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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
3 evaluation.

4
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18
19

20 **Abstract**

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

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

35 This method permits the determination of 100 pollutants in a single run, including those
36 requiring a derivatization step, with very low quantification and detection limits. Indeed,
37 ATD-GC/MSMS technic presents very low LOD (0.002 to 0.17 ng) and LOQ (0.007 to 0.56
38 ng) values while SPME-GC/MSMS displays slightly higher LOD (0.044 to 12.3 ng) and LOQ
39 (0.10 to 37.0 ng) ranges.

40

41

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

43

44

45 **1. Introduction**

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

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

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

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

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

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

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

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

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

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

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

145

146

147 **2. Materials and methods**

148

149 *2.1. Reagents and solutions*

150

151 Acetonitrile (ACN) of HPLC quality , PDMS 100 μ m Supelco SPME fibers and Radiello®
152 Tenax®-TA adsorbing cartridges (100 mesh, 4.8 mm diameter) were supplied from Sigma-
153 Aldrich (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.

157 Standards of individual pesticides of Pestanal® quality (> 99 % purity), phthalates,
158 alkylphenols and *N-tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MtBSTFA) were
159 purchased from Fluka (Sigma Aldrich, St. Quentin Fallavier, France), Dr Ehrenstorfer GmbH
160 (Cluzeau Info Labo, St. Foy la Grande, France) or Riedel de Haën (Sigma Aldrich, St.
161 Quentin Fallavier, France). Stock solutions of each standard were dissolved in ACN (HPLC
162 grade supplied by Sigma Aldrich, St. Quentin Fallavier, France) at a concentration of 1 g L⁻¹.

163 For PAHs and PCBs, two mixtures at 0.1 g L⁻¹ of 16 PAHs and 22 PCBs respectively were
164 purchased from Cluzeau Info Labo (St. Foy la Grande, France).

165 Internal standards; naphthalene-d₈, trifluralin d₁₄, nitrophenol d₄, *pp'*-DDE d₈, *pp'*-DDT d₈,
166 DEHP d₄ and *trans*-cypermethrin d₆ were obtained from Sigma-Aldrich (L'Isle d'Abeau,
167 France) and Cambridge isotope laboratories (Cluzeau Info Labo, St. Foy la Grande, France).

168 Calibration and internal standard mixtures at 10 mg L⁻¹ were prepared by appropriate
169 dilution with ACN in vials.

170

171 2.2. Cleaning and storage of passive Tenax®-TA tubes, PDMS fibers and SiC© foam

172

173 to be introduced in and Tenax®-TA adsorbing cartridges were conditioned at 350°C for 45
174 min under 45 mL min⁻¹ Helium (He) flow (99,9999% purity) and were then stored in capped
175 glass tubes surrounded with Teflon rubber at room temperature until exposure or spiking.
176 After exposure, passive sampling tubes were stored in the dark at -18°C in capped glass tubes
177 surrounded with Teflon rubber.

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

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

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

193

194 *2.3. Air and dust sampling*

195

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

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

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

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

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

219 The sampling was done on a 2 m² surface of the corridor or the living room in order to
220 accumulate enough dust. After sampling, the SiC© foam was placed in an aluminum foil and
221 stored at -18°C before weighting, extraction and analysis.

222

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

224

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

231 under a fume hood and then completed up to this volume with ACN in order to obtain a
232 known volume.

233

234 *2.5. Bioaccessibility experiments*

235

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

241

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

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

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

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

255 evaluate the potential effects of enzymes and salts from the synthetic mimicking solutions
256 compared to a simpler medium like pure water.

257

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

259

260 *2.6.1. Passive tubes*

261 Tenax®-TA tubes were placed upside down in empty stainless steel tubes (89 mm x 5 mm
262 i.d.). Then 100 µL of ACN, 10 µL of a mix of internal standards (naphthalene-d₈, trifluralin
263 d₁₄, nitrophenol d₄, *pp'*-DDE d₈, *pp'*-DDT d₈, DEHP d₄, *trans*-cypermethrin d₆) and 10 µL of
264 the derivatization agent, *Mt*BSTFA, were added. The liquid was then allowed to spread
265 during 5 min before the tube being flipped and placed on the ATD autosampler. ACN was
266 added in order to create a medium comparable to the dust samples analysis and the calibration
267 procedure.

268

269 *2.6.2. Dust samples*

270 For dust particles, an extra-step involving spiking the tube placed upside down with 100
271 µL of dust extract is required. For this, conditioned Tenax®-TA clean passive sampling tubes,
272 placed in empty stainless steel tubes (89 mm × 5 mm i.d.), were used as support for analysis.
273 As for passive samplers, 10 µL of a mix of internal standards (naphthalene-d₈, trifluralin-d₁₄,
274 nitrophenol-d₄, *pp'*-DDE-d₈, *pp'*-DDT-d₈, DEHP-d₄, *trans*-cypermethrin-d₆) and 10 µL of the
275 derivatization agent, *Mt*BSTFA, were deposited. The liquid was then allowed to spread
276 during 5 min before returning the tube and inserting it in the ATD autosampler.

277

278 *2.7. ATD procedure*

279

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

289

290 2.8. SPME procedure

291

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

297

298 2.9. GC/MSMS analysis

299

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 µm 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

304 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
305 total acquisition program of 45 min.

306 Spectra of compounds were obtained in electron impact (EI) ionization mode at 70 eV
307 electron energy. Transfer line temperature was set up at 300°C and source temperature at
308 200°C. The most abundant ion of a full scan analysis of each compound was selected as
309 precursor ion for the second ionization step. Collision induced dissociation (CID) was
310 performed in resonant mode. The highest abundant product ions were then selected as
311 characteristic ions for each compound. The selected ions for MSMS analysis, the CID
312 excitation voltage, and the retention times are presented in table 1.

313

314

315 **3. Results and discussion**

316

317 *3.1. SiC© foam*

318

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

329

330 *3.2. Storage and QA/QC of samples*

331

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

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

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

352

353 *3.3. Bioaccessibility experiment*

354

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

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

365

366 *3.4. GC/MSMS liquid injection*

367

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

376 Concerning the inlet liner, it has been observed that the use of a liner SKY provided by
377 RESTEK© permits, in particular at the end of the temperature gradient, to increase the
378 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 for
380 liquid and SPME injections.

381

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

383 Tenax®-TA passive sampling tubes do not require any steps before analysis. They can be
384 analyzed directly after spiking with an internal standard mixture and a derivatization agent.
385 The derivatization is required for some pesticides in order to improve their volatilisation
386 before analysis in ATD-GC-MS/MS and occurs directly in the gas phase in the Tenax®-TA
387 tube during the first thermal desorption step, avoiding a tedious sample preparation prior to
388 analysis. The procedure used for the analysis of passive tubes is synthetized in figure 2. The
389 method developed is derived from Raepfel et al. [29] for pesticides and was extended with
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
392 done in order to confirm these points and it was demonstrated that previously published
393 general conditions are optimum also for PAHs, PCBs, phthalates and phenols desorption.
394 However, it was not possible to include PBDEs in this method due to the known problem of
395 temperature stability for some of these compounds (i.e. BDE 209) in particular with a long
396 length capillary column.

397 As dust samples cannot be directly introduced into empty thermal desorption tubes, an
398 extraction and concentration step before analysis is required. For this purpose, the use of ASE
399 conditions developed for XAD-2® resin passive samplers was chosen [42]. As the ASE cells
400 used are 33 mL, the final volume of ACN was 80 mL and this volume was reduced to 1 mL
401 into a fume hood at laboratory temperature. Fume hood was chosen as this slow technique
402 (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 all
404 compounds.

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

412 An aliquot of the extract (100 µL) was then deposited on a clean Tenax®-TA passive
413 sampling tube and internal standard mixture and derivatization agent were added. This
414 procedure permits to increase drastically the sensitivity by comparison with a classical liquid
415 injection of 1 µL of extract. Even if the extract was concentrated to a lower amount than
416 1 mL, the sensitivity was not comparable to the one obtained by the deposition on a Tenax®-
417 TA tube. The procedure for dust samples analysis is synthetized in figure 2.

418

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

420

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

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

437

438 *3.7. Calibration, recovery, and sensitivity*

439

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

444 For ATD-GC/MSMS, spiking each tube is done the same way as for standards and
445 samples: tube upside down with 100 μL of solution at different concentrations, 10 μL of
446 internal standards mixture and 10 μL of *Mt*BSTFA allowing liquid to spread in the tubes for
447 5 min before analysis.

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

452 All calibrations were performed in triplicates.

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

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

465

466 *3.8. Application to environmental samples*

467

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

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

483 Concerning bioaccessibility experiments, about 100 mg of indoor dust were treated using
484 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
493 pollutants of various chemical families in different matrices with a very good sensitivity and
494 accuracy. In particular, the use of thermal desorption for the quantification of polar and/or
495 thermolabile molecules was possible by the addition of an “in-tube” derivatization step. The
496 use of thermal desorption instead of classical liquid injection for the quantification of indoor
497 dust after solid/liquid extraction was also found to be very sensitive and simple. For
498 bioaccessibility experiments, SPME were chosen as it permits without interferences to analyse
499 directly the bioaccessibility solutions, avoiding any procedure like Liquid-Liquid or Solid-
500 Phase extraction. The proposed protocol for the evaluation of the bioaccessibility along the
501 gastrointestinal tractus was also found to be representative to real conditions.

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

506

507 **Credit author statement**

508 Alexandre Sonnette has performed the development of the method

509 Laurent Alleman and Olivier Delhomme have participated to the supervision of Alexandre
510 Sonnette work.

511 Maurice Millet, Laurent Alleman and Patrice Coddeville have applied and obtained the
512 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

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

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528

529

530 **References**

531

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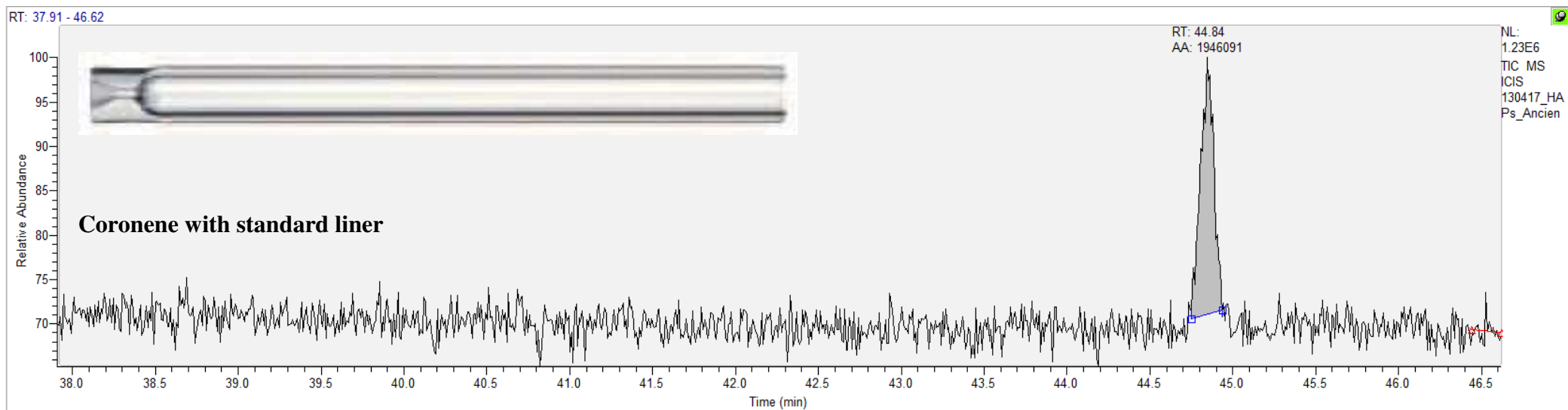
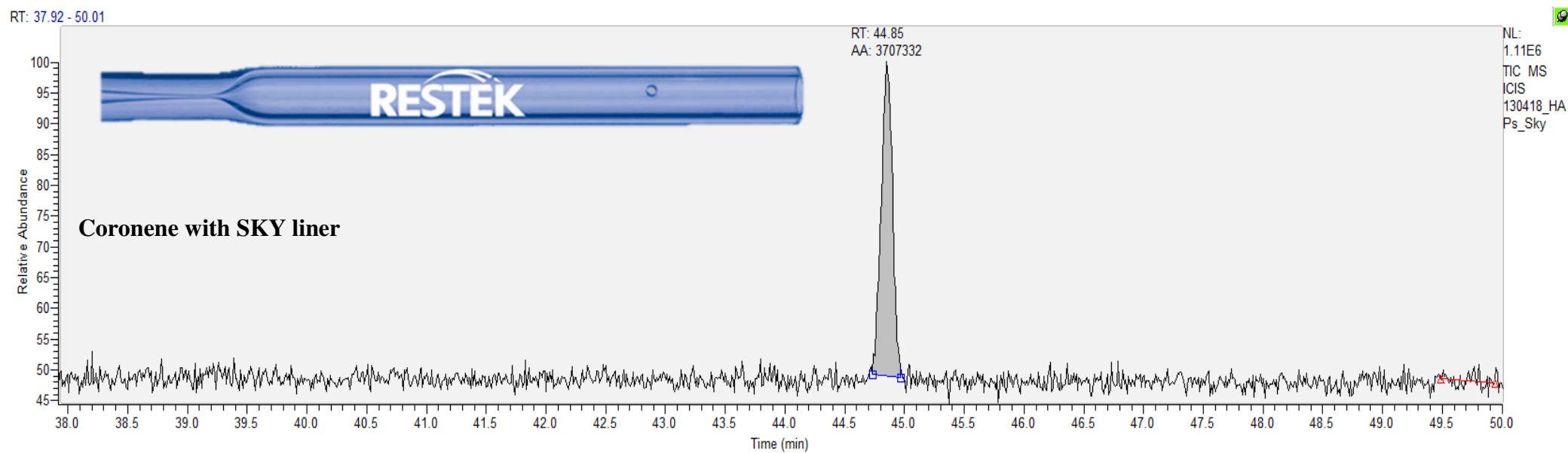


Fig. 1. Comparison between SKY liner and standard liner for the analysis of 10 mg.L^{-1} coronene ($1 \mu\text{L}$ injection in splitless mode, full scan)

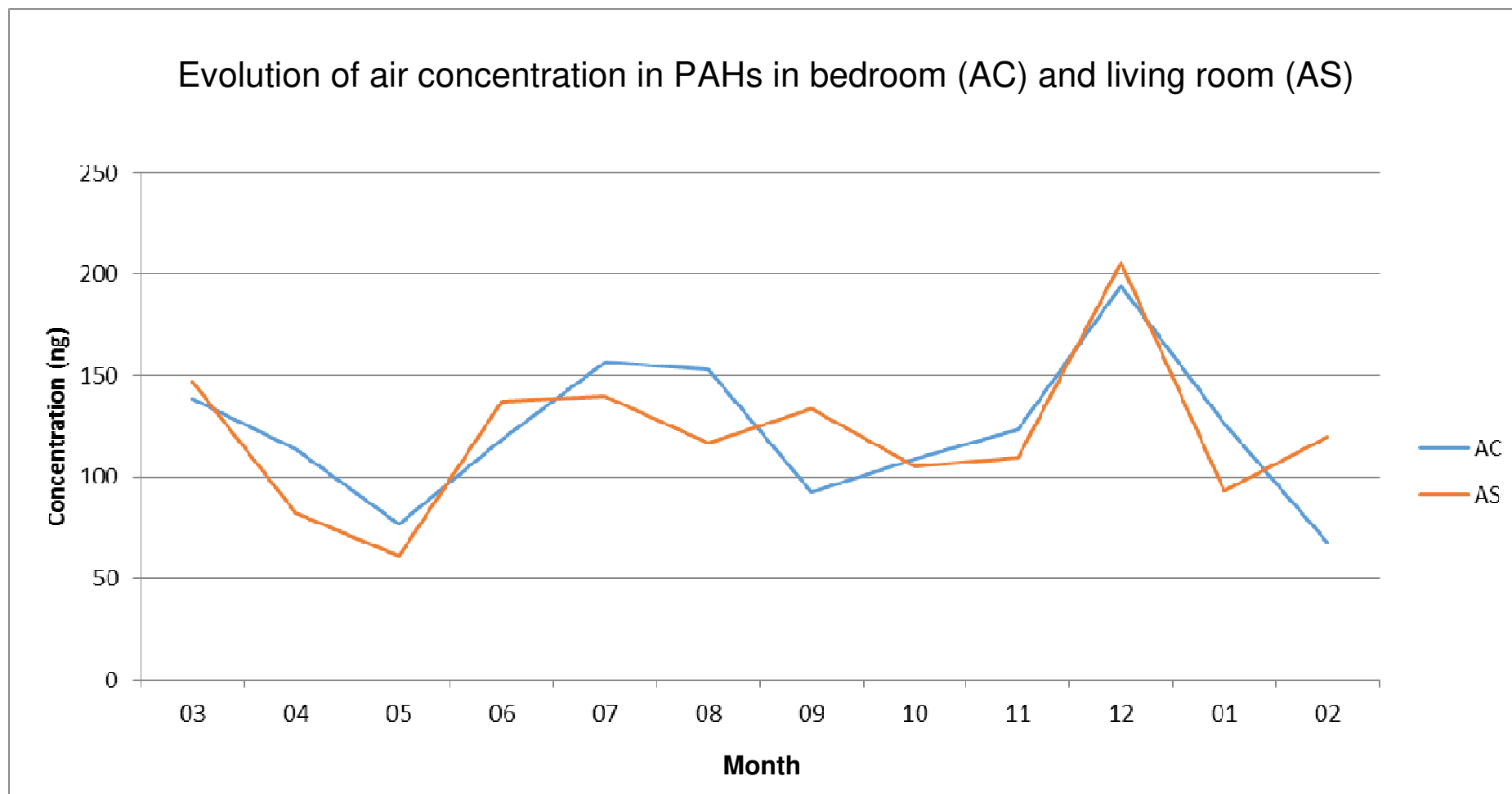


Fig. 3. Evolution of air concentration of the mean value of the Σ PAHs for all the sampled houses (n = 10) in the living room (AS) and in the bedroom (AC).

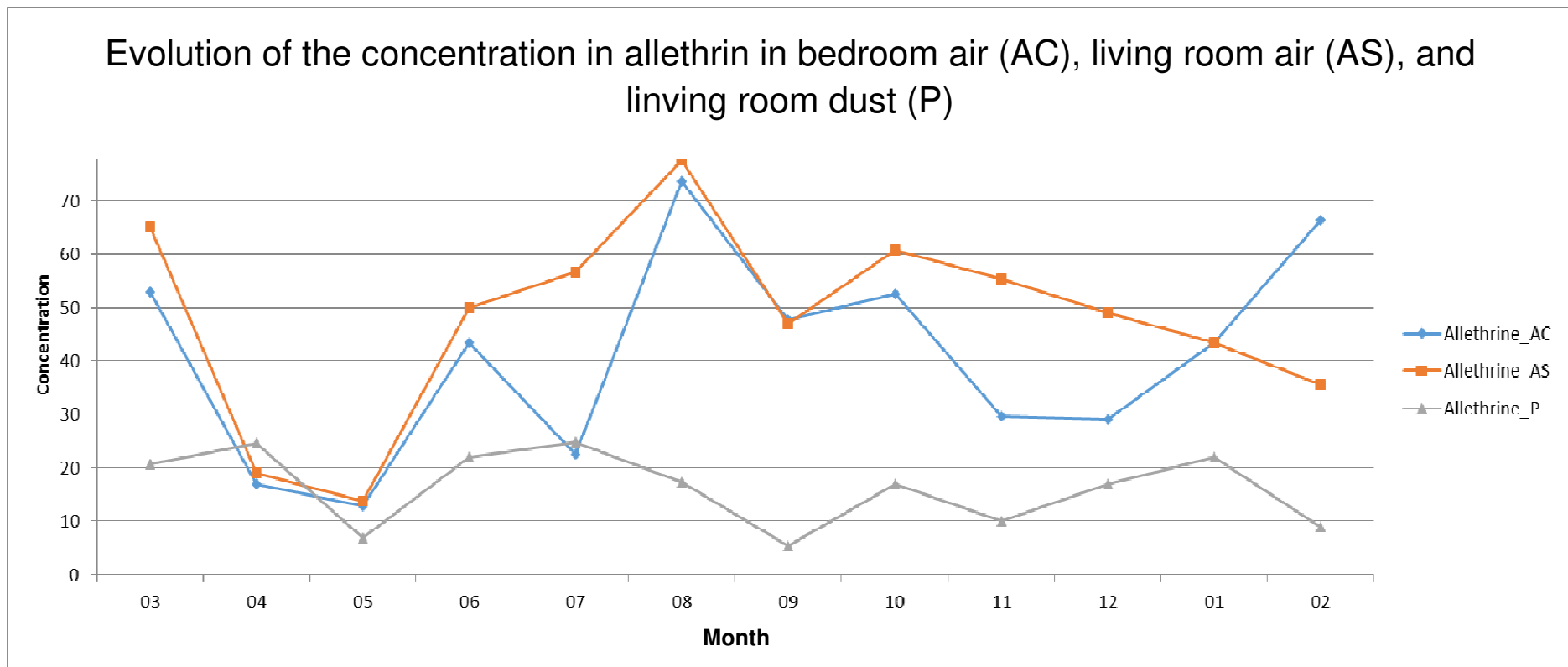


Fig. 4. Evolution of the concentration of allethrin (mean concentration for each month on the 10 houses) in the living room and in the bedroom for air and in dust (only living room).

Table 1.

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

	Compounds	RT (min)	Precursor ion (m/z)	Excitation voltage (V)	Product ions (m/z)
ISTDs	naphthalene d8	9.25	136	1,5	108/132/84/82/80
	trifluralin d14	11.18	315	0,8	267/209
	nitrophenol d4	12.28	200	1	139/154/182
	DDE d8	18.10	254	1,3	184/149/219
	DDT d8	20.20	173	1,6	137/138
	phthalate d4	24.43	153	1	153
	<i>trans</i> -cypermethrin d6	27.54	183	0,9	168/165/153
PAHs	naphthalene	9.31	128	1,2	102/126/76/77/78
	acenaphthene	10.83	153	1,3	150/151/126
	fluorene	11.47	165	1,2	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
	pyrene	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	29.71	252	1,3	250/226
	benzo[e]pyrene	30.75	252	1,3	250/226
	benzo[a]pyrene	30.98	252	1,3	250/226
	dibenzo[a,h]anthracene	34.43	278	1,5	276
	indeno[1,2,3]pyrene	34.45	276	1,4	274
	benzo[g,i,h]perylene	35.93	276	1,4	274
PCBs	PCB 18	12.73	256	1,2	186/221
	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
	γ -HCH	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 determination and variation and recovery for each compound in ATD GC/MSMS

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

mecoprop-p	$Y = 0.00562118xx$	0.9838	25.9	72.1	
dicamba	$Y = 0.0009972xx+6.67454e-005xx^2$	0.9986	10.4	54.8	
2,4-MCPA	$Y = 0.00172559xx+1.85696e-005xx^2$	0.9918	19.5	47.4	
acetochlor	$Y = 0.0116542xx+0.00024495xx^2$	0.9997	16.4	39.7	
alachlor	$Y = -0.0646043xx+0.0158739xx^2$	0.9999	20.0	80.9	
dichlorprop	$Y = 0.253175xx+0.00107106xx^2$	0.9921	29.2	47.2	
chlorothalonil	$Y = 0.585031xx+0.00132817xx^2$	0.9961	21.8	64	
2,4-D	$Y = 0.139607xx+0.00133056xx^2$	0.9976	22.3	40.3	
metolachlor	$Y = 0.0450239xx+0.000169866xx^2$	0.9995	17.7	46.9	
aldrin	$Y = 0.0003578xx+5.32758e-005xx^2$	0.9991	2.8	65.1	
triclopyr	$Y = 0.0008511xx+2.90409e-005xx^2$	0.9990	16.9	47.8	
esbiothrin	$Y = -0.208025xx+0.01518xx^2$	0.9929	10.2	62.5	
allethrin	$Y = -0.0164852xx+0.00809853xx^2$	0.9987	11.3	78.4	
cyprodinil	$Y = 0.589763xx+0.0100304xx^2$	0.9981	23.3	59.1	
prallethrin	$Y = 0.0170286xx+0.000584419xx^2$	0.9988	1.9	68.3	
metazachlor	$Y = -0.0173222xx+0.00198511xx^2$	0.9921	15.0	92	
o,p'-DDE	$Y = 0.214587xx+0.00369748xx^2$	0.9984	18.6	53.7	
pentachlorophenol	$Y = 1.52246xx$	0.9982	6.8	47.2	
oxadiazon	$Y = 0.259649xx+0.0123259xx^2$	0.9988	6.4	62.8	
fluroxypyr	$Y = 0.0219126xx+0.000295729xx^2$	0.9988	14.2	62	
α -endosulfan	$Y = -0.347037xx+0.0550062xx^2$	0.9999	13.4	84.1	
buprofezin	$Y = 3.1903xx+0.00150316xx^2$	0.9980	1.7	87.4	
p,p'-DDE	$Y = 0.3688745xx+0.0256874xx^2$	0.9978	26.1	53.2	
o,p'-DDD	$Y = 0.8796485xx+0.00365894xx^2$	0.9968	15.7	38.5	
myclobutanil	$Y = -0.0119564xx+0.00126635xx^2$	0.9990	16.9	54.2	
dieldrin	$Y = -0.0404649xx+0.00861221xx^2$	0.9990	11.8	80.6	
picloram	$Y = 0.02547874xx+0.0014587xx^2$	0.9984	12.5	47.8	
imiprothrin	$Y = 0.0129142xx+0.00181641xx^2$	0.9984	10.1	69.5	
p,p'-DDD	$Y = 2.356898xx+0.0158745xx^2$	0.9990	4.1	54	
o,p'-DDT	$Y = 1.254693xx+0.3675841xx^2$	0.9999	11.3	53	
β -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	$Y = 0.281072xx+0.00212207xx^2$	0.9857	17.1	32.8	
p,p'-DDT	$Y = -8.06502xx+0.356577xx^2$	0.9991	3.8	44.3	
diflufenican	$Y = -0.01458741xx+0.1547854xx^2$	0.9975	6.7	62.9	
tebuconazole	$Y = 0.0291554xx+0.000119102xx^2$	0.9999	33.5	65.1	
bifenthrin	$Y = 0.282973xx+0.0229783xx^2$	0.9999	18.4	67.7	
tetramethrin	$Y = 0.0196582xx+0.000315872xx^2$	0.9999	4.3	56.2	
cyphenothrin	$Y = 6.14848xx+0.0565313xx^2$	0.9999	5.5	74.5	
permethrin	$Y = -0.00643462xx+0.0177379xx^2$	0.9999	19.5	78.1	
α -cypermethrin	$Y = 0.399647xx+0.00944233xx^2$	0.9990	8.7	69.9	
τ -fluvalinate	$Y = 0.445412xx+0.00651781xx^2$	0.9964	6.9	45.2	
deltamethrin	$Y = 0.315458xx+0.0875697xx^2$	0.9996	25.0	42.2	
Alkylphenols	4-octylphenol	$Y = 1.09579xx+0.00399132xx^2$	0.9967	26.3	54.3
	4-nonylphenol	$Y = 0.385576xx+6.17678e-005xx^2$	0.9976	28.4	47.2
	octylphenol monoethoxylate	$Y = 1.214587xx+0.0025784xx^2$	0.9957	20.6	32.2
	octylphenol diethoxylate	$Y = 3.589745xx+0.0214587xx^2$	0.9954	13.0	37.5
	bisphenol A	$Y = -0.00726143xx+0.00136089xx^2$	0.9999	23.7	28.5
Phthalates	phthalate DMP	$Y = 0.0567936xx+0.000260551xx^2$	0.9996	19.9	114.8

phthalate DEP	$Y = 0.0192154xx + 8.60562e-005xx^2$	0.9968	7.0	102.3
phthalate DBP	$Y = -0.818309xx + 0.162187xx^2$	0.9999	4.1	109.6
phthalate DIBP	$Y = 0.00245352xx + 0.00350707xx^2$	0.9999	9.7	99.4
phthalate DPP	$Y = -0.06246xx + 0.00616563xx^2$	0.9943	17.2	100.4
phthalate BBP	$Y = 0.0231804xx$	0.9996	11.7	99.9
phthalate DEHP	$Y = 0.114715xx$	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 -HCH	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	γ -HCH	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
PCB	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	0.22	0.07	2.1	7.0	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	0.09	0.03	0.6	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	1.8	1	5
ISTD	<i>trans</i> -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)

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 %