

## PCDD/Fs and PCBs in urban ambient air: gas-particle partitioning, size distribution and inhalation risk

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### Introduction

Atmospheric pollutants concern the whole environment, because ambient air constitutes an entry point into the trophic chains, through deposition (both dry and wet) and the exchange between air, soil and vegetation. The adverse effects of air pollution are especially severe in urban locations, because they are very populated areas, where there are potentially polluting activities such as the production and use of electric energy, road traffic, and heating and burning of biomass for domestic use<sup>1</sup>.

Ambient air is the main transport route for most of POPs, including polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs), which can partition between the gas phase and suspended particulate matter (PM), due to their low vapor pressures<sup>2</sup>. Consequently, there is a need of knowledge related to the distribution of these compounds in gas and particulate phases, and among different particle sizes in the atmosphere, which determines the health effects of suspended particles and its mobilization in the environment. Large particles are more likely to undergo sedimentation processes, depositing in closer areas to their release site, whereas small particles are able to travel great distances<sup>3</sup>. The latter have a greater capacity of penetration and deposition in the human body, being those with a diameter < 1  $\mu\text{m}$  ( $\text{PM}_{10}$ ) capable to reach the alveoli and even bloodstream, and develop inflammatory responses and respiratory and cardiovascular disorders<sup>4,5</sup>.

In order to better understand the concentrations and distribution of PCDD/Fs and PCBs in urban ambient air, and thus their mobilization and impact on health, an annual basis experiment was conducted. The ambient air levels, gas/particle partitioning, size particle distribution, congener profiles and toxic contents of the 17 toxic congeners of PCDD/Fs, the 12 dioxin-like PCBs (dl-PCBs; non-ortho-substituted congeners (no-PCBs) and mono ortho-PCBs (mo-PCB), and 6 indicator PCBs (i-PCBs) were evaluated in the city of Madrid (Spain).

### Materials and methods

68 ambient air samples were collected at the Center for Energy, Environmental and Technological Research (CIEMAT, 40° 27' 27" N, 3° 43'23" W), in the city of Madrid (Spain) during 15 sampling campaigns, from January to December 2013. Gas and particle phases were collected simultaneously using four high-volume active samplers (HVS, CAV A/m model; MCV Spain) working at 30  $\text{m}^3 \text{h}^{-1}$  flow rate. Polyurethane foam cylinders (PUF, 10 cm diameter, 10 cm height, and 0.03  $\text{g cm}^{-3}$  density; TechnoSpec, Spain) and circular glass fiber filters (GFF, 15 cm diameter; 0.26 mm thickness; GF/A grade; Whatman, UK) were used for gas phase and particle sampling, respectively. One of the HVSs was equipped with a circular filter holder to collect the total suspended particulates (TSP), followed by a PUF holder (CBE-CAV model; MCV, Spain) in order to sample the gas phase. The remaining HVSs were equipped with  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  cutoff inlets (PM1025-CAV model; MCV Spain), and a  $\text{PM}_{10}$  cutoff inlet (DIGITEL DPM01/30/00), to collect particulate matter with an aerodynamic diameter equal or <10, 2.5 and 1  $\mu\text{m}$ , respectively. Handling and sampling procedures were performed following the guidelines of EN 12341:1999 and EN 14907:2006 standards.

Calibration of the sampling flow rate was conducted prior to the sampling campaigns, using an adequate flow meter, and repeated after the first 6 months of sampling. Field blanks were taken to evaluate the possible contamination due to the deployment and handling of the samples. They were extracted and analyzed following the same procedures as the samples, and data were blank corrected subtracting the amount of contaminant quantified in the blank to the amount measured in the sample.

The analytical procedure was carried out in accordance with the USEPA 1613B and the 1668A Methods for PCDD/Fs and PCBs. Instrumental analysis were performed in an Agilent GC 6890N coupled to a Micromass Ultima NT HRMS, at 10,000 resolving power (10% valley) and working in selected ion monitoring (SIM). GC column was a 60 m × 0.25 mm × 0.25 μm film thickness (DB-5MS, Agilent J&W). Quantification was carried out using isotopic dilution method.

### Results and discussion:

Total air concentrations (sum of PUF and TSP) obtained in the present work, indicated that levels of TPCBs (437 pg m<sup>-3</sup>; median) were orders of magnitude higher than TPCDD/Fs (0.07 pgm<sup>-3</sup>). Besides, PCB pattern ranked ( $p < 0.01$ ) as follows: i-PCBs (309 pg m<sup>-3</sup>) > mo-PCBs (110 pg m<sup>-3</sup>) >> no-PCBs (0.81 pg m<sup>-3</sup>), with no seasonal variability.

TPCBs (Total PCBs) showed significantly ( $p < 0.05$ ) higher levels in warm seasons (spring and summer) than in autumn and winter. Similar results have been described in the literature in relation to locations with similar climates<sup>6,7</sup> and are corroborated by positive correlations between TPCBs and temperature ( $r = 0.635$ ,  $p < 0.05$ ).

The concentration differences between gas phase and total particulate matter were very significant for both i-PCBs ( $p < 0.00001$ ) and dl-PCBs ( $p < 0.01$ ), with higher levels in the gas phase (99 and 98% of i-PCBs and dl-PCBs) than in particulate matter. However, no statistically significant differences were detected between the different particle sizes, suggesting that most of dl-PCB and i-PCB content in TSP is mainly associated with the smallest particles (PM<sub>1</sub>), since the addition of larger ones does not reflect statistically significant changes in their concentrations.

The Ti-PCB (sum of PUF and TSP) pattern closely resembles the one obtained in the gas phase, that is dominated by PCB-101 (35%, penta-CB) and PCB-52 (30%, tetra-CB), followed by PCB-138~PCB-153 (14%), PCB-28 (5%) and PCB-180 (2%). Presence of major i-PCBs in gas (PCB-101) and particle phase (PCB 138) could reflect the historical use of commercial formulations such as: Kanechlor 500, Clophen A-50, Aroclor 1254, and Sovol in which they are constituents (30–36%)<sup>8</sup>. The use of PCBs was banned in Spain in 1986, however buildings near (<100 m) the sampling site date back to the early 1950s, so presence of PCBs in construction materials cannot be ruled out. Additionally, traffic road emissions could influence the presence of these congeners both in particulate and gas phase. All samples present a similar dl-PCB congener pattern: PCB-118 > PCB-105 > PCB-156 > PCB-167. This result can be clearly associated with global production/utilization of PCB-118, since this congener was included in large quantities in various commercial mixtures of PCBs<sup>9</sup>.

Data of total concentration (PUF + TSP) obtained for TPCDD/Fs, ranging between 0.04 and 0.41 pg m<sup>-3</sup>, are comparable to those described for another urban background area in Athens<sup>10</sup>, however they are lower than the concentrations found in urban center zones<sup>11</sup>. Besides, TPCDD/F levels showed statistically significant seasonal differences ( $p < 0.05$ ), exhibiting maxima during the winter. Concentrations of TPCDD/Fs showed negative correlations with ambient temperature ( $r = -0.730$ ,  $p < 0.01$ ) and wind speed ( $r = -0.618$ ;  $p < 0.05$ ), and positive correlation with relative humidity ( $r = 0.686$ ,  $p < 0.01$ ). These three meteorological variables were combined during winter (high relative humidity, low temperature and wind speeds) with respect to the rest of the year. It is interesting to highlight this season is characterized by an increase in the combustion processes (which are related to the emission of dioxins and furans) associated with heating.

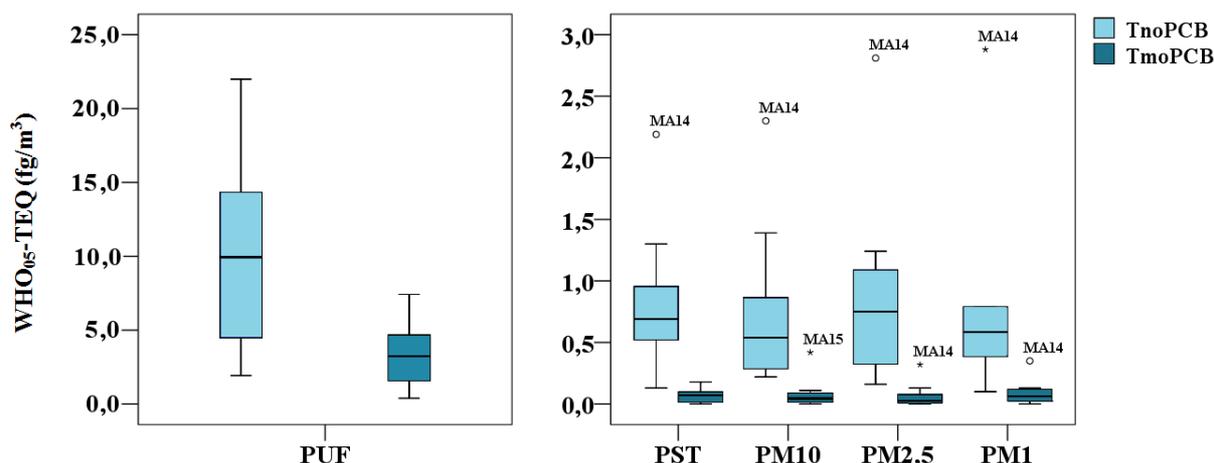
Levels of PCDD/F in the gas phase (0.004–0.14 pg m<sup>-3</sup>, range) were significantly ( $p < 0.05$ ) lower than those found in the particulate phase (0.02–0.34 pg m<sup>-3</sup>). Similar concentrations in all size fractions, even increasing the cutoff size, indicate that PCDD/Fs in the ambient air of the study area are associated with the smallest particle sizes (PM<sub>1</sub>). This result agrees with those obtained in other studies<sup>12</sup> reporting that 90% of PCDD/Fs were associated with particles <1.35 μm.

When the seasonal contribution (%) in each phase (PUF/TSP) to the total concentration of PCDD/Fs was analyzed, a significant increase in the contribution of the gas phase in spring and summer was observed

(Kruskal-Wallis,  $p < 0.05$ ). The higher contribution of PCDD/Fs to the gas phase in periods of higher ambient temperature has also been reported in other studies<sup>6,13</sup>.

PCDD/F pattern revealed OCDD (26%), 1,2,3,4,6,7,8-HpCDF (12%), 1,2,3,4,6,7,8-HpCDD (9%) and OCDF (9%) as the main congeners (PUF + TSP). Similar results have been reported in ambient air from urban areas and have been widely attributed in the literature to road traffic emissions.

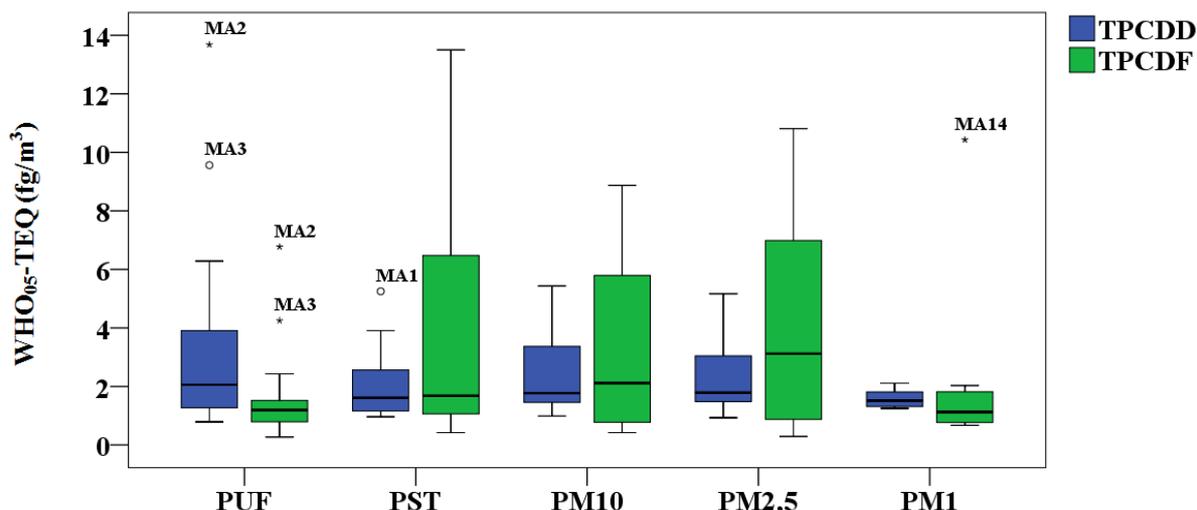
Toxicity attributable to dl-PCBs was higher (68% of total TEQ, in PUF+TSP) than that obtained for TPCDD/F. Gas phase toxicity was mainly due to dl-PCBs (12.6 and 1.82 fg-TEQ<sub>05</sub> m<sup>-3</sup>; median values for dl-PCBs and PCDD/Fs), while in particulate matter the main contributors to total TEQ were PCDD/Fs (0.80 and 3.01 fg-TEQ<sub>05</sub> m<sup>-3</sup>). Related to dl-PCBs, no statistically significant differences were detected among the evaluated fractions of PM, indicating that the toxic content of these compounds in the particulate phase is mainly due to the smaller particles (PM<sub>1</sub>), see Figure 1. Additionally, no significant differences were detected between TEQ of PCDD/Fs in gas (2.96 fg-TEQ<sub>05</sub> m<sup>-3</sup>; median) and particulate phase (3.01 fg-TEQ<sub>05</sub> m<sup>-3</sup>) and, as happened for dl-PCBs, there were also no significant differences between toxicity of the different sizes of particulate matter, being mainly attributable to the smaller particle sizes (PM<sub>1</sub>), see Figure 2.



**Figure 1.** Box and whisker plots of the toxic content related to dl-PCBs (Tmo-PCB and Tno-PCB), in gas phase (PUF) and particles (PST, PM<sub>10</sub>, PM<sub>2,5</sub> and PM<sub>1</sub>), expressed in WHO<sub>05</sub>-TEQ fg m<sup>-3</sup>.

The toxic concentrations of PCDD/Fs and dl-PCBs measured in ambient air were used to assess inhalation risk in the studied area. Thus, the results of daily inhalation dose ranged from 0.004 to 0.02 pg-TEQ<sub>05</sub> kg<sup>-1</sup> day<sup>-1</sup>, which are two and three orders of magnitude lower than the recommended tolerable daily intakes (TDI) of 1–4 pg-WHO-TEQ kg<sup>-1</sup> day<sup>-1</sup> proposed by the WHO European Centre for Environment and Health<sup>14</sup>, and 2 pg-WHO-TEQ kg<sup>-1</sup> day<sup>-1</sup> recommended by the UK Committee on the Toxicity of Chemical in Food, Consumer Products and the Environment<sup>15</sup>.

In addition to the daily intakes estimated for inhalation, cancer risk for a whole life exposure (average 70 years) was also calculated. The values obtained were in a low range ( $5.4 \times 10^{-7}$ – $2.2 \times 10^{-6}$ ) compared to the range considered as acceptable ( $1 \times 10^{-6}$ – $1 \times 10^{-4}$ ) by the US Environmental Protection Agency<sup>16</sup>.



**Figure 2.** Box and whisker plots of the toxic content related to PCDD/Fs (TPCDD and TPCDF), in gas phase (PUF) and particles (PST, PM<sub>10</sub>, PM<sub>2,5</sub> and PM<sub>1</sub>), expressed in WHO<sub>05</sub>-TEQ fg m<sup>-3</sup>.

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