical procedure has been described by Rudel *et al* [11], consisting in the collection of dust samples using a mite vacuum cleaner modified to collect dust in a cellulose extraction thimble. Since phthalates are closely associated to the plastic materials, a custom crevice tool with a holder for the extraction thimble was constructed in PTFE to avoid dust contact with any plastic part of the cleaner. Prior to extraction, dust was weighed and sieved to <150 μm. Aliquots for the analysis (0.047 to 1.6 g) were spiked with the surrogate solution (*p*-terpenyl-d_{14}), let to equilibrate at room temperature, and then Soxhlet extracted (table 8). After concentration and clean-up of the extract, the GC/MS determination of the phthalates was performed. Recoveries of the method ranged from 40 to 220% with RSD < 20% and LOD values of 0.1 to 24 μg g^{-1}.

8.2. Brominated flame retardants

Extraction of BFRs from dust has been mainly carried out by Soxhlet [11, 24,141,143,145,147] using solvents like toluene, DCM or different organic mixtures. Wilford *et al*. [147] reported mean recoveries of 99 %, RSD of 19 % and LODs in the range of 0.1-14 ng g^{-1} for tri- to decaBDE after Soxhlet extraction of 0.25 g dust with DCM for 15 h and treatment with concentrated sulphuric acid.

PSE has also been employed for extraction of this kind of brominated compounds from house dust [40,142,143,148]. A PSE-based method was developed for Stapleton *et al* [142] for the analysis of PBDEs in house dust and clothes dryer lint. The extraction was carried out with DCM at 100 ºC and 2000 psi for 5 min during 3 cycles. LODs ranged from 1 to 6 ng g^{-1} after a simple clean-up procedure on silica SPE cartridges and volume concentration. Harrad *et al* [40] reported recoveries from 45 to 67 % for the PSE extraction from dust of tri- to hexaBDEs using n-hexane at 150 ºC and 1500 psi for 5 min. An in-cell clean-up with Florisil during the extraction and further purification with concentrated sulphuric acid and a Florisil column were used.

Recently, the use of microwave-assisted extraction (MAE) has been demonstrated as a valuable alternative, providing satisfactory results for the extraction of PBDEs from indoor dust [56,144,146]. Regueiro *et al* [56,144] performed the extraction of tetra- to decaBDE by MAE using 8 mL n-hexane in the presence of 4 mL 10 % $NaOH_{(aq)}$ at 80 ºC for 15 min. Recoveries higher than 90 %, RSD lower than 16 % and LODs from 0.0439 to 1.44 ng g^{-1} were reported after a simple on-batch clean-up by addition and shaking of a small amount of Florisil.

Determination of BFRs in dust is commonly carried out by GC/MS operating in the negative ionization with SIM [24,142,143,145-147], which allows to obtain LODs in the low ng g^{-1} level. Nevertheless, MS in the EI mode with SIM [11,40,141,143], tandem mass spectrometry (MS/MS) [144] or even micro-electron capture detection (μECD) [56] have also been used. HBCD has been recently determined in house dust using LC coupled to ESI negative mode MS/MS [148]. In contrast to GC, this technique is a versatile tool for the isomer-specific determination, enabling the separation and quantification of α-, β- and γ-HBCD.

8.3. Organophosphate esters

Organophosphate flame retardants have been extracted from house dust by Soxhlet [62], ultrasound-assisted extraction (USAE) [151], MAE [150] and matrix solid-phase dispersion (MSPD) [149].

Marklund *et al*. [151] carried out the US extraction of 12 organophosphate flame retardants with 25 mL DCM for 20 min followed by a simple filtration and a volume concentration. An average recovery of 97 % and LODs ranging between 7 and 60 ng g^{-1} were obtained for the different compounds.

MSPD has been recently applied for the extraction of these compounds from house dust [149]. An amount of 0.5 g dust was mixed with 0.5 g anhydrous sodium sulphate and

dispersed with 0.5 g Florisil in a glass mortar. After loading the blend in a cartridge containing alumina on the bottom, compounds were eluted with acetone and finally volume reduced. Recoveries higher than 80 % and RSD lower than 13 % were achieved. Separation and quantification is typically performed by GC with NPD [149-151], although GC coupled to MS in the EI mode with SIM has also been used [62].

8.4. Synthetic musk fragrances

Synthetic musk fragrances have been mainly extracted from house dust by PSE [11,145]. Fromme *et al*. [12] carried out the PSE extraction of both polycyclic and nitromusk in indoor dust with n-hexane/DE (19:1) and further determination by GC/MS operating in the EI mode with SIM. Recently, Peck *et al* [153] reported the extraction of musk compounds from the indoor dust standard reference material SRM 2585 with DCM at 100 ºC and 2000 psi. After clean-up on an alumina SPE cartridge, a GPC column and volume concentration, recoveries in the range 73-90 % were obtained.

MAE has also been applied for the extraction of nitromusk compounds from house dust samples [152]. Dust (0.8 g) was extracted at 80 ºC for 10 min using a mixture of 8 mL n-hexane and 4 mL H_2SO_4(aq) 1M containing ascorbic acid 0.10 %. Clean-up was performed by addition and shaking of partially deactivated Florisil. Extracts were further analyzed by GC/μECD. Under these conditions, recoveries between 88 and 97 % and LODs from 1.03 to 3.26 ng g^{-1} were reported.

8.5 . Pesticides

Common household pesticide levels are generally higher indoors, and are also present in dust and PM. Analytical procedures for the determination of pesticides in dust and PM are reported in Tables 8 and 10 Mukerjee *et al* [124] measured 24 pesticide, including 18 insecticides, two herbicides, and a fungicide concentrations and their overall occurrence in house dust by season. Rudel *et al* identified EDC, including phthalates, alkylphenols, pesticides, PBDEs, among other compounds, in dust from 120 homes [11]. In this study, 27 pesticides were detected in dust, the most abundant being permethrins and the synergist piperonyl butoxide. The 90th percentile concentrations for these pesticides ranged from 1.7 to 17 μg g^{-1} in dust. The prevalence indoors of pesticides that have been banned or restricted for many years, such as DDT, chlordane, heptachlor, methoxychlor, dieldrin and pentachlorophenol, suggests that degradation is negligible indoors. This observation is further supported by the abundance of DDT in dust relative to its degradation product 1,1-dichloro-2,2-bis(p-dichlorodiphenyl)ethylene (DDE).

Schieweck *et al* [108] analyzed biocides in dust samples in different rooms of a museum. A distinction between old and fresh dust was made. While the age of old dust is unknown, fresh dust was defined as dust whose age is determined by the measurement planning and is known exactly, usually 1-2 weeks. The concentrations of pentachlorophenol and lindane in a sample of old dust taken directly from a sculpture were exceptionally high with 117 and 14 $\mu g\ g^{-1}$, respectively. In the fresh dust samples taken from the floor, considerably increased concentration up to 30 (for pentachlorophenol, PCP) and 5 $\mu g\ g^{-1}$ (for lindane) were also found, which probably resulted from the intensive treatment of the wooden sculpture for purposes of conservation. This result gave evidence for a possible exposure of museum staff and visitors. Berger-Preiss *et al* measured indoor pyrethroid exposure in 80 homes with woollen textile floor coverings [160]. While permethrin concentrations in house dust were high (mean: 53.7 $\mu g\ g^{-1}$), the permethrin concentrations in suspended particles were very low (mean: 2.8 ng m^{-3}). Leng *et al*. found positive correlations between pyrethroids in house dust and in airborne particles, especially one day after pest control operation [158]. Concentrations of pyrethroids in indoor suspended PM and household dust were also measured over a period of 25 months in an experiment simulating indoor pest control [97]. House dust was collected using a modified vacuum cleaner, where the usual dust bag was replaced by Soxhlet filter tubes, which were preferred as they allowed a quantitative transfer of the particles into de Soxhlet extractor. Moreover, it was found that the Soxhlet filter tubes retained (90%) smaller particles better than the usual dust bags (30%). Initial concentrations of deltamethrin and permethrin were 150-800 and 50 $\mu g\ g^{-1}$, depending on the commercial formulation applied. The concentration levels of both compounds decreased by a factor of about 10 within the first 12 months, but remained practically constant the following year. Roinestad *et al* identified 30 pesticides in household dust ranging from 80 (diazinon) to 15000 (chlorpyrifos) ng g^{-1} [100]. Permethrin levels decreased from 2550-3850 (just after application) to 550-675 ng g^{-1} 8 weeks after pesticide application. However, dichlorvos and o-phenylphenol levels remained relatively constant suggesting that dust sampling may be a more appropriate method for determining chronic risk assessment of indoor pesticides than air. Children of agricultural families are likely to be exposed to agricultural chemicals, even it they are not involved in farm activities. Household dust samples were collected in 59 residences [161]. Household dust concentrations for all four organophosphorous pesticides were significantly lower in reference homes (up to 820 ng g^{-1}) when compared to farmer homes (up to 17100 ng g^{-1}). A statistical comparison indicated that agricultural families had significantly higher concentrations of azinphosmethyl,

chlorpyrifos, and parathion. These results demonstrate that children of agricultural families have higher potential for exposure to these chemicals than children of non-farm families. In this way, Lu *et al* [89] estimated organophosphorus exposures of preschool children in agricultural and non-agricultural areas. Detectable levels of diazinon and azinphosmethyl in house dust were found in most of the agricultural homes, whereas only diazinon was found in the metropolitan homes in the summer.

8.6 . Organotin and perfluoroalkyl compounds

Extraction of perfluoroalkyl compounds has been carried out by both Soxhlet [129] and USAE [154,155]. Moriwaki *et al* [154] developed a US-based method for the determination of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in indoor dust. Compounds were US extracted with methanol for 60 min and determined using LC coupled to ESI MS/MS. Recoveries higher than 73 % and LODs in the range 10-50 ng g^{-1} were reached. Soxhlet extraction with DCM during 24 h was applied by Shoeib *et al* [129] for the extraction of perfluoralkyl sulfonamides (PFASs) in indoor dust. No further extract preparation than volume concentration was performed before analysis by GC/EI-MS in the SIM mode.

Organotin compounds have also been determined in house dust [156]. USAE was conducted with ethanol, followed by derivatization with sodium tetraethylborate (STEB) and liquid-liquid extraction with n-hexane. Recoveries higher than 70 % and average LODs of 10 ng g^{-1} were reported.

9. References

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Table 1. Analytical procedures for the analysis of phthalate esters in indoor air

Ref	Analytes	Sampling	Desorption/Extraction	Extract treatment	Determination	Recovery (%)	RSD (%)	LOD
5	DEP, DBP, BBP, DEHP	Cartridge filled with charcoal granules in 2 layers, one for sampling and other for breakthrough (1L min^{-1}, 3 days, 4.3 m^3)	US with 1 mL toluene	Centrifugation	GC/EI-MS (SIM), GC/FPD	97.5-115	~10	25.6-118.6 ng m^{-3}
10	DEP, BBP, DBP, DEHP, DHP, DAMP, DPP, DCHP, DIBP	Cartridge filled with QFF, XAD-2 and PUF (3.8 L min^{-1}, 0.29-5.9 m^3)	Soxhlet with 200 mL of 6% DE-hexane, 16 h	Addition of sodium sulphate and concentration to 1 mL 10% DE-hexane. Silylation.	GC/EI-MS (SIM)	95-129 (DEP)	0-8	0.0045-1.64 µg per extract (BBP, present in the blanks)
11	DEP, DBP, BBP, DEHP, DCHP, DPP, DIBP	URG personal pesticide sampling cartridges (impactor inlet followed by a cartridge fitted with QFF, XAD-2 and PUF plugs) (8-9 L min^{-1}, 10-14 m^3)	Soxhlet with 150 mL of 6% DE-hexane, 16 h	Addition of sodium sulphate and concentration to 2 mL 10% DE-hexane.	GC/EI-MS (SIM)	40-220	15-25	2-75 ng m^{-3}
12	DMP, DEP, DPP, DBP, DIBP, DCHP, BBP, DEHP, DOP	Active with PUF (5 L min^{-1}, 2 m^3)	PSE with hexane-DE 95:5.	Concentration	GC/EI-MS (SIM)	91-100	NR	Determination limits: 10 ng m^{-3}
13	DEP, DBP	Active using Tenax GR sorbent tubes (200 ml min^{-1}, 0.1 m^3).	TD (290ºC, 10 min) to a cold trap (-30ºC) followed by TD (325ºC, 15 min)	None	GC/EI-MS	94-96	NR	5 ng m^{-3}
14	Phthalates	Medium volume sampler on a QFF and two PUF plugs during 24 h.	NR	NR	NR	NR	NR	NR
15	DBP, DEHP	Active on sorption tubes packed with 5% PDMS on Chromosorb, (500 mL min^{-1}, 15–30 min, 15 L).	TD (300 ºC, 10 min)	None	GC/MS	NR	NR	1 ng m^{-3}
16	DBP, DEHP	Active using SepPak PS (2 L min^{-1}, 20–24 h).	5 mL acetone.	Concentration to 5 mL	GC/EI-MS (SIM)	100-102	1.5-2.3	100 ng m^{-3} (2.88 m^3 air sample)

NR: Not reported data

Table 2. Concentration of organic contaminants in indoor air

	Home	**Office**	**Schools, kindergartens and daycare centers**	**Stores, markets and shops**
Phthalates (ng m^{-3})	DBP: 110-600, DEHP: 40-230, BBP: <1-100, DEP: 50-190 [5] DBP: 52-1100, DEHP: <59-1000, BBP: <31-480, DEP: 130-4300 [11] DBP: 1083, DEHP: 191, BBP: 37, DEP: 807, DMP: 1182 [12] DBP: 410, DEHP: 110, BBP: 35, DEP: 350 [22]	DBP: <50-780, DEHP: <100-200 [16]	DBP: 2395, DEHP: 599, DEP: 396, DMP: 1034 [12]	NR
BFR (pg m^{-3})	Tri-hexaBDEs: <2.3-171, BDE209: <173-257 [24] Tri-hexaBDEs: 0.04-25.2, BDE183: 0.40 [37] Tetra-hexaBDEs: <1-1330 [38] Tri-hexaBDEs: <LOD-1600 [39] ΣPBDEs (tri-hexaBDEs): 4-245 [40] ΣPBDEs (tri-heptaBDEs): 2.5-139 [41] Di-pentaBDEs: <LOD-3200, HBCD: <LOD-24000 [42] Tri-hexaBDEs: <2.8-2371, BDE209: <47.8-1636 [43] ΣPBDEs (tri-heptaBDEs): 76.3-2088 [45] Tri-hexaBDEs: 0.3-1710, BDE183: 1.8-375.7, BDE209: 39-11468 [48] HCDBCO: <LOD-3000 [50]	Tetra-hexaBDEs: <2-<100, BDE183: 4.6-12, BDE209: <40-87, BTBPE: <3-5.8, TBBPA: 10-70 [35] Tetra-hexaBDEs: <1-7140 [38] ΣPBDEs (tri-hexaBDEs): 10-1416 [40] ΣPBDEs (tri-heptaBDEs): 2-385 [41] Di-pentaBDEs: <LOD-21500, HBCD: <LOD-29500 [42] Tri-pentaBDEs: 18-468 [47] Tri-hexaBDEs: 0.7-4925, BDE183: 1.4-259, BDE209: 80.1-13732 [48]	NR	NR

OFR (ng m^{-3})	TBP: 36.6, TEP:214, TCEP: 1.2, TCPP:5.5 [42] TiBP: 7, TBP: 11, TCEP: 31, TCPP: 1130 [64] TBP:14-120, TCEP:0.4-3.0, TCPP: 38-210 [65] TBP: 4-7, TCEP: 5-15, TCPP: 700-730 [67]	TiBP:17, TCEP: 7.4, TCPP: 0.2-7.0 [57] TiBP: 25, TCEP: 11, TCPP:1.4-31 [61] TBP: 8.2, TCEP: 730, TCPP: 160 [65] TBP: 18, TCEP: 37, TCPP: 432 [66] TBP: 5, TCEP:5, TCPP: 120 [67] TBP: <LOD-8.1, TCEP: 6.1-56, TPhP: 0.93-3.1 [120]	TiBP: 7.6-35, TCEP: 18-250, TCPP:14-41 [61] TBP: 3.7, TCEP: 2.5, TCPP: 28 [65]	NR
Musks (ng m^{-3})	HHCB: 143-1129, AHTN: 21-77, ADBI: 2.6 AHMI: 8.5 [76]	HHCB: 57, AHTN: 21[76]	AHTN: 47, HHCB: 119, AHMI: 22 [12]	MX: 1.0, MK: 0.3, AHTN: 13.4, HHCB: 44.3, ATII: 5.2 [70]
Pesticides (ng m^{-3})	3.0-970 [11] 0.3-256 [81] 0.012-7.3[d] [83] 3.0-1651 [85] 10-1117 [86] 0.001-68 [87] 1-50 [89] 20-1000 [90] 1-4500 [91] 1.5-12 [97] 0.2-20 [98] 5.7-255 [100] 0.46-130 [101] 10000-300000 [102] 0.3-27.8 [124]	NR	73.3-193 [80]	0.2-28.6 [81]
Organotin and perfluorinated compounds (ng m^{-3})	MeFOSE: 0.366-8.19, EtFOSE: 0.227-7.74, MeFOSEA: 0.012-0.109 [129] TPTC: 0.40-0.60 [131] MeFOSE: 1.546-8.315, EtFOSE: 0.289-1.799, MeFOSEA: <LOD-0.283 [133]	MeFOSE: 0.727, EtFOSE: 0.305, EtFOSA:0.188 [130]	NR	NR

Table 2. Concentration of organic contaminants in indoor air (continued)

	Laboratory, hospital	**Restaurant, bar, pub, cinema, theatre, museum**	**Car, truck, garage, petrol stations, mechanic shop, public transport, station, airport, tollbooth**	**Greenhouse**	**Other workplaces and indoor environments**
Phthalates (ng m^{-3})	NR	NR	NR	DBP: 1910, DEHP: 550, DEP: 32, DMP: 56 [17]	DBP: <100, DEHP: <100 [16] DBP: 120, DEP: <50 [13]
BFR (pg m^{-3})	Tetra-pentaBDEs: 7-59 [32] ΣPBDEs (tri-heptaBDEs): 358-410 [45]	NR	ΣPBDEs (tri-hexaBDEs): 11-8184 [40]	NR	Tetra-hexaBDEs: <2-11000, BDE183: 4.8-44000, BDE209: <40-70000, BTBPE: <3-67000, TBBPA: 3.1-61000 [35] Tri-hexaBDEs: 10-25000, BDE183: 140-32000, BDE209: 1300-61000, BTBPE: 600-39000 [36] Tetra-hexaBDEs: <LOD-7800, BDE183: 5900-33000, BDE209: 10-600000 [44] Mono-hexaBDEs: <LOD-320, BDE183: 1290, BDE209: 590 [46] TBBPA: 13800 [49] DeBDethane: 700 [51]
OFR (ng m^{-3})	TEP: 0.60, TBP: 1.3, TCEP: 0.65, TCPP: 0.95, TBEP: 4.9 [42] TBP: 5.4, TCEP: 320, TCPP: 69 [65]	NR	TBP:2.5-14, TCEP: <LOD-9.4, TPhP: 0.36-0.90 [58]	NR	TPhP: 12-40, TBP: 9-18, TCEP: 15-36, TCPP: 10-19, TBEP: 20-36 [35]

Musks (ng m^{-3})	MX: 0.3, MK: 0.1, AHTN: 1.9, HHCB: 5.6, ATII: 0.3 [70] MX: 0.5, MK: 0.1, AHTN: 0.6, HHCB: 2.5, ATII: 0.4 [71]	AHTN: 11.6, HHCB: 35.3, ATII: 4.8 [70]	NR	NR	MX: 0.4-1.0, MK: 0.1-0.3, AHTN: 5.8-13.4, HHCB: 18.9-44.3, ATII: 0.8-5.2 [70] AHTN: 724, HHCB: 4505, AHMI:32, DPMI: 119 [72]
Pesticides (ng m^{-3})	NR	1600 [108]	NR	0.1-220 [81] 500-85900 [84] 200000-500000 [88] 69400-85900 [95] 2900-3500 [96] <200-28000 [99]	0.3-52.9 [81] 2150-187420 [82]
Perfluorinated compounds (ng m^{-3})	MeFOSE: 0.011-1.698, EtFOSE: 0.00475-1.92 [133]	NR	NR	NR	NR

Table 3. Analytical procedures for the determination of BFR in indoor air

Ref.	Analytes	Sampling	Desorption/Extraction	Extract preparation	Determination	Recovery (%)	RSD (%)	LOD
11	Tetra-PentaBDEs	Active (10-14 m^3, 8-9 L min^{-1}) with 3 URG cartridges in parallel containing a QFF and XAD-2 resin between 2 PUF plugs	Soxhlet with 150 mL hexane-DE (6%) containing a deuterated SS (p-terphenyl-d_{14}), 16 h	Concentration to 2 mL and addition of deuterated IS (PAHs)	GC/EI-MS (SIM)	40-220	NR	NR
24	Tri-DecaBDE, BTBPE, DeBDethane	Hi-vol sampler (25 m^3, flow 50 L min^{-1}) using n GFF, cellulose pad and XAD-2	Soxhlet with toluene, 16 h, previous addition of ^{13}C-labeled SS	Clean-up on treated (KOH+ H_2SO_4) silica column, elution with hexane, clean-up on a GPC-system, elution with hexane-DCM 1:1, concentration to a small volume and addition of tetradecane and ^{13}C-labeled IS	GC/NCI-MS (SIM)	12-97	NR	2.30-173 pg m^{-3}
36	Tri-HeptaBDEs, TBBPA, 2,4,6-TBPh	1) Passive: adsorption on glass funnel surface. 2) Lo-vol sampler (0.18 m^3, flow 4 L min^{-1}) collection on SPE cartridge (Isolute ENV+, 200 mg, 6mL)	Elution with 6 mL DCM-MeOH 7:3	Concentration to 30 µL, derivatization with 50µL diazomethane and addition of IS (TBB)	GC/NCI-MS	NR	NR	NR
39	Tetra-DecaBDE, BTBPE, BB-209, TBBPA	1) Lo-vol sampler (1.5 m^3, flow 3 L min^{-1}): collection on GFF and 2 PUF plugs in series. 2) Hi-vol sampler (3.6 m^3, flow 9 L min^{-1}): collection on GFF, cellulose pad and 2 PUF plugs in series	US (bath 50 W, 48 kHz) extraction with 5 mL DCM 20 min (x2), addition of SS (BDE-128, TrBCBPA)	Solvent exchange to hexane, concentration to 0.1 mL and LLE with 2 mL methanolic KOH (≥ 50 %) twice: 1) Neutral fraction (hexane): clean-up on a silica/ H_2SO_4 (2:1) column and elution with 8 mL hexane 2) Aqueous fraction: acidification with HCl and LLE with hexane/MTBE 1:1. Separation of organic phase, concentration to 1 mL and derivatization of phenolic compounds with 0.2 mL diazomethane, 1h, in a refrigerator. Clean-up on a silica/ H_2SO_4 (2:1) column and elution with 8 mL DCM	GC/NCI-MS (SIM)	~97 (23-60 for BTBPE, TBBPA)	3-10	LOQ: 3-100 pg m^{-3}
40	Tri-DecaBDE, BTBPE, DeBDethane	Personal sampler (1 m^3, flow 2 L min^{-1}) with GFF, cellulose pad and XAD-2	Soxhlet with 250 mL toluene, 16 h , previous addition of ^{13}C-labeled SS	Concentration to 0.5 mL, clean-up on treated (KOH+ H_2SO_4) silica column and GPC, solvent exchange to nonane and concentration to 40 µL	GC/NCI-MS (SIM)	NR	0.3-9.5	0.01-1.3 ng m^{-3}

41	Tri-heptaBDEs	Passive using organic films from window surfaces (exposition < 4 months) collected using kimwipes wetted with isopropyl alcohol	Soxhlet with toluene-acetone (4:1), 18 h, previous addition of ^{13}C-labeled SS	Acid-base washing (H_2SO_4 and KOH), concentration to dryness, reconstitution in DCM-hexane 1:1. Clean-up on a multilayer acidic/basic silica column, elution with DCM-hexane 1:1 and solvent exchange to hexane. Clean-up on a copper column, elution with hexane, clean-up on an alumina column, elution with DCM-hexane 1:1, concentration to dryness and reconstitution in toluene	GC/EI-MS (SIM)	35-119	NR	NR
42	Tetra-HexaBDEs	Hi-vol sampler (300 m^3 flow 0.6-0.8 m^3 min^{-1}) using a GFF and a PUF plug	Soxhlet with DCM-hexane 1:1, 16-24 h, previous addition of ^{13}C-labeled SS	Treatment with $H_2SO_{4(c)}$, clean-up on acidic silica, elution with hexane, clean-up on florisil, concentration to a small volume and solvent exchange to nonane	GC/EI-MS (SIM)	54-104	4-22	1 pg m^{-3}
43	Tri-HexaBDEs	Passive with a PUF disk (21 days, uptake rate 2.5 m^3 day^{-1}: 50 m^3) previous addition of SS (BDE-3, d6-γ-HCH, PCB-107, PCB-198)	Soxhlet with PE, 21 h, previous addition of SS (BDE-2, BDE-35)	Concentration to 0.5 mL, solvent exchange to isooctane and addition of IS (Mirex)	GC/NCI-MS (SIM)	110-116	16-25	1.2-18 pg m^{-3}
44	Tri-HexaPBDEs	Passive with a PUF disk (28 days, uptake rate 1.1-1.9 m^3 day^{-1}: 31-53 m^3), previous addition of SS (PCB19, PCB147)	Soxhlet with hexane, 8 h, previous addition of ^{13}C-labeled SS	Concentration to 2 mL, treatment with 2 mL $H_2SO_{4(c)}$, LLE with DMSO, clean-up on florisil, elution with 20 mL hexane. Concentration to a small volume, solvent exchange to 20 µL nonane and addition of IS (PCB-29, PCB-129)	GC/EI-MS (SIM)	45-67	0.9-6	0.1 pg m^{-3}
45	Tri-heptaBDEs	Passive with a PUF disk (42 days, uptake rate 2.5 m^3 day^{-1}: 105 m^3)	Soxhlet with DCM-hexane 1:1, previous addition of SS (BDE-35, BDE-181)	Concentration to a small volume, solvent exchange to hexane, clean-up on a silica/alumina (2:1) column, elution with 100 mL hexane-DCM 1:1, concentration to a small volume, solvent exchange to dodecane and addition of IS (Mirex)	GC/NCI-MS (SIM)	80-90	NR	0.2-0.5 pg m^{-3}
46	Di-decaBDE, 2,4,6-TBPh, PBPh, HBB, HBCD	Active (14.4 m^3, flow 10 L min^{-1}) using QFF and SPE disk (Empore C18)	US extraction with 10 mL acetone	Concentration of 5 mL of extract to 0.5 mL and addition of deuterated IS	GC/AED	81 -91	2-9	0.47-9.9 ng m^{-3}

47	Tri-DecaBDE	Lo-vol sampler (9 m^3, 2 L min^{-1}) using GFF and a PUF plug	PSE extraction (100 ºC, 1500 psi, 5 min, 3 cycles): GFF with DCM and PUF with PE, previous addition of ^{13}C-labeled SS	Concentration to 0.2 mL and filtration through glass wool	GC/NCI-MS (SIM)	NR	~6	NR
48	Tri-DecaBDE	Lo-vol sampler (6-26 m^3, flow 13-18 L min^{-1}) using QFF and XAD-2	Soxhlet with DCM, 24 h	Concentration to a small volume, clean-up on silica, elution with 50 mL DCM, concentration to 0.3-0.5 mL, solvent exchange to isooctane and addition of IS	GC/NCI-MS (SIM)	64-90	NR	NR
49	Tetra-HeptaBDEs	Hi-vol sampler (100-200 m^3, flow 0.4 m^3 min^{-1}) using 2 GFF and 2 PUF plugs in series	Soxhlet 18-24h: GFF with DCM and PUF with PE-acetone 1:1	Concentration to 1 mL, solvent exchange to isooctane, addition of ^{13}C-labeled SS, clean-up on a multilayer (basic, neutral, acidic, neutral) silica column and elution with 60 mL DCM-hexane 1:1. Clean-up on alumina, elution with 60 mL DCM-hexane 1:1, concentration to < 10 mL and addition of ^{13}C-labeled IS	GC/EI-MS	> 98	NR	0.3-20 pg m^{-3}
50	Mono-DecaBDE	Lo-vol sampler (2 m^3, flow 3 L min^{-1}) with a GFF and 2 PUF plugs in series	US extraction with 5 mL DCM, 20 min (x2), previous addition of ^{13}C-labeled SS	Concentration to 1 mL, solvent exchange to hexane, concentration to 1 mL, clean-up on a SPE cartridge (Isolute NH_2)	GC/NICI-MS (SIM)	NR	NR	NR
51	Tri-pentaBDEs	Passive with a PUF disk (50 days, uptake rate 1.12-1.95 m^3 day^{-1}: 56-98 m^3), previous addition of SS (PCB-19, PCB-147)	Soxhlet with 200 mL hexane, 8 h , previous addition of ^{13}C-labeled SS	Concentration to 2 mL, treatment with 2 mL $H_2SO_{4(c)}$, LLE with DMSO, clean-up on florisil, elution with 20 mL hexane. Concentration to a small volume, solvent exchange to 20 µL nonane and addition of IS (PCB-29, PCB-129)	GC/EI-MS (SIM)	42-80	~18	NR
52	Tri-DecaBDE	Hi-vol sampler (0.4-0.7 m^3 min^{-1}, indoor: 175-385 m^3) using a GFF and a PUF plug	Soxhlet with acetone-hexane 1:1, 72 h, previous addition of ^{13}C-labeled SS	Addition of activated copper, concentration to a small volume and clean-up on an acid/basic multilayer silica column, concentration to 0.2 mL and addition of ^{13}C-labeled IS	GC/NCI-MS (SIM)	74-87	< 15	0.28-28.6 pg m^{-3}
55	TBBPA	Lo-vol sampler (3 m^3, 3 L min^{-1}) with a GFF and 2 PUF plugs in series	US extraction with 5 mL ACN, 20 min (x2), previous addition of ^{13}C- labeled SS	Concentration to 0.5 mL, filtration through a syringe filter, elution with 5 mL MeOH, concentration to 0.1 mL and addition of 0.075 mL water	LC/ESI-MS (SIM)	75-107	4.9-6.4	NR

56	HCDBCO	Passive using a PUF disk (21 days, uptake rate 2.5 m^3 day^{-1}: 52.5 m^3)	Soxhlet with PE, 21 h	Concentration to 0.5 mL, solvent exchange to isooctane	GC/NCI-MS (SIM)	NR	NR	1.3 pg m^{-3}
57	DeBDethane	Lo-vol sampler (1 m^3, 3 L min^{-1}) with a GFF and 2 PUF plugs in series	US extraction with 10 mL DCM, 20 min (x2), previous addition of SS (Dechlorane)	Solvent exchange to hexane, concentration to 1 mL, clean-up on SPE cartridge (Isolute NH_2) and elution with 10 mL hexane	GC/NCI-MS	NR	NR	NR

Table 4. Analytical procedures for the determination of OP esters in indoor air

Ref.	Analytes	Sampling	Desorption/Extraction	Extract treatment	Determination	Recovery (%)	RSD (%)	LOD
35	TPhP, IPPDPP, PPDPP, TBPDPP, TBP, TCEP, TCPP, TBEP	1) Lo-vol sampler (1.5 m^3, 3 L min^{-1}) with GFF and 2 PUF plugs in series 2) High-vol sampler (3.6 m^3, 9 L min^{-1}) with GFF, cellulose pad and 2 PUF plugs in series	US (bath 50 W, 48 kHz) extraction with 5 mL DCM 20 min (x2), previous addition of SS (MDPP)	Concentration to 0.1 mL	GC/NPD	> 95	NR	NR
42	TMP, TEP, TPP, TBP, TCPP, TCEP, TEHP, TBEP, TDCPP, TPhP, TCrP	Active (14.4 m^3, flow 10 L min^{-1}) Collected on QFF and SPE disk (Empore C18)	US extraction with 10 mL acetone	Concentration of 5 mL of extract to 0.5 mL and addition of IS (tris(1H,1H,5H-octafluoropentyl)phosphate)	GC/FPD	90-100	1.2-7	0.24-3.5 ng m^{-3}
57,61	TiBP, TBP, TCEP, TCPP, TPhP, TBEP, TEHP	Personal sampler (2.1 m^3, flow 3.0 L min^{-1}) with a GFF and 2 PUF plugs in series	US (bath 50 W, 48 kHz) extraction with 5 mL DCM 20 min (x2), previous addition of SS (TPP)	Filtration through glass wool, concentration to a small volume and addition of IS (ABP)	GC/NPD	>95	8-22	0.1 ng m^{-3}
58	TBP, TCEP, TPhP, TBEP, TEHP, TCrP, TCPP, TDCPP	Lo-vol sampler (1.4-3.4 m^3,flow 4 L min^{-1}) with a PUF plug	US (bath 50 W, 48 kHz) extraction with 37 mL DCM, 20 min (x2), previous addition of SS (TPP)	Solvent exchange to hexane, concentration to 0.1 mL and addition of IS (Phenanthrene-d_{10})	GC/EI-MS	62-100	NR	0.073-0.41 ng m^{-3}
62	TCEP, TCPP	Lo-vol sampler (1 m^3, 5 L min^{-1}) with a PUF cartridge (Orbo 1000, Supelco)	Soxhlet with hexane-acetone 4:1, 8 h	Concentration to small volume	GC/EI-MS (SIM)	NR	NR	1 ng m^{-3} (LOQ)
63	TEP, TPP, TiPP, TiBP, TCEP, TCPP	Dynamic sampling with controlled linear airflow (7cm s^{-1}) using non-equilibrium SPME (100 µm PDMS, 60 min)	Thermal desorption (2 min, 250 ºC)	-	GC/NPD	NR	8-10	~2 ng m^{-3}
64	TEP, TPP, TiBP, TBP, TCEP, TCPP	Dynamic sampling with controlled linear airflow (10 cm s^{-1})using equilibrium SPME (7 µm PDMS 12 h or 100 µm PDMS 24 h)	Thermal desorption (2 min, 250 ºC)	-	GC/NPD	NR	5-17	7 µm PDMS 0.1 ng m^{-3} 100 µm PDMS 0.01 ng m^{-3}

65	TMP, TPP, TBP, TCPP, TCEP, TDCPP,TPhP, TBEP, TEHP, DOPP, TEEdP, CLP1	Lo-vol sampler (1.0-2.7 m^3, flow 2.5 L min^{-1}) with a SPE cartridge (Isolute NH_2, 25 mg, 1 mL)	Elution with 10 mL DCM, previous addition of SS (TPeP)	Concentration to dryness, dissolution in DCE and concentration to 0.1 mL	GC/NPD	82-110 (34–58 TEEdP, TMP, TPhP)	4-18	0.1-3.9 ng m^{-3}
66	TEP, TPP, TiBP, TCEP, TCPP	Dynamic sampling with controlled linear airflow (10-35 cm s^{-1}: flow 1.1-3.8 L min^{-1}) using non-equilibrium SPME (100 µm PDMS, 40-90 min) or equilibrium SPME (30 µm PDMS, >18 h)	TD (2 min, 250 ºC)	-	GC/NPD	NR	13-18	NR
67	TMP, TEP, TPP, TiPP, TiBP, TBP, TCEP, TCPP, TPhP, TTP	Lo-vol sampler (1.4 m^3, flow 3 L min^{-1}) with a GFF and a cellulose filter, previous addition of SS (MDPhP)	US extraction with DCM, 20 min (x2)	Concentration to a small volume	GC/PCI-MS/MS	NR	4-22	0.1-1.4 ng m^{-3}
68	TCrP, TEP, TPhP, TPP, TBEP, TCEP, TDCPP, TEHP	Active with a QFF disk and an SPE disk (Empore C18) (7.2 m^3, flow 5 L min^{-1})	US extraction with 8 mL acetone, 15 min, and shaking, 10 min	Centrifugation (2000 rpm, 10 min), decantation of 5 mL supernatant, addition of IS (fluoranthene-d_{10}) and concentration to 0.3 mL	GC/EI MS (SIM)	94-112	1.3-12	0.1-0.6 ng m^{-3}
69	TEP, TiPP, TPP, TBP, TCEP, TCPP, TDCPP, TBEP, TPhP, DPEHP, TEHP, TTP	Active (1.5 m^3, flow 2.5-3.3 L min^{-1}) with SPE cartridge (Isolute NH_2, 25 mg, 1 mL)	Elution with 5 mL MTBE, previous addition of SS (THP)	Addition of IS (TPeP)	GC/NPD	~ 100 %	1-9	0.1-0.3 ng m^{-3}

Table 5. Analytical procedures for the determination of synthetic musks in indoor air

Ref.	Analytes	Sampling	Desorption/Extraction	Extract preparation	Determination	Recovery (%)	RSD (%)	LOD
12	HHCB, AHTN, ATII, ADBI, AHMI, DPMI, MX, MK	Lo-vol sampler (2 m^3, 5 L min^{-1}) using a PUF plug	PSE with hexane-DE 19:1, previous addition of deuterated SS	Concentration to a small volume	GC/EI-MS (SIM)	91-100	NR	10 ng m^{-3}
70,71	HHCB, AHTN, ATII, MX, MK	Lo-vol sampler (36-108 m^3, 25-38 L min^{-1}) using GFF and 2 PUF plugs in series	Soxhlet with 300 mL hexane-DE 9:1, 8h, previous addition of deuterated SS	Concentration to 0.5 mL, clean-up on silica, elution with 50 mL of hexane EtAcO 9:1, concentration to 0.2 mL and addition of IS (TCN)	GC/EI-MS (SIM), GC/NCI-MS (SIM) for nitromusks	69-126	1-9	EI: Polycyclic (5-45 pg m^{-3}) NCI: Nitromusk (4-12 pg m^{-3})
72	HHCB, AHTN, ATII, ADBI, AHMI,DPMI	Hi-vol sampler (72 m^3, 0.3-0.4 m^3 min^{-1}) with a GFF and a PUF plug	Soxhlet with DCM, 72 h	Concentration, clean-up on a silica-alumina (2:1) column, elution with DCM, solvent exchange to hexane, concentration to 0.2-0.5 mL and addition of IS (HMB)	GC/EI-MS	57-107	3-12	60-120 pg m^{-3}
76	HHCB, AHTN, ATII, ADBI, AHMI, DPMI, MX, MK, MM	Lo-vol sampler (1-10 m^3, 100 L min^{-1}) using a SPE device filled with 25 mg Tenax	Addition of 100 µL acetone followed by HS-SPME (DVB/CAR/PDMS fiber, (30 min, 100ºC)	None	GC/EI-MS (ITD)	85-103	3-15	29-380 pg m^{-3}

Table 6. Analytical procedures for the determination of pesticides in indoor air

Ref	Analyte	Sampling	Desorption/Extraction	Extract treatment	Determination	Recovery (%)	RSD (%)	Limits of detection
11	39 pesticides	Active with cartridges containing an impactor, QFFs and XAD-2 resin sandwiched between 2 PUF plugs (4-9 L min^{-1}, 24 h, 4-14 m^3)	Soxhlet with 150 mL DE in hexane (6%), 16 h	Addition of a deuterated surrogate, drying with sodium sulphate, concentration and adjusting to a final volume of 2 mL using 10% DE in hexane	GC/EI-MS (SIM)	60-150	< 20%	1-6 ng m^{-3}
68	19 insecticides, 1 synergist, 1 fungicide	Active with a QFF and an Empore disk (5 L min^{-1}, 24 h, 7.2 m^3)	US with 8 mL acetone (15 min) followed by shaking (10 min)	Centrifugation 2000 rpm (10 min). Addition of IS and concentration (N_2) to 0.3 mL	GC/EI-MS (SIM)	>85	<14	0.1-2.0 ng m^{-3} (7.2 m^3)
80	Pentachlorophenol, bisphenol- A and nonylphenol	Active using glass cartridge containing a QFF followed by XAD-2 resin (48 h, 4 L min^{-1})	Soxhlet with DCM	Concentration (K-D), SPE with florisil and concentration. Addition of SS	GC/MS	55-120	NR	0.09 ng m^{-3}
81	38 pesticides: herbicides, pyrethroids, organophosphate and organochlorine insecticides, fungicides	Active using a glass cartridge containing PUF and a QFF (24 h, 5 L min^{-1}, 7.1 m^3)	Soxhlet with 150 mL DCM, 16 h	Concentration in a rotary evaporator to 100 µL followed by dilution in 2 mL acetone	GC/ECD, GC/TSD, HPLC/UV (DAD)	73.1-120.2	<8	LOQs = 0.1-562 ng m^{-3}
82	Disinfectants: Quaternary Ammonium Compounds (QACs)	Active with a tube containing XAD-2 resin (1 Lmin^{-1}, 100 L)	US with 5 mL ACN, 10 min	None	IC (Cationic preconcentration column), LC-MS/MS	99.83-101.00	NR	28 µg m^{-3} (100 L, IC), 5 ng m^{-3} (100 L, LC-MS-MS)
83	Insecticides (pyrethroids)	Passive with SPMDs suspended about 2 m height (48 h)	MAE (2x20 min) with 30 mL hexane-acetone (1:1).	Concentration (rotary evaporator), reconstitution in 5 mL hexane, and extraction with ACN (3x5 mL). Clean-up with alumina-C_{18} and elution with 10 mL ACN. Evaporation almost to dryness in a rotary evaporator and finally to dryness with N2. Addition of IS in isooctane	GC/EI-MS/MS	61-103 (after 2nd extraction)	2.9-9.4	0.3-0.9 ng per SPMD
84	4 fungicides, 1 insecticide and 1 acaricide	Active using stainless steel tubes filled with Supelpak or C18 distributed in 2 beds (front one 250 mg and back one 150 mg)	SE with acetone or EtOAc by shaking (20 min)	Centrifugation at 3500 rpm (10 min)	GC/NPD, HPLC/UV	79-102 (Supelpak), 84-106 (C_{18})	0.23-6.3	LOQ=0.2-20 µg m^{-3} (60 L)

85	11 pyrethroids, 1 synergist, 1 fungicide, 1 carbamate	Active with a glass tube containing 25 mg Tenax (100 L min^{-1}, 1 m^3)	US with 1 mL EtOAc, 10 min	None	GC/MS (ITD), GC/µECD	81-114	<10	0.03-4.1 ng m^{-3} (µECD), 1.4-9.1 ng m^{-3} (MS)
86	10 pyrethroids, 1 synergist, 1 fungicide, 1 carbamate	Active with a glass tube containing 25 mg Florisil (100 L min^{-1}, 1 m^3)	Addition of 100 µL acetone followed by HS-SPME (PA fiber, 30 min, 100ºC)	None	GC/MS (ITD), GC/µECD	76-119	<20	0.001-2.1 ng m^{-3} (µECD), 0.046-7.1 ng m^{-3} (MS)
87	3 chlordanes and 2 nonachlors	Active with a MSP sampler modified by addition of a stainless steel cylinder with a PUF plug and QFFs (10 L min^{-1}, 29 m^3)	SE with 40 mL of hot (50ºC) hexane-DCM 4:1 (1h, for PUF)	Rinsed (x2) with 20 mL of hot hexane:DCB (4:1). Concentration by rotary evaporation followed by concentration with N_2. Clean-up on microcolumns of silicic acid. Elution with 2 mL hexane:DCM 9:1. Reduction (N_2) to ~0.1 mL, addition of deuterated PAHs as IS and final reduction to ~0.05 mL	GC/EI-MS (SIM)	82-91	≤17	0.018-0.140 ng (gas phase)
88	11 pesticides: pyrethroids, carbamates, organophosphorous, etc	The output knob of a 250-mL glass flask is connected to a pump and the input knob is just open to the air. The SPME fiber (PDMS) is inserted into the sampling flask through a septum and exposed to the air stream (dynamic mode, 40 min)	TD	-	GC/EI-MS (ITD, SIM)	NR	1.9-7.6	0.03-76.7 µg m^{-3}
89	8 pesticides : malathion, chlorpyrifos, diazinon, etc	Active using PUF cartridges (30-40 L min^{-1}, 24 h)	SE with 2 mL toluene-acetone 9:1 (NIOSH 5600)	None	GC/MS (SIM)	NR	NR	0.001-0.002 µg m^{-3}
90	Chlorpyrifos	Active using OVS samplers (QFF with two beds of XAD-2 sandwiched between PUF partitions, 1.0 L min^{-1}, 24 h) and PUF tubes (3.8 L min^{-1}, 24 h)	Soxhlet with 5% DE in hexane (PUF) SE with 5% DE in hexane followed by shaking (2500 rpm, 1 h)	Addition of decachlorobiphenyl as surrogate and 2,4,5-tribromobiphenyl as IS	GC/ECD, GC/MS (confirmation)	98-120	30	NR
91	17 insecticides and acaricides: pyrethroids, organophosphates, carbamates, etc	Active with PUF plugs and GFFs (50 L min^{-1})	SE soaking in 50 mL EtOAc, and squeezed periodically in an US bath for 2 min (PUF plugs). US with 10 mL EtOAc for 5 min (x3) (GFFs)	Concentration (N_2) to 0.5 mL, filtration through a pipette with silanized glass wool, washing with 0.4 mL ethyl acetate and adjusting to 1 mL.	GC/EI-MS (SIM)	85-109 (matrix-matched calibration)	2.8-11.4	0.1-5 ng m^{-3} (10 m^3)

92	29 pesticides: 9 organophosphates, 6 carbamates, 2 pyrethroids, 6 herbicides, 5 fungicides, 1 repellant	Active with a filter and a PUF plug (4 L min^{-1}, 48 h, 11.5 m^3). Spiked with terphenyls-d_{14} as a recovery surrogate	Soxhlet with 6% DE in hexane, 16 h	Concentration to 1 mL	GC/MS	NR	NR	0.2-0.7 ng m^{-3} (air)
93	Chlorpyrifos	Passive with a porous PTFE tube filled with 0.75 g Supelpak	SE with 3 mL toluene by shaking (1 h)	Concentration to almost dryness (N_2) in a K-D evaporator with a cooling pump	GC/MS (SIM)	NR	NR	NR
94	5 insecticides pyrethroids	100 mL air dissolved in 25 mL acetone using a syringe	The syringe is washed with 10 mL acetone (x4)	The washings are combined and concentrated	GC/ECD	NR	9.6-11.4	NR
95	Insecticide and acaricide (malathion and some of its metabolites)	Active with a PUF plug (2 L min^{-1})	Soxhlet with 100 mL acetone (8 h)	Evaporation until almost dryness. Addition of IS and dilution to 4 mL	GC/MS-MS	93.2-94.1	≤6	0.01-0.07 ng L^{-1}
96	11 pesticides: 2 fungicides, 1 carbamate, 2 pyrethroids, 1 dinitroaniline, etc	Active with sampling tubes containing 100 mg (front layer) and 50 mg (backup layer) Tenax and intermediate glass wool plugs (2.1 L min^{-1}, 8 h)	Incubation with 5 mL methanol (5 min) with occasional shaking and US (3 min)	After sedimentation, 1 mL of the supernatant is filtered through a 0.45 µm GFF. Addition of IS and adjusting to the final volume with water	HPLC/UV (DAD)	70-100	≤4	1.0-9.1 µg m^{-3} (1 m^3)
97	Insecticides: pyrethrins, pyrethroids and a synergist	Active with GFF and 2 PUF plugs (3 m^3 h^{-1}, 10 m^3)	US with 10 mL EtOAc (x3) (GFFs) US with 150 mL EtOAc (x3) (PUF)	The extracts were combined, filtered through silanized glass wool and reduced (rotary evaporator) to a final volume of 1 mL	GC/ECD, GC/FID, HPLC/UV	75.5-113.9	4.9-13.2	NR
98	aldrin, dieldrin, 4 chlordanes, pentachloroanisole and HCHs	Active using 2 hi-vol samplers with PUF plugs (30 m^3 h^{-1}, 50-100 m^3)	Spiking with isotopically labelled IS. Soxhlet with hexane in acetone (50%) 24 h	Reduction to 0.1 mL, purification using SPE cartridges containing 1 g silica and final elution using 10 mL hexane, 10 mL 50% hexane in DCM and 10 mL DCM	GC/MS	NR	NR	NR
99	7 pesticides: 1 carbamate, 3 pyrethroids, 1 phenylsulfamide, etc	Active with tubes containing Tenax and glass wool plugs (0.528-1.261 L min^{-1}, 60 min)	SE with 2 mL acetone followed by shaking (5 min)	Filtration through a paper filter, rinsing with 2 mL acetone, evaporation (N_2) and redissolution with n-hexane or acetone	GC/ECD, GC/NPD	75-89	NR	LOQs=0.1-0.2 µg m^{-3}
100	23 pesticides	Active with tubes packed with 25 mg Tenax and plugged with 2 portions of silanized glass wool (4h, 1m^3)	SE with 5 mL acetone followed by shaking (30 min)	Filtration through glass wool. Addition of filtered acetone, concentration (N_2) to 200 µL, addition of IS and final concentration (N_2) to 40 µL	GC/CI-MS	50.7-110.9	<15	0.5-30 ng m^{-3} (1 m^3 air)
101	Insecticides (chlordanes)	Active with a glass-lined stainless-steel tube packed with 0.4 g Tenax and sealed with 2 silica-wool plugs (1-2 L min^{-1}, 50-100 L)	TD	-	GC/EI-MS (SIM)	NR	1.1-5.1	0.25 ng m^{-3} (20 L)

102	6 pyrethrins and 7 pyrethroids	Active using glass tubes filled with 4 g silica gel (0.5 m^3 h)	SE with 50 mL hexane	Transferred into glass columns and elution with 50 mL hexane:ethyl acetate (1.1). Final concentration	HRGC/ECD	NR	NR	NR
103	3 pesticides: chlorpyrifos, malathion and methomyl	Active using a hi-vol sampler loaded with XAD-4 resin (1 m^3 min^{-1}, 3 h, 180 m^3)	SE with 250 mL EtOAc, followed by shaking (1.5 h) and filtration. Addition of 100 mL EtOAc, shaking (1 h) and filtration. Combination of extracts.	HPLC fractionation. Concentration by rotary evaporator to 5 mL. Centrifugation with 5 mL ethyl acetate and final concentration (N_2) to 1 mL	GC/FID, GC/ECD	72-81	8-12	0.3-1 ng m^{-3}

Table 7. Analytical procedures for the determination of organotin and perfluorinated alkyl compounds in indoor air

Ref.	Analytes	Sampling	Desorption/Extraction	Extract preparation	Determination	Recovery (%)	RSD (%)	LOD
129	MeFOSE, EtFOSE, EtFOSA, MeFOSEA	Passive using a PUF disk (21 days, uptake rate 2.5 m^3 day^{-1}: 52.5 m^3)	Soxhlet with PE, 21 h	Concentration to 0.5 mL, and addition of IS (Mirex)	GC/EI-MS (SIM)	64-89	5-6	0.01-7.1 pg m^{-3}
130	FTOHs, MeFOSA, EtFOSA, MeFOSE, EtFOSE	Lo-vol sampler (20-100 m^3, 1.1 m^3 h^{-1}) using a SPE cartridge (Isolute ENV+), previous addition of SS (7:1 FA)	Elution with 34 mL EtAcO	Concentration to a small volume, addition of isooctane, concentration to 0.2 mL, and addition of IS (TCN)	GC/PCI-MS (SIM)	17-400	NR	3-300 pg m^{-3}
131	DBTC, TBTC, DPTC, TPTC	Active (7.2 m^3, 5 L min^{-1}) using 2 QFFs and an activated carbon-fibre filter	US with 10 mL HCl/MeOH (1 M), 10 min (x2), and with 2.5 mL benzene, 10 min (x2)	Centrifugation (1700 g), 10 min, washing with 15 mL NaCl (10%), drying over Na_2SO_4 and concentration to 1 mL. Derivatization by addition 1 mL propylmagnesium (2 M), 40 ºC, 30 min. Addition of 10 mL H_2SO_4 (0.5 M), addition of 10 mL MeOH, LLE with 2.5 mL hexane (x2), and concentration to 0.5 mL	GC/FPD	95-99	4-6	0.2-0.4 ng m^{-3}
133	MeFOSE, EtFOSE, MeFOSEA	Active using a hi-vol sampler (100-200 m^3, 400 L min^{-1}) with collection on a GFF and 2 PUF plugs in series	Soxhlet, 18-24 h, with DCM for GFF, and with PE/acetone 1:1 for PUF	Concentration to 1 mL, solvent exchange to EtAcO, and addition of IS (Mirex)	GC/EI-MS (SIM)	47-60	5.8-7.2	0.3-20 pg m^{-3}
134	FTOHs, MeFOSE, MeFOSA, EtFOSE, EtFOSA, MeFOSEA	Passive using a PUF disk impregnated with XAD-4 powder (83 days, uptake rate 1.4-4.6 m^3 day^{-1}, 116-382 m^3)	Soxhlet with PE/acetone 1:1, 24h, previous addition of ^{13}C-labeled and deuterated SS	Concentration to 0.5 mL, centrifugation (4000 rpm), 10 min, and addition of IS (N,N-Me_2FOSA)	GC/PCI-MS (SIM)	86-126	15-50	NR

Table 8. Analytical procedures for the determination of pesticides in air suspended particulate matter

Ref	Analytes	Sampling	Desorption/Extraction	Extract treatment	Determination	Recovery (%)	RSD (%)	LOD
87	Chlordanes	QFF (10 L min^{-1}, 29 m^3)	Addition of a SS. US with 25 mL DCM (35 min, x2)	Concentration with rotary evaporation and N_2. Clean-up on microcolumns of silicic acid followed by rinsing with 2 mL hexane-DCM (9:1), concentration (N_2), addition of IS and concentration to 0.01 mL	GC/MS (SIM)	62-90	NR	0.032-0.146 ng
97	Insecticides: pyrethrins, pyrethroids and a synergist	GFF (10 m^3, 3 m^3 h^{-1}). Also, an impactor was used.	US with 10 mL EtAcO (x3)	Filtration through silanized glass wool and concentration to 1 mL by rotary evaporation	GC/ECD, GC/FID, HPLC/UV	88-100	≤15	0.5-250 ng m^{-3} (10 m^3)
121	Permethrin	GFF (2 L min^{-1}, 6 h)	SE with 3 mL MeOH	Dilution with phosphate buffer (1:20) for ELISA-optical detection	LC, ELISA-optical detection	92-129 (LC), 118-240 (ELISA)	3-12 (LC), 25-34 (ELISA)	2 ng mL^{-1} (ELISA), 300 ng mL^{-1} (LC)
158,160	Pyrethroids	Pallflex filter (10 m^3, 2.6-3 m^3)	US with 10 mL EtAcO (x3)	Filtration through sylanized glass wool and concentration to 1 mL by rotary evaporation	GC/EI-MS	108-110	<12	1.0-3.0 ng m^{-3}
164	Permethrin and fenvalerate	Millipore filter (1-2 L min^{-1}, 60 min)	SE with acetone	Partition between hexane and water	GC/ECD	90-100	NR	1 µg m^{-3} (1-2 L min^{-1}, 60 min)

Table 9. Concentrations of organic contaminants in indoor suspended particulate matter and dust

	Home	**Office**
PM (μg m^{-3})		
Pesticides	≤0.002 [87] 0.005-40 [97]	NR
Dust (μg g^{-1})		NR
Phthalates	DBP: <24-352, DEHP: 16.7-7700, BBP: 3.87-1310, DEP: <4-111 [10,11] DBP: 56, DEHP: 776, BBP: 86, DEP: 45, DMP: 11 [12] DBP: 226 (0-5446), DEHP: 1310 (0-40459), BBP: 319 (0-45549), DEP: 31 (0-2425) [139,163]	DEHP: 980-3000 [140]
BFR	Tetra-pentaBDEs: <LOD-22.5 [11] Tri-hexaBDEs: 0.0022-0.079, BDE183: 0.0048, BDE209: 0.470, BTBPE: 0.0048, BeBDethane: 0.047 [24] ΣPBDEs (tri-hexaBDEs): 0.0162-0.6254 [40] Tetra-hexaBDEs: 0.000286-0.060, BDE183: 0.00455-0.142, BDE209: 0.0584-1.615 [56] Tetra-hexaBDEs: <LOD-2.85, BDE183: 0.0009-0.464, BDE209: 0.137-19.1 [141] Tri-hexaBDEs: <LOD-13.8, BDE183: 0.0013-0.162, BDE209: 0.137-8.75 [142] Tetra-hexaBDEs: <LOQ-0.0642 [144] Tri-hexaBDEs: <LOD-0.06515, BDE183: <LOD-0.02461 , BDE209: 0.0008-0.3381 [145] Tri-hexaBDEs: <LOD-6.3, BDE183: 0.0015-0.180 , BDE209: 0.068-13.0 [146] Tri-hexaBDEs: <LOD-60.0, BDE183: <LOD-0.650, BDE209: 0.074-10.0 [147] HBCD: 0.064-110.0 [148]	ΣPBDEs (tri-hexaBDEs): 0.0162-0.6254 [40] HBCD: 0.09-3.6 [148]

OFR	TCEP: 3.75, TCPP: 2.35 [62] TBP: 0.040-0.90, TCEP: 0.090-40, TCPP: 1.2-39.6, TPhP: 0.36-4.9 [149] TBP: 0.070-0.226, TCEP: 0.25-9.8, TCPP: 0.35-10.3, TPhP: 0.29-9.5 [150] TBP: 0.21-0.61,TCEP: 0.19-0.27, TCPP: 0.47-0.93, TPhP: 0.85-0.99, TBEP: 18-25 [151]	TBP: 0.18-0.35,TCEP:1.0-48, TCPP: 5.3-73, TPhP: 2.2-6.8, TBEP: 120-270 [151]
Musks	HHCB: 1.3, AHTN: 1.0, MK: 0.3 [12] HHCB: 1.46, AHTN: 1.65, AHMI: 0.202, MX: 0.895, MK: 0.477 [62] MX: <LOD-0.6916, MM: <LOD-0.01494, MK: 0.01436-2.303 [152]	NR
Pesticides	0.221-228 [11] 0.707-4.220 [80] 0.13-4.5 [89] <0.2-130 [97] 0.080-15 [100] <0.019.0-3.125 [124] 0.0007-0.067 [157]	NR
Other organic pollutants	MeFOSE: 0.0033-8.86, EtFOSE: 0.0014-75.44, MeFOSEA: 0.0007-0.044 [129] PFOS: 0.011-2.5, PFOA: 0.069-3.7 [154] PFOS: 0.00228-5.065, PFOA: 0.00115-1.234 [155] MBT: 0.16, DBT: 0.51, TBT: 0.02 [156]	NR

Table 10. Analytical procedures for the determination of organic contaminants in indoor dust

Ref	Analytes	Sampling	Desorption/Extraction	Extract treatment	Determination	Recovery (%)	RSD (%)	LOD
11	DEP, DBP, BBP, DEHP, DCHP, DnHP, DiBP	Collection in cellulose extraction thimble placed in a PTFE holder inside a vacuum cleaner.	Addition of the SS (p-terphenyl-d_{14}), equilibration at room T (30 min) and Soxhlet with 6% DE in hexane, 16 h	Concentration to 10 mL and 1-mL aliquot cleaned on a florisil column, elution with 20 mL 10% acetone in hexane, concentration to 2 mL with 10% DE in hexane	GC/MS	40-220	<20	0.1-24 μg g^{-1}
12	DMP, DEP, DPP, DBP, DiBP, DCHP, BBP, DEHP, DOP, Musks	Collection in bags of vacuum cleaners (1 g dust).	Addition of deuterated SS, PSE with hexane-DE 95:5.	None	GC/EI-MS (SIM)	91-100	NR	Determination limit= 0.5 μg g^{-1}
139	DEP, DIBP, DBP, BBP, DEHP, DINP.	Cellulose membrane filters in holders of styrene-acrylonitrile polymer mounted on a sampler of polypropylene connected to a vacuum cleaner (>25 mg dust).	Agitation 30 min with 2 mL DCM (x2).	NR	GC/MS, GC/FID	NR	NR	NR
14	Phthalates, PCBs, PCDDs, PCDFs, PBDEs, PFCs	Collection in special filter bags by slowly vacuum-cleaning the floor of the room during 10 min.	NR	NR	GC/FID, GC/ECD	NR	NR	NR
140	Phthalates	Dust from a vacuum cleaner with an inserted particle filter was sieved through 2 mm pore size.	10 mL hexane	Clean-up by SPE with silica gel.	GC/ECD/FID	NR	NR	NR

10	PAHs, phthalates, PCBs, pesticides	Dust (1.4-12.1 g) collected in a cellulose thimble	Soxhlet with 200 mL hexane-DE 94:6, 16 h, after addition of a deuterated surrogate	Treatment with anhydrous sodium sulphate, concentration to 2.5 mL cleanup with florisil, concentration to 2 mL in 10% DE in hexane and silylation	GC/EI-MS (SIM)	110-378	12-175	NR
141	Tetra-DecaBDE	Dust (10 g) from vacuum cleaners	Soxhlet with 300 mL toluene, 24 h	Addition of ^{13}C-labelled SS, clean-up on a multilayer (acidic, neutral, basic, neutral) silica column and elution with 150 mL hexane. Clean-up on alumina, elution with 100 mL hexane/DCM 1:1, clean-up on a GPC column, elution with cyclohexane/EtAcO 1:1, clean-up on alumina, elution with 10 mL hexane/DCM 1:1, addition of ^{13}C-labeled IS and concentration to 0.1mL.	GC/EI-MS (SIM)	NR	NR	NR
11	Tetra-pentaBDEs	Dust (0.047-1.6 g) from vacuum cleaners passed through a 150µm mesh sieve	Soxhlet with hexane/DE 6%, 16 h, previous addition of deuterated SS	Concentration to 10 mL, clean-up on florisil of an 1 mL aliquot, elution with 20 mL acetone/hexane (10 %), solvent exchange to DE/hexane (10 %) and concentration to 2 mL	GC/EI-MS (SIM)	40-220	< 20	0.2-0.4 µg g^{-1}
142	Tri-DecaBDE	Dust (0.1-0.5 g) from vacuum cleaners passed through a 1mm mesh sieve	PSE (100 ºC, 2000 psi, 5 min, 3 cycles) with DCM, previous addition of ^{13}C-labeled SS	Concentration to 0.5 mL, solvent exchange to hexane, clean-up on SPE cartridge (Silica Sep-Pak), elution with 20 mL hexane, and concentration to 0.5 mL	GC/NCI-MS (SIM)	NR	< 25	1-6 ng g^{-1}
40	Tri-HexaBDEs	Dust (1 g) from vacuum cleaners passed through a 500 µm mesh sieve	PSE (150 ºC, 1500 psi, 5 min, 1 cycle) with hexane and florisil on the bottom of extraction cell, previous addition of ^{13}C-labeled SS	Concentration to 2 mL, treatment with 2 mL $H_2SO_{4(c)}$, LLE with DMSO, clean-up on florisil, elution with 20 mL hexane, concentration to a small volume, solvent exchange to 20 µL nonane, and addition of IS (PCB-29, PCB-129)	GC/EI-MS (SIM)	45-67	0.9-6	0.03 ng g^{-1}

143	Tri-DecaBDE	Dust (0.5-1 g) from vacuum cleaners (SRM 2585) passed through a 100 µm mesh sieve	1) PSE (100 ºC, 2000 psi, 5 min, 3 cycles) with DCM, previous addition of ^{13}C-labeled SS. 2) Soxhlet with DCM, previous addition of ^{13}C-labeled SS	1A) Concentration to a small volume, clean-up on SPE cartridge (Silica Sep Pak), elution with 20 mL hexane, concentration to 0.5 mL. 1B) Concentration to a small volume, clean-up on a SPE cartridge (alumina), elution with 10 mL DCM/hexane (35%), clean-up on a GPC column, concentration and solvent exchange to 0.5 mL isooctane. 2) Concentration to a small volume, clean-up on alumina, elution with 20 mL PE, concentration to a small volume, solvent exchange to isooctane	GC/EI-MS (SIM), GC/NCI-MS (SIM)	NR	NR	NR
144	Tetra-HexaBDEs	Dust (0.8 g) from vacuum cleaners passed through a 60 µm mesh sieve	MAE (80 ºC, 15 min) with a mixture of 8 mL hexane and 4 mL NaOH 10 % (w/w), previous addition of ^{13}C-labeled SS	Centrifugation, separation of organic phase, on-batch clean-up by addition of 100 mg florisil per mL extract, shaking 2 min, and filtration. An aliquot of 2 mL concentrated to 0.2 mL	GC/EI-MS (MS/MS)	92-114	11-16	0.29-0.55 ng g^{-1}
145	Tri-DecaBDE	Dust (3.4 g) from vacuum cleaners passed through a 2 mm mesh sieve	Soxhlet with DCM/hexane (1:1), previous addition of SS (BDE-35, BDE-181)	Concentration to a small volume, solvent exchange, clean-up on a silica-alumina column 2:1, elution with 100 mL hexane/DCM (1:1), addition of 50 µL dodecane, concentration to < 0.1 mL, and addition of IS (Mirex)	GC/NCI-MS (SIM)	70-84	5-10	0.032-0.305 ng g^{-1}
56	Tetra-DecaBDE	Dust (0.8 g) from vacuum cleaners passed through a 60 µm mesh sieve	MAE (80 ºC, 15 min) with a mixture of 8 mL hexane and 4 mL NaOH 10 % (w/w), previous addition of SS (PCB-30)	Centrifugation, separation of organic phase, on-batch clean-up by addition of 100 mg florisil per mL extract, shaking 2 min and filtration.	GC/µECD	90-108	4-13	0.0439-1.44 ng g^{-1}
146	Tri-DecaBDE	Dust (0.2 g) from air conditioning units	MAE (115ºC, 15 min) with 25 mL hexane/DCM (1:1) in the presence of Na2SO4, previous addition of 1 3C-labeled SS	Clean-up on acidic silica (H_2SO_4) column, elution with 100 mL hexane and 50 mL hexane/DCM 2:3, clean-up on a GPC, elution with 30 mL hexane/DCM 1:1, addition of dodecane, concentration to 25 µL, and addition of ^{13}C-labeled IS	GC/NCI-MS (SIM)	71-130	0.4-32	0.02-40 ng g^{-1}

147	Tri-DecaBDE	Dust (0.25 g) from vacuum cleaners passed through a 150 µm mesh sieve	Soxhlet with DCM, 15 h, previous addition of SS (BDE-35)	Concentration to 4 mL, solvent exchange to PE/isooctane up to 10 mL, a 5 mL aliquot concentrated to 3 mL, and treatment with 1-2 mL H_2SO_4 (x2). Concentration to 1 mL in isooctane and addition of IS (Mirex)	GC/NCI-MS (SIM)	≈ 99	≈ 19	0.1-14 ng g^{-1}
41	Tri-DecaBDE, BTBPE, DeBDethane	Dust from vacuum cleaners	Soxhlet with toluene, 16 h , previous addition of ^{13}C-labeled SS	Clean-up on treated (KOH+ H_2SO_4) silica column, elution with hexane, clean-up on GPC, elution with hexane/DCM 65:35, concentration to a small volume, and addition of tetradecane and ^{13}C-labeled IS	GC/NCI-MS (SIM)	45-184	NR	0.169-10.1 ng g^{-1}
148	HBCD (α,β,γ)	Dust (1 g) from vacuum cleaners passed through a 500 µm mesh sieve	PSE (90 ºC, 1500 psi, 5 min, 3 cycles) with hexane/DCM (1:1) and florisil on the bottom of extraction cell, previous addition of ^{13}C-labeled SS	Concentration to 0.5 mL, treatment with H_2SO_4, clean-up on florisil, elution with 30 mL hexane/DCM 1:1, concentration to a small volume, solvent exchange to MeOH and addition of deuterated IS	LC/ESNCI-MS (MS/MS)	82-88	5-8	0.1 ng g^{-1}
62	TCEP, TCPP	Dust from vacuum cleaners	Soxhlet with hexane/acetone (4:1) 8 h, previous addition of SS	Concentration to a small volume	GC/EI-MS (SIM)	NR	NR	100 ng g^{-1}
149	TiBP, TBP, TCEP, TCPP, TDCPP, TPhP, TBEP	Dust from vacuum cleaners passed through a 60µm mesh sieve	MSPD: 0.5 g dust mixed with Na_2SO_4 (0.5 g) and dispersed with florisil (0.5 g) in a glass mortar	Loading the blend in a cartridge containing alumina on the bottom, rinsing with 2 mL hexane, and elution with 3 mL acetone. Addition of 1 mL EtAcO, concentration to 0.5 mL and addition of IS (TPP)	GC/NPD	80-116	4-13	LOQ: 40-50 ng g^{-1}
150	TiBP, TBP, TCEP, TCPP, TDCPP, TPhP, TBEP, TEHP, TPPO	Dust (0.5 g) from vacuum cleaners passed through a 60µm mesh sieve	MAE with 10 mL acetone (130ºC, 30 min)	Centrifugation (3000 rpm, 5 min), decantation, addition to 500 mL ultrapure water, SPE (Oasis HLB), elution with 2 mL EtAcO, clean-up on a silica cartridge, elution with 5 mL EtAcO and concentration to 1 mL	GC/NPD	85-104	3-13	LOQ: 40-50 ng g^{-1}
151	TBEP, TCEP, TCPP, TDCPP, TPhP, TEEdP, TEHP, TBP, DOPP, CLP1, TPhP, TMP	Dust (1-2 g) from vacuum cleaners	US with 25 mL DCM 20 min	Filtration through paper filters, concentration to a small volume and addition of IS (TEP)	GC/NPD	97	6-18	7-60 ng g^{-1}

12	HHCB, AHTN, ATII, ADBI, AHMI, DPMI, MX, MK	Fine dust fraction from vacuum cleaners (1 g)	PSE with hexane/DE (19:1), previous addition of deuterated SS	-	GC/EI-MS (SIM)	NR	NR	LOQ: 500 ng g^{-1}
152	MX, MK, MM	Dust (0.8 g) from vacuum cleaners passed through a 60µm mesh sieve	MAE with a mixture of 8 mL hexane and 4 mL H_2SO_4(aq) 1M containing ascorbic acid 0.10 % (w/w) (80 ºC, 10 min), previous addition of SS (PCB-166, PCB-195)	Centrifugation, separation of organic phase, on-batch clean-up by addition of 100 mg florisil per mL extract, shaking 2 min and filtration	GC/µECD	88-97	6-8	1.03-3.26 ng g^{-1}
153	HHCB, AHTN, ATII, ADBI, AHMI, MX, MK	SRM 2585 Organics in House Dust	PSE: Dust mixed with H_2SO_4 and extracted (100 ºC, 2000 psi) with DCM, previous addition of deuterated IS (Fluoroanthene-d_{10})	Concentration to a small volume, solvent exchange to 0.5 mL isooctane, clean-up on SPE cartridge (5 % deactivated alumina), elution with 9 mL DCM/hexane (35 %), concentration to a small volume, solvent exchange to 1 mL DCM, clean-up on GPC, elution with 5.5 mL DCM, concentration to 1mL	GC/EI-MS (SIM)	73-90	4-13	NR
154	PFOS, PFOA	Dust (0.5 g) from vacuum cleaners	US with 10 mL MeOH 60 min	Centrifugation (1500 rpm) 10 min, filtration, and addition of deuterated IS	LC/ESI-MS (MS/MS)	73-89	11	10-50 ng g^{-1}
155	PFOS, PFOA, PFBS, PFOSA, PFHS	Dust (0.5 g) from vacuum cleaners passed through a 150 µm mesh sieve	US with 5 mL ACN 5 min (x2)	Clean-up of a 2 mL aliquot on a SPE cartridge (C18 Waters), elution with 7 mL ACN, concentration to dryness, reconstitution in 0.2 mL ACN, and addition of ^{13}C-labled IS	LC/ESI-MS (MS/MS)	46-101	1.7-6.3	0.99-4.56 ng g^{-1}
129	MeFOSE, EtFOSE, EtFOSA, MeFOSEA	Dust (0.25 g) from vacuum cleaners passed through a 150 µm mesh sieve	Soxhlet with DCM, 24 h	Concentration to 0.5 mL and addition of IS (Mirex)	GC/EI-MS (SIM)	NR	NR	NR
156	MBT, DBT, TBT, MOT, DOT, TPT	Dust (0.5-1.0 g) from vacuum cleaners	US with ethanol	Buffering with sodium acetate (pH 4.5), derivatization with sodium tetraethylborate (STEB) and LLE with hexane	GC/EI-MS (SIM)	> 70	NR	10 ng g^{-1}

157	41 PCBs and 7 pesticides	Dust collection from the filters of air conditioning units or the blades of ceiling fan using a small pair of steel tweezers rinsed with n-hexane	Addition of IS (0.2 g dust), MAE with 25 mL n-hexane-DCM (1:1) in the presence of sodium sulfate (2 g)	Acid silica gel column, elution with 100 mL n-hexane and subsequently with 50 mL n-hexane-DCM (2:3). GPC packed with Biobeads (6 g) per column using n-hexane-DCM (1:1) as a mobile phase. Concentration to 0.5 mL (N_2). Further concentration to 25 µL after addition of IS.	GC-MS/EI (SIM)	70-126	<19	0.2-1.0 ng mL^{-1} (on column)
80	Pentachlrophenol, bisphenol-A, nonylphenol	HVS3 vacuum sampler	ASE with acetone	Concentration, addition of IS (dicamba-d_3), followed by methylation or silylation. Clean-up by SPE with Florisil and final concentration	GC/MS	NR	NR	2.0 ng g^{-1}
108	Biocides	Manual wiping with Soxhlet-extracted paper towels (20 h toluene and 20 h acetone). Also, collection in a cleaned glass vial using metallic spoons.	Soxhlet or US with acetone-hexane 50:50	NR	GC/ECD, GC/MS	NR	NR	LOQ < 1 µg g^{-1}
158	4 pyrethroids	Dust collected using a modified vacuum cleaner where the usual dust bag was replaced by a Soxhlet filter tube	Soxhlet with EtAcO, 15 h	Concentration, solvent exchange into hexane, clean-up with silica gel and elution with DCM-hexane 30:70. Solvent exchange to EtAcO	GC/EI-MS	NR	NR	0.5 µg g^{-1}
159	6 PCDDs, 9 PCDFs, 12 PCBs	NR	ASE (150ºC, 12 min, 2000 psi)	Concentration (N2) using a Turbovap. Clean-up with multi-layered silica chromatography column and microcolumns packed with Florisil. Elution with DCM-hexane (1:49) for PCBs and with DCM for PCDD/Fs. Solvent exchanged with nonane and addition of IS. For PCB fractions collected after Florisil clean-up, concentration to 0.5 mL, additional clean-up on alumnia (16 h, 200ºC), elution with 25 mL DCM-hexane (3:7), solvent exchanged with nonane and addition of IS	GC/LRMS (SIM), HRGC/HRMS/positive ion mode (SIM)	58-112	≤41	1.0-12 pg g^{-1}

89	8 Organophosphorous pesticides	Hi-vol Surface Sampler HVS3 with a Teflon catch bottle, sieving through a 150-µm stainless steel mesh	US with 50 mL acetone, 1 min	Concentration, solvent exchange into cyclohexane, filtration through PTFE membrane filters, GPC, and elution with cyclohexane. Final concentration to 2 mL	GC/MS (SIM)	NR	NR	0.18-0.56 µg g^{-1}
11	15 pesticides	Vacuum cleaner modified to collect dust into a cellulose extraction thimble (45-90 min, 4g/sample)	Addition of a SS (p-terphenyl-d_{14}) and/or matrix spike solutions in hexane. Equilibration for 30 min, and Soxhlet with 6% DE in hexane, 16 h	Concentration to 10 mL, clean-up in a Florisil column, elution with 20 mL acetone-hexane (10%), concentration and elution with 2 mL DE-hexane (10%)	GC/MS (SIM)	NR	NR	0.2-1 µg g^{-1}
160	2 insecticides: permethrin and cyfluthrin	Dust collected with a vacuum cleaner (10-770 g) and sieved into two fractions; a fine fraction (<2 mm) and a coarse fraction (> 2 mm)	Soxhlet with EtAcO, 15 h	Concentration, solvent exchange into hexane, clean-up with silica gel and elution with DCM-hexane 30:70. Solvent exchange to EtAcO	GC/EI-MS	93.9-109.1	3.0-5.8	0.5 µg g^{-1}
97	Insecticides: pyrethrins, pyrethroids and a synergist	Dust collected using a modified vacuum cleaner where the usual dust bag was replaced by a Soxhlet filter tube	Soxhlet with 250 mL EtAcO, 15 h	Concentration, clean-up on a silica gel mini-column. Elution with 12 mL DCM-hexane 20:80 for 2 pyrethroids, elution with 13 mL EtAcO-hexane 15:85, solvent exchange to ACN (HPLC) or EtAcO (GC)	GC/ECD, GC/FID, HPLC/UV	95.3-116.8	1.6-6.3	LOQ = 0.05-0.5 µg g^{-1}
124	24 pesticides: 18 insecticides, 2 herbicides, 1 fungicide	HVS3 vacuum cleaner (high volume small surface sampler, 4-180 g), sieving to a size fraction < 53 µm, and resuspension using a fluidized bed generator (FBG).	Addition of a SS (p-terphenyl-d_{14}). Soxhlet with DE in hexane (6%, 16-18 h)	Concentration to 20 mL by rotary evaporation (40ºC, N_2)	GC/MS (SIM)	NR	NR	NR

161	4 organophosphorous pesticides	HSV3 sampler (cyclone-equipped vacuum sampler, which collects small particles in a Teflon catch bottle, 5 g). Particles sieved through a 150-µm stainless steel mesh	US with 50 mL acetone, 1 min	Concentration (N_2), solvent exchange into cyclohexane, filtration through PTFE membrane filters, GPC, and elution with cyclohexane. Concentration with K.D. and final concentration to 2 mL (N_2)	GC/MS	72-106	≤20	LOQ = 11-40 ng g^{-1}
100	23 pesticides	Dust collected using a vacuum cleaner and homogenizated in a food processor	SE with 5 mL acetone by shaking, 45 min	Filtration through a funnel containing glass wool and concentration to 1 mL (N_2). Addition of IS	GC/CI (with isobutene)-MS	60.7-135	1.4-18.3	25-100 ng g^{-1}