**Supplementary Material**

**Traditional and novel halogenated flame retardants in urban ambient air: gas-particle partitioning, size distribution and implications for health**

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## Calculation of air volume sampled by passive samplers

In this study a theoretical model has been applied (described by Shoeib and Harner, 2002) to calculate the volume of air sampled by passive sensors. A template provided by the Global Atmospheric Passive Sampling (GAPS) Network (Harner, 2017) was used. The equation used to calculate the volume of air sampled (Eq S1) takes into account both the physical characteristics of the PUF and the meteorological conditions of the study area, as well as physical-chemical characteristics of the pollutant studied through its octanol-air partition coefficient (Koa).

(Eq S1)

Where:

* Vair = effective air volume (m3)
* K'PUF-a = ratio between the concentration of analyte in the PUF and in the air when equilibrium is reached = KPUF-a ρPUF  (dimensionless)
* ρPUF = PUF´s density = Mass PUF / VPUF (g m-3)
* VPUF = PUF´s volume (m3)
* log KPUF-a = 0.6366 log Koa -3.1774
* Koa = octanol-air partition coefficient
* KA = air-side mass transfer coefficient (m day -1) = R (Surface area PUF  (m2)) -1
* R = sampling rate (m3 day-1) (4 m3 day-1 assumed)
* t = deployment time (days)
* Dfilm (m) = effective film thickness = VPUF (m3) (Surface area PUF  (m2)) -1

## Human respiratory risk assessment

Human respiratory risk assessment was carried out adopting International Commission on Radiological Protection (ICRP) model (1995) as described by (Lyu et al., 2016). Briefly, particle deposition efficiencies (DE) of head airway (HA), tracheobronchial (TB) and alveoli (AV) regions were calculated by Equations S2, S3 and S4, where is the diameter of the particle, and IF is the inhalable fraction of all particles (Eq S5)

Then, the deposition flux (; pg h-1) of inhaled particulate PBDE is calculated (Eq S6), where is the congener concentration in particles, *DEi* is the particle deposition efficiency in each respiratory system region for *Dpi* (average diameter of each particle size fraction, µm), and V is the breathing rate (normal conditions of 0.45 m3 h-1was considered; Zhang et al., 2012)

Hazard quotient (HQ) was calculated by Eq S7, where *DI* is the daily intake (pg day-1; Eq S8), BW is the mean body weight of and adult (60 kg), and RfD is the reported oral reference dose for PBDEs, DP and BB-153 (pg kg-1 bw day-1; (US EPA, 2014, 2010, 2008a, 2008b, 2008c, 2004; Wang et al., 2013). DI is calculated by Eq S8, where ET is the average exposure time (h day-1), for which a conservative value of 24 h day-1 was assumed.

**Tables:**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
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| **Table S1**  Meteorological data monitored during sampling campaigns. Seasonal average ± SD were calculated. | | | | | | | | | | | | | | | | | | | | | |
|  | **Winter** | | | | **Spring** | | | | | **Summer** | | | | | | | **Autumn** | | | | |
| **Active**  **Sampling** | **A1** | **A2** | **A3** |  | **A4** | **A5** | **A6** | |  | **A7** | **A8** | **A9** | **A10** | | **A11** |  | **A12** | **A13** | **A14** | **A15** |  |
| Date | 28-1 | 4-2 | 13-2 | x̄ ± SD | 17-4 | 22-4 | 22-5 | | x̄ ± SD | 26-6 | 3-7 | 10-7 | 17-7 | | 24-7 | x̄ ± SD | 15-10 | 28-10 | 5-11 | 12-11 | x̄ ± SD |
| T low (ºC) | 5.4 | 8.7 | 9.7 | 7.9 ± 1.8 | 20.4 | 14.0 | 15.7 | | 16.7 ± 2.7 | 24,3 | 28,4 | 27,6 | 26,3 | | 28,8 | 27,1 ± 1,6 | 17,1 | 11,9 | 16,1 | 14,4 | 14,9 ± 2,0 |
| T top (ºC) | 7.6 | 10.5 | 11.1 | 9.7 ± 1.5 | 21.6 | 14.5 | 15.6 | | 17.3 ± 3.1 | 23,9 | 28,3 | 27,7 | 26,3 | | 29,0 | 27,1 ± 1,8 | 17,3 | 12,0 | 16,3 | 14,8 | 15,1 ± 2,0 |
| Wind direction1 | SW | WNW | SSW | SSW | SW | NE | ENE | | NE | NE | NE | NE | NE | | SW | NE | SW | NNE | WSW | NE | NE |
| Wind speed (m/s) | 1.6 | 2.7 | 2.0 | 2.1 ± 0.5 | 2.9 | 4.2 | 3.6 | | 3.6 ± 0.6 | 4,5 | 5,4 | 4,0 | 4,3 | | 3,5 | 4,4 ± 0,6 | 1,7 | 3,9 | 2,8 | 5,4 | 3,5 ± 1,4 |
| Relative humidity (%) | 72 | 64 | 66 | 67 ± 4 | 44 | 42 | 46 | | 44 ± 2 | 25 | 33 | 31 | 36 | | 26 | 30 ± 4 | 72 | 56 | 71 | 62 | 65 ± 7 |
| Pressure (hPa) | 949 | 946 | 943 | 946 ± 2 | 941 | 941 | 939 | | 940 ± 1 | 943 | 942 | 935 | 940 | | 937 | 939 ± 3 | 944 | 942 | 942 | 944 | 943 ± 1 |
| Solar irradiance  (W/m2) | 267 | 300 | 301 | 289 ± 16 | 533 | 531 | 509 | | 524 ± 11 | 578 | 503 | 394 | 470 | | 514 | 492 ± 60 | 318 | 317 | 300 | 192 | 282 ± 52 |
|  | | | | | | | | | | | | | | | | | | | | | |
| **Passive Sampling** | **P1** | | **P2** | | **P3** | | | **P4** | | **P5** | | | | **P6** | | | **P7** | | | **P8** | |
| **Date** | 14-01 / 14-02 | | 14-01 / 14-03 | | 17-04 / 07-05 | | | 17-04 / 17-06 | | 03-07 / 05-08 | | | | 03-07 / 03-09 | | | 18-10 / 20-11 | | | 18-10 / 20-12 | |
| T low (ºC) | 6.6 ± 3.2 | | 6.8 ± 3.2 | | 13.9 ± 5.3 | | | 15.4 ± 6.0 | | 26.9 ± 4.8 | | | | 26.4 ± 4.9 | | | 11.7 ± 4.7 | | | 8.6 ± 5.3 | |
| T top (ºC) | 7.6 ± 2.9 | | 7.6 ± 3.0 | | 14.5 ± 5.1 | | | 15.8 ± 5.8 | | 27.0 ± 4.4 | | | | 26.5 ± 4.6 | | | 12.1 ± 4.3 | | | 9.6 ± 4.5 | |
| Wind direction | WNW | | SW ≈ WSW | | NE | | | NE | | NE | | | | NE | | | SW > NE | | | NE | |
| Horizontal speed (m/s) | 4.7 ± 3.0 | | 4.5 ± 2.7 | | 3.8 ± 2.3 | | | 3.9 ± 2.3 | | 3.7 ± 1.8 | | | | 3.8 ± 1.9 | | | 3.1 ± 2.2 | | | 3.1 ± 2.1 | |
| Relative humidity (%) | 67 ± 18 | | 70 ± 18 | | 54 ± 20 | | | 51 ± 20 | | 31 ± 14 | | | | 32 ± 14 | | | 67 ± 17 | | | 65 ± 18 | |
| Pressure (hPa) | 939 ± 9 | | 936 ± 8 | | 937 ± 6 | | | 937 ± 5 | | 939 ± 3 | | | | 939 ± 3 | | | 941 ± 4 | | | 943 ± 5 | |
| Solar irradiance  (W/m2) | 259 ± 180 | | 254 ± 190 | | 427 ± 292 | | | 460 ± 301 | | 531 ± 295 | | | | 517 ± 288 | | | 261 ± 190 | | | 259 ± 173 | |

1Wind direction refers to the most frequent direction during the sampling period

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| **Table S2** | |
| Labelled surrogate standards added to the samples before extraction (LCS) and instrumental analysis (ISS). | |
|  | **Solution** |
| **Surrogate standard solutions (LCS)** | BFR-LCS containing: 13C12 -BDE-3, -15, -28, 47, -77, -99, -100, -126, -153, -154, -169, -183, -197, -205, -207, -209, 13C14-DBDPE, 13C12 –HBB, 13C12 –BB-153, 13C12 –BTBPE,  13C12-*syn*-DP and 13C12-*anti*-DPb |
| **Internal Standard Spiking Solution (ISS)** | BFR-ISSa containing: 13C12 BDE-79, -139, 180, 206 |
| **Calibration Solutions** | BFR-CVSa; *syn*-DPb , *anti*-DPb, Dec-602c, Dec-603 c, Dec-604 c, CP a and Mirexb |

*a Wellington Labs (Canada) and b Cambridge Isotope Labs (USA) trading houses; c Toronto Research Chemical Inc. (Toronto, ON, Canada).*

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| **Table S3** |
| Gas chromatographic and mass spectrometric method conditions. |

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|  | **HRGC** | **MS** |
| **BFR1** | Flow rate:1 mL/min  Inyector: 280ºC Splitless  Oven: 100ºC (1 min) - 25ºC/min - 250ºC - 1.5ºC/min -260ºC (7,7min) - 25ºC/min -325ºC | Autospec Ultima (HRMS)  Transfer line: 280ºC  Source: 280ºC  EI (35 eV) 10.000 |
| **Dechloranes2** | Flow rate:1 mL/min  Inyector: 140ºC (1 min) -20ºC/min -310ºC  Pulsed Splitless (30 psi)  Oven: 140ºC(1 min) – 20ºC/min -310ºC (9.5 min) | Agilent 5973 MSD (LRMS)  Transfer line: 300ºC  Source:150ºC  Quadrupole:150ºC  ECNI (Methane: 40%) |

1 BFR = PBDE, PBEB, HBB, BB-153, DBDPE y BTBPE; 2 Dechloranes = DP, Dec 602, Dec 603, Dec 604, CP and Mirex

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| **Table S4** | | | | | | |
| Recoveries (mean ± standard deviation, %) obtained for each matrix with active and passive samplers. | | | | | | |
|  | **High Volume Samplers (active)** | | | | | **Passive Samplers** |
| **PUF** | **TSP** | **PM10** | **PM2.5** | **PM1** | **PUF** |
| 13C12-PBDE | 82 ± 23 | 91 ± 26 | 90 ± 37 | 97 ± 27 | 69 ± 31 | 80 ± 18 |
| 13C6-BTBPE | 62 ± 14 | 64 ± 40 | 107 ± 81 | 67 ± 38 | 95 ± 81 | 71 ± 35 |
| 13C12-BB-153 | 93 ± 29 | 102 ± 38 | 106 ± 38 | 114 ± 38 | 95 ± 31 | 87 ± 28 |
| 13C12-HBB | 81 ± 52 | 60 ± 43 | 61 ± 61 | 68 ± 66 | 45 ± 41 | 69 ± 54 |
| 13C10-TDP | 78 ± 23 | 77 ± 24 | 80 ± 23 | 83 ± 24 | 77 ± 23 | 78 ± 18 |

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| **Table S5**  Native, surrogate (LCS) and internal (ISS) solutions, limits of detection (LOD) and quantification (LOQ). | | | | |
| **Analyte** | **Surrogate standard**  **solutions**  **(LCS)** | **Internal Standard**  **Spiking Solution**  **(ISS)** | **Limit of**  **detection**  **(LOD)**  **(fg/m3)** | **Limit of**  **quantification**  **(LOQ)**  **(fg/m3)** |
| **BFR** | **BFR-LCS** | **BDE-CVS-EISS** |  |  |
| BDE-17 |  | 13C12 -BDE-79 | 0.10 | 0.34 |
| BDE-28 | 13C12 -BDE-28 | 0.11 | 0.35 |
| BDE-30 |  | 0.14 | 0.46 |
| BDE-47 | 13C12 -BDE-47 | 0.02 | 0.05 |
| BDE-66 | 13C12 -BDE-77 | 0.02 | 0.08 |
| BDE-77 |  | 0.01 | 0.05 |
| BDE-85 | 13C12 -BDE-126 | 0.06 | 0.19 |
| BDE-99 | 13C12 -BDE-99 | 0.04 | 0.12 |
| BDE-100 | 13C12 -BDE-100 | 0.02 | 0.08 |
| BDE-119 | 13C12 -BDE-99 | 0.04 | 0.14 |
| BDE-126 | 13C12 -BDE-126 | 0.04 | 0.14 |
| BDE-138 |  | 13C12 -BDE-139 | 0.31 | 1.01 |
| BDE-139 | 13C12 -BDE-169 | 0.28 | 0.92 |
| BDE-140 |  | 0.27 | 0.89 |
| BDE-153 | 13C12 -BDE-153 | 0.18 | 0.58 |
| BDE-154 | 13C12 -BDE-154 | 0.13 | 0.42 |
| BDE-156 &169 | 13C12 -BDE-169 | 0.37 | 1.22 |
| BDE-171 |  | 13C12 -BDE-180 | 0.16 | 0.52 |
| BDE-180 |  | 0.19 | 0.62 |
| BDE-183 | 13C12 --BDE-183 | 0.11 | 0.35 |
| BDE-184 |  | 0.10 | 0.33 |
| BDE-191 |  | 0.17 | 0.57 |
| BDE-196 | 13C12 -BDE-205 | 0.26 | 0.86 |
| BDE-197 | 13C12 -BDE-197 | 0.23 | 0.74 |
| BDE-201 | 0.35 | 1.16 |
| BDE-203 | 13C12 -BDE-205 | 0.27 | 0.90 |
| BDE-204 | 13C12 -BDE-197 | 0.32 | 1.06 |
| BDE-205 | 13C12 -BDE-205 | 0.46 | 1.52 |
| BDE-206 |  | 0.65 | 2.15 |
| BDE-207 | 13C12 -BDE-207 | 13C12 -BDE-206 | 0.51 | 1.69 |
| BDE-208 |  | 0.62 | 2.06 |
| BDE-209 | 13C12 -BDE-209 | 1.76 | 5.82 |
| BTBPE | 13C6 -BTBPE | 13C12 -BDE-180 | 1.20 | 3.95 |
| BB-153 | 13C12 -BB-153 | 13C12 -BDE-139 | 0.06 | 0.21 |
| PBEB | 13C12 -HBB | 13C12 -BDE-139 | 0.08 | 0.25 |
| HBB | 0.09 | 0.31 |
| DBDPE | 13C14 -DBDPE | 13C12 -BDE-206 | 0.58 | 1.91 |
|  |  |  |  |  |
| syn-DP | 13C12 -syn-DP | 13C12 -anti-DP | 18 | 60 |
| anti-DP | 102 | 340 |
| Dec 604 | 36 | 120 |
| Dec 603 | 2 | 7 |
| Dec 602 | 8 | 27 |
| CP | 9 | 30 |
| Mirex | 2 | 7 |

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| **Tab1e S6**  Pearson correlation matrix for f1ame retardants concentrations (**PUF+TSP**) and meteorologica1variab1es | | | | | | | | | | | | | | | | | | |
|  | **TPBDE** | **BDE-209** | **BDE-207** | **BDE-206** | **BDE-99** | **BDE-47** | **BB-153** | **HBB** | **PBEB** | **TDP** | **Mirex** | ***f*anti** | **T** | **W** | **H** | **P** | **S** |
| **TPBDE** | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-209** | 0.968\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-207** | 0.766\*\* | 0.740\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-206** | 0.850\*\* | 0.900\*\* | 0.784\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-99** | 0.577\* | 0.436 | 0.105 | 0.188 | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-47** | 0.224 | 0.071 | -0.289 | -0.146 | 0.852\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |
| **BB-153** | 0.208 | 0.274 | -0.082 | 0.133 | 0.272 | 0.307 | 1 |  |  |  |  |  |  |  |  |  |  |
| **HBB** | 0.559 | 0.481 | 0.342 | 0.259 | 0.718 | 0.669 | 0.785 | 1 |  |  |  |  |  |  |  |  |  |
| **PBEB** | 0.282 | 0.375 | -0.112 | 0.247 | 0.341 | 0.703\* | 0.319 | 0.754 | 1 |  |  |  |  |  |  |  |  |
| **TDP** | -0.038 | 0.013 | -0.082 | 0.144 | -0.100 | -0.095 | 0.077 | 0.480 | 0.088 | 1 |  |  |  |  |  |  |  |
| **Mirex** | -0.195 | -0.102 | -0.514 | -0.258 | -0.097 | 0.651 | 0.212 | 0.843 | 0.880\*\* | 0.227 | 1 |  |  |  |  |  |  |
| ***f*anti** | -0.588\* | -0.527 | -0.635\* | -0.633\* | -0.398 | -0.100 | 0.432 | 0.374 | 0.149 | 0.193 | 0.551 | 1 |  |  |  |  |  |
| **T** | 0.269 | 0.300 | -0.278 | 0.210 | 0.551\* | 0.668\*\* | 0.404 | 0.446 | 0.776\*\* | 0.203 | 0.630 | -0.109 | 1 |  |  |  |  |
| **W** | -0.200 | -0.155 | -0.538\* | -0.276 | 0.284 | 0.372 | 0.368 | -0.322 | 0.203 | -0.185 | 0.353 | 0.106 | 0.545\* | 1 |  |  |  |
| **H** | -0.205 | -0.290 | 0.234 | -0.257 | -0.386 | -0.381 | -0.506 | -0.020 | -0.417 | -0.220 | -0.365 | 0.171 | -0.832\*\* | -0.640\* | 1 |  |  |
| **P** | -0.175 | -0.256 | 0.208 | -0.153 | -0.359 | -0.341 | -0.168 | -0.043 | -0.439 | -0.346 | -0.691\* | 0.018 | -0.725\*\* | -0.386 | 0.697\*\* | 1 |  |
| **S** | -0.029 | 0.041 | -0.212 | 0.181 | 0.034 | 0.152 | 0.304 | -0.482 | 0.171 | 0.308 | 0.271 | -0.195 | 0.641\* | 0.347 | -0.832\*\* | -0.525\* | 1 |

T = temperature; W = wind speed; H = re1ative humidity; P = atmospheric pressure; S= solar radiation; **\*** (*p* < 0.05); **\*\*** (*p* < 0.01)

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| **Tab1e S7**  Pearson corre1ation matrix for flame retardants concentrations (**PUF**) and meteoro1ogical variables | | | | | | | | | | | | | | | |
|  | **BDE-47** | **BDE-99** | **BDE-100** | **BDE-28** | **BB-153** | **HBB** | **PBEB** | **TDP** | **Mirex** | ***f*anti** | **T** | **W** | **H** | **P** | **S** |
| **BDE-47** | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-99** | 0.927\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-100** | 0.952\*\* | 0.969\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-28** | 0.910\*\* | 0.890\*\* | 0.892\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |
| **BB-153** | -0.119 | -0.168 | -0.190 | -0.517 | 1 |  |  |  |  |  |  |  |  |  |  |
| **HBB** | 0.852\* | 0.822\* | 0.853\* | 0.734 | -0.054 | 1 |  |  |  |  |  |  |  |  |  |
| **PBEB** | 0.770\*\* | 0.770\*\* | 0.799\*\* | 0.485 | -0.371 | 0.810 | 1 |  |  |  |  |  |  |  |  |
| **TDP** | -0.017 | -0.074 | -0.169 | 0.333 | 0.374 | 0.827\* | 0.217 | 1 |  |  |  |  |  |  |  |
| **Mirex** | 0.871\* | 0.709 | 0.703 | 0.687 | 0.189 | 0.896 | 0.787\* | 0.890\*\* | 1 |  |  |  |  |  |  |
| ***f*anti** | -0.106 | -0.267 | -0.237 | -0.165 | 0.516 | -0.396 | -0.107 | 0.425 | 0.659 | 1 |  |  |  |  |  |
| **T** | 0.707\*\* | 0.753\*\* | 0.686\*\* | 0.733\*\* | -0.299 | 0.607 | 0.766\*\* | 0.231 | 0.746 | -0.123 | 1 |  |  |  |  |
| **W** | 0.426 | 0.542\* | 0.543\* | 0.253 | 0.208 | -0.484 | 0.123 | -0.039 | 0.407 | 0.224 | 0.545\* | 1 |  |  |  |
| **H** | -0.430 | -0.576\* | -0.513 | -0.574 | 0.190 | -0.028 | -0.360 | -0.129 | -0.510 | 0.084 | -0.832\*\* | -0.638\* | 1 |  |  |
| **P** | -0.387 | -0.537\* | -0.401 | -0.610\* | -0.010 | -0.076 | -0.389 | -0.149 | -0.701 | 0.075 | -0.725\*\* | -0.386 | 0.694\*\* | 1 |  |
| **S** | 0.191 | 0.194 | 0.204 | 0.333 | -0.399 | -0.354 | 0.176 | 0.175 | 0.600 | 0.113 | 0.641 | 0.347 | -0.835\*\* | -0.525\* | 1 |

T = temperature; W = wind speed; H = relative humidity; P = atmospheric pressure; S= solar radiation; **\*** (*p* < 0.05); **\*\*** (*p* < 0.01)

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| **Tab1e S8**  Pearson correlation matrix for flame retardants concentrations (**TSP**) and meteorological variables. | | | | | | | | | | | | | | | | |
|  | **BDE-209** | **BDE-207** | **BDE-206** | **BDE-99** | **BDE-47** | **BB-153** | **HBB** | **PBEB** | **TDP** | **Mirex** | ***f*anti** | **T** | **W** | **H** | **P** | **S** |
| **BDE-209** | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-207** | 0.743\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-206** | 0.890\*\* | 0.788\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-99** | 0.393 | 0.844\*\* | 0.457 | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-47** | 0.126 | 0.565\* | 0.193 | 0.871\*\* | 1 |  |  |  |  |  |  |  |  |  |  |  |
| **BB-153** | 0.526 | 0.069 | 0.539 | -0.282 | -0.421 | 1 |  |  |  |  |  |  |  |  |  |  |
| **HBB** | 0.262 | 0.101 | 0.010 | 0.239 | 0.174 | 0.328 | 1 |  |  |  |  |  |  |  |  |  |
| **PBEB** | -0.287 | -0.344 | -0.463 | -0.235 | -0.071 | -0.212 | 0.445 | 1 |  |  |  |  |  |  |  |  |
| **TDP** | 0.125 | -0.015 | 0.287 | -0.078 | -0.020 | 0.663 | 0.489 | 0.007 | 1 |  |  |  |  |  |  |  |
| **Mirex** | 0.345 | 0.402 | 0.302 | -0.016 | -0.131 | -0.205 | -0.056 | -0.840 | 0.091 | 1 |  |  |  |  |  |  |
| ***f*anti** | -0.394 | -0.605\* | -0.594\* | -0.551\* | -0.381 | 0.254 | 0.622 | 0.065 | -0.084 | -0.021 | 1 |  |  |  |  |  |
| **T** | 0.272 | -0.293 | 0.192 | -0.624\* | -0.754\*\* | 0.716\* | 0.037 | -0.131 | 0.252 | 0.375 | 0.402 | 1 |  |  |  |  |
| **W** | -0.158 | -0.500 | -0.245 | -0.707\*\* | -0.772\*\* | 0.591 | -0.114 | -0.228 | -0.150 | 0.224 | 0.509 | 0.545\* | 1 |  |  |  |
| **H** | -0.236 | 0.215 | -0.259 | 0.514 | 0.655\*\* | -0.809\*\* | 0.150 | 0.531 | -0.385 | -0.261 | -0.283 | -0.832\*\* | -0.638\* | 1 |  |  |
| **P** | -0.246 | 0.215 | -0.142 | 0.531 | 0.682\*\* | -0.279 | 0.147 | 0.226 | -0.362 | -0.836\* | -0.122 | -0.725\*\* | -0.386 | 0.694\*\* | 1 |  |
| **S** | 0.008 | -0.204 | 0.183 | -0.399 | -0.488 | 0.707\* | -0.513 | -0.406 | 0.489 | 0.002 | 0.091 | 0.641\* | 0.347 | -0.835\*\* | -0.525\* | 1 |

T = temperature; W = wind speed; H = relative humidity; P = atmospheric pressure; S= solar radiation; **\*** (*p* < 0.05); **\*\*** (*p* < 0.01)

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| **Tab1e S9**  Pearson correlation matrix for flame retardants concentrations (**PM10**) and meteorological variables. | | | | | | | | | | | | | |
|  | **BDE-209** | **BDE-207** | **BDE-206** | **BDE-47** | **BDE-99** | **BB-153** | **TDP** | ***f*anti** | **T** | **W** | **H** | **P** | **S** |
| **BDE-209** | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-207** | 0.459 | 1 |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-206** | 0.842\*\* | 0.764\*\* | 1 |  |  |  |  |  |  |  |  |  |  |
| **BDE-47** | -0.471 | 0.275 | -0.192 | 1 |  |  |  |  |  |  |  |  |  |
| **BDE-99** | -0.411 | 0.373 | -0.091 | 0.829\*\* | 1 |  |  |  |  |  |  |  |  |
| **BB-153** | 0.334 | -0.021 | 0.277 | -0.565 | -0.411 | 1 |  |  |  |  |  |  |  |
| **TDP** | 0.392 | 0.044 | 0.207 | -0.312 | -0.373 | -0.199 | 1 |  |  |  |  |  |  |
| ***f*anti** | 0.378 | -0.008 | 0.218 | -0.461 | -0.593 | -0.409 | 0.902\*\* | 1 |  |  |  |  |  |
| **T** | 0.586 | -0.275 | 0.324 | -0.805\*\* | -0.725\* | 0.592 | 0.499 | 0.527 | 1 |  |  |  |  |
| **W** | 0.193 | -0.445 | -0.095 | -0.803\*\* | -0.858\*\* | 0.346 | 0.068 | 0.199 | 0.545\* | 1 |  |  |  |
| **H** | -0.562 | 0.223 | -0.286 | 0.850\*\* | 0.725\* | -0.756\* | -0.599 | -0.401 | -0.832\*\* | -0.638\* | 1 |  |  |
| **P** | -0.577 | 0.196 | -0.263 | 0.688\* | 0.524 | -0.139 | -0.568 | -0.473 | -0.725\*\* | -0.386 | 0.694\*\* | 1 |  |
| **S** | 0.220 | -0.341 | 0.041 | -0.549 | -0.422 | 0.610 | 0.482 | 0.231 | 0.641\* | 0.347 | -0.835\*\* | -0.525\* | 1 |

T = temperature; W = wind speed; H = relative humidity; P = atmospheric pressure; S= solar radiation; **\*** (*p* < 0.05); **\*\*** (*p* < 0.01)

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| **Table S10**  Pearson correlation matrix for flame retardants concentrations (**PM2.5**) and meteorological variables. | | | | | | | | | | | | | | | |
|  | **BDE-209** | **BDE-207** | **BDE-206** | **BDE-99** | **BDE-47** | **BB-153** | **HBB** | **PBEB** | **TDP** | ***f*anti** | **T** | **W** | **H** | **P** | **S** |
| **BDE-209** | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-207** | 0.213 | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-206** | 0.798\*\* | 0.681\* | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-99** | -0.007 | 0.805\*\* | 0.366 | 1 |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-47** | -0.149 | 0.297 | -0.024 | 0.682\* | 1 |  |  |  |  |  |  |  |  |  |  |
| **BB-153** | 0.370 | -0.223 | 0.174 | 0.159 | 0.351 | 1 |  |  |  |  |  |  |  |  |  |
| **HBB** | -0.051 | -0.425 | -0.517 | -0.234 | 0.041 | -0.366 | 1 |  |  |  |  |  |  |  |  |
| **PBEB** | 0.415 | -0.122 | -0.032 | 0.129 | 0.309 | -0.031 | 0.847\* | 1 |  |  |  |  |  |  |  |
| **TDP** | 0.219 | -0.142 | 0.109 | -0.259 | -0.358 | -0.321 | 0.948\*\* | -0.087 | 1 |  |  |  |  |  |  |
| ***f*anti** | 0.326 | -0.400 | 0.167 | -0.483 | -0.499 | 0.197 | 0.141 | -0.055 | 0.377 | 1 |  |  |  |  |  |
| **T** | 0.343 | -0.451 | 0.015 | -0.571 | -0.676\* | 0.176 | -0.238 | -0.317 | 0.138 | 0.559 | 1 |  |  |  |  |
| **W** | 0.357 | -0.451 | 0.083 | -0.632\* | -0.635\* | 0.413 | -0.218 | 0.047 | 0.019 | 0.453 | 0.545\* | 1 |  |  |  |
| **H** | -0.386 | 0.356 | -0.105 | 0.565 | 0.574\* | -0.266 | 0.530 | 0.453 | -0.147 | -0.447 | -0.832\*\* | -0.638\* | 1 |  |  |
| **P** | -0.510 | 0.179 | -0.267 | 0.521 | 0.772\*\* | 0.129 | 0.010 | -0.113 | -0.277 | -0.359 | -0.725\*\* | -0.386 | 0.694\*\* | 1 |  |
| **S** | 0.052 | -0.503 | -0.167 | -0.531 | -0.394 | 0.324 | -0.557 | -0.538 | 0.252 | 0.552 | 0.641\* | 0.347 | -0.835 | -0.525\* | 1 |

T = temperature; W = wind speed; H = relative humidity; P = atmospheric pressure; S= solar radiation; **\*** (*p* < 0.05); **\*\*** (*p* < 0.01)

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| **Table S11**  Pearson correlation matrix for flame retardants concentrations (**PM1**) and meteorological variables | | | | | | | | | | | | | |
|  | **BDE-209** | **BDE-207** | **BDE-206** | **BDE-99** | **BDE-47** | **BB-153** | **TDP** | ***f*anti** | **T** | **W** | **H** | **P** | **S** |
| **BDE-209** | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-207** | 0.269 | 1 |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-206** | 0.545 | 0.562 | 1 |  |  |  |  |  |  |  |  |  |  |
| **BDE-99** | 0.432 | -0.608 | -0.347 | 1 |  |  |  |  |  |  |  |  |  |
| **BDE-47** | 0.514 | -0.292 | -0.438 | 0.595 | 1 |  |  |  |  |  |  |  |  |
| **BB-153** | 0.467 | 0.217 | 0.865 | -0.450 | -0.593 | 1 |  |  |  |  |  |  |  |
| **TDP** | 0.852 | -0.137 | 0.196 | 0.816\* | 0.904\*\* | 0.072 | 1 |  |  |  |  |  |  |
| ***f*anti** | 0.262 | 0.060 | 0.180 | 0.509 | 0.451 | 0.036 | 0.397 | 1 |  |  |  |  |  |
| **T** | 0.074 | -0.466 | 0.077 | 0.387 | -0.363 | 0.423 | -0.097 | -0.026 | 1 |  |  |  |  |
| **W** | 0.100 | -0.260 | 0.287 | -0.257 | -0.233 | 0.572 | -0.270 | -0.396 | 0.545\* | 1 |  |  |  |
| **H** | 0.201 | 0.631 | -0.052 | -0.287 | 0.493 | -0.487 | 0.170 | -0.066 | -0.832\*\* | -0.638\* | 1 |  |  |
| **P** | 0.093 | 0.704 | 0.714 | -0.830\*\* | -0.253 | 0.603 | -0.501 | -0.539 | -0.725\*\* | -0.386 | 0.694\*\* | 1 |  |
| **S** | -0.541 | -0.458 | 0.107 | -0.065 | -0.726\* | 0.396 | -0.567 | -0.268 | 0.641\* | 0.347 | -0.835\*\* | -0.525\* | 1 |

T = temperature; W = wind speed; H = relative humidity; P = atmospheric pressure; S= solar radiation; **\*** (*p* < 0.05); **\*\*** (*p* < 0.01)

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| **Tab1e S12**  Pearson correlation matrix for flame retardants concentrations obtained with passive samplers (PAS) and meteorological variables. | | | | | | | | | | | | | |
|  | **BDE-209** | **BDE-207** | **BDE-206** | **BDE-99** | **BDE-47** | **PBEB** | **TDP** | ***f*anti** | **T** | **W** | **H** | **P** | **S** |
| **BDE-209** | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-207** | 0.819\* | 1 |  |  |  |  |  |  |  |  |  |  |  |
| **BDE-206** | 0.953\*\* | 0.841\* | 1 |  |  |  |  |  |  |  |  |  |  |
| **BDE-99** | -0.346 | -0.308 | 0.061 | 1 |  |  |  |  |  |  |  |  |  |
| **BDE-47** | -0.380 | -0.337 | -0.061 | 0.806 | 1 |  |  |  |  |  |  |  |  |
| **PBEB** | -0.916 | -0.662 | -0.789 | 0.287 | 0.863 | 1 |  |  |  |  |  |  |  |
| **TDP** | 0.809 | 0.590 | 0.813\* | -0.160 | -0.058 | -0.392 | 1 |  |  |  |  |  |  |
| ***f*anti** | 0.670 | 0.476 | 0.535 | 0.242 | -0.098 | -0.822 | 0.570 | 1 |  |  |  |  |  |
| **T** | -0.710 | -0.585 | -0.538 | 0.607 | 0.935\*\* | 0.957\* | -0.490 | -0.451 | 1 |  |  |  |  |
| **W** | 0.906\* | 0.913\*\* | 0.968\*\* | -0.076 | -0.043 | -0.608 | 0.805\* | 0.513 | -0.233 | 1 |  |  |  |
| **H** | 0.574 | 0.475 | 0.386 | -0.690 | -0.981\*\* | -0.938\* | 0.352 | 0.298 | -0.981\*\* | 0.126 | 1 |  |  |
| **P** | -0.495 | -0.702 | -0.466 | -0.091 | 0.085 | 0.958\* | -0.246 | -0.746 | -0.051 | -0.704 | 0.113 | 1 |  |
| **S** | -0.532 | -0.459 | -0.379 | 0.798 | 0.979\*\* | 0.802 | -0.330 | -0.061 | 0.921\*\* | -0.069 | -0.957\*\* | -0.303 | 1 |

T = temperature; W = wind speed; H = relative humidity; P = atmospheric pressure; S= solar radiation; **\*** (*p* < 0.05); **\*\*** (*p* < 0.01)

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| **Tab1e S13**  AEROWIN v1.0 (EPI suite) results for analites evaluated in ambient air at 25 ºC | | | | | | |
|  | CAS Number | LogKoaa | Ps  (Pa)b | Kp  ( m3 µg-1)c | Phi d |
| BDE-209 | 001163-19-5 | 14.98 | 6.32E-07 | 4.75 | 0.997 |
| BDE-99 | 32534-81-9 | 11.32 | 4.13E-06 | 0.72 | 0.983 |
| BDE-47 | 5436-43-1 | 10.54 | 2.11E-04 | 0.01 | 0.533 |
| Dec 602 | 031107-44-5 | 12.27 | 5.85E-05 | 0.05 | 0.804 |
| Dec 603 | 013560-89-9 | 11.83 | 2.13E-05 | 0.14 | 0.918 |
| Dec 604 | 031107-44-5 | 13.22 | 1.27E-05 | 0.23 | 0.950 |
| Dec 605 (DP) | 013560-89-9 | 12.26 | 7.87E-06 | 0.38 | 0.968 |
| CP | 013560-89-9 | 11.25 | 7.01E-05 | 0.04 | 0.774 |
| DBDPE | 84852-53-9 | 19.20 | 9.33E-09 | 321 | 1 |
| HBB | 000087-82-1 | 9.13 | 5.65E-03 | 5.31E-04 | 0.041 |
| PBEB | 000085-22-3 | 9.97 | 8.53E-03 | 3.52E-04 | 0.027 |
| BTBPE | 037853-59-1 | 15.67 | 3.23E-06 | 0.93 | 0.987 |
| BB-153 | 059080-40-9 | 12.01 | 2.03E-05 | 0.18 | 0.922 |
| a Octanol air partition coefficient (KOA) (Cetin and Odabasi, 2008; Lee et al., 2016; Sverko et al., 2011; EPIWEB 4.1), b Vapor pressure (Liquid/subcooled), c Particle gas coefficient (Mackay model), d Fraction sorbed to airborne particulates (Mackay model). | | | | | |

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| **Tab1e S14**  Deposition fluxes (DF pg h-1) and Hazard Quotients(HQ) obtained for particles between PM10 and PM2.5 | | | | | | | |
| **Compound** | **Ci**  **(pg m-3)** | **DFHA**  **(pg h-1)** | **DFTB**  **(pg h-1)** | **DFAR**  **(pg h-1)** | **DF total-**  **(pg h-1)** | **RfDa**  **(pg Kg-1 day-1)** | **HQ** |
| BDE-209 | 3.63 | 1.4 | 0.06 | 3.6E-03 | 1.49 | 7E+06 | 9E-08 |
| BDE-206 | 0.16 | 0.06 | 2.5E-03 | 1.96 | 2.03 | 5E+06 | 2E-07 |
| BDE-207 | 0.26 | 0.10 | 4.0E-03 | 2.6E-04 | 0.11 | 5E+06 | 8E-09 |
| BDE-208 | 0.05 | 0.02 | 8.3E-04 | 5.3E-05 | 0.02 | 5E+06 | 2E-09 |
| BDE-197 | 0.03 | 0.01 | 4.4E-04 | 2.8E-05 | 0.01 | 3E+06 | 2E-09 |
| BDE-171 | 2.1E-03 | 8.2E-04 | 3.2E-05 | 2.1E-06 | 8.5E-04 | 2E+05 | 2E-09 |
| BDE-180 | 2.5E-03 | 1.0E-03 | 3.9E-05 | 2.5E-06 | 1.0E-03 | 2E+05 | 2E-09 |
| BDE-191 | 0.01 | 3.1E-03 | 1.2E-04 | 7.9E-06 | 3.2E-03 | 2E+05 | 6E-09 |
| BDE-183 | 0.01 | 4.8E-03 | 1.9E-04 | 1.2E-05 | 0.01 | 2E+05 | 1E-08 |
| BDE-184 | 1.1E-05 | 4.2E-06 | 1.7E-07 | 1.1E-08 | 4.4E-06 | 2E+05 | 9E-12 |
| BDE-85 | 0.01 | 2.1E-03 | 8.4E-05 | 5.4E-06 | 2.2E-03 | 1E+05 | 9E-09 |
| BDE-119 | 3.2E-03 | 1.3E-03 | 5.0E-05 | 3.2E-06 | 1.3E-03 | 1E+05 | 5E-09 |
| BDE-100 | 4.2E-04 | 1.6E-04 | 6.5E-06 | 4.2E-07 | 1.7E-04 | 1E+05 | 7E-10 |
| BDE-47 | 4.3E-03 | 1.7E-03 | 6.8E-05 | 4.4E-06 | 1.8E-03 | 1E+05 | 7E-09 |
| TPBDE | 4.10 | 1.61 | 0.06 | 4.1E-03 | 1.68 | 1E+06 | 3.0E-07 |
| TDP | 0.45 | 0.18 | 0.01 | 0.00 | 0.19 | 1.E+07 | 7.E-09 |
| a(US EPA, 2014, 2010, 2008a, 2008b, 2008c, 2004; Wang et al., 2013) | | | | | | | |

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| **Tab1e S15**  Deposition fluxes (DF pg h-1)and Hazard Quotients(HQ) obtained for particles between PM2.5 and PM1 | | | | | | | |
| **Compound** | **Ci**  **(pg m-3)** | **DFHA**  **(pg h-1)** | **DFTB**  **(pg h-1)** | **DFAR**  **(pg h-1)** | **DF total**  **(pg h-1)** | **RfDa**  **(pg Kg-1 day-1)** | **HQ** |
| BDE-209 | 1.15 | 0.28 | 0.03 | 3.4E-03 | 0.31 | 7E+06 | 1.7E-08 |
| BDE-206 | 0.13 | 0.03 | 3.2E-03 | 4.0E-04 | 0.04 | 5E+06 | 2.9E-09 |
| BDE-207 | 0.16 | 0.04 | 3.7E-03 | 4.6E-04 | 0.04 | 5E+06 | 3.3E-09 |
| BDE-208 | 0.09 | 0.02 | 2.1E-03 | 2.6E-04 | 0.02 | 5E+06 | 1.9E-09 |
| BDE-203 | 0.15 | 0.04 | 3.5E-03 | 4.4E-04 | 0.04 | 3E+06 | 5.2E-09 |
| BDE-196 | 0.06 | 0.01 | 1.5E-03 | 1.8E-04 | 0.02 | 3E+06 | 2.2E-09 |
| BDE-197 | 0.06 | 0.01 | 1.3E-03 | 1.7E-04 | 0.01 | 3E+06 | 2.0E-09 |
| BDE-201 | 0.08 | 0.02 | 1.8E-03 | 2.3E-04 | 0.02 | 3E+06 | 2.8E-09 |
| BDE-171 | 4.1E-03 | 9.9E-04 | 9.7E-05 | 1.2E-05 | 1.1E-03 | 2E+05 | 2.2E-09 |
| BDE-180 | 0.01 | 1.4E-03 | 1.4E-04 | 1.7E-05 | 1.5E-03 | 2E+05 | 3.1E-09 |
| BDE-191 | 0.01 | 2.3E-03 | 2.3E-04 | 2.9E-05 | 2.6E-03 | 2E+05 | 5.2E-09 |
| BDE-183 | 0.09 | 0.02 | 2.2E-03 | 2.8E-04 | 0.03 | 2E+05 | 5.0E-08 |
| BDE-184 | 0.01 | 3.5E-03 | 3.5E-04 | 4.4E-05 | 3.9E-03 | 2E+05 | 7.9E-09 |
| BDE-138 | 0.01 | 2.3E-03 | 2.3E-04 | 2.9E-05 | 2.6E-03 | 2E+05 | 5.2E-09 |
| BDE-153 | 0.05 | 0.01 | 1.2E-03 | 1.5E-04 | 0.01 | 2E+05 | 2.7E-08 |
| BDE-154 | 0.02 | 0.01 | 5.4E-04 | 6.8E-05 | 0.01 | 2E+05 | 1.2E-08 |
| BDE-126 | 4.5E-03 | 1.1E-03 | 1.1E-04 | 1.3E-05 | 1.2E-03 | 1E+05 | 4.8E-09 |
| BDE-85 | 0.01 | 1.7E-03 | 1.7E-04 | 2.1E-05 | 1.9E-03 | 1E+05 | 7.5E-09 |
| BDE-99 | 0.08 | 0.02 | 1.9E-03 | 2.4E-04 | 0.02 | 1E+05 | 8.7E-08 |
| BDE-119 | 0.01 | 1.8E-03 | 1.8E-04 | 2.3E-05 | 2.0E-03 | 1E+05 | 8.2E-09 |
| BDE-100 | 0.02 | 0.01 | 5.4E-04 | 6.8E-05 | 0.01 | 1E+05 | 2.4E-08 |
| BDE-77 | 4.7E-03 | 1.1E-03 | 1.1E-04 | 1.4E-05 | 1.2E-03 | 1E+05 | 4.9E-09 |
| BDE-66 | 0.01 | 2.1E-03 | 2.1E-04 | 2.6E-05 | 2.3E-03 | 1E+05 | 9.4E-09 |
| BDE-47 | 0.03 | 6.6E-03 | 6.5E-04 | 8.1E-05 | 0.01 | 1E+05 | 2.9E-08 |
| BDE-17 | 2.8E-03 | 6.7E-04 | 6.6E-05 | 8.3E-06 | 7.4E-04 | 1E+05 | 3.0E-09 |
| TPBDE | 2.28 | 0.55 | 0.05 | 0.01 | 0.61 | 1E+06 | 3.3E-07 |
| TDP | 0.36 | 0.09 | 0.01 | 0.00 | 0.10 | 1.E+07 | 4.E-09 |
| a(US EPA, 2014, 2010, 2008a, 2008b, 2008c, 2004; Wang et al., 2013) | | | | | | | |

**Figures:**



**Fig. S1**. Box and whisker p1ots of concentration in air (pg m-3; PUF+TSP) of TPBDE, TDP, Mirex, PBEB and BB-153 seasonal - c1ustered (WI = Winter; SP = Spring; SU = Summer; AU = Autumn). Upper edge of the box, 1ine within the box and 1ower edge of the box, represents the 75th, 50th, and 25th percenti1es. Vertical 1ines extend from the minimum to the maximum va1ue, exc1uding out1iers (circ1es) and extreme (asterisks) va1ues which were labeled with sampling campaign code (see Tab1e S1).



**Fig. S2**. PBDE congeners pattern obtained with (a) active (PUF+TSP) and (b) passive (PAS) samp1ers



**Fig. S3**. Fraction of PBDE concentrations partitioned onto TSP, PM10, PM2.5 and PM1 versus the logarithm of the octanol-air partition coefficient (KOA)



**Fig. S4**. Concentrations (pg m-3) of a) TPBDE, b) BDE-209, c) BDE-47d) BDE-99 and e) TDP obtained with passive (orange) and active (green) samplers.



**Fig. S5**. Seasona1 evo1ution of BB-153 in PUF-TSP, averaged temperature and re1ative humidity (RH) for the period of study.

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