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1 **Endocrine disrupting compounds in gaseous and particulate outdoor air**
2 **phases according to environmental factors**

3
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19 phase, particulate phase
20

21 **Abstract**

22

23 This study investigated, for the first time in France, the spatial and temporal patterns of 55 endocrine
24 disrupting chemicals (EDCs) in ambient air at three sites (urban, suburban and forest) under two
25 climatic periods (warm/cold) for 2 successive years. All EDCs, except tetrabromobisphenol A
26 (TBBPA), were encountered with various frequencies of up to 100%. Phthalate diesters (PAEs) were
27 the most abundant chemicals with total concentrations as the sum of compounds, ranging from 10 to
28 100 ng m⁻³ of total air, followed by alkylphenols (APs) and polycyclic aromatic hydrocarbons (PAHs),
29 which were both approximately 1 ng m⁻³. Polychlorinated biphenyl (PCBs) and bisphenol A (BPA)
30 concentrations were notably lower (approximately 0.1 ng m⁻³). Air concentrations, depending on the
31 considered compounds, were from 1.2 to 2 times higher in the urban than the suburban area and from
32 2 to 5 times higher in the urban than the forest site. PAH emissions were higher in the cold period, due
33 to combustion processes. This finding is contrary to the other EDCs that are more abundant in the
34 summer and governed by volatilisation. Most of the EDCs were largely distributed in the gaseous
35 phase (> 80% in the summer). The octanol/air partition coefficient (K_{OA}) and vapour pressure (V_p)
36 were relevant parameters for predicting EDC partitioning and direct relationships ($p < 0.001$) were
37 observed i) between log K particle/gas partitioning ($\log K_p$) and $\log K_{OA}$ and ii) between EDC ratios
38 in the gaseous phase and log vapor pressure ($\log V_p$).

39

40 **Highlights**

41 EDCs in the Paris area were similar to Western countries except PAHs and PBDEs

42 PCBs and PAEs showed an urban signature

43 AP, PAH and PBDE sources were more distributed along a urban-suburban transect

44 EDCs prevailed in gaseous phase whatever the season except DEHP and heavy PAHs

45

46 **1. Introduction**

47 The continuous release of a number of endocrine disrupting chemicals (EDCs), such as
48 bisphenol A (BPA), tetrabromobisphenol A (TBBPA), phthalate diesters (PAEs),
49 alkylphenols (APs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers
50 (PBDEs) and polycyclic aromatic hydrocarbons (PAHs), to the environment generates new
51 concerns regarding human exposure to low doses of toxic mixtures and possible subsequent
52 effects on health (Benachour et al., 2007; Woodruff, 2011).

53 The emission sources of these chemicals have greatly increased and diversified over the
54 past decades (EEA, 2013); and therefore, they have appeared as major air contaminants,
55 particularly because of their semi-volatile properties (Rudel and Perovich, 2009). Thus, PAEs,
56 APs, PCBs and PBDEs that are not chemically bound to matrices might become easily
57 dispersed by volatilisation (Palm et al., 2002; Fujii et al., 2003; Liang and Xu, 2014).

58 PAEs can be emitted into the atmosphere from commonly used products, plastics,
59 detergents, building materials or furniture (Wormuth et al., 2006). To date, despite a wide use
60 of BPA in polycarbonate and epoxy resin production, emission sources and subsequent
61 impacts upon ambient air quality remain poorly documented (Huang et al., 2012).

62 APs are by-products of alkylphenol ethoxylates largely used in household detergents. The
63 European directive 2003/53/EC that came into force in January 2005 restrained the use of
64 products containing more than 0.1% nonylphenols (NP) or nonylphenol ethoxylates.
65 However, alkylphenol ethoxylates are still applied as dispersing agents in pulp and paper
66 production, emulsifying agents in latex paints, glue and pesticides or in the preparation of
67 antioxidants, curing agents and heat stabilisers for polymer resins and may be emitted to the
68 environment from building materials (Saito et al., 2004).

69 PBDEs, a major class of flame retardants used in a number of manufactured goods to
70 reduce their flammability, were composed of three major commercial formulations: penta-

71 BDE, octa-BDE and deca-BDE (de Wit et al., 2010). Since 2003, penta- and octa-BDE were
72 banned of use in all applications for the European Union market (Directive2003/11/EC) Deca-
73 BDE was registered under the “Registration, Evaluation, Authorisation and Restriction of
74 Chemicals” (REACH) in 2010 and thus its uses have been restricted to applications such as
75 automotive equipment, textiles and construction and suppressed for electric and electronic
76 equipment (Deca-BDE, 2012). Tetrabromobisphenol A (TBBPA) is used as a reactive or
77 additive flame retardant in polymers such as ABS, epoxy and polycarbonate resins,
78 polystyrene, phenolic resins or adhesives (Who, 1995).

79 Chlorinated compounds such as hexachlorobenzene (HCB) and PCBs have been
80 classified as persistent organic pollutants in the 1998 Aarhus Protocol (Aarhus, 24 June 1998),
81 in the framework of the Geneva Convention on long-range transboundary air pollution.
82 Dispersive uses of PCBs were banned in France by the Decree of 8 July 1975 and their uses
83 were restricted to in-service equipment by a second decree in February 1986. Finally, in
84 February 2003, a decree on the elimination of all equipment containing PCBs before the end
85 of 2010 has been published. An unknown stock of PCBs is within now buried landfills and
86 other waste-handling facilities as well as diffuse sources such as electrical wiring and paints
87 (Diamond et al, 2010). Most recently, new “non-aroclor” PCBs were detected as byproduct of
88 diarylide yellow (Rodenburg et al., 2010) and other pigment production (Anezaki et al.,
89 2015).

90 Although HCB production has ceased since 1993, this compound is still being generated
91 inadvertently as a by-product and/or an impurity in several chemical processes (Bonnomet et
92 al., 2011) and pentachlorobenzene (PeCB) occurs as a by-product of HCB degradation
93 (Brignon, 2005).

94 PAHs are continuously produced by combustion processes, mainly from domestic heating
95 and automobile traffic (Katsoyiannis et al., 2011; Tobiszewski and Namieśnik, 2012). Despite

96 PAHs are not considered as POPs, they were included to the Aarhus protocol. The objective
97 was to reduce their emissions from stationary sources below their levels in 1990. For the
98 emission inventories, the four indicator compounds shall be used: benzo(a)pyrene,
99 benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene.

100 Consequently, EDCs might undergo local or long range transport and their residence time
101 in the air depends on climatic conditions and pollutant partitioning between the gaseous and
102 particulate phases (Wania, 2003).

103 This study investigated for the first time in France, the atmospheric fate of a wide variety
104 of EDCs (n=55) including PCBs, PBDEs, PAHs, APs, PAEs, HCB, PeCB, BPA and TBBPA,
105 and considering both their gaseous and particulate phases. The target compounds were
106 selected according to suspicion of endocrine disrupting properties, to their classification as
107 POPs and semi-volatile organic compounds and to their environmental occurrence. The
108 concentration levels for the different EDC families were first considered, in order to highlight
109 the general trends of EDC distribution in France and to compare with the contamination in
110 other countries. As EDCs result from various sources, the spatial variations between three
111 sites located respectively in urban, suburban and forest areas were studied. In addition,
112 temporal variations between two contrasted seasons with and without domestic heating and
113 between two successive years were investigated. Next, the particle/gas partitioning was
114 examined on the basis of compound molecular properties. Last, relationships between outdoor
115 temperature, suspended particles < 10 µm (PM10) and EDC air concentrations were explored
116 at the most polluted site.

117

118 **2. Material and Methods**

119 **2.1 Sampling schedule**

120 The three sampling sites belonged to the local air monitoring network of the Ile-de-

121 France district (Airparif) (Fig. Supplementary Material – SM 1).

122 Two sampling campaigns were carried out at the following 3 sampling sites in the Paris
123 region: urban centre residential (population density: 20 000 inhab km⁻²) - Paris 13th (75013),
124 suburban residential area (population density 4 400 inhab km⁻²) - Lognes (77185 – Seine et
125 Marne) and forest area (population density: 87 inhab km⁻²) - Fontainebleau (77186 – Seine et
126 Marne). The prevailing wind direction was W/NW. Because of logistical constraints, only two
127 sites per year were simultaneously sampled: first, Paris/Fontainebleau (distance between the 2
128 sites, 56.5 km) and then Paris/Lognes (distance 20 km).

129 The first campaign was carried out for two periods: summer 2010 and winter 2010/2011
130 at the urban (Paris 13th) and the forest (Fontainebleau) sites. The second campaign was carried
131 out in summer 2011 and winter 2011/2012 and was performed at the urban and the suburban
132 sites i.e., Paris and Lognes.

133 Each sampling period consisted of three successive and individual samples over 14 d,
134 accounting for 42 sampling days. Sampling conditions are presented in Table SM.1. Air
135 sample volumes ranged from 276 to 555 m³.

136

137 **2.2 Sample collection and treatment**

138 The particulate phases were sampled onto quartz fibre filters (porosity 0.3 µm supplied
139 by Whatman) and gaseous phases onto XAD-2 resin (20-60 mesh). The resin from Sigma-
140 Aldrich (Saint-Quentin Fallavier, France) was cleaned and dried under vacuum, and 75 g were
141 introduced into two brass cartridges (2 cm diameter; 20 cm length). The filters were put on
142 open aluminium filter holders (Ecomesure, Janvry, France) and used in total suspended
143 particle mode (Granier and Chevreuril, 1997). The sampler (filter and resin) was connected to
144 a sampling pump (Busch, model SV1005GP) with a paddle dryer combined with a timer and
145 an air flow meter (Hivolin, Germany). To secure the trapping of all EDCs, air speed through

146 the system was $< 170 \text{ cm s}^{-1}$ as stated in the IEPA method (IEPA/APC/85-003, 1985). The air
147 flow in the sampler remained constant, from 1.2 to $1.8 \text{ m}^3 \text{ h}^{-1}$ (Table SM.1). The outdoor
148 temperatures and the concentrations of particulate matter $< 10 \mu\text{m}$ in diameter (PM10) were
149 supplied by Airparif (Table SM.1).

150 The entire experimental procedures (sampling + clean-up + fractionation) and validations
151 for sampling, extraction and analytical methods (Tables SM.2 to SM.7) were previously
152 described (Alliot et al., 2014). The XAD-2 resins and filters were extracted separately. An
153 aliquot of each extract was kept for AP analyses using a method previously developed
154 (Cladière et al., 2013). Laboratory blanks were run for each series with clean XAD-2 resins
155 and clean filters (matrix blank). They were subtracted from sample values. Internal standards
156 were added to samples prior to extraction and compounds were quantified by internal
157 calibration. Syringe standards were added to vials prior to analyses to determine internal
158 standard recoveries.

159

160 **2.3 Presentation of the results**

161 The results for each site are presented as the mean \pm standard deviation ($n = 6$) and as the
162 median. Mean gaseous and particulate phase concentrations ($n = 3$) are calculated for each
163 season. PAEs are expressed both as individual compounds and as the sum of 7 PAEs
164 ($\Sigma 7\text{PAEs}$). APs are expressed as the sum of octylphenol and 4-nonylphenols ($\Sigma\text{OP+NP}$).
165 PCBs are expressed as ΣPCBi (the sum of 7 PCB indicators for the monitoring of PCBs in
166 Europe: CB28, 52, 101, 118, 138, 153 and 180), $\Sigma\text{PCB-DL}$ (the sum of CB77, 81, 126, 169
167 for the non-ortho polychlorinated dibenzo-p-dioxins-like PCBs and CB105, 114, 118, 123,
168 156, 157, 167, 189 for the mono-ortho polychlorinated dibenzo-p-dioxins-like PCBs) and
169 $\Sigma 19\text{PCBs}$. PBDEs are expressed as individual compounds and as $\Sigma 8\text{PBDEs}$ (the sum of
170 BDE28, 47, 99, 100, 153, 154, 183 and 209). PAHs are expressed as the individual

171 compounds of the French regulation (Decree of 02/02/1998) for atmospheric emissions
172 (ATEP9870017A, 1998): fluorene (FLU), phenanthrene (PHE) and benzo(a)pyrene (BaP),
173 \sum 8PAHs (the sum of fluoranthene – FTH, benzo(a)anthracene - BaA, benzo(b)fluoranthene -
174 BbF, benzo(k)fluoranthene - BkF, BaP, indeno(1,2,3-cd)pyrene – IcdP,
175 dibenzo(a,h)anthracene – DahA, and benzo(g,h,i)perylene - BghiP) and as \sum 15PAHs (Table
176 SM.6).

177 The EDC groups were represented by compounds with low and high molecular weights
178 to give a comprehensive view of their behaviour. Relationships between i) compounds as % in
179 the gaseous phase and log of their vapour pressure (log V_p , Pa at 25 °C) and ii) between log K
180 particle/gas partitioning (log K_p) and log octanol/air partition coefficient (log K_{OA}) were
181 explored.

182 Statistical analyses of spatial and temporal variations were performed with the non-
183 parametric test of Mann-Whitney, and correlation significances were expressed by
184 Spearman's r coefficient at $\alpha = 0.05$. A principal component analysis - PCA (XLSTAT PRO
185 software; Copyright holder CC-BY-SA-3.0, Addinsoft, Paris, France) was used for the Paris
186 site with a diagram sorting out the main trends of the different EDC concentrations for the
187 two campaigns. When the measured concentration was < the limit of quantification (LOQ),
188 the LOQ value divided by 2 was used for the mean calculation and for the PCA analysis
189 (Decree, July 08 2010).

190

191 **3. Results and Discussion**

192 **3.1. General trends**

193 All of the targeted EDCs except for TBBPA were quantified in the ambient air at the
194 urban, suburban and forest sites (Table 1 and Table 2). The patterns for each site and season
195 are shown in Fig. 1. In decreasing order, the overall concentration (\sum of gaseous and

196 particulate phases) trends were similar and are as follows, PAEs > APs \geq PAHs > PCBs >
197 BPA > HCB > PeCB > PBDEs.

198 PAEs were encountered in all air samples, and their concentrations ranged from 6.8 to
199 165 ng m⁻³ as the Σ 7PAEs. The main compound was DEHP (from 0.1 to 156 ng m⁻³)
200 followed by DiBP (from 3.2 to 30 ng m⁻³) and DnBP (from 0.1 to 11 ng m⁻³). These
201 compounds were detected at a frequency of 100%. DEHP concentrations are in accordance
202 with those previously measured in Paris (France) (Teil et al., 2006) and in the Netherlands
203 (Peijnenburg and Struijs, 2006).

204 APs and PAHs were the second most abundant EDC group (Fig. 1). OP and NP were
205 always detected and their concentrations ranged respectively, from 0.034 to 0.657 ng m⁻³ and
206 from 0.216 to 2.08 ng m⁻³. NP represented the major constituent of the total APs (72 to 88%).
207 This is consistent with literature data i.e., NP concentrations from 0.15 to 1 ng m⁻³ in the gas
208 phase and from 0.0017 to 0.117 ng m⁻³ in the particulate phase of ambient air in NE-Bavaria,
209 Germany ((Berkner et al., 2004).

210 The Σ 8PAHs were quantified in all samples with concentrations ranging from 0.215 to
211 1.93 ng m⁻³. PAH concentrations in decreasing order were PHE > FLU > FTH (Table SM.8).
212 A similar sequence was observed at a suburban site located nearby in Paris in 2010 (Motelay-
213 Massei et al., 2003). Literature data are scarce for periods similar to this study. Our
214 concentrations remained lower than those of high volume air sampling (5.3 to 71.6 ng m⁻³ as
215 Σ 14 PAHs) at four locations in the Chesapeake bay (USA) in 1994 (Gustafson and Dickhut,
216 1997). In Bursa (Turkey), for the period 2008-2009, residential and suburban sites showed
217 average concentrations of respectively, 77 and 30 ng m⁻³ as Σ 12PAHs, PHE and FLU being
218 the predominant compounds (Birgul and Tasdemir, 2015).

219 PCB_i were present in all samples with the concentration of the Σ PCB_i ranging from
220 0.024 to 0.327 ng m⁻³ (Table 1 and Table 2). These values are consistent with those found in

221 Northern France in 2002 (Blanchard et al., 2006) but were much lower than those of the Paris
222 area in the 1980s (Granier and Chevreuil, 1997). Thus, after a significant drop linked to the
223 French regulation since the 1970s, a steady state was observed due to the persistence of
224 diffuse sources. Mean concentrations from high volume sampling in urban/industrial location
225 in Barcelona (Spain), in 2005, were similar to ours: 0.17 ng m^{-3} (Mari et al., 2008)

226 The order of PCBi abundance was $\text{CB52} > \text{CB101} > \text{CB28} > \text{CB153} > \text{CB138} > \text{CB118}$
227 $> \text{CB180}$ (Table SM.8). $\sum\text{PCB-DL}$ represented only 8 to 12% of the total PCBs. Among the 4
228 non-ortho substituted congeners, that share a structural similarity and toxic mode of action
229 with polychlorinated dibenzo-p-dioxins, only CB77 and CB81 were detected at a few pg m^{-3}
230 with a frequency approximately 10%. Both congeners were the most abundant coplanars, and
231 this has been found to be the case in the commercial Aroclor and Clophen mixtures (Schulz et
232 al., 1989) and in indoor air (Kohler et al., 2002). However, toxic effects such as endocrine
233 disruption are also associated with other congeners within the group (Caserta et al., 2008).

234 The occurrence of PBDEs depends on the congeners considered, and the concentrations
235 were low, from 0.001 to 0.016 ng m^{-3} as $\sum 8\text{PBDEs}$. PBDE concentrations were 10- to 30-fold
236 lower than PCBs. These concentrations are in accordance with total air concentrations found
237 in the Paris centre in 2008-2009 (Tlili et al., 2012) and in Munich (Germany) in 2008
238 (Fromme et al., 2009).

239 BDE47 was quantified with a frequency up to 100%, whereas BDE209 was detected in
240 only 50% of the samples. A higher LOQ for BDE209 compared to BDE47 could contribute to
241 such results. Two different potential sources of PBDEs were reported in urban ambient air, in
242 Taiwan: the lighter brominated PBDEs were mainly originated from indoor air, while their
243 highly brominated ones were attributed to combustion sources, such as vehicles (Wang et al.,
244 2011).

245 HCB and PeCB were detected in 100% of samples and displayed low concentrations, <

246 0.06 ng m⁻³. HCB production and commercialisation in Europe ceased in 1993, however it is
247 still released into the environment as a by-product or impurity from the manufacture of
248 chlorinated solvents, aromatics and pesticides. The European Chlorinated Solvent Association
249 reported that 4 000 tons of HCB were produced in Europe for 1996, during the manufacture of
250 tetrachlorethylene and that over 99% were incinerated at high temperature (Bonnomet et al.,
251 2011). Another potential source of HCB to the environment is from the bioisomerization of
252 lindane in agricultural soil (Waliszewski, 1993).

253 BPA was quantified in 75% of the samples and at low concentrations, ranging from 0.01
254 to 0.1 ng m⁻³. However, these results need to be confirmed because of low recoveries of the
255 deuterated internal standard, owing to the deuterium/hydrogen exchange in hydroxyl groups
256 when BPA-D₁₆ was dissolved into a protic solvent such as methanol/water (Ballesteros-
257 Gomez et al., 2009).

258

259 **3.2. Spatial trends**

260 **3.2.1. Urban centre/suburban area (Paris/Lognes 2011/2012)**

261 Despite the high population density of 20 000 inhabitants per km⁻² in the Paris area (urban)
262 versus 4 400 inhabitants per km⁻² at Lognes (suburban; 20 km from the sampling site of Paris),
263 differences between ambient air concentrations at the two sampling sites were minor (Table 1).
264 No differences were observed for PAHs, APs, PBDEs, HCB and PeCB. For PCBi and PAEs,
265 the concentrations were two times lower at the suburban site than at the urban site ($p < 0.05$).
266 Thus, PCBs and PAEs showed an urban signature, whereas AP, PBDE and PAH sources were
267 more distributed along the urban-suburban transect. In the Great Lakes basin (USA), PCBs
268 opposite to PAHs showed a strong urban signature (Hafner and Hites, 2003).

269 For PAHs, the source regions were less distinct as the molecular weight of the
270 compounds increased. Indeed, the PAHs in gaseous phase are more susceptible than those

271 adsorbed on particles to degradation *via* reaction with OH-radical, ozone and NO_x or
272 photolysis. For FLU, PHE, FTH and PYR well known to be emitted from gasoline engine,
273 coal combustion and coke ovens, atmospheric lifetime under OH-reaction varied from 26 h
274 (FLU), to 5.6 h (FHE) and 3-5 h (FLU and PYR) (Atkinson and Arey, 1994). As a major
275 source of OH-radicals in the atmosphere is the photolysis of ozone (Alvarez et al., 2013), the
276 degradation potentials were estimated by ozone concentrations at the urban and the suburban
277 site. They remained very similar as no differences were observed in ozone concentrations
278 (Table SM.1).

279 For APs, wastewater treatment plants, usually located outside urban areas, were identified
280 as a major source to ambient air during water-air exchange processes (Salgueiro-González et
281 al., 2015).

282 Population density is a major factor impacting semi-volatile organic compound emissions
283 in urban area as reported in a study in USA that noted indoor sources as the predominant
284 factor influencing outdoor ambient air concentrations in densely populated areas (Rudel and
285 Perovich, 2009). Indeed, in a major UK conurbation, the principal contemporary source of
286 PCBs appears to be the ventilation of indoor air (Jamshidi et al., 2007). Moreover, emissions
287 from indoor air to outdoors for BDE209 and sum of BDE28, 47, 99, and 153, were roughly
288 estimated to represent close to 90% of total emissions to outdoor air in Sweden, indicating
289 that contaminated indoor air is an important source of PBDE contamination (Björklund et al.,
290 2012).

291 However, Lognes is located under prevailing westerly winds (frequency > 25%) passing
292 first over the Paris centre. Thus, recirculation of the contaminated air mass over the urban
293 zone can also impact the contamination level at the suburban site located 20 km far from the
294 urban site and under the air mass plume. Similarly, in the UK, a direct correlation between
295 wind direction and PCB ambient air concentration was observed, in accordance with inputs

296 from winds passing over the Birmingham city centre (3 km away from the sampling site)
297 because the main source of tri- and tetra-chlorinated congeners is a non-equilibrium, short-
298 range transport (Currado and Harrad, 2000).

299

300 **3.2.2. Urban centre/forest area (Paris/Fontainebleau 2010/2011)**

301 Spatial differences of compound concentrations were observed from the urban site to the
302 forest site, 56.5 km apart ($p < 0.05$) (Table 2), with decreases ranging from 2- to 5-fold,
303 according to the compounds.

304 Differences were clearly shown for $\sum 7\text{PAEs}$ (concentration ratio between the urban and
305 the forest site = 5, $p < 0.001$, Mann-Whitney test) and APs (ratio = 3, $p < 0.05$) and at a lower
306 magnitude for $\sum 8\text{PAHs}$ and $\sum \text{PCBi}$ (ratio = 2, $p < 0.2$). In contrast, no differences were
307 observed for $\sum 8\text{PBDEs}$, HCB and PeCB, as previously observed for the urban/suburban sites.

308 Several processes might explain that spatial distribution. First, emissions related to high
309 building density in urban areas might constitute the major source of PAEs and APs to ambient
310 air. Indeed, in California (USA), of all of the chemicals studied in paired indoor and outdoor
311 air samples, most supported the hypothesis of dominant indoor sources except for PAHs,
312 which had a significant outdoor contribution (Rudel et al., 2010). However, in Stockholm
313 (Sweden) the indoor environment contributes only about 25% of BDE209 to the air pollution
314 load (Cousins et al., 2014) suggesting the existence of additional sources in the outdoor
315 environment.

316 Less marked variations in concentrations of PCBs and PBDEs between the urban and the
317 forest area were consistent with their persistence far away from their emission sources, with
318 half-lives under photo-degradation conditions ranging from 3 to 120 d for PCBs (Bunce et al.,
319 1989) and from 2 to 94 d for PBDEs (Wania and Dugani, 2003). In the Toronto area
320 (Canada), data from PUF passive samplers showed that PBDEs were fairly uniform along an

321 urban-rural transect, in accordance with our observations (Harner et al., 2006). In the same
322 area, 95% of PCB and 70% of PBDE emissions undergo atmospheric transport from the city,
323 the urban air plume reaching about 50 km in the direction of prevailing winds (Csiszar et al.,
324 2014).

325 Opposite, PAEs and APs were characterised by short half-lives under photodegradation
326 in ambient air, from 5 h to 18 d for PAEs, DEHP being more persistent than low molecular
327 weight PAEs (Staples et al., 1997), and from 10 to 15 h for APs (Neamțu and Frimmel, 2006),
328 leading to a decrease of their ambient air concentrations in the absence of local emission
329 sources, which is documented by the detection of OP in rain and snow (Fries and Püttmann,
330 2004)

331 Concerning PAH concentrations, the small differences found between the 2 sites can be
332 supported by a higher degradation in urban site related to elevated OH-radical, ozone and NO_x
333 concentrations compared to the forest site. As a matter of fact, for FLU, PHE and FTH, a
334 major removal mechanism from the gaseous phase by reaction with OH radicals in temperate
335 atmosphere has been reported (Halsall, 2001).

336 Moreover, we observed an increase spatial homogeneity in winter (1.93 ng m⁻³ - urban
337 site/1.18 ng m⁻³ - forest site) compared to summer (0.918 ng m⁻³ - urban site/0.215 ng m⁻³ -
338 forest site) (Table 2). A similar result was observed in Toronto (Canada) as emissions from
339 domestic heating, with a large part played by natural gas (94%) in urban area, corresponded to
340 relatively low PAH emissions, compared to gasoil or wood, and lead to a greater increase in
341 the rural compared to the urban concentrations in winter (Melymuk, 2012). Last, the vicinity
342 of main highways crossing the forest area could contribute to local PAH emissions.

343 For HCB a steady concentration of approximately 0.05 ng m⁻³ was found, suggesting that
344 there is no major primary source of HCB in the Paris area. Opposite, a spatial variation of
345 HCB in air from an urban-rural transect across Tianjin (China) was shown, related to

346 unintentionally in course of substantial chlor-alkali production ((Zheng et al., 2010).

347

348 **3.3. Temporal trends**

349 **3.3.1. Summer/winter variations**

350 Clear variations for the three sites were observed between summer and winter for PAHs,
351 APs, PAEs and PCBs (Table 1 and Table 2). The most marked difference was found for BaP
352 concentrations, with summer/winter increases up to 14-fold. For the Σ 8PAHs, a 2- to 5-fold
353 concentration increase in the winter of 2011 and a 2-fold increase in the winter of 2012 were
354 found. The winter season corresponds to lower degradation processes and to high domestic
355 heating activities, that contributes to explain the summer/winter differences. Photochemical
356 reactions of PAHs may constitute important decay routes for these compounds in the
357 atmosphere (Albaigés et al., 1991). A main source of OH-radicals that oxidize compounds in
358 the atmosphere, being the photolysis of ozone (Alvarez et al., 2013), a 2- to 3-fold decrease of
359 ozone concentration in winter due to the attenuation of solar radiation (Table SM.1) could
360 result to a decrease in PAH photolysis.

361 In contrast, OP concentrations decreased 4- to 7-fold in the winter, depending on the sites
362 ($p < 0.05$). NP concentrations showed lower discrepancies than OP, with a 3- to 4-fold
363 decrease in the winter of 2011 and no variations in the winter 2012. NP and OP exhibited
364 seasonal dependence with higher gas-phase concentrations during summer than during fall
365 and early winter in the lower Hudson river estuary (USA), suggesting that temperature is a
366 driving factor for their atmospheric occurrence (Van Ry et al., 2000)

367 The variations of PCB and DEHP concentrations were similar to that of APs, with a 2- to
368 7-fold decrease in the winter. However, CB52 which represent a low molecular weight PCB
369 displayed maximal decrease whereas CB153, a heavier and less volatile congener, showed
370 minor variation. A highly significant relationship between temperature and partial pressure of

371 PCBs, PBDEs and PAHs was reported in the ambient air of Toronto (Canada), their dominant
372 emissions originated from temperature-controlled processes such as volatilisation from local
373 sources under warm temperatures and condensation/deposition under cold temperature
374 (Melymuk et al., 2012).

375 PBDE concentrations varied little. The restriction in uses for PBDEs which lead to a
376 decrease in emission sources, coupled to their persistence in the environment could contribute
377 to the background level observed, this result being confirmed by low variation of
378 concentrations along the transect urban/suburban/forest area.

379 Among the compounds emitted by combustion and industrial processes, only HCB, PeCB
380 and FLU remained steady over the year at the three sites. This is consistent with the lack of a
381 major primary source for HCB and PeCB, whereas FLU has been identified as a good marker
382 of emission from diesel vehicles (Fang et al., 2004) that prevail among road traffic in France
383 and remain constant throughout the year. Moreover, degradation processes by atmospheric
384 reactive species reported inside samplers (Menichini, 2009; Melymuk et al., 2014), even for
385 compounds adsorbed on particles (Menichini, 2009), can lead to underestimate EDC
386 concentrations in the two phases, particularly for the summer period.

387

388 **3.3.2. Pollutant phase partitioning**

389 The average distribution in the gaseous phase for the different compounds in summer and
390 winter is shown in Fig. 2. In the summer, the high outdoor temperature (approximately 20 °C)
391 and low PM10 concentrations ($< 22 \mu\text{g m}^{-3}$), in contrast to the winter season with low
392 temperatures ($< 6.5 \text{ }^\circ\text{C}$) and high PM10 concentrations (up to $38 \mu\text{g m}^{-3}$) (Table SM1), leads
393 to the prevalence of most compounds in the gaseous phase. Thus, the proportions of the
394 different APs and PCBs compounds in the gaseous phase were always $> 50\%$ of the total
395 concentrations and were often up to 100%. Other compounds such as DEHP tended to

396 increase in the particulate phase, up to 80% in the cold season (Table 1 and 2). However, in
397 summer, the high proportion of DEHP in gaseous form was more linked to the increase of its
398 gaseous phase concentration (up to 32-fold at the urban area) than to the decrease of its
399 particle phase concentration (2-fold).

400 Because of their high volatility (vapour pressure, VP, 0.63 Pa at 25 °C for NP) compared
401 to the other EDCs, APs prevailed in the gaseous phase in all seasons. A similar phase
402 distribution was reported at an urban site of Germany, with NP concentrations ranging from
403 0.15 to 1.0 ng.m⁻³ in the gaseous phase and from 0.002 to 0.117 ng.m⁻³ in the particulate phase
404 (Berkner et al., 2004).

405 PCBs occurred in the gaseous phase, from 97% for the lower chlorinated congeners to 12%
406 for the highly chlorinated ones as they display a wide range of VP (from 5.8 to 0.00005 Pa)
407 (Table SM.9). A prevailing occurrence in the gaseous phase associated with a decreasing
408 concentration of the highly chlorinated congeners in winter was reported at an industrial
409 location in North China (Li et al., 2015).

410 HCB (VP: 2.3 x 10⁻³ Pa) was only detected in the gaseous phase, which confirms
411 previous observations in Ontario (Canada) (Lane et al., 1992).

412 PBDEs were in the gaseous phase from 34% to 99%. These results are consistent with
413 previous studies that indicated that tri- to hepta-BDEs dominated the gaseous phase,
414 accounting for 77% of the total PBDE levels (Tlili et al., 2012).

415 Except for BaP, BaA and BghiP, which are mainly associated with particles, PAHs were
416 predominantly in the gaseous phase (Fig. 2). In summer, the most volatile PAHs (VP from 4.1
417 Pa to 5.7 x 10⁻² Pa) were found at rates up to 100% in the gaseous phase, whereas CHR was
418 equally distributed in both phases. Compound occurrence in the gaseous phase decreased
419 from summer to winter from 50% to 25% of the total concentration for CHR; whereas, for the
420 most volatile PAHs, the gaseous phase remained the predominant phase. This is in accordance

421 with literature data (Terzi and Samara, 2004; Ballesteros-Gomez et al., 2009). The molecular
422 weight of CHR (M_w 228 g mol⁻¹) corresponds to the dividing line for the distribution of PAH
423 compounds preferentially in the gaseous or the particulate phase (Lu et al., 2008).

424 Direct relationships were found between log K_p of EDCs and log K_{OA} ($R^2 = 0.335$, $p <$
425 0.001) and also between the EDC occurrence in the gaseous phase and their log V_p ($R^2 =$
426 0.571 , $p < 0.001$) for the summer period (Fig. 3, Table SM.9). Thus, V_p and K_{OA} are relevant
427 parameters for predicting EDC distribution in ambient air, as reported in previous studies
428 (Falconer and Bidleman, 1994; Harner and Bidleman, 1998; Paasivirta et al., 1999).

429 Other environmental parameters, such as UV index or sunshine duration, size and nature
430 of the particles and hygrometry, might interfere with EDC partitioning in ambient air
431 (Cousins and Mackay, 2001). In addition, for FLU, PHE and FTH, a major removal
432 mechanism from the gaseous phase, by reaction with OH radicals, in temperate atmosphere,
433 has been reported, (Halsall et al., 2001).

434

435 **3.3.3. Two year variations at the Paris site – impact of ambient parameters**

436 **(temperature and PM10)**

437 Annual EDC concentrations in ambient air in the Paris centre (Table 1 and Table 2) were
438 about two-fold lower for the second campaign (2011/2012) than for the first one (2010/2011)
439 for PAEs, APs and PBDEs, and there was less variation for PCBs and PAHs. Inter-annual
440 variations were mainly characterised by lower summer concentrations during the campaign
441 2011/2012. The average air temperature higher in summer 2010 (20.9 °C) than in summer
442 2011 (19.2 °C) was in favour of volatilisation particularly for the most volatile compounds
443 like OP, NP, FLU, PHE and CB52, which presented higher gaseous phase concentrations
444 (Table 1 and Table 2).

445 To enhance knowledge about the influence of ambient parameters upon EDC variability,

446 a principal component analysis (PCA) was performed at a significance level of 95%. EDC
447 concentrations in the ambient air of the urban area were examined in relation to outdoor
448 temperature and PM10 concentrations. PM10 that are from 2 origins, local and regional, may
449 increase with emissions, thermal inversion phenomenon, low wind speed, and air mass
450 recirculation in continental environments and anti-cyclonic conditions with East/North-East
451 wind direction. Two predominant compounds within each chemical group, one of low
452 molecular weight and one of high molecular weight were considered to perform the PCA
453 analysis. Two clusters were identified corresponding to winter and summer samples (Fig. 4).

454 The correlation matrix for $p < 0.05$ (Table 3) showed a direct correlation between
455 temperature and CB52 or CB153, OP and DEP. In the summer of 2011, the ambient
456 temperature reached a higher value than in the summer of 2012, which can favour
457 volatilisation from contaminated sites and materials and contribute to the explanation of
458 higher air concentrations for PAEs, APs and PBDEs in 2011. On the contrary, a positive
459 correlation between BaP and PM10 concentrations and a negative correlation between BaP
460 and temperature were found. This result is a consequence of their high production and
461 emission levels in winter and their tendency to be adsorbed upon particles. High PAH
462 concentrations and high PM10 levels during poor vertical mixing associated with the strong
463 barrier of surface inversions were reported in ambient air from rural residential areas in
464 southern Germany (Bari et al., 2010).

465

466 **4. Conclusions**

467 This study, considering both the gaseous and particulate phases of ambient air, constitutes
468 a first approach to examine multi-residue contamination of ambient air by 55 EDCs in France
469 and provides useful insights into the growing concern regarding chronic exposure to these
470 compounds. The human exposure to indoor air contamination in France was estimated *via*

471 indoor air concentration data. But, due to the lack of data for outdoor air concentrations (more
472 especially total and gaseous phase concentrations), most of the studies concerning the
473 particles, it remains difficult to estimate the exposure from outdoor air.

474 The high volume sampling conditions allowed the quantification of all EDCs except
475 TBBPA. Our findings are consistent with molecular properties, environmental conditions and
476 published literature.

477 Environmental data about ambient air contamination improves the knowledge of
478 distribution variability that depends on location characteristics (urban, suburban, forest) and
479 mainly on temperature conditions (summer, winter). The general trend for seasonal variations
480 was of lower concentrations in winter for most compounds, except for PAHs and in particular
481 BaP, that depend i) on their lower photochemical reaction linked to the increase in the
482 adsorbed form ii) on the decrease in atmospheric reactive species like ozone and iii) on the
483 increase in combustion processes, during the cold season.

484 Compound distribution between gaseous and particulate phases depends on compound
485 properties such as $\log K_{OA}$ and on particulate aerosol concentrations and ambient air
486 temperature. The EDCs studied are largely distributed in the gaseous phase, which leads to
487 the ubiquity of these SVOCs, even far away from their emission source locations.

488 Our study highlights priority SVOCs that may be considered for monitoring air quality or
489 for the control of diffuse emission sources. Thus, molecules belonging to the PAE and AP
490 families which are already listed as priority compounds for the protection of aquatic
491 environments (DCE - 2000), are both ubiquitous and relatively abundant in the atmosphere. In
492 Europe, PAHs are regulated both in ambient air and emissions. The objective of this
493 regulation is to assess the population exposure to air pollution and to improve air quality.
494 Therefore, some PAE compounds like DEHP and some APs could be associated with PAH
495 monitoring.

496

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506

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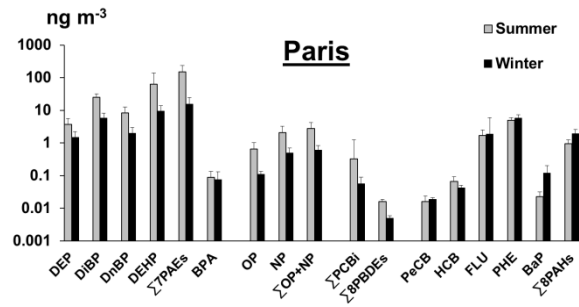
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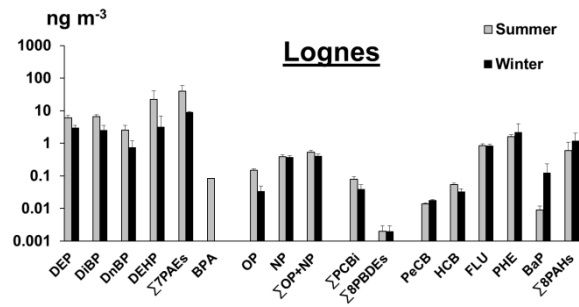
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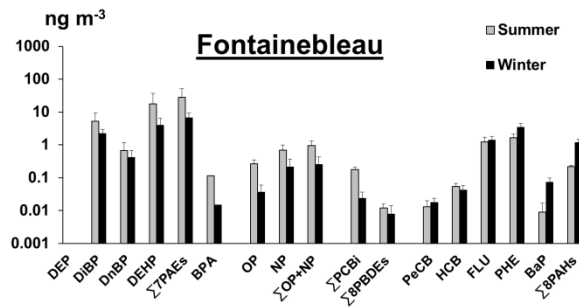
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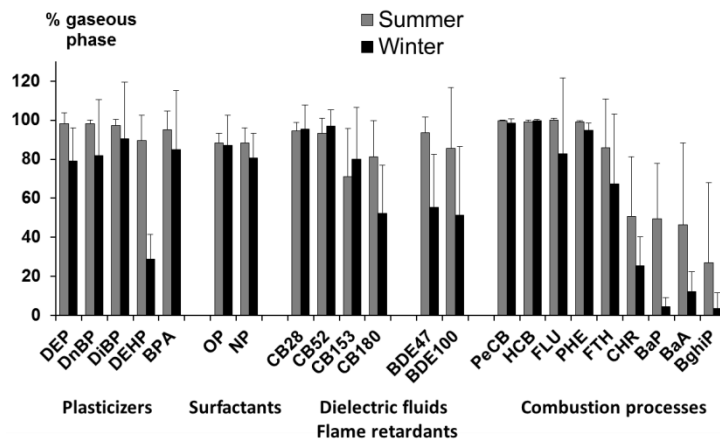


713

714 Fig. 1: Concentrations as ng m⁻³ (mean ± SD, n = 3) of EDCs at Paris, Lognes and

715 Fontainebleau in summer and winter.

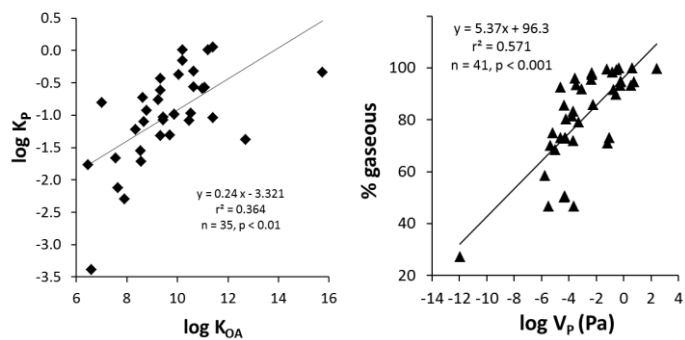
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719 Fig. 2: Compound distribution in the gaseous phase as % of total (mean \pm SD, n = 9), at the
720 three sites, during summer and winter.

721

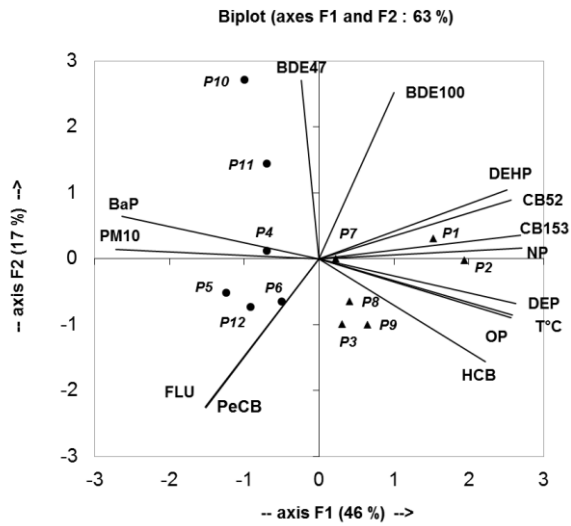


722

723 Fig. 3: Log K_p against $\log K_{OA}$ (at 25 °C) and compound as % gaseous phase against $\log V_p$

724 (Pa at 25 °C) for the summer period, all sites included.

725



726

727 Fig. 4: PCA projections of the 12 air samples corresponding to the two sampling campaigns at
 728 the Paris location (▲ summer and ● winter) and of the 14 variables (solid lines).

729

730 Table 1: Concentrations of different EDCs as annual concentrations in total air (mean \pm SD),
 731 as seasonal concentrations in the gaseous, the particulate phases and the total air (ng m⁻³) and
 732 as gaseous (% of total air) at Paris and at Lognes, during summer 2011 and winter 2011-2012.

compound	Annual concentration (n=6)				Summer 2011 (n=3)				Winter 2011-2012 (n=3)				
	Total (ng m ⁻³)	Gaseous (ng m ⁻³)	Particulate (ng m ⁻³)	% gaseous	Total (ng m ⁻³)	Gaseous (ng/m ³)	Particulate (ng m ⁻³)	% gaseous	Total (ng m ⁻³)	Gaseous (ng m ⁻³)	Particulate (ng m ⁻³)	% gaseous	Total (ng m ⁻³)
Paris													
OP	0.142 \pm 0.105	0.191	0.034	85	0.225 \pm 0.082	0.056	0.004	94	0.060 \pm 0.019				
NP	0.468 \pm 0.140	0.287	0.084	77	0.371 \pm 0.108	0.541	0.023	96	0.564 \pm 0.095				
Σ OP+NP	0.610 \pm 0.118	0.478	0.118	80	0.596 \pm 0.155	0.597	0.027	96	0.624 \pm 0.101				
BPA	0.05 \pm 0.05	0.076	<LOQ	100	0.076	0.039	0.032	55	0.071 \pm 0.057				
TBBPA		<LOQ	<LOQ	-	-	0.010	0.001	96	0.013 \pm 0.022				
FLU	1.09 \pm 0.60	1.16	0.001	100	1.16 \pm 0.33	1.00	0.018	98	1.02 \pm 0.871				
PHE	2.57 \pm 1.48	2.35	0.016	99	2.37 \pm 0.56	2.52	0.26	91	2.80 \pm 2.20				
BaP	0.07 \pm 0.08	0.006	0.003	38	0.009 \pm 0.003	0.002	0.125	1	0.127 \pm 0.084				
Σ 8PAHs	1.05 \pm 0.61	0.470	0.185	72	0.655 \pm 0.107	0.512	0.930	36	1.44 \pm 0.666				
HCB	0.054 \pm 0.027	0.068	<LOQ	100	0.068 \pm 0.03	0.046	<LOQ	100	0.046 \pm 0.016				
PeCB	0.018 \pm 0.009	0.019	<LOQ	99	0.019 \pm 0.008	0.022	<LOQ	100	0.022 \pm 0.008				
CB52	0.047 \pm 0.022	0.059	<LOQ	100	0.059 \pm 0.025	0.034	<LOQ	100	0.035 \pm 0.014				
CB153	0.012 \pm 0.005	0.015	0.001	84	0.016 \pm 0.004	0.007	0.001	87	0.008 \pm 0.002				
Σ PCBi	0.129 \pm 0.063	0.169	0.005	84	0.170 \pm 0.068	0.084	0.005	95	0.089 \pm 0.021				
Σ PCB-DL	0.016 \pm 0.007	0.021	0.005	94	0.021 \pm 0.006	0.011	0.001	93	0.012 \pm 0.002				
DEP	6.99 \pm 1.55	6.69	0.436	94	7.13 \pm 0.55	4.81	2.05	70	6.86 \pm 2.37				
DiBP	7.85 \pm 1.60	7.30	0.330	96	7.63 \pm 2.21	8.07	<LOQ	100	8.07 \pm 1.15				
DnBP	2.10 \pm 0.88	2.66	0.156	94	2.81 \pm 0.65	1.39	<LOQ	100	1.39 \pm 0.093				
DEHP	25.1 \pm 11.4	21.8	8.9	71	30.7 \pm 14.7	3.62	15.8	19	19.5 \pm 4.0				
Σ 7Phthalates	36.3 \pm 17.1	40.2	10.0	80	50.2 \pm 12.2	18.1	4.2	81	22.4 \pm 3.4				
BDE47	0.0022 \pm 0.0019	0.001	0.0001	83	0.001	0.001	0.003	23	0.004 \pm 0.003				
BDE209		<LOQ	<LOQ	-	-	<LOQ	<LOQ	-	-				
Σ 8PBDEs	0.0043 \pm 0.0051	0.0011	0.0003	77	0.0015 \pm 0.0004	0.0009	0.006	13	0.007 \pm 0.006				
Lognes													
OP	0.94 \pm 0.066	0.129	0.025	84	0.154 \pm 0.015	0.030	0.004	89	0.034 \pm 0.015				
4-NP	0.38 \pm 0.12	0.354	0.035	90	0.389 \pm 0.053	0.314	0.059	84	0.373 \pm 0.246				
Σ OP+NP	0.48 \pm 0.17	0.483	0.060	89	0.543 \pm 0.052	0.344	0.063	85	0.407 \pm 0.256				
BPA		0.084	<LOQ	100	0.084	<LOQ	<LOQ	85					
TBBPA		<LOQ	<LOQ	-	-	0.008	<LOQ	98	0.008 \pm 0.01				
FLU	0.84 \pm 0.36	0.853	0.001	100	0.853 \pm 0.113	0.814	0.014	98	0.828 \pm 0.012				
PHE	1.9 \pm 0.96	1.56	0.024	99	1.58 \pm 0.224	2.000	0.194	91	2.19 \pm 1.81				
BaP	0.067 \pm 0.075	0.008	0.001	89	0.009 \pm 0.003	0.002	0.123	1	0.124 \pm 0.111				
Σ 8PAHs	0.90 \pm 0.57	0.283	0.322	47	0.604 \pm 0.477	0.368	0.818	31	1.19 \pm 0.87				
HCB	0.053 \pm 0.021	0.055	<LOQ	100	0.055 \pm 0.005	0.033	<LOQ	100	0.033 \pm 0.007				
PeCB	0.016 \pm 0.0038	0.014	<LOQ	100	0.014 \pm 0.001	0.017	<LOQ	100	0.018 \pm 0.001				
CB52	0.022 \pm 0.010	0.029	<LOQ	100	0.029 \pm 0.007	0.014	<LOQ	100	0.014 \pm 0.008				
CB153	0.006 \pm 0.003	0.007	0.0002	98	0.008 \pm 0.001	0.003	0.0007	75	0.004 \pm 0.001				
Σ PCBi	0.059 \pm 0.026	0.077	0.001	99	0.079 \pm 0.017	0.034	0.005	87	0.039 \pm 0.015				
Σ PCB-DL	0.006 \pm 0.003	0.008	0.001	93	0.009 \pm 0.001	0.004	0.0002	95	0.004 \pm 0.002				
DEP	3.78 \pm 1.81	5.99	0.436	99	6.03 \pm 1.09	2.52	0.50	83	3.02 \pm 0.48				
DiBP	3.56 \pm 2.39	6.42	0.330	97	6.60 \pm 0.99	2.29	0.255	90	2.54 \pm 0.97				
DnBP	1.20 \pm 1.10	2.45	0.156	95	2.57 \pm 0.96	0.742	<LOQ	100	0.742 \pm 0.446				
DEHP	12.8 \pm 15.7	21.3	1.20	95	22.5 \pm 17.9	1.41	1.75	45	3.16 \pm 3.7				
Σ 7Phthalates	24.1 \pm 20.4	37.7	1.57	96	39.3 \pm 18.6	7.16	1.81	80	8.97 \pm 0.47				
BDE47	0.001 \pm 0.0003	0.001	0.0005	92	0.001	0.0002	0.00055	30	0.0008 \pm 0.0003				
BDE209		<LOQ	<LOQ	-	-	<LOQ	<LOQ	-	-				
Σ 8PBDEs	0.0014 \pm 0.0006	0.0011	0.0006	82	0.001	0.0004	0.0013	22	0.002 \pm 0.002				

733 <LOQ: below the limit of quantification

734 Table 2: Concentrations of different EDCs as annual concentrations in total air (mean \pm SD),
 735 as seasonal concentrations in the gaseous, the particulate phases and the total air (ng m⁻³) and
 736 as gaseous (% of total air) at Paris and at Fontainebleau, during summer 2010 and winter
 737 2010-2011.

compound	Annual concentration (n=6)		Summer 2010 (n=3)		Winter 2010-2011 (n=3)				
	Total (ng m ⁻³)	Gaseous (ng m ⁻³)	Particulate (ng m ⁻³)	Gaseous (%)	Total (ng m ⁻³)	Gaseous (ng/m ³)	Particulate (ng m ⁻³)	Gaseous (%)	Total (ng m ⁻³)
Paris									
OP	0.38 \pm 0.38	0.625	0.032	95	0.657 \pm 0.379	0.094	0.014	87	0.11 \pm 0.024
NP	1.14 \pm 0.45	1.98	0.099	95	2.08 \pm 1.15	0.392	0.094	81	0.49 \pm 0.21
Σ OP+NP	1.66 \pm 1.49	2.60	0.131	95	2.74 \pm 1.44	0.49	0.11	82	0.59 \pm 0.23
BPA	0.048 \pm 0.053	0.073	0.017	81	0.089 \pm 0.047	0.011	<LOQ	100	0.011
TBBPA		<LOQ	<LOQ			<LOQ	<LOQ		
FLU	1.8 \pm 0.7	1.72	<LOQ	100	1.72 \pm 0.79	1.88	<LOQ	100	1.88 \pm 4.08
PHE	5.4 \pm 1.2	5.01	0.003	99	5.01 \pm 1.02	5.76	0.089	98	5.85 \pm 1.46
BaP	0.07 \pm 0.07	0.005	0.018	23	0.023 \pm 0.009	0.019	0.102	16	0.121 \pm 0.083
Σ 8PAHs	1.4 \pm 0.7	0.897	0.051	95	0.948 \pm 0.304	1.22	0.71	63	1.93 \pm 0.62
HCB	0.054 \pm 0.022	0.066	0.001	99	0.067 \pm 0.027	0.042	<LOQ	100	0.042 \pm 0.009
PeCB	0.017 \pm 0.005	0.015	<LOQ	97	0.016 \pm 0.008	0.019	<LOQ	100	0.019 \pm 0.002
CB52	0.065 \pm 0.047	0.091	0.012	88	0.103 \pm 0.033	0.027	0.002	96	0.029 \pm 0.016
CB153	0.023 \pm 0.007	0.026	0.018	59	0.044 \pm 0.023	0.023	0.007	77	0.03 \pm 0.02
Σ PCBi	0.19 \pm 0.16	0.267	0.060	82	0.327 \pm 0.091	0.055	0.002	96	0.057 \pm 0.033
Σ PCB-DL	0.020 \pm 0.025	0.032	0.002	94	0.034 \pm 0.032	0.006	0.001	87	0.007 \pm 0.004
DEP	1.85 \pm 2.32	3.67	<LOQ	100	3.67 \pm 1.90	<LOQ	<LOQ		<LOQ
DiBP	15.0 \pm 11.9	24.7	0.211	99	24.9 \pm 7.17	5.05	0.128	82	5.19 \pm 4.17
DnBP	4.49 \pm 5.08	8.3	<LOQ	100	8.31 \pm 4.54	0.671	<LOQ	100	0.671 \pm 0.523
DEHP	60.3 \pm 71.3	58.7	3.8	93	62.6 \pm 75.8	1.8	7.7	19	9.5 \pm 4.4
Σ 7Phthalates	83.3 \pm 91.0	151	14.9	90	165 \pm 91.6	7.55	8.1	48	15.7 \pm 9.2
BDE47	0.001	0.001	<LOQ	100		<LOQ	<LOQ	64	0.02 \pm 0.01
BDE209	0.007 \pm 0.003	0.007	0.002	75	0.009 \pm 0.004	0.004	0.002	70	0.006 \pm 0.001
Σ 8PBDEs	0.0098 \pm 0.0011	0.013	0.002	85	0.016 \pm 0.003	0.004	0.001	88	0.005 \pm 0.001
Fontainebleau									
OP	0.15 \pm 0.14	0.238	0.029	89	0.267 \pm 0.087	0.033	0.004	88	0.037 \pm 0.023
NP	0.45 \pm 0.27	0.626	0.065	91	0.691 \pm 0.03	0.162	0.054	75	0.216 \pm 0.157
Σ OP+NP	0.60 \pm 0.41	0.864	0.094	90	0.957 \pm 0.109	0.195	0.058	77	0.253 \pm 0.179
BPA	0.116	0.116	<LOQ	100	0.116	0.015	<LOQ	100	0.015
TBBPA		<LOQ	<LOQ			<LOQ	<LOQ		
FLU	1.3 \pm 0.42	1.22	<LOQ	100	1.22 \pm 0.51	1.41	<LOQ	100	1.41 \pm 0.39
PHE	2.6 \pm 1.2	1.65	<LOQ	100	1.65 \pm 0.44	3.432	0.050	99	3.48 \pm 1.02
BaP	0.050 \pm 0.037	0.004	0.005	48	0.009 \pm 0.008	<LOQ	0.073	0	0.073 \pm 0.026
Σ 8PAHs	0.70 \pm 0.57	0.200	0.015	93	0.215 \pm 0.024	0.646	0.531	55	1.18 \pm 0.33
HCB	0.048 \pm 0.015	0.053	0.001	99	0.054 \pm 0.014	0.042	<LOQ	100	0.042 \pm 0.016
PeCB	0.015 \pm 0.006	0.012	<LOQ	98	0.013 \pm 0.007	0.018	<LOQ	100	0.018 \pm 0.006
CB52	0.026 \pm 0.023	0.053	0.009	85	0.062 \pm 0.009	0.019	0.002	89	0.021 \pm 0.017
CB153	0.017 \pm 0.012	0.010	0.013	43	0.023 \pm 0.008	0.009	0.002	86	0.011 \pm 0.005
Σ PCBi	0.10 \pm 0.09	0.134	0.045	75	0.180 \pm 0.031	0.021	0.004	85	0.024 \pm 0.013
Σ PCB-DL	0.0068 \pm 0.0059	0.007	0.004	62	0.012 \pm 0.004	0.001	0.001	70	0.002 \pm 0.002
DEP	0.78 \pm 0.92	1.51	<LOQ	100	1.51 \pm 0.721	<LOQ	<LOQ		
DiBP	4.02 \pm 2.50	5.83	<LOQ	100	5.83 \pm 2.30	1.53	0.695	60	2.21 \pm 0.80
DnBP	1.20 \pm 1.07	1.99	<LOQ	100	1.99 \pm 0.99	0.367	0.061	94	0.416 \pm 0.273
DEHP	10.9 \pm 14.4	17.8	<LOQ	100	17.8 \pm 19.3	1.32	2.72	33	4.0 \pm 2.5
Σ 7Phthalates	17.3 \pm 18.3	27.7	0.02	99.7	27.9 \pm 22.4	3.24	3.56	48	6.8 \pm 2.8
BDE47	0.0006 \pm 0.0005	0.001	<LOQ	100	0.001 \pm 0.001	0.000	<LOQ	84	<LOQ
BDE209	0.0088 \pm 0.0048	0.006	0.003	66	0.010 \pm 0.004	0.007	0.001	90	0.008 \pm 0.006
Σ 8PBDEs	0.0103 \pm 0.0065	0.009	0.004	70	0.012 \pm 0.004	0.007	<LOQ	98	0.008 \pm 0.006

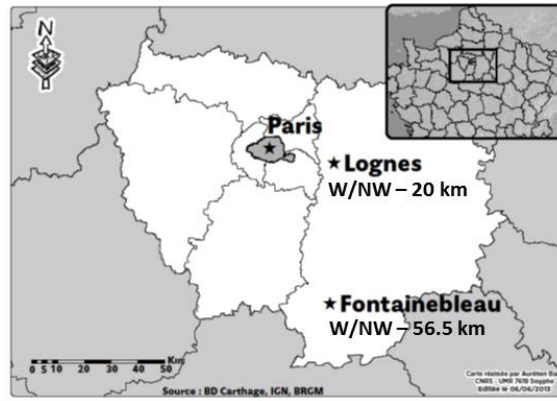
738 <LOQ: below the limit of quantification

739

740 Table 3: Spearman's coefficient between air temperature, PM10 and EDC ambient air
 741 concentrations at Paris (bold: significant r values for p<0.05, n=14).

	T°C	PM10	CB52	CB153	HCB	PeCB	DEP	DEHP	BDE47	BDE100	FLU	BaP	OP	NP
PM10	-0.585	1												
CB52	0.720	-0.472	1											
CB153	0.832	-0.574	0.832	1										
HCB	0.692	-0.373	0.462	0.573	1									
PeCB	0.070	0.278	-0.294	-0.196	0.259	1								
DEP	0.606	-0.691	0.613	0.620	0.577	-0.437	1							
DEHP	0.538	-0.521	0.636	0.832	0.315	-0.538	0.472	1						
BDE47	-0.182	0.028	0.238	0.126	-0.259	0.084	-0.282	0.091	1					
BDE100	0.049	-0.201	0.594	0.413	-0.112	-0.378	0.077	0.434	0.573	1				
FLU	-0.154	0.225	-0.364	-0.280	-0.147	0.329	-0.148	-0.336	-0.252	-0.420	1			
BaP	-0.825	0.803	-0.490	-0.706	-0.517	0.105	-0.577	-0.587	0.091	0.028	0.350	1		
OP	0.839	-0.592	0.762	0.762	0.629	-0.252	0.859	0.531	-0.357	0.091	-0.042	-0.615	1	
NP	0.266	0.067	0.434	0.469	0.322	0.049	0.225	0.259	-0.077	0.350	0.133	0.126	0.469	1

742



743

744 Fig. SM.1: Location of the sampling sites of Airparif (1: urban site - Paris 13th; 2: suburban site - Lognes; 3: forest site - Fontainebleau),
745 prevailing wind direction and distance from the urban site.

746

747 Table SM.1: Sampling conditions for two campaigns at the urban (Paris), the suburban (Lognes) and the forest (Fontainebleau) sites.

Season	Sunshine duration (hours)	Period	Sites	Ozone $\mu\text{g m}^{-3}$	Air sample volume (m^3) (mean \pm SD)	Air flow ($\text{m}^3 \text{h}^{-1}$) (mean \pm SD)	Air temperature ($^{\circ}\text{C}$)	PM10 concentrations <i>Airparif</i> ($\mu\text{g m}^{-3}$)	Cumulative precipitation (mm)
Summer 2010	195	06/01 - 06/16/10	Paris	65.7 \pm 36.9	276 \pm 135	1.4 \pm 0.3	20.9 \pm 3.1	22.2 \pm 3.2	90.3
		06/16 - 06/30/10 06/30 - 07/13/10	Fontainebleau	70.4 \pm 34.4	357 \pm 13	1.3 \pm 0.1	19.2 \pm 2.7	18.0 \pm 0.9	95.6
Winter 2010/2011	36	01/06 - 01/20/11	Paris	23.5 \pm 17.9	331 \pm 79	1.2 \pm 0.3	6.3 \pm 3.4	28.7 \pm 9.6	43.4
		01/20 - 02/02/11 02/02 - 02/16/11	Fontainebleau	44.8 \pm 18.7	401 \pm 7	1.4 \pm 0.1	4.7 \pm 3.3	24.5 \pm 9.2	50.4
Summer 2011	158	05/30 - 06/14/11	Paris	57.9 \pm 29.5	499 \pm 82	1.7 \pm 0.2	19.2 \pm 1.0	19.3 \pm 2.3	86.2
		06/14 - 06/28/11 06/28 - 07/12/11	Lognes	61.8 \pm 32.5	555 \pm 59	1.9 \pm 0.1	18.4 \pm 1.0	16.8 \pm 1.7	98.9
Winter 2011/2012	107	01/24 - 02/08/12	Paris	19.8 \pm 16.5	454 \pm 38	1.5 \pm 0.1	4.0 \pm 4.1	37.9 \pm 4.8	19.4
		02/08 - 02/21/12 02/21 - 03/06/12	Lognes	24.7 \pm 18.5	475 \pm 98	1.6 \pm 0.2	3.0 \pm 4.3	32.7 \pm 1.8	27.4

748

749 Table SM.2: Specifications for the GC analyses

Compound	Chromatography	Apparatus	Injector	Column	Oven parameters	Vector gas
PAHs	GCMS-EI	Agilent GC (7890)-MS (5975)	pulsed Splitless 280°C; 1 µL	ZB-5MS (30 m, 250 µm ID, 0.25 µm film thickness from Phenomenex) with a deactivated silica pre-column (1 m; 0.25 mm ID from Restek)	90°C for 1 min, then 10°C/min to 160°C for 0 min, 5°C/min to 240°C for 10 min and 4°C/min to 300°C for 2 min	Helium 1mL/min
PCBs HCB PeCB	GCMSMS-EI	GC (7890) triple Quad (7000A)	pulsed Splitless 280°C; 1 µL	HT8 (50 m, 250 µm ID, 0.25 µm; from SGE) with a deactivated silica pre-column (1 m; 0.25 mm ID from Restek)	80 °C for 2 min, then 30 °C/min to 170 °C for 0 min and 3 °C/min to 300 °C for 3 min	Helium 40 psi
PAEs	GCMS-EI	Agilent GC (7890)-MS (5975)	splitless 290°C; 1 µL	ZB-5MS (30 m, 250 µm ID, 0.25 µm film thickness from Phenomenex) with a deactivated silica pre-column (1 m; 0.25 mm ID)	50°C for 1 min, then 30°C/min to 280°C and 15°C/min to 310°C for 4 min	Helium 1mL/min
PBDEs	GCMSMS-EI	GC (7890) triple Quad (7000A)	pulsed Splitless 285°C; 1 µL	J&W HP-5MS analytical column (15 m, 250 µm ID, 0.25 µm film thickness) with a deactivated silica pre-column (1 m; 0.25 mm ID)	102 °C for 0.8 min, then 25 °C/min to 185 °C for 0 min, 15 °C/min to 270 °C for 0 min, 5 °C/min to 285 °C for 0 min and 30 °C/min to 315 °C for 3.1 min	Helium 1.8 mL/min

750 Table SM.3: Specifications for the LC-MS/MS analyses

Compound	Chromatography		Apparatus	Injector	Column	Mobile phase	Flow				
BAP TBBPA	LCMSMS-ESI		Agilent LC (SL serie 1200) triple Quad (G6410 BA)	Standard: 10 µL	Zorbax Eclipse XDB-C18 (4.6 X 50 mm; 1.8 µm; Agilent). Chauffée à 50°C.	Methanol/water Gradient: 40/60 at 0 min then 100/0 from 0 to 10 min, 100/0 from 10 to 12 min and 40/60 from 12 to 17 min.	0.5 mL/min				
Alkylphenols	LCMSMS-ESI		AQUITY UPLC®/TQD (Waters).	Standard: 10 µL	AQUITY UPLC/BEH C18 (2.1 mm X 100 mm; 1.7 µm; Water). Chauffée à 40°C.	Methanol and water with ammonium hydroxyde 0,05% Gradient:50/50 at 0 min then 95/5 from 0 to 3 min, 100/0 from 3 to 5 min and 50/50 from 5 to 8 min.	0.4 mL/min				
EDs	Compounds	Internal standard	RT(min)	Source	m/z precursor ion	Fragmentor (V)	m/z quantification		m/z qualification		Collision
							ion fils	Ce(eV)	ion fils	Ce (eV)	
	OP	n-NP	3.25	ESI negatif ; N ₂ ; 380°C ; gas flow: 800 L/h; Capillaire: 2800 V	205	45	134.2	17	133.2	30	Ar (0.25 mL/min)
	NP	n-NP	3.52		219	40	133.2	26	147.2	26	
	BPA	BPA-d16	5.35		227.1	125	212.1	12	133.1	20	
	TBBPA	¹³ C ₁₂ -TBBPA	9.3	ESI negatif ; N ₂ ; 350°C ; gas flow: 660 L/h; Capillaire: 4000 V	543	130	81	60	417.8	40	
	Ethyl-P		4.1		165.1	110	92	20	137	8	N ₂
	Propyl-P		5.4		179.1	80	92	24	136	12	
	Butyl-P		6.5		193.1	110	92	20	136	12	

751

752 RT: Retention Time; Ce: Collision energy; ESI: Electro Spray Ionization

753 Table SM.4: Specifications for the GC-MS/MS analyses (Q: transition for quantification; q:
754 transition for qualification).

Family	Compounds	Internal standard	m/z precursor	m/z product	Dwell Time (ms)	Ec	Others
PCBs	PeCB	CB30	250	215 Q	50	25	Source: 300 °C Interface: 250 °C Quadrupoles: 150 °C
			250	142 q	50	40	
	HCB	CB30	249	214 Q	50	13	
			284	249 q	50	18	
	Tri	CB30	256	186 Q	50	25	
			256	151 q	50	25	
	Tetra	CB30	292	222 Q	25	27	
			292	220 q	25	27	
	Penta	CB107	326	256 Q	25	27	
			326	254 q	25	27	
	Hexa	CB107	360	290 Q	25	27	
			360	325 q	25	12	
	Hepta	CB107	394	324 Q	60	20	
			394	359 q	60	20	
13C12 PCB 194	Syringe standard	442	370 Q	60	40		
		440	370 q	60	40		
PBDEs	BDE28	13C BDE47	407.8	247.9 Q	90	20	
			247.9	139 q	90	30	
	BDE47	13C BDE47	485.7	325.9 Q	80	25	
			325.9	138 q	80	55	
	BDE100	13C BDE47	403.7	137 Q	75	55	
			565.7	405.9 q	75	25	
	BDE99	13C BDE47	403.7	137 Q	75	55	
			565.7	405.9 q	75	25	
	BDE154	13C BDE153	643.6	483.9 Q	75	25	
			483.9	376.8 q	75	40	
	BDE153	13C BDE153	643.6	483.9 Q	75	25	
			483.9	376.8 q	75	40	
	BDE183	BDE181	561.6	454.6 Q	75	40	
			721.6	561.6 q	75	30	
	BDE209	13C BDE209	799.7	640 Q	75	55	
			797.7	637.7 q	75	55	
	13C12 BDE47	IS	497.7	337.9 Q	80	25	
			337.9	148.9 q	80	55	
	13C12 BDE153	IS	655.7	495.8 Q	75	25	
			495.7	335.8 q	75	40	
	BDE181	IS	561.6	454.6 Q	75	40	
			721.6	561.6 q	75	30	
	13C12 BDE209	IS	811.4	651.4 Q	75	55	
809.4			649.5 q	75	55		
BB209	IS	943.5	783.7 Q	70	30		
		783.7	625.7 q	70	45		
CB209	IS	499.7	427.9 Q	75	30		
		427.9	357.8 q	75	45		

755

756 Table SM.5: Specifications for the GC/MS analysis.

Compounds	Internal standards	m/z ion quantification	m/z ion qualification	Others
Acenaphthylene	Phenanthrene d10	152	151	
Acenaphthene	Phenanthrene d10	153	154	
Fluorene	Phenanthrene d10	166	165	
Phenanthrene	Phenanthrene d10	178	179	
Anthracene	Phenanthrene d10	178	179	
Fluoranthene	Pyrene d10	202	200	
Pyrene	Pyrene d10	202	200	Source: 230 °C
Benzo(a)anthracene	Benzo(a)anthracene d12	228	226	
Chrysene	Benzo(a)anthracene d12	228	226	Interface: 250 °C
Benzo(b)fluoranthene	Benzo(a)anthracene d12	252	253	
Benzo(k)fluoranthene	Benzo(a)anthracene d12	252	253	Quadrupoles: 150 °C
Benzo(a)pyrene	Benzo(a)anthracene d12	252	253	
Indeno(1,2,3-cd)pyrene	Benzo(a)anthracene d12	276	274	
Dibenzo(a,h)anthracene	Benzo(a)anthracene d12	278	276	
Benzo(g,h,i)perylene	Benzo(a)anthracene d12	276	274	
Phenanthrene d10		188	189	
Pyrene d10		212	213	
Benzo(a)anthracene d12		240	236	
Benzyl benzoate	Syringe standard	105	212	
DMP	DPP	163	194	
DEP	DPP	149	177	
DiBP	DPP	149	104	
DnBP	DPP	149	223	Source: 230 °C
BBP	DPP	149	104	
DEHP	DPP	149	279	Interface: 200 °C
DnOP	DPP	149	279	
DiNP	DPP	293	149	Quadrupoles: 150 °C
DiDP	DPP	307	149	
DPP		149	104	
Benzyl benzoate	Syringe standard	105	212	

757

758 Table SM.6: Calibration ranges, correlations of the linear responses and quantities of native
759 compounds for the spiked matrices.

Compounds	Calibration ranges (pg)	r^2	Quantity (ng)
BPA	2-20000	> 0.997	50
TBBPA	2-20000	> 0.999	50
PAHs	10-1000	> 0.996	100
HCB	0.8-800	> 0.999	100
PeCB	0.8-800	> 0.999	100
PCBs	0.8-800	> 0.999	50
PAEs	31.25-8000	> 0.998	2000
PBDEs	35-476	> 0.999	25
BDE209	350-4760	> 0.998	250

760

761 Table SM.7: Instrument detection limits (IDLs - pg on column for the low standard
762 solutions, as the concentration with a signal/noise ratio of 3 peak to peak), limits of
763 quantification (LOQs - pg m⁻³), recoveries (as % in spiked XAD-2 and filter matrices) and
764 average blanks (pg m⁻³) for gaseous and particulate phases. For LOQs and recoveries, XAD-2
765 resin and quartz filters were spiked, before extraction, with all native compounds. After
766 extraction, the ISs were added and the extract followed the entire procedure. The LOQ was
767 considered as the concentration (in pg m⁻³) with a signal/noise ratio of 9 (peak to peak).
768

Family	Compounds	IDLs (pg on column)	LOQ Gaseous phase	LOQ Particulate phase	Recovery Gaseous phase	Recovery Particulate phase	Average blanks Gaseous phase (pg m ⁻³)	Average blanks Particulate phase (pg m ⁻³)		
PBDEs	BDE28	0.30	0.2	1.0	87	95	0.2			
	BDE47	0.24	0.6	4.1	98	94	0.8	< LOQ		
	BDE100	0.66	0.6	1.6	102	86	< LOQ	< LOQ		
	BDE99	0.51	0.6	1.6	107	88	< LOQ	< LOQ		
	BDE154	2.04	1.5	0.8	92	89	< LOQ	< LOQ		
	BDE153	1.41	1.8	1.0	100	94	< LOQ	< LOQ		
	BDE183	1.35	1.7	14.9	103	89	< LOQ	< LOQ		
	BDE209	7.5	9.9	79.1	98	93	< LOQ	< LOQ		
	PeCB	0.1	0.2	0.3	50	61	1.6	0.37		
	HCB	0.12	0.3	0.6	57	62	2.0	< LOQ		
PCBs	Indicators	CB28	0.03	0.9	0.4	90	95	4.1	2.7	
		CB52	0.09	0.2	0.1	93	100	17.7	11.9	
		CB101	0.1	1.1	0.2	96	101	8.6	5.2	
		CB118	0.09	0.4	0.3	125	115	4.3	2.9	
		CB138	0.27	0.4	0.5	124	107	18.0	22.3	
		CB153	0.16	0.1	0.2	109	109	17.4	22.8	
		CB180	0.11	0.2	0.4	133	109	3.3	15.2	
		CB77	0.05	0.6	0.8	98	96	< LOQ	< LOQ	
		CB81	0.06	0.3	0.4	102	101	< LOQ	< LOQ	
	DL	CB126	0.18	0.6	0.3	127	112	< LOQ	< LOQ	
		CB169	0.07	0.2	0.3	136	113	< LOQ	< LOQ	
		CB105	0.09	0.4	2.4	113	111	1.1	< LOQ	
		CB114	0.10	0.4	0.3	113	105	< LOQ	< LOQ	
		CB123	0.10	0.4	0.3	125	103	< LOQ	< LOQ	
		Others	CB156	0.07	0.1	0.3	82	107	0.3	0.8
			CB157	0.06	0.4	0.3	134	108	< LOQ	< LOQ
			CB167	0.07	2.2	1.4	135	106	< LOQ	< LOQ
			CB189	0.13	0.2	0.5	133	117	0.2	< LOQ
CB110	0.1		2.1	0.9	65	63	4.9	3.1		
PAEs	DMP	0.08	50.0	6.0	91	78	247	51		
	DEP	0.09	50	0.7	90	83	1017	549		
	DiBP	0.09	83	5.7	101	77	2615	2998		
	DnBP	0.06	69	9.6	102	89	1050	590		
	BBP	0.90	49	3.8	127	98	469	617		
	DEHP	0.30	92	2.8	56	101	2133	2092		
	DnOP	0.30	254	11	63	102	< LOQ	970		
PAHs	Acenaphthylene	0.27	46	1.6	54	47	< LOQ	< LOQ		
	Acenaphthene	0.12	9.2	2.1	67	50	< LOQ	< LOQ		
	Fluorene	0.09	137	0.4	90	54	< LOQ	< LOQ		
	Phenanthrene	0.18	2.7	2.1	76	55	193	16.3		
	Anthracene	0.19	6.6	2.1	67	55	< LOQ	< LOQ		
	Fluoranthene	1.50	8.1	0.3	71	56	14.7	11.9		
	Pyrene	1.58	1.0	0.3	61	55	11.8	11.6		
	Benzo(a)anthracene	0.63	1.0	1.8	53	53	< LOQ	2.4		
	Chrysène	0.60	0.7	1.8	61	52	< LOQ	6.8		
	Benzo(b)fluoranthene	0.86	0.7	0.5	59	51	< LOQ	< LOQ		
	Benzo(k)fluoranthene	0.61	4.6	0.5	67	54	< LOQ	< LOQ		
	Benzo(a)pyrene	2.50	4.6	0.4	60	46	< LOQ	< LOQ		
	Indeno(1.2.3.c d)pyrene	0.48	4.5	0.6	58	45	< LOQ	< LOQ		
	Dibenzo(a,h)anthracene	0.50	1.4	0.5	54	45	< LOQ	< LOQ		
Benzo(g,h,i)perylene	0.27	2.8	0.5	87	95	< LOQ	1.2			
Phenols	BPA	4.4	5.4	18	120	22	300	196		
	TBBPA	0.48	103	39	12	29	< LOQ	< LOQ		

769 < LOQ : under limit of quantification

770 Table SM.8: Annual compound concentrations as mean \pm SD (n = 6) and median for the
 771 phthalates as compounds and Σ 7PAEs, for the PAHs as compounds, Σ 8PAHs (bold) and
 772 Σ 15PAHs and for the PCBs as compounds, Σ PCBi (bold), Σ PCB-DL (italic) and Σ 19PCBs.

	Fontainebleau (2010-2011)			Lognes (2011-2012)			Paris (2010-2011)			Paris (2011-2012)		
	Mean	SD	Median	Mean	SD	Median	Mean	SD	Median	Mean	SD	Median
DMP	0.03	0.04	0.01	0.41	0.30	0.43	0.11	0.13	0.08	0.46	0.29	0.41
DEP	0.76	0.95	0.39	4.53	1.81	4.30	1.84	2.35	0.74	6.99	1.55	7.39
DiBP	4.03	2.51	3.31	4.58	2.39	4.34	15.0	12.0	12.4	7.85	1.60	7.73
DnBP	1.20	1.08	0.95	1.66	1.20	1.51	4.49	5.09	2.22	2.10	0.89	1.95
BBP	0.02	0.02	0.01	0.24	0.19	0.25	0.15	0.22	0.01	0.33	0.33	0.28
DEHP	10.9	14.4	5.07	12.8	15.7	4.63	60.2	71.3	21.6	25.1	11.5	21.30
DnOP	0.31	0.62	0.07	0.29	0.26	0.32	0.08	0.09	0.03	0.30	0.33	0.26
Σ 7PAEs	17.3	18.3	8.55	24.13	20.4	13.7	83.3	91.0	39.0	36.3	17.2	31.3
Acenaphthylene	0.001	0.002		0.265	0.425	0.004	0.225	0.549		0.175	0.422	0.003
Acenaphthene	0.539	0.335	0.405	0.403	0.337	0.490	0.787	0.620	0.687	0.642	0.419	0.571
Fluorene	1.32	0.417	1.48	0.840	0.461	0.903	1.80	0.694	1.64	1.09	0.596	1.35
Phenanthrene	2.57	1.23	2.48	1.89	1.20	1.65	5.43	1.220	5.56	2.57	1.48	2.66
Anthracene	0.002	0.002	0.001	0.032	0.051	0.003	0.002	0.003	0.001	0.034	0.052	0.004
Fluoranthene	0.453	0.322	0.386	0.616	0.432	0.469	1.04	0.310	1.01	0.747	0.381	0.674
Pyrene	0.260	0.216	0.250	0.316	0.289	0.177	1.02	0.675	0.880	0.450	0.332	0.282
Benzo(a)anthracene	0.032	0.037	0.020	0.074	0.105	0.027	0.076	0.072	0.073	0.082	0.097	0.043
Chrysene	0.076	0.084	0.050	0.120	0.142	0.067	0.130	0.107	0.136	0.145	0.165	0.082
Benzo(b)fluoranthene	0.083	0.098	0.056	0.082	0.119	0.027	0.115	0.158	0.056	0.109	0.135	0.051
Benzo(k)fluoranthene	0.002	0.005	0.000	0.001	0.003	0.000	0.001	0.001	0.003	0.003	0.005	0.000
Benzo(a)pyrene	0.041	0.039	0.030	0.067	0.094	0.022	0.072	0.075	0.047	0.068	0.084	0.031
Indeno(1,2,3,c,d)pyrene	0.004	0.006		< LOQ			0.007	0.011	< LOQ	< LOQ		
Dibenzo(a,h)anthracene	< LOQ			< LOQ			< LOQ		< LOQ	< LOQ		
Benzo(g,h,i)perylene	0.081	0.086	0.059	0.056	0.080	0.017	0.13	0.137	0.096	0.040	0.038	0.030
Σ 8PAHs	0.696	0.567	0.543	0.895	0.705	0.685	1.44	0.696	1.24	1.05	0.607	0.852
Σ 15PAHs	5.46	2.228	5.195	4.761	3.08	4.22	10.834	2.74	9.98	6.160	3.21	6.01
CB28	0.0121	0.0117	0.0095	0.0085	0.0044	0.0052	0.0237	0.0199	0.0215	0.0131	0.0055	0.0118
CB52	0.0364	0.0287	0.0340	0.0216	0.0102	0.0222	0.065	0.0472	0.0623	0.0469	0.0224	0.0422
CB101	0.0257	0.0235	0.0226	0.0123	0.0067	0.0108	0.0506	0.0459	0.0390	0.036	0.0271	0.0267
CB110	0.0156	0.0140	0.0139	0.0058	0.0029	0.0054	0.0330	0.0294	0.0293	0.0183	0.0131	0.0138
CB81	0.00001			0.00003			0.00001			0.00004		
CB77	0.00029	0.00021	0.00022	0.00013	0.00011	0.00008	0.00033	0.00023	0.00034	0.00040	0.00048	0.00024
CB123	0.0001	0.0003		0.0001	0.0002		0.0018	0.0024	0.0006	0.0002	0.0003	
CB118	0.0034	0.0031	0.0032	0.0045	0.0016	0.0045	0.0087	0.0078	0.0070	0.0111	0.0040	0.0106
CB114	0.0002			0.0003			< LOQ		< LOQ			
CB153	0.0123	0.0121	0.0111	0.0058	0.0026	0.0047	0.0233	0.0270	0.0145	0.0123	0.0051	0.0121
CB105	0.0011	0.0010	0.0010	0.0014	0.0008	0.0014	0.0027	0.0023	0.0024	0.0040	0.0018	0.0036
CB138	0.0100	0.0099	0.0091	0.0040	0.0017	0.0046	0.0188	0.0213	0.0124	0.0079	0.0021	0.0072
CB126	< LOQ			< LOQ			< LOQ		< LOQ			
CB167	0.00007	0.00008	0.00005	0.00006	0.00005	0.00006	0.00006	0.00007	0.00005	0.00015	0.00012	0.00013
CB156	0.0002	0.0001	0.0002	0.0001	0.0002	0.0001	0.0004	0.0003	0.0003	0.0004	0.0003	0.0003
CB157	0.00147	0.00357	0.0001	0.00004	0.00004	0.00004	0.00037	0.00035	0.00033	0.00039	0.00028	0.00031
CB180	0.0019	0.0018	0.0013	0.0024	0.0026	0.0011	0.0022	0.0021	0.0018	0.0020	0.0012	0.0022
CB169	< LOQ			< LOQ			< LOQ		< LOQ			
CB189	0.00009	0.00011	0.00003	0.00004	0.00005	0.00000	0.0065	0.0155	0.0004	0.00002	0.00003	0.00000
Σ PCBi	0.102	0.0878	0.0907	0.0589	0.0259	0.0514	0.192	0.160	0.159	0.129	0.0634	0.112
Σ PCB-DL	0.0068	0.0059	0.0062	0.0065	0.0027	0.0065	0.021	0.025	0.011	0.016	0.0067	0.015
Σ 19PCBs	0.121	0.103	0.111	0.067	0.030	0.059	0.237	0.198	0.192	0.153	0.079	0.131
BDE28	< LOQ			< LOQ			0.0001			0.0001		
BDE47	0.001	0.001		0.001			0.0017	0.0019	0.0008	0.0023	0.0022	0.0012
BDE100	< LOQ			< LOQ			0.0005	0.0008	0.0001	0.0006	0.0009	0.0002
BDE99	< LOQ			0.001			0.0013	0.0015	0.0006	0.0013	0.0020	0.0002
BDE154	< LOQ			< LOQ			< LOQ			< LOQ		
BDE153	< LOQ			< LOQ			0.0002	0.0005		< LOQ		
BDE183	< LOQ			< LOQ			0.0010	0.0028		< LOQ		
BDE209	0.0088	0.0048	0.0096	< LOQ			0.0048	0.0044	0.0055	< LOQ		
Σ 8PBDEs	0.0103	0.0065	0.0103	0.0014	0.0006	0.0011	0.0098	0.0120	0.0072	0.0043	0.0051	0.0017

773

774 Table SM.9: EDC vapor pressure (Pa, at 25 °C), log K_{OA} (at 25 °C), EDC distribution (as %
775 of total concentration) in gaseous phase of the ambient air and K_p, considering the mean of
776 the three sites during summer (mean temperature 20 °C) and winter (mean temperature 4.5
777 °C).

Compound	Vapor pressure Pa at 25°C	Log K _{OA} at 25°C	% in gaseous phase		K _p	
			Summer	Winter	Summer	Winter
OP	6.27E-01	9.24	88.2	87.1	1.71E-01	2.10E-01
NP	6.00E-01	8.62	88.2	80.6	1.85E-01	2.43E-01
CB28	5.81E+00	8.35	94.5	95.6	6.01E-02	7.12E-02
CB52	3.30E+00	8.68	93.2	97.1	7.99E-02	3.95E-02
CB101	5.55E-01	9.45	93.1	97	8.39E-02	3.64E-02
CB105	8.67E-04	9.88	91.8	91.3	1.03E-01	1.13E-01
CB110	9.50E-04	9.45	90	93	9.28E-02	1.02E-01
CB118	1.75E-01	9.88	91.5	94.4	1.02E-01	6.96E-02
CB138	6.85E-02	10.21	68	75.2	1.01E+00	6.53E-01
CB153	9.11E-02	10.21	71	80	6.92E-01	1.25E-01
CB156	2.10E-04	10.65	83.2	67.7	2.70E-01	2.37E+00
CB157	2.10E-04	10.65	71.8	70.9	4.78E-01	2.64E-01
CB169	6.31E-05	11.08	80.3	69.5	2.65E-01	3.03E-02
CB180	1.73E-04	10.98	81.3	52.2	2.60E-01	3.30E+00
CB189	5.01E-05	11.41	72.9	12.1	1.12E+00	1.76E+00
HCB	3.07E-01	7.64	99.3	99.7	7.50E-03	2.70E-03
PeCB	2.67E+02	6.46	99.7	98.4	1.70E-02	2.70E-03
BPA	5.33E-05	12.70	95.2	85	4.20E-02	1.38E-01
DMP	2.63E-01	7.01	89.7	77.8	1.56E-01	3.82E-01
DEP	1.47E-01	7.55	98.2	79.2	2.18E-02	1.58E-01
DnBP	4.73E-03	8.56	98.1	81.7	1.92E-02	6.99E-01
DiBP	4.73E-03	8.54	97.4	90.6	2.82E-02	1.34E-02
BBP	2.50E-05	8.78	92.4	88.9	1.17E-01	1.93E+00
DEHP	2.50E-05	10.53	89.7	29	1.08E-01	4.61E+00
DnOP	1.84E-06	10.04	58.5	19.5	4.22E-01	3.11E+01
BDE28	2.70E-04	9.70	95.9	99.1	4.93E-02	5.50E-03
BDE47	3.30E-04	10.46	93.7	55.3	8.24E-02	4.88E+00
BDE100	4.69E-05	11.40	85.5	51.4	9.17E-02	1.27E+00
BDE99	4.69E-05	11.20	50	34	1.02E+00	6.38E+00
BDE209	4.60E-06	15.73	70	80	4.62E-01	3.34E-01
Acenaphtene	4.14E+00		100	100		
Fluorene	4.50E-01	7.19	100	82.9	4.00E-04	4.70E-03
Phenanthrene	5.70E-02	7.90	99.2	94.8	5.00E-03	4.20E-02
Fluoranthene	5.60E-03	9.32	85.8	67.2	2.41E-01	3.33E-01
Benzo(a)pyrene	3.20E-06	9.32	49.5	4.4	3.71E-01	4.47E+01
Pyrene	4.10E-03	9.32	95.5	75.6	4.85E-02	4.45E-01
Benzo(a)anthracene	2.30E-04		46.6	12.2	7.29E-01	1.53E+01
Chrysene	4.80E-05		50.6	25.4	5.97E-01	1.16E+01
Benzo(g,h,i)perylene	1.10E-12		27.1	3.6	2.62E-01	5.66E+01

778 PAH compounds detected only in winter and at low levels were not taken in account for the gaseous/particulate phase
779 distribution.

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