

A versatile method for the quantification of 100 SVOCs from various families. Application to indoor air, dust and bioaccessibility evaluation.

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- 1 A versatile method for the quantification of 100 SVOCs from various
- 2 families: Application to indoor air, dust and bioaccessibility

з evaluation.

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20 Abstract

A method coupling automated thermal desorption (ATD) with in-tube derivatization and solid 21 22 phase micro-extraction (SPME), with on-injector derivatization gas chromatography - tandem 23 mass spectrometry (GC/MSMS) was developed and used for the simultaneous quantification of 100 semivolatile (SVOCs) pollutants (50 pesticides, 16 PAHs, 22 PCBs, 7 phthalates and 5 24 alkylphenols) in indoor air, indoor dust, and for bioaccessibility evaluation. Chemical 25 compounds in indoor air were sampled on Tenax-TA passive samplers (PAS) exposed for 15 26 days, while dust was collected on silicon carbide (SiC©) foam using a custom made vacuum 27 cleaner head. After sampling, Tenax tubes from PAS were introduced directly into a thermal 28 29 desorption tube while dust was extracted using accelerated solvent extractor (ASE). Extract is then used to spike clean Tenax-TA tube that is then treated as a Tenax from PAS. The 30 31 derivatization agent (MtBSTFA) and a mix of internal standards were added into the tubes before thermal desorption and analysis by GC/MSMS. 32

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The SPME technique was applied to extract the 100 SVOCs from the different tested
bioaccessibility solutions (saliva, gastric, intestinal).

This method permits the determination of 100 pollutants in a single run, including those requiring a derivatization step, with very low quantification and detection limits. Indeed, ATD-GC/MSMS technic presents very low LOD (0.002 to 0.17 ng) and LOQ (0.007 to 0.56 ng) values while SPME-GC/MSMS displays slightly higher LOD (0.044 to 12.3 ng) and LOQ (0.10 to 37.0 ng) ranges.

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42 **Keywords** thermal-desorption; SPME; indoor air; dust; bioaccessibility; derivatization

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45 **1. Introduction**

In Europeans countries, most of the population spends considerable amount of time in 46 confined spaces. This term refers to houses, dwellings, workplaces (offices, factories, etc.), 47 schools, leisure areas (cinemas, restaurants, swimming pools, sports halls, etc.), and transport 48 (personal vehicles or public transport). On average, a person spends between 80% and 90% of 49 50 time indoors [1-4]. This statement may vary depending on countries, lifestyles (rural or urban), seasons or the general climate, but gives a good idea of the potential importance of 51 exposure to the indoor environment [1]. Mrs Marie-Christine Blandin, "Nord-Pas-de-Calais" 52 senator, made public a report devoted to the daily chemical risks evoking one "major sanitary 53 stake" [5]. Indoor air pollutants form a "risk cocktail" where health effects are not yet 54 correctly evaluated, because indoor environments are still regarded as being protected from 55 external pollution, and considered as safe. According to the "Global Burden of Disease" 56 study, 1.6 million people died prematurely in 2017 as a result of indoor air pollution [6]. 57

Indoor environments are known to be a source of diverse airborne pollutants which could 58 59 induce adverse health effects. Among these pollutants, volatile organic compounds (VOCs) are a class of molecules present in the gas phase including alkanes, alkenes, monoaromatics, 60 terpenes, aldehydes, ketones, esters, etc. Some VOCs are known to be toxic to humans and 61 are intensively monitored and regulated (benzene, formaldehyde, limonene, etc.) [7-10]. A 62 second class of molecules is of increasing interest in the last two decades and corresponds to 63 semi-volatile organic compounds (SVOC) which can be present both in the gas and 64 condensed phase (aerosol and dust) [11-13]. Some of these compounds are suspected to be 65 neurotoxic or reprotoxic and may be classified as endocrine disruptors [3]. 66

67 House dust is considered as an important exposure pathway to pollutants [14-17]. Indeed, it can be resuspended in living areas [15, 17-18] and can easily enter the body through 68 inhalation, carrying along various substances [1, 15]. Ingestion of dust is also an important 69 70 way of exposure, especially among young children where hand/mouth contact is frequent [17]. A great diversity of compounds that can be found in the dust (pesticides, polycyclic 71 72 aromatic compounds (PAHs), polychlorobiphenyls (PCBs), polybromodiphenylethers 73 (PBDEs), phthalates, etc.) [4] with a large variability of physicochemical properties. Consequently, the analysis of dust by a multi-residue approach is difficult and requires the 74 75 development of complex analytical methods including a large variety of molecules with very diverse properties. 76

For a complete evaluation of exposure via indoor environment, the simultaneous sampling and analysis of indoor air, airborne particles in addition to deposited dust is required in particular since the distribution of pollutants is not equal in each matrices and depend strongly of their physical and chemical properties. The composition of an indoor environment (air and dust) is directly related to the building materials used, the furnishings and the activity performed in the building [19]. It also depends on other parameters such as ventilation

systems or air renewal as well as outdoor parameters such as meteorological conditions and 83 84 outdoor chemical composition (i.e. pesticides application close to the building) [19-23]. One common explanation for poor indoor air quality is that indoor pollutants (confined to 85 buildings and therefore more concentrated than outdoor) are less subject to weather hazards 86 such as wind rain, solar radiation (photochemical degradation) or oxidizing compounds that 87 are more easily found in open environments. These pollutants come from a variety of sources, 88 89 some of which from outdoor while most of them originates from the indoor environment like furnishing and decoration materials, electronic equipment, or activities of the occupants like 90 biocides application [24]. 91

92 Collecting a representative sample of indoor air and dust is crucial. Active sampling on filter followed by an adsorbent for the collection of the particle and gas phase respectively is 93 the common method used for indoor air while vacuum cleaner is commonly used to collect 94 95 dust in bags [25-27]. Active sampling for indoor air is efficient but samplers require excessive time as the number of samplers is limited thus prohibiting parallel sampling in multiple 96 97 dwellings, are noisy and expensive, when undertaking large scale studies considering spatial and temporal variations of indoor pollutants. Passive sampling can be used as an alternative as 98 no pump or power supply are needed. It is simple enough to be handled by occupants 99 themselves and deployed in large scale during a long period and is quiet, which is an 100 important criteria indoor. Passive sampling of indoor air has been extensively used in the past 101 for different kind of pollutants like pesticides, PAHs, PCBs, PBDEs, etc. [28-30]. 102

103 The United States Environment Protection Agency (US EPA) has developed a vacuum 104 cleaner devoted to indoor sampling named "High volume small surface sampler (HVS3)" 105 which can be operated for many surfaces [4]. The standardized method from the American 106 Society for Testing Materials; "D54385 Standard practice for collection of floor dust for 107 chemical analysis" permits the determination of concentration and the charge of the sampled

surfaces if the exact surfaces areas are defined. This HVS3 collect dust in a filter bag and
potential losses of volatile and semi-volatile molecules (SVOCs) cannot be excluded and have
to be taken into account [14].

After sampling, common extraction techniques and analytical methods used for indoor air 111 and dust generally include a solvent extraction with Soxhlet, accelerated solvent extraction 112 (ASE) or microwave assisted extraction (MAE) followed by purification steps and an 113 114 injection on gas chromatography - GC or liquid chromatography - LC instruments. Extraction techniques using thermal desorption followed by direct injection into the GC can be used for 115 the desorption of molecules adsorbed on a trap as an alternative to these techniques. Thermal 116 117 desorption presents some advantages as it substantially simplifies analyses (no concentration step is needed) and increases sensitivity (a large part of the pre-concentrated material may be 118 recovered for determination). Moreover, detection limits and background noise are lower 119 120 because of the disappearance of solvent components [31-34]. Passive sampling on Tenax® adsorbent followed by thermal desorption and GC/MS analysis have been used for pesticides 121 122 and PAHs in indoor air [29-30]. The significant increase of sensitivity allowed by thermal desorption can be used for other matrices than passive sampling on Radiello® Tenax® 123 cartridges designed to be directly introduced in thermal desorption tubes. In fact, this 124 technique allows introducing an amount of concentrated liquid extract, obtained from ASE 125 extraction for example, largely higher than the classic liquid injection (about 1-2 µL in 126 splitless mode) into the GC column and detector. For this purpose, between 10 and 100 µL of 127 sample extract can be deposited on a clean Radiello® Tenax® tube and this extract is subject 128 to thermal desorption allowing the direct introduction of all the molecules present in this large 129 sample's volume in the GC system [30]. 130

Solid phase micro extraction (SPME) is also an interesting pre-concentration technique, in
 particular when samples are mainly composed of water, allowing a sensitivity increase
 compared to liquid injection on GC/MS [35-39].

In general, it is desirable to perform a multi-residue analysis to minimize sample handling 134 and reduce the number of extraction steps. In this study, an original method allowing, in one 135 unique injection, the quantification of 100 compounds from five families: pesticides, 136 137 phthalates, PCBs, PAHs, and alkylphenols in air, dust as well as aqueous solutions from bioaccessibility testing has been developed. This method associate thermal desorption and 138 quantification by GC/MSMS for air and dust samples, and the SPME coupled to GC/MSMS 139 140 for the bioaccessibility experiments. This method described also a new sampling head for the collection of dust from different floors. All parameters of these methods in terms of 141 performance, sensitivity, usefulness will be described and discussed. The environmental 142 validation was done by the analysis of different samples collected indoor in several French 143 houses and dwellings. 144

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147 **2.** Materials and methods

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149 2.1. Reagents and solutions

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Acetonitrile (ACN) of HPLC quality, PDMS 100 µm Supelco SPME fibers and Radiello®
Tenax®-TA adsorbing cartridges (100 mesh, 4.8 mm diameter) were supplied from SigmaAldrich (L'Isle-d'Abeau, France).

154 Perkin Elmer® ATD-empty tubes (89 mm x 5 mm i.d.) were purchased from PerkinElmer

155 Corp. (Norwalk, CT, USA) and SiC[®] foam were obtained from SICAT SARL (Strasbourg,

156 France) at desired dimensions.

Standards of individual pesticides of Pestanal® quality (> 99 % purity), phthalates, 157 alkylphenols and *N-tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MtBSTFA) were 158 purchased from Fluka (Sigma Aldrich, St. Quentin Fallavier, France), Dr Ehrenstorfer GmbH 159 (Cluzeau Info Labo, St. Foy la Grande, France) or Riedel de Haën (Sigma Aldrich, St. 160 Quentin Fallavier, France). Stock solutions of each standard were dissolved in ACN (HPLC 161 grade supplied by Sigma Aldrich, St. Quentin Fallavier, France) at a concentration of 1 g L^{-1} . 162 For PAHs and PCBs, two mixtures at 0.1 g L⁻¹ of 16 PAHs and 22 PCBs respectively were 163 purchased from Cluzeau Info Labo (St. Foy la Grande, France). 164 Internal standards; naphthalene-d₈, trifluralin d₁₄, nitrophenol d₄, *pp*'-DDE d₈, *pp*'-DDT d₈, 165 DEHP d₄ and *trans*-cypermethrin d₆ were obtained from Sigma-Aldrich (L'Isle d'Abeau, 166 France) and Cambridge isotope laboratories (Cluzeau Info Labo, St. Foy la Grande, France). 167 Calibration and internal standard mixtures at 10 mg L⁻¹ were prepared by appropriate 168 169 dilution with ACN in vials. 170 171 2.2. Cleaning and storage of passive Tenax®-TA tubes, PDMS fibers and SiC© foam 172 to be introduced in and Tenax®-TA adsorbing cartridges were conditioned at 350°C for 45 173 min under 45 mL min⁻¹ Helium (He) flow (99,9999% purity) and were then stored in capped 174 glass tubes surrounded with Teflon rubber at room temperature until exposure or spiking. 175 After exposure, passive sampling tubes were stored in the dark at -18°C in capped glass tubes 176

surrounded with Teflon rubber.

ASE 300 (Dionex Corporation, St Louis, US) is used to clean SiC© foam before sampling. Foams were placed in 33 mL stainless steel cells that are filled with hexane and dichloromethane mix (50:50 v/v) and heated at 150°C and 103 bars of pressure for 10 /min. They were rinsed with the same solvent mixture and a high purity nitrogen flow was then

applied to purge cells content in glass jars and dry cells during 5 min. The same process was repeated with 100 % ACN. SiC© foam was then placed in aluminum foil, weighted and stored in a beaker at 50°C. After a period of storage of two week in these conditions, SiC© foam was extracted and analyzed in order to evaluate the potential contamination during the storage period. No compounds were detected confirming that the SiC© foam can be used on the field without risk of contamination during storage.

Before use, the PDMS fiber is conditioned at 280°C during 30 min in the split/splitless injector. After three extractions, the fiber is washed in ACN (30 min immersion at room temperature) and thermally desorbed for 15 min in the GC injector at 250°C. This washing step is required in order to remove any memory effect which can occur, in particular with high molecular weight PAHs.

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194 *2.3. Air and dust sampling*

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Radiello® Tenax-TA® passive sampling tubes (figure S1) were placed in a plastic shelter in order to protect the samplers mainly from wind variations when exposed indoor. This shelter is derived from the one developed by Wania et al. [40] for ambient air passive sampling with XAD-2© resin. Tenax-TA® was chosen as it correspond to a polymeric material (styrene polyvinylbenzene) commonly used as an adsorbent for semi-volatile compounds specifically treated to sustain high temperatures.

Passive samplers were placed indoor (1 in the living room and 1 in the bedroom in 10 different houses) and exposed for 15 days. After that, Tenax®-TA passive samplers were returned in their glass tube, capped and stored in a freezer at -18°C until analysis.

A custom made vacuum cleaner head was used for collection of indoor dust on a SiC© foam placed between the head and a commercial vacuum cleaner tube (figure S2). The

sampling head was designed to maintain the SiC foam (figure S2) and is made of aluminum in 207 order to decrease phthalates contamination. The extremity of the head present a reduction of 208 diameter allowing to increase the air linear velocity, facilitating the impaction of dust on the 209 210 whole surface of the SiC[©] foam. The use of adsorbent foam in the sampler head is a guaranty that no losses of the more volatile compounds will occur during sampling. As the SiC© foam 211 is extracted after the sampling with ASE, the particulate and volatilized fraction of the studied 212 molecules will be extracted together. Before sampling and before extraction, SiCO foams 213 214 were weighed to obtained the mass of dust sampled. After extraction, SiCO were ultrasonicated in ACN for the complete removing of dust particles before re-use. 215

The head was also conceived to meet the standards sizes of commercial vacuum cleaners pipes, allowing the use of any vacuum cleaner on the field and consequently, eliminating the need to carry one in every sampled dwelling.

The sampling was done on a 2 m² surface of the corridor or the living room in order to accumulate enough dust. After sampling, the SiC $^{\odot}$ foam was placed in an aluminum foil and stored at -18 $^{\circ}$ C before weighting, extraction and analysis.

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223 2.4. Accelerated solvent extraction (ASE) of dust samples

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Indoor dust extraction was carried out with an ASE 300. SiC© foam were placed in 33 mL stainless steel cells. Cells were then filled with pure ACN and heated at 150°C under the pressure of 103 bars for 10 min. A high purity nitrogen flow was then applied to purge and dry the cells content for 5 min, and extracts were recovered in clean glass jars. The process was repeated only twice as a third extraction cycle did not improve the compounds recovery. The extract was evaporated to a volume less than or equal to 1 mL by natural evaporation under a fume hood and then completed up to this volume with ACN in order to obtain aknown volume.

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234 2.5. Bioaccessibility experiments

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Bioaccessibility experiments were performed on dust spiked with all the molecules of interest. The dust used was previously collected (about 100 mg) on the field using a metallic shovel and spatula previously cleaned to avoid contamination by phthalates during sampling. Before spiking, dust samples have been cleaned from any organic contaminant by ASE extraction following the protocol used for SiC© dust sampling.

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A volume of 10 mL of synthetic saliva was mixed with 100 mg of spiked dust during 10 seconds under stirring. Immediately, 1 mL of the solution was collected and the rest was transferred in a jar containing 100 mL of the gastric solution maintained at 37°C under stirring for 2 hours. Then, 1 mL of this gastric juice was collected and the remaining solution was adjusted to pH 7 with sodium hydrogenocarbonate. Pancreatine was added to mimic an intestinal solution that was stirred at 37°C for 2 hours. After that, 1 mL was again collected.

The analysis of each 1 mL solution permits the determination of the quantity of pollutant solubilized by each synthetic solution by comparison with the initial pollutants concentration in the dust samples.

The same experiment was repeated but the last step involving the intestinal solution was replaced by a colon solution.

In addition, a last experiment was carried out by placing the spiked dust in ultrapure water under the same conditions (stirring and 37°C). Samplings were done at regular intervals to

evaluate the potential effects of enzymes and salts from the synthetic mimicking solutionscompared to a simpler medium like pure water.

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258 2.6. Preparation of samples for analysis by ATD-GC/MSMS

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- 260 *2.6.1. Passive tubes*

Tenax®-TA tubes were placed upside down in empty stainless steel tubes (89 mm x 5 mm i.d.). Then 100 μ L of ACN, 10 μ L of a mix of internal standards (naphthalene-d₈, trifluralin d₁₄, nitrophenol d₄, *pp*'-DDE d₈, *pp*'-DDT d₈, DEHP d₄, *trans*-cypermethrin d₆) and 10 μ L of the derivatization agent, M*t*BSTFA, were added. The liquid was then allowed to spread during 5 min before the tube being flipped and placed on the ATD autosampler. ACN was added in order to create a medium comparable to the dust samples analysis and the calibration procedure.

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269 *2.6.2. Dust samples*

For dust particles, an extra-step involving spiking the tube placed upside down with 100 μ L of dust extract is required. For this, conditioned Tenax®-TA clean passive sampling tubes, placed in empty stainless steel tubes (89 mm × 5 mm i.d.), were used as support for analysis. As for passive samplers, 10 μ L of a mix of internal standards (naphthalene-d₈, trifluralin-d₁₄, nitrophenol-d₄, *pp*'-DDE-d₈, *pp*'-DDT-d₈, DEHP-d₄, *trans*-cypermethrin-d₆) and 10 μ L of the derivatization agent, M*t*BSTFA, were deposited. The liquid was then allowed to spread during 5 min before returning the tube and inserting it in the ATD autosampler.

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278 *2.7. ATD procedure*

Analyses were carried out by using an automatic thermal desorption system (ATD 350, 280 PerkinElmer Corp.; Norwalk, CT, USA) connected to a Trace 1300 GC coupled to an ITQ 281 900 mass spectrometer (Thermo Scientific). ATD 350 was coupled to a GC-MS/MS system 282 via a valve and a transfer line maintained at 280°C and 300°C respectively. The thermal 283 desorption is a two steps desorption. First, a 2 min tube purge with helium (He) at a flow rate 284 of 45 mL min⁻¹ take place; then, a desorption step occurs when the sample tube is heated at 285 300°C during 30 min under a He flow stream (45 mL min⁻¹). All compounds are refocused in 286 a cold trap maintained at -30°C by Peltier effect. At the end, the trap is heated to 300°C by 287 induction (temperature rate 40° C s⁻¹) for a flash desorption step. 288

289

290 *2.8. SPME procedure*

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Prior to GC-MS/MS injection, 1 mL of bioaccessibility solutions was added in a vial filled to 19 mL of 1.5 % NaCl ultrapure water and pre-concentrated by SPME using a CTC CombiPAL autosampler. The SVOCs were extracted for 45 min at 60°C using a PDMS (100 μ m) fiber. Just before the PDMS fiber desorption, 2 μ L of M*t*BSTFA, used as derivatisation agent, were manually and directly injected to the GC injection port [29, 41].

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298 2.9. GC/MSMS analysis

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300 Compounds from ATD and SPME desorption were separated on a Macherey-Nagel 301 OPTIMA XLB capillary column (60 m × 0.25 mm i.d.; 0.25 μ m film thickness) with He as 302 carrier gas with an electronically regulated constant flow of 1.2 mL min⁻¹. The GC oven 303 temperature ramp starts at 50°C, hold 3 min, then increasing at a rate of 40°C min⁻¹ to 240°C

then 1.5°C min⁻¹ to 255°C hold for 5 min, and a rate of 20°C min⁻¹ to 330°C hold 18 min for a
total acquisition program of 45 min.

Spectra of compounds were obtained in electron impact (EI) ionization mode at 70 eV electron energy. Transfer line temperature was set up at 300°C and source temperature at 200°C. The most abundant ion of a full scan analysis of each compound was selected as precursor ion for the second ionization step. Collision induced dissociation (CID) was performed in resonant mode. The highest abundant product ions were then selected as characteristic ions for each compound. The selected ions for MSMS analysis, the CID excitation voltage, and the retention times are presented in table 1.

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- 314

315 **3. Results and discussion**

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317 *3.1. SiC*[©] foam

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SiC[©] is a mesoporous to macroporous material, initially used as catalyst support, which has 319 shown interesting properties as passive air sampler [39]. The diversity of pore size (ranging 320 321 from 2 nm to 50 nm for the internal structure and from 0.5 to 4 mm for the peripheral structure) allows simultaneous sampling of gaseous and particulate phases, which is 322 323 interesting in the case of active sampling where most volatiles compounds may be transferred from the particulate to the gas phase due to the depression created by the vacuum cleaner. The 324 mean specific surface area of the SiC[©] material is 30 m² g⁻¹ which is close to the Tenax[®] (35 325 m² g⁻¹). SiC[©] foams were designated with precise dimensions (laser cutting) in order to fit in 326 327 the sampling device and in Accelerated Solvent Extractor stainless steel cells (33 mL) with 328 low remaining space.

331

Stability was tested by spiking previously conditioned Tenax®-TA sampling tubes and 332 333 cleaned SiC[©] foams with standard mix (10 ng of each compound deposited) and stored in the dark at -18°C in capped glass tubes surrounded by Teflon rubber and aluminium foil, for 334 passive tubes and SiC[©] foam respectively, for two months, period that largely exceed the real 335 delay applied during these experiments. After the storage period, Tenax®-TA tubes and SiC 336 foams were extracted and analyzed. No loss of compounds was observed (100 % recovery for 337 all molecules), demonstrating that the storage procedure did not alter the quality of the 338 sample. 339

Some passive tubes and SiC foams were stored immediately after cleaning for two months as blanks. No molecules under study were detected confirming the efficiency of the cleaning and storage procedure used. Some others were wrapped in aluminum foil and exposed in the field for 15 days for passive samplers and 30 days for SiC foam. Their extraction and analysis did not show any compounds under study.

Phthalates are a category of molecules which are analyzed with the developed method. It is known that phthalates are ubiquitous contaminants and some false positive can occurred. In order to evaluate the potential contamination by phthalates during all analytical procedure, some experiments were done. The first one consists to equip a shelter with a clean passive sampling tube and covered it entirely with an aluminum foil. After 15 days, the foil is removed, and the passive tube is analyzed. No phthalates were detected confirming that no emissions of phthalates occur from the shelter.

352

353 *3.3. Bioaccessibility experiment*

Digestion was done using a rotary evaporators allowing the continuous stirring (20 rpm) of 355 356 the solution at constant temperature (37°C) in order to simulate the physiological conditions. Different synthetic solutions mimicking body fluids were tested successively; saliva, gastric, 357 intestinal and colon. The composition of the solutions is summarized in table S1.. This 358 experimental system simplifies the procedure when the digestive procedure includes 359 successive steps (contacts with saliva followed by gastric and intestinal solutions). The 360 361 diverse solutions were added in an ovoid balloon foiled with an aluminum foil as the digestive process occurs in the dark. The part of the evaporator devoted to the condensation of vapors is 362 plugged in order to isolate the system from the environment. 363

364

Two systems were used in parallel to perform the experiments in duplicates.

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366 *3.4. GC/MSMS liquid injection*

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The separation optimization of the target compounds and the MSMS development was 368 369 performed by liquid injection of individual and the total set of compounds. The flow rate of He was first fixed at 1.5 mL min⁻¹ as the column is connected to the ATD system [29] and 370 reduced to 1.2 mL min⁻¹ for the optimization of the temperature gradient. An isotherm for 371 372 3 min at 50°C was also fixed to allow the compounds desorbed from ATD of SPME fiber to be accumulated in the top of the column before starting the temperature gradient. This 373 gradient was identical to the one used for thermal desorption and is already described in the 374 Material and Methods section. 375

Concerning the inlet liner, it has been observed that the use of a liner SKY provided by RESTEK© permits, in particular at the end of the temperature gradient, to increase the chromatographic resolution and the sensitivity of very low volatile molecules like coronene in

379 comparison to classic SSL liner as shown in figure 1. This inlet liner was then selected for380 liquid and SPME injections.

381

382 *3.5. Thermal desorption conditions for passive samplers and dust samples*

Tenax®-TA passive sampling tubes do not require any steps before analysis. They can be 383 analyzed directly after spiking with an internal standard mixture and a derivatization agent. 384 The derivatization is required for some pesticides in order to improve their volatilisation 385 before analysis in ATD-GC-MS/MS and occurs directly in the gas phase in the Tenax®-TA 386 tube during the first thermal desorption step, avoiding a tedious sample preparation prior to 387 388 analysis. The procedure used for the analysis of passive tubes is synthetized in figure 2. The method developed is derived from Raeppel et al. [29] for pesticides and was extended with 389 390 success for PAHs, PCBs, phthalates and phenols without changing the desorption flow rate, 391 time and temperature, trap head and velocity of trap desorption. Some experiments have been done in order to confirm these points and it was demonstrated that previously published 392 general conditions are optimum also for PAHs, PCBs, phthalates and phenols desorption. 393 However, it was not possible to include PBDEs in this method due to the known problem of 394 temperature stability for some of these compounds (i.e. BDE 209) in particular with a long 395 length capillary column. 396

As dust samples cannot be directly introduced into empty thermal desorption tubes, an extraction and concentration step before analysis is required. For this purpose, the use of ASE conditions developed for XAD-2© resin passive samplers was chosen [42]. As the ASE cells used are 33 mL, the final volume of ACN was 80 mL and this volume was reduced to 1 mL into a fume hood at laboratory temperature. Fume hood was chosen as this slow technique (one night) allows avoiding the evaporation of the more volatile compounds with ACN as 403 long as one takes care that no dryness occurs in the vial to avoid irremediable loss of all404 compounds.

Recoveries were determined by spiking SiC© resin with a mixture of compounds under study that were treated as a normal sample (extraction + evaporation step). Recovery percentage of known amount of standard extracted from dust shows good capabilities of ASE to recover most of the pollutants despite their different physicochemical properties. Some of the recovery percentages are greater than 100% due to uncertainties. The lowest recovery rate is obtained for Bisphenol A with 28.5%. Mean recoveries obtained for each compound are summarized in table 1.

An aliquot of the extract (100 μ L) was then deposited on a clean Tenax®-TA passive sampling tube and internal standard mixture and derivatization agent were added. This procedure permits to increase drastically the sensitivity by comparison with a classical liquid injection of 1 μ L of extract. Even if the extract was concentrated to a lower amount than 1 mL, the sensitivity was not comparable to the one obtained by the deposition on a Tenax®-TA tube. The procedure for dust samples analysis is synthetized in figure 2.

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419 *3.6. SPME pre-concentration of bioaccessibility solutions*

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All bioaccessibility solutions (saliva, gastric and intestinal fluids) are aqueous and consequently, the quantification of pollutants requires an extraction step such as liquid-liquid (LLE) or Solid-Phase Extraction (SPE) followed by an evaporation step. The use of SPME allows avoiding these steps by extracting the compounds directly in a low concentrated aqueous solution with very low LOQs (table 3). The final procedure for SPME analysis is synthetized in figure 2.

The choice of the phase for SPME extraction was done regarding previous studies on 427 SPME made by Mokbel et al. [37], Levy et al. [42] and Al-Alam et al. [43]. Generally, 428 Polyacrylate fiber (PA - 65 µm) is chosen for pesticides while Polydimethylsiloxane (PDMS -429 100 µm) is preferred for PAHs and PCBs. The performance of the PDMS fiber for pesticides, 430 phthalates and alkylphenols was evaluated and compared to PA fiber and PDMS was selected 431 since the slightly lower efficiency for pesticides, phthalates and alkylphenols is compensated 432 by the better efficiency of PDMS, PAHs and PCBs. These are usually extracted at 80°C [42] 433 but in order to prevent potential degradation of some pesticides by long exposure at this 434 temperature, it was decided to choose 60°C for the temperature of extraction as it does not 435 436 change the recovery of compounds on the fiber.

437

438 3.7. Calibration, recovery, and sensitivity

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Calibration curves for the quantification of the SVOCs by ATD and SPME were obtained
by analysis of 8 tubes and 8 fibers spiked with increasing amount of a target compounds
mixture (1, 2.5, 5, 7.5, 10, 25, 50, 100 ng respectively). The amount of internal standards was
the same for ATD and SPME.

For ATD-GC/MSMS, spiking each tube is done the same way as for standards and samples: tube upside down with 100 μ L of solution at different concentrations, 10 μ L of internal standards mixture and 10 μ L of M*t*BSTFA allowing liquid to spread in the tubes for 5 min before analysis.

For SPME injection, calibration was carried out by preparing 20 mL aqueous flasks (1.5% NaCl) filled with increasing amount of the molecules. After the exposition time of the fiber and just before injection into the SSL injector, 2 μ L of M*t*BSTFA were added for the derivatization step.

- 452 All calibrations were performed in triplicates.
 - 18

Regression equations and associated coefficient (R²) are presented in table 2 for ATD GC/MSMS. Linear regressions were used when possible, but most of the compounds calibration curves are better fitted with quadratic regression, which can be explained by an influence of the thermal desorption step, maybe a concentration-dependent desorption kinetic, as liquid injection gives linear calibration. The same tendency was also observed for SPME injections and these results are in accordance with previous studies [36, 39, 43, 44-46].

The limits of detection (LOD) and quantification (LOQ) were determined using a graphical approach. The LOD and LOQ represent three and ten times respectively, the ratio between the averaged noise height on each side of a known amount of a compound's peak and the height of the peak. The aim is to determinate the minimal peak heights that can be used to discriminate a compound's peak from the noise found on each side of the peak. LOD and LOQ are presented in table 3.

465

466 *3.8. Application to environmental samples*

467

A sampling campaign was performed in 10 homes at various location around Strasbourg, 468 France (between 0 and 10 kilometers from the Strasbourg center) chosen for their contrasted 469 localization (urban, per-urban, rural, proximity to heavy traffic road,...). Passive air sampling 470 was done on a 15 days basis while dust samples were collected each month during one year. 471 Some results are presented in figures 4 and 3. In figure 4 is presented the mean value for the 472 10 houses of the Σ PAHs in the living room and in the bedroom. It can be observed that 473 474 concentrations present the same evolution whatever the sampling location. In figure 3 is presented the evolution of the concentration of insecticide allethrin. For pesticides, it is better 475 to discuss by molecules as pesticides display very different structure, mode and period of 476 application. Allethrin is commonly used in electric diffusing spray devices against mosquitos. 477

This use can be seen on the graph as concentrations increase during spring and summer periods in the air. The difference observed for the living room and the bedroom can be explained by the difference of ventilation between these two rooms. The allethrin concentration in dust is relatively homogeneous which can be explained by the mode of application by diffusion in the air of this insecticide.

Concerning bioaccessibility experiments, about 100 mg of indoor dust were treated using the protocol defined in the Materials and Method section. Some results are presented in table 485 4 and the comparison of the quantities of analytes in the dust samples and those found in the 486 biological fluids lead to a percentage of bioaccessibility for each compound. The quantity of 487 analytes in the dust was obtained by ASE extraction and analysis by ATD-GC/MSMS [30].

488

489

490 **4. Conclusion**

491

492 The method developed in this work allows the analysis of a large set of indoor air organic pollutants of various chemical families in different matrices with a very good sensitivity and 493 accuracy. In particular, the use of thermal desorption for the quantification of polar and/or 494 thermolabile molecules was possible by the addition of an "in-tube" derivatization step. The 495 use of thermal desorption instead of classical liquid injection for the quantification of indoor 496 dust after solid/liquid extraction was also found to be very sensitive and simple. For 497 bioaccessibility experiments, SPME were chosen at it permits without interferences to analyse 498 499 directly the bioaccessibility solutions, avoiding any procedure like Liquid-Liquid of Solid-Phase extraction. The proposed protocol for the evaluation of the bioaccessibility along the 500 501 gastrointestinal tractus was also found to be representative to real conditions.

With the proposed method coupling Accelerated Solvent Extraction, thermal desorption and GC/MSMS, it will be possible to consider analyzing other type of samples than dust following the same procedure like soils, sediments, plants, fruits, or other biological matrices like pine needles, snails or earthworms, ... for biomonitoring purposes.

506

507 **Credit author statement**

508 Alexandre Sonnette has performed the development of the method

Laurent Alleman and Olivier Delhomme have participated to the supervision of AlexandreSonnette work.

511 Maurice Millet, Laurent Alleman and Patrice Coddeville have applied and obtained the512 funding of the Alexandre Sonnette Ph.D grant.

513 Maurice MILLET has participated to the supervision of the development of the 514 methodology and of the co-supervision of Alexandre Sonnette thesis with Patrice Coddeville.

515 All authors took part in the writing of the manuscript.

516

517 Declaration of Competing Interest

518

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

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528

529

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Fig. 1. Comparison between SKY liner and standard liner for the analysis of 10 mg.L⁻¹ coronene (1 µL injection in splitless mode, full scan)



Fig. 2. Details of the three analytical methods developed.



Fig. 3. Evolution of air concentration of the mean value of the \sum PAHs for all the sampled houses (n = 10) in the living room (AS) and in the bedroom (AC).



Fig. 4. Evolution of the concentration of allethrin (mean concentration for each month on the 10 houses) in the living room and in the bedroom for air and in dust (only living room).

Table 1.

Retention time (RT), precursor ion and product ions with associated dissociation energy value in GC-MSMS for each compound

	Compounds	RT (mn)	Precursor ion (m/z)	Excitation voltage	Product ions (m/z)
ISTDs	nanththalene d8	9.25	136	(V) 15	108/132/84/82/80
10125	trifluralin d14	11 18	315	0.8	267/209
	nitrophenol d4	12.28	200	1	139/154/182
	DDF d8	18.10	254	13	184/149/219
	DDE d8	20.20	173	1,5	137/138
	nhthalate d4	20.20	153	1,0	153
	<i>trans</i> -cypermethrin d6	27.54	183	0.9	168/165/153
PAHs	napththalene	9.31	128	1.2	102/126/76/77/78
11115	acenaphthene	10.83	153	13	150/151/126
	fluorene	11.47	165	1,3	163/139/115
	phenanthrene	13.26	178	1.2	152/176/151
	anthracene	13.35	178	1.2	152/176/151
	fluoranthene	17.23	202	1.3	200
	nvrene	18.39	202	1,2	200
	benzo[a]anthracene	25.75	228	1,2	226/202
	chrysene	25.92	228	1.2	226/202
	benzo[b]fluoranthene	29.57	252	1.3	250/226
	benzo[k]fluoranthene	29.57	252	13	250/226
	benzo[e]pyrene	30.75	252	1,3	250/226
	benzo[a]pyrene	30.98	252	13	250/226
	dibenzo[a h]anthracene	34.43	232	1,5	276
	indeno[1 2 3]pyrene	34 45	276	1,5	274
	henzo[g.i.h]pervlene	35.93	276	1.4	274
PCBs	PCB 18	12.73	256	1,1	186/221
1020	PCB 31	13.78	256	1.2	186/151/150
	PCB 28	13.85	256	1.2	186/151/150
	PCB 52	14.47	292	1.2	222/220/257/255
	PCB 44	15.03	292	1.2	222/220/257/255
	PCB 70	16.42	292	1.3	222/220/185/150
	PCB 101	16.93	326	1.2	256/254/291
	PCB 81	18.82	292	1.3	222/220/185/150
	PCB 149	19.45	360	1,2	290/288/325/323
	PCB 123	19.94	326	1,3	256/254
	PCB 153	20.53	360	1,3	290/288
	PCB 114	20.49	326	1,3	256/254
	PCB 118	20.18	326	1,3	256/254
	PCB 105	21.36	326	1,4	256/254
	PCB 138	22.13	360	1,3	290/288/325
	PCB 126	23.59	326	1,4	256/254
	PCB 167	24.16	360	1,5	290/288/218
	PCB 156	25.33	360	1,5	290/288/218
	PCB 180	25.56	396	1,3	324/326/361
	PCB 157	25.44	360	1,5	290/288/218
	PCB 169	26.66	360	1,5	290/288/218

	PCB 189	27.42	396	1,8	326/324
Pesticides	dichlobenil	10.06	171	1,8	100/136
	trifluralin	11.23	264	1,5	206/188/171/160
	propachlor	11.33	120	1,4	117/103/92/77
	α-HCH	12.26	183	1,3	147/148/145/146/109
	clopyralid	12.42	248	1,5	204/168/146
	flazasulfuron	12.49	231	1,5	216/188/131
	ү-НСН	12.83	183	1,4	147/148/145/146/109
	mecoprop-p	12.94	225	1,5	209/197/163
	dicamba	13.14	279	1,4	264/235/205
	2,4-MCPA	13.42	211	1,3	183
	acetochlor	13.47	146	1,5	131/118/91
	alachlor	13.64	160	0,9	132/117/145
	dichlorprop	13.70	245	1,2	209/229/217
	chlorothalonil	14.12	266	1,7	170/205/231
	2,4-D	14.30	213	1,5	183/198/163
	metolachlor	14.59	162	1	133/118
	aldrin	15.00	263	1,8	193/191/227/228
	triclopyr	15.00	312	1,4	254
	esbiothrin	15.36	123	1,2	81/95
	allethrin	15.36	123	1,2	81/79/95/77/67
	cyprodinil	15.63	224	2,1	208
	prallethrin	15.82	123	1,3	81/95
	metazachlor	15.94	132	1,6	117
	o,p'-DDE	16.70	246	1,9	150/176
	pentachlorophenol	16.86	323	1,5	288/214/252
	oxadiazon	17.29	175	1,1	146/112/140
	fluroxypyr	17.15	253	1,5	217/159/182
	α-endosulfan	17.81	241	1,6	206/204/170/171
	buprofezin	17.63	105	1,2	77
	p,p'-DDE	18.07	246	1,9	176/150
	o,p'-DDD	18.20	235	1,4	199/165/200/163
	myclobutanil	18.90	179	1,2	125/144/152
	dieldrin	18.88	279	1,6	243/241/206/209/207
	picloram	19.19	297	2	253/217/189
	imiprothrin	19.71	123	1,3	81/95
	p,p'-DDD	20.74	235	1,5	165/163/199/200
	o,p'-DDT	20.12	235	1,5	199/165/200/163
	β-Endosulfan	21.15	195	1,6	159/160/123/125
	propiconazole	22.07	173	1,6	144/108
	piperonyl butoxide	22.05	176	1,4	131/117/145/161
	p,p'-DDT	22.22	235	1,5	165/199/163/200
	diflufenican	23.00	266	1,7	218/245/183
	tebuconazole	23.42	125	1,4	89/99
	bifenthrin	23.51	181	1,6	166
	tetramethrin	24.42	164	1,4	107/93/135
	cyphenothrin	26.81	181	1,7	152
	permethrin	27.33	183	1,5	168/165/153
	α-cypermethrin	28.96	181	1,8	152

	τ-fluvalinate	29.91	250	1,7	250
	deltamethrin	31.17	181	1,6	152
Alkylphenols	4-octylphenol	14.70	165	0,9	135/91
	4-nonylphenol	16.03	165	0,8	135/91
	octylphenol monoethoxylate	16.90	307	0,9	177/195/161
	octylphenol diethoxylate	23.57	233	1	159/177/135/131/149/163
	bisphenol A	26.94	441	1,8	327/233/267/269/323
Phthalates	phthalate DMP	10.35	163	1	133/105/135
	phthalate DEP	11.01	149	1	121/93/131
	phthalate DBP	12.72	149	1	121/93
	phthalate DIBP	13.87	149	1	121/93
	phthalate DPP	16.41	149	1	121/93
	phthalate BBP	20.80	149	1	121/93/126
	phthalate DEHP	24.86	149	1	121/93/122

Table 2.

Calibration curve,	coefficient of	f determination	and variation and	revovery for each	compound in ATD GC/MSMS
,				2	1

	Compounds	Equation	R ²	CV %	Recovery (%)
PAHs	napththalene	$Y = 0.616764 \times x$	0.9893	13.0	89.5
	acenaphthene	$Y = 0.583448 \times x$	0.9999	1.9	85.7
	fluorene	$Y = 4.29551 \times x + 0.0394102 \times x^2$	0.9985	2.0	126.7
	phenanthrene	$Y = 0.03390 \times x + 9.76278e - 005 \times x^2$	0.9985	9.9	98.5
	anthracene	$Y = 0.0516385 \times x$	0.9966	8.0	106.8
	fluoranthene	$Y = 2.28229 \times x + 0.347818 \times x^2$	0.9996	3.4	62
	pyrene	$Y = 83.0575 \times x + 4.90224 \times x^2$	0.9992	14.4	61.9
	benzo[a]anthracene	$Y = 3.77313 \times x$	0.9959	9.2	64.3
	chrysene	$Y = 66.2729 \times x + 0.0710232 \times x^2$	0.9978	32.8	57.8
	benzo[b]fluoranthene	$Y = -1.76584 \times x + 0.708726 \times x^2$	0.9995	13.4	72.3
	benzo[k]fluoranthene	$Y = 25.1649 \times x + 0.712638 \times x^2$	0.9991	21.3	68.7
	benzo[e]pyrene	$Y = 10.3666 \times x + 0.694201 \times x^2$	0.9972	18.1	52.9
	benzo[a]pyrene	$Y = -0.466507 \times x + 1.82594 \times x^2$	0.9995	13.2	43.6
	dibenzo[a,h]anthracene	$Y = 0.0579948 \times x$	0.9999	12.8	39.2
	indeno[1,2,3]pyrene	$Y = 1.58456 \times x + 0.0058964 \times x^2$	0.9995	21.0	48.5
	benzo[g,i,h]perylene	$Y = -1.97786 \times x + 0.782992 \times x^2$	0.9977	26.5	34.3
PCBs	PCB 18	$Y = 0.420817 \times x + 0.0138768 \times x^2$	0.9982	22.4	63.4
	PCB 31	$Y = 0.416784 \times x + 0.0138563 \times x^2$	0.9982	7.9	78.2
	PCB 28	$Y = -0.0276346 \times x + 0.00100019 \times x^2$	0.9972	10.4	59.5
	PCB 52	$Y = -0.0158671 \times x + 0.0142522 \times x^2$	0.9999	17.0	90.7
	PCB 44	$Y = -12.1124 \times x + 0.540317 \times x^2$	0.9729	5.2	61.1
	PCB 70	$Y = 0.158359 \times x + 0.00168774 \times x^2$	0.9979	20.9	64.1
	PCB 101	$Y = 0.511832 \times x + 0.0149724 \times x^2$	0.9982	20.6	85.2
	PCB 81	$Y = 0.00703438 \times x + 3.15341e - 005 \times x^{2}$	0.9976	27.5	94.4
	PCB 149	$Y = -2.376 \times x + 0.556923 \times x^2$	0.9999	14.7	59.9
	PCB 123	$Y = 0.0689715 \times x + 0.0196883 \times x^2$	0.9999	18.9	113.4
	PCB 153	$Y = 0.937165 \times x + 0.0460618 \times x^2$	0.9991	18.6	102.3
	PCB 114	$Y = 0.86283 \times x + 0.0193347 \times x^2$	0.9997	22.9	105.2
	PCB 118	Y = -0.0590285×x+0.00503843×x ²	0.9998	16.9	96.1
	PCB 105	$Y = 3.72731 \times x + 0.230528 \times x^2$	0.9993	11.1	71.3
	PCB 138	$Y = 9.48637 \times x + 0.390604 \times x^2$	0.9988	5.3	68.9
	PCB 126	$Y = 3.9681 \times x + 0.228819 \times x^2$	0.9993	17.5	108.6
	PCB 167	$Y = 5.22717 \times x + 0.303399 \times x^2$	0.9992	4.2	76
	PCB 156	$Y = 4.81961 \times x + 0.315149 \times x^2$	0.9993	18.0	60.4
	PCB 180	$Y = 4.80883 \times x + 0.326963 \times x^2$	0.9994	5.9	74.5
	PCB 157	$Y = -3.45235 \times x + 0.573913 \times x^2$	0.9990	2.0	102.4
	PCB 169	$Y = 0.812695 \times x + 0.0719567 \times x^2$	0.9996	38.4	85.4
	PCB 189	$Y = 1.24203 \times x + 0.0235986 \times x^2$	0.9994	16.8	72.9
Pesticides	dichlobenil	$Y = 0.584311 \times x + 0.0149806 \times x^2$	0.9998	25.7	95.5
	trifluralin	$Y = 0.0281514 \times x + 0.00370642 \times x^{2}$	0.9971	27.5	81.6
	propachlor	$Y = -0.0193467 \times x + 0.00101959 \times x^2$	0.9988	14.1	57.2
	α-ΗCΗ	$Y = 0.00314032 \times x + 0.000537147 \times x^2$	0.9991	18.1	77.4
	clopyralid	$Y = -0.229071 \times x + 0.00931519 \times x^2$	0.9988	4.7	59.8
	flazasulfuron	$Y = -0.2983 \times x + 0.0353428 \times x^2$	0.9999	15.4	44.2
	ү-НСН	$Y = -0.664516 \times x + 0.0304934 \times x^2$	0.9992	5.8	80.6

	mecoprop-p	$Y = 0.00562118 \times x$	0.9838	25.9	72.1
	dicamba	$Y = 0.0009972 \times x + 6.67454 e - 005 \times x^2$	0.9986	10.4	54.8
	2,4-MCPA	$Y = 0.00172559 \times x + 1.85696e - 005 \times x^2$	0.9918	19.5	47.4
	acetochlor	$Y = 0.0116542 \times x + 0.00024495 \times x^2$	0.9997	16.4	39.7
	alachlor	$Y = -0.0646043 \times x + 0.0158739 \times x^2$	0.9999	20.0	80.9
	dichlorprop	$Y = 0.253175 \times x + 0.00107106 \times x^2$	0.9921	29.2	47.2
	chlorothalonil	Y = 0.585031×x+0.00132817×x ²	0.9961	21.8	64
	2,4-D	$Y = 0.139607 \times x + 0.00133056 \times x^2$	0.9976	22.3	40.3
	metolachlor	Y = 0.0450239×x+0.000169866×x ²	0.9995	17.7	46.9
	aldrin	Y = 0.0003578×x+5.32758e-005×x ²	0.9991	2.8	65.1
	triclopyr	Y = 0.0008511×x+2.90409e-005×x ²	0.9990	16.9	47.8
	esbiothrin	$Y = -0.208025 \times x + 0.01518 \times x^2$	0.9929	10.2	62.5
	allethrin	$Y = -0.0164852 \times x + 0.00809853 \times x^2$	0.9987	11.3	78.4
	cyprodinil	$Y = 0.589763 \times x + 0.0100304 \times x^2$	0.9981	23.3	59.1
	prallethrin	$Y = 0.0170286 \times x + 0.000584419 \times x^{2}$	0.9988	1.9	68.3
	metazachlor	$Y = -0.0173222 \times x + 0.00198511 \times x^{2}$	0.9921	15.0	92
	o.p'-DDE	$Y = 0.214587 \times x + 0.00369748 \times x^{2}$	0.9984	18.6	53.7
	pentachlorophenol	$Y = 1.52246 \times x$	0.9982	6.8	47.2
	oxadiazon	$Y = 0.259649 \times x + 0.0123259 \times x^2$	0.9988	6.4	62.8
	fluroxypyr	$Y = 0.0219126 \times x + 0.000295729 \times x^2$	0.9988	14.2	62
	α-endosulfan	$Y = -0.347037 \times x + 0.0550062 \times x^{2}$	0.9999	13.4	84.1
	buprofezin	$Y = 3.1903 \times x + 0.00150316 \times x^2$	0.9980	1.7	87.4
	n.n'-DDE	$Y = 0.3688745 \times x + 0.0256874 \times x^2$	0.9978	26.1	53.2
	o.p'-DDD	$Y = 0.8796485 \times x + 0.00365894 \times x^{2}$	0.9968	15.7	38.5
	myclobutanil	$Y = -0.0119564 \times x + 0.00126635 \times x^2$	0.9990	16.9	54.2
	dieldrin	$Y = -0.0404649 \times x + 0.00861221 \times x^2$	0.9990	11.8	80.6
	nicloram	$Y = 0.02547874 \times +0.0014587 \times x^{2}$	0 9984	12.5	47.8
	imiprothrin	$Y = 0.0129142 \times x + 0.00181641 \times x^2$	0 9984	10.1	69.5
	n n'-DDD	$Y = 2.356898 \times x + 0.0158745 \times x^2$	0 9990	4 1	54
	o p'-DDT	$Y = 1.254693 \times x + 0.3675841 \times x^2$	0.9999	11.3	53
	B-endosulfan	$Y = 0.0507626xx + 0.000120145xx^2$	0.9992	8.0	72.1
	propiconazole	$Y = 0.0189758xx+0.874589xx^2$	0.9996	8.5	41 7
	piperonyl butoxide	$Y = 0.281072 x + 0.00212207 x x^{2}$	0.9857	17.1	32.8
	n n'-DDT	$Y = -8.06502xx + 0.356577xx^{2}$	0.9091	3.8	44 3
	diflufenican	$Y = -0.01458741 \times \pm 0.1547854 \times x^2$	0.9975	67	62.9
	tebuconazole	$Y = 0.0291554xx + 0.000119102xx^2$	0.9999	33.5	65.1
	hifenthrin	$V = 0.282973 \times 10.000119102 \times 10^{-1}$	0.9999	18.4	67.7
	tetramethrin	$Y = 0.0196582 \times x + 0.000315872 \times x^2$	0.9999	43	56.2
	cyphenothrin	$V = 6.14848xx \pm 0.0565313xx^2$	0.9999	5.5	74 5
	permethrin	$V = -0.00643462 \times x \pm 0.0177379 \times x^2$	0.9999	19.5	78.1
	g_cypermethrin	$V = 0.300647 \times v \pm 0.00044233 \times v^2$	0.0000	87	69.9
	α-cyperinetinin τ-fluvalinate	$V = 0.445412xx \pm 0.00651781xx^2$	0.9990	6.9	45.2
	deltamethrin	$Y = 0.315458 \times 10.00031761 \times 10^{-1}$	0.9904	0.9 25 0	42.2
Alladabaaala	4 octulnhonol	V = 1.00570xy + 0.00200122xy2	0.0067	25.0	54.2
rankyipitettois	4-nonvlnhenol	Y = 0.3855765516 (000000000000000000000000000000000000	0.9907	20.5	лт о
		$\mathbf{Y} = 0.3033703340.17076000333^{2}$ $\mathbf{V} = 1.21458755710.0025784552^{2}$	0.9970	20.4 20.6	+1.4
	octylphenol disthermulate	$1 = 1.214307 \times 100023704 \times 2$ $V = 3.520775 \times 100217597 \times 2$	0.9937	20.0 13.0	37.5
	bisphenol A	$I = 3.307/43XX+0.021438/XX^{2}$ $V = 0.00726142xy+0.00126090x^{-2}$	0.9934	13.0	28.5
Dhthalata-	phthelata DMD	$\mathbf{V} = 0.05670265702657172$	0.9999	10.0	114.9
r numanates	philatale DMP	$1 = 0.0307930XX + 0.000200331XX^2$	0.9990	17.7	114.0

phthalate DEP	$Y = 0.0192154 \times x + 8.60562e - 005 \times x^2$	0.9968	7.0	102.3
phthalate DBP	$Y = -0.818309 \times x + 0.162187 \times x^2$	0.9999	4.1	109.6
phthalate DIBP	$Y = 0.00245352 \times x + 0.00350707 \times x^2$	0.9999	9.7	99.4
phthalate DPP	$Y = -0.06246 \times x + 0.00616563 \times x^2$	0.9943	17.2	100.4
phthalate BBP	$Y = 0.0231804 \times x$	0.9996	11.7	99.9
phthalate DEHP	$Y = 0.114715 \times x$	0.9991	10.3	122.5

Table 3.	
LOQ and LOD for each of the injection techniques used (ATD, SPME and Liquid))

	Compounds	LOQ ATD (ng)	LOD ATD (ng)	LOQ SPME (ng)	LOD SPME (ng)	LOQ Liq. Inj.(ng)	LOD Liq. Inj.(ng)
ISTD	naphthalene d8	-	-	-	-		
PAH	naphthalene	0.09	0.03	1	2	1	5
Pesticides	dichlobenil	0.25	0.08	1.5	5	2	10
Phthalates	phthalate DMP	0.09	0.03	0.5	2	2	10
PAH	acenaphthene	0.09	0.03	0.75	2	1	5
Phthalates	phthalate DEP	0.09	0.03	0.50	19	1	5
ISTD	trifluralin d14	-	-	-	-		
Pesticides	trifluralin	0.01	0.002	0.04	0.1	0.5	3
Pesticides	propachlor	0.25	0.08	2.0	7	5	10
PAH	fluorene	0.09	0.03	0.9	3.0	5	10
Pesticides	α-НСН	0.22	0.07	1.19	4.0	10	30
ISTD	nitrophenol d4	-	-	-	-		
Pesticides	clopyralid	0.25	0.08	2.0	7.5	8	25
Pesticides	flazasulfuron	0.44	0.13	3	9.5	10	30
PCB	PCB 18	0.04	0.01	0.25	1	1	5
Pesticides	ү-НСН	0.22	0.07	1.75	6	2	10
Phthalates	phthalate DBP	0.09	0.03	0.50	2	1	5
Pesticides	mecoprop-p	0.44	0.13	2	6.5	5	10
Pesticides	dicamba	0.44	0.13	2.5	7.5	10	30
PAH	phenanthrene	0.09	0.03	0.55	2.5	1	5
PAH	anthracene	0.09	0.03	0.55	2.5	1	5
Pesticides	2.4-MCPA	0.44	0.13	2	7.5	10	30
Pesticides	acetochlor	0.25	0.08	8.0	24.0	10	30
Pesticides	alachlor	0.44	0.13	2.75	9.0	5	10
Pesticides	dichlorprop	0.44	0.13	3.25	11	10	30
PCB	PCB 31	0.04	0.01	0.25	0.85	1	5
PCB	PCB 28	0.04	0.01	0.25	0.6	1	5
Phthalates	phthalate DIBP	0.09	0.03	0.70	2.5	3	15
Pesticides	chlorothalonil	0.25	0.08	1.2	4.0	5	10
Pesticides	2.4-D	0.44	0.13	2.35	7.8	5	10
PCB	PCB 52	0.04	0.01	0.25	0.8	1	5
Pesticides	metolachlor	0.44	0.13	2.85	9.5	5	15
Phenols	4-octylphenol	0.04	0.01	0.18	0.6	1	5
Pesticides	aldrin	0.22	0.07	1.5	4.75	10	30
PCB	PCB 44	0.04	0.01	0.2	0.6	1	5
Pesticides	triclopyr	0.44	0.13	3.25	11	10	30
Pesticides	esbiothrin	0.22	0.07	1.82	6.1	10	30
Pesticides	allethrin	0.22	0.07	1.61	5.4	10	30

Pesticides	cyprodinil	0.44	0.13	2.34	7.8	5	10
Pesticides	prallethrin	0.22	0.07	1.47	4.9	10	30
Pesticides	metazachlor	0.44	0.13	3.12	10.4	5	15
Phenols	4-nonylphenol	0.04	0.01	0.15	0.5	1	5
Phthalates	phthalate DPP	0.09	0.03	0.63	2.1	5	10
PCB	PCB 70	0.04	0.01	0.19	0.6	2	8
Pesticides	o.p'-DDE	0.44	0.13	3.25	10.8	10	30
Phenols	octylphenol monoethoxylate	0.56	0.17	4.25	14.2	10	30
Pesticides	pentachlorophenol	0.44	0.13	3.12	10.4	5	15
PCB	PCB 101	0.04	0.01	0.27	0.9	2	8
PAH	fluoranthene	0.15	0.05	1.5	5.0	5	10
Pesticides	oxadiazon	0.44	0.13	2.47	8.2	5	10
Pesticides	fluroxypyr	0.25	0.08	2	6.7	10	30
Pesticides	α-Endosulfan	0.25	0.08	1.52	5.1	5	10
Pesticides	buprofezin	0.44	0.13	3.9	13.0	10	30
ISTD	DDE d8	-	-	-	-		
Pesticides	p.p'-DDE	0.44	0.13	3.5	14.5	10	30
Pesticides	o.p'-DDD	0.44	0.13	3.5	14.5	10	30
PAH	pyrene	0.15	0.05	0.8	2.7	5	10
PCB	PCB 81	0.04	0.01	0.22	0.7	1	5
Pesticides	myclobutanil	0.18	0.05	0.85	2.8	1	5
Pesticides	dieldrin	0.22	0.07	1.05	3.5	5	15
Pesticides	picloram	0.44	0.13	3.51	11.7	10	30
PCB	PCB 149	0.04	0.01	0.16	0.5	1	5
Pesticides	imiprothrin	0.22	0.07	1.47	4.9	5	10
ISTD	DDT d8	-	-	-	-		
PCB	PCB 123	0.04	0.01	0.15	0.5	1	
PCB	PCB 153	0.04	0.01	0.2	0.7	1	5
Pesticides	p.p'-DDD	0.44	0.13	4	15	10	30
PCB	PCB 114	0.04	0.01	0.22	0.7	1	5
Pesticides	o.p'-DDT	0.44	0.13	-	-	5	15
PCB	PCB 118	0.09	0.03	0.78	2.6	5	8
Phthalates	phthalate BBP	0.09	0.03	0.9	3.0	5	10
Pesticides	β-Endosulfan	0.22	0.07	1.82	6.1	5	10
PCB	PCB 105	0.09	0.03	0.81	2.7		5
Pesticides	propiconazole	0.44	0.13	3.8	11.4	5	15
15Pesticides	piperonyl butoxide	0.44	0.13	4.5	12.5	5	10
Pesticides	p.p'-DDT	0.44	0.13	4.5	15	10	30
PCB	PCB 138	0.09	0.03	0.45	1.5	1	5
Pesticides	diflufenicanil	0.22	0.07	2.03	6.8	5	10
Pesticides	tebuconazole	0.44	0.13	3.38	11.3	5	10
Phenols	octylphenol diethoxylate	0.56	0.17	10.1	30.3		
Pesticides	bifenthrin	0.22	0.07	1.05	3.5	5	10
РСВ	PCB 126	0.09	0.03	0.72	2.4	1	5
PCB	PCB 167	0.09	0.03	0.84	2.8	1	5

Pesticides	tetramethrin	amethrin 0.22 0.07 2.1 7.0 5				5	10
ISTD	phthalate d4	-	-	-	-		
Phthalates	phthalate DEHP	0.09	0.03	0.48	1.6	1	5
PCB	PCB 156	0.09	0.03	0.78	2.6	1	5
PCB	PCB 180	0.09	0.03	0.6	2.0	1	5
PCB	PCB 157	0.09	0.03	0.54	1.8	1	5
PAH	benzo[a]anthracene	0.15	0.05	1.15	3.8	2	12
PAH	chrysene	0.15	0.05	1.45	4.8	5	10
Pesticides	cyphenothrin	0.22	0.07	1.61	5.4	5	10
PCB	PCB 169	PCB 169 0.09 0.03 0.6 2		2.0	1	5	
Phenols	bisphenol A	0.09	0.03	-	-	5	10
Pesticides	permethrin	0.22	0.07	1.4	4.7	5	10
PCB	PCB 189	0.09	0.03	0.54	0.54 1.8		5
ISTD	trans-cypermethrin d6	-	-	-	-		
Pesticides	α-cypermethrin	0.36	0.11	3.19	10.6	10	25
PAH	benzo[b]fluoranthene	0.15	0.05	0.8	2.7	5	10
PAH	benzo[k]fluoranthene	0.15	0.05	0.75	2.5	1	5
Pesticides	tau-fuvalinate	0.36	0.11	2.2	7.3	5	10
PAH	benzo[e]pyrene	0.25	0.08	1.76	5.9	5	10
PAH	benzo[a]pyrene	0.25	0.08	1.76	5.9	5	10
Pesticides	deltamethrin	0.44	0.13	-	-	2	8
PAH	dibenzo[a.h]anthracene	0.25	0.08	12.3	37.0	35	85
PAH	indeno[1.2.3]pyrene	0.25	0.08	-	-	35	85
PAH	benzo[g.i.h]perylene	0.25	0.08	-	-	35	85

Table 4.

Quantities and bioaccessibility ratio for some compounds (S=Saliva. G=Gastric. I=Intestinal)

C	·····	I I I I I I I I I I I I I I I I I I I		,	
Compound	Dust	S+G	S+G+I	%S+G	%S+G+I
fluorene	210 ng/g	2.77 ng/g	3.11 ng/g	1.3 %	1.5 %
PCB 52	10.1 ng/g	1.43 ng/g	2.78 ng/g	14.2 %	27.5 %
α-HCH	186.3 ng/g	2.23 ng/g	2.34 ng/g	1.2 %	1.3 %