Gas/particle partitioning and particle size distribution of PCDD/Fs and PCBs in urban ambient air

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HIGHLIGHTS

- PCBs were detected in gas phase (99%) regardless of season considered.
- PCDD/Fs were mainly bounded to particulate matter (PM$_1$).
- PCBs and PCDDFs displayed maximum levels in warm and cold seasons, respectively.
- Risk assessment reflected low risk of cancer through inhalation.

GRAPHICAL ABSTRACT
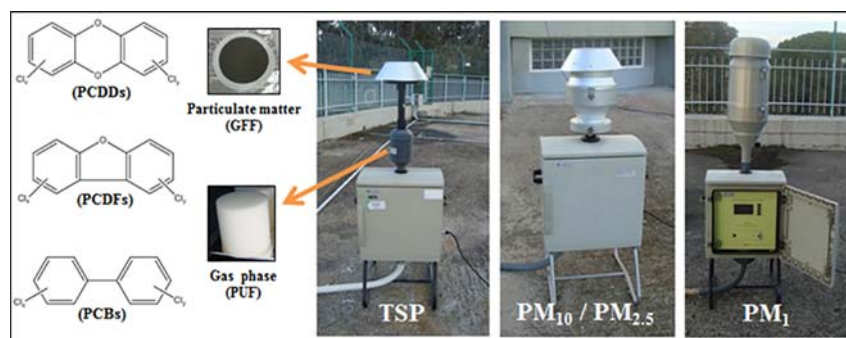
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ABSTRACT

Urban ambient air samples, including gas-phase (PUF), total suspended particulates (TSP), PM$_{10}$, PM$_{2.5}$ and PM$_1$ airborne particle fractions were collected to evaluate gas-particle partitioning and size particle distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs). Clausius-Clapeyron equation, regressions of logKp vs logP_L and logK_{OA}, and human respiratory risk assessment were used to evaluate local or long-distance transport sources, gas-particle partitioning sorption mechanisms, and implications for health. Total ambient air levels (gas phase + particulate phase) of TPCBs and TPCDD/Fs, were 437 and 0.07 pg m^{-3} (median), respectively. Levels of PCDD/F in the gas phase (0.004–0.14 pg m^{-3}, range) were significantly ($p < 0.05$) lower than those found in the particulate phase (0.02–0.34 pg m^{-3}). The concentrations of PCDD/Fs were higher in winter. In contrast, PCBs were mainly associated to the gas phase, and displayed maximum levels in warm seasons, probably due to an increase in evaporation rates, supported by significant and strong positive dependence on temperature observed for several congeners. No significant differences in PCDD/Fs and PCBs concentrations were detected between the different particle size fractions considered (TSP, PM$_{10}$, PM$_{2.5}$ and PM$_1$), reflecting that these chemicals are mainly bounded to PM$_1$. The toxic content of samples was also evaluated. Total toxicity (PUF + TSP) attributable to dl-PCBs (13.4 fg-TEQ$_{05}$ m^{-3}, median) was higher than those reported for PCDD/Fs (6.26 fg-TEQ$_{05}$ m^{-3}). The inhalation risk assessment concluded that the inhalation of PCDD/Fs and dl-PCBs pose a low cancer risk in the studied area.

1. Introduction

Air pollution continues to be a major health, environmental, and economic issue, because it leads to health problems, premature deaths and damage to ecosystems, crops and buildings. Atmospheric pollutants

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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 (EEA, 2013). There are a large number of atmospheric pollutants, such as the persistent organic pollutants (POPs), which are matter of great concern for human health and natural ecosystems, because they are toxic, bioaccumulative and persistent. POPs are also prone to long-range atmospheric transport, and can travel and accumulate far from the areas where they were used or emitted. Ambient air is the main transport route for most of POPs, which can partition between the gas phase and suspended particulate matter (PM), due to their low vapor pressures (10^{-4}–10^{-11} atm at 25 °C, Fernández and Grimalt, 2003). This issue will be also influenced by meteorological parameters such as ambient temperature, humidity, wind speed and the physical-chemical properties of each compound.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are among the POPs which can be found in the ambient air. PCDD/Fs are unintentionally produced organic contaminants obtained as impurities in industrial processes involving chlorinated compounds (such as production of chlorophenol), and in combustion processes of chlorine-containing substances (such as incineration of waste, or production of steel and iron, among others) (WHO, 2000). In contrast, polychlorinated biphenyls (PCBs) are industrial chemical compounds widely used as dielectric and heat transfer fluids in transformers and capacitors, plasticizers, hydraulic fluids, adhesives and flame retardants in plastics and lubricants (Stackelberg, 2011) that were banned in most countries throughout the 1970s, even though their presence in the environment, transfer from one environmental compartment to another through atmospheric transport, deposition and subsequent re-volatilization continues to be a problem nowadays.

POP studies in air reporting data as total concentrations (sum of gas phase and particulate matter) may lead to a significant loss of information. 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 (Lohmann et al., 2000). The latter have a greater capacity of penetration and deposition in the human body, being those with a diameter <1 μm (PM_1) capable to reach the alveoli and even bloodstream, and develop inflammatory responses and respiratory and cardiovascular disorders (Brown et al., 1950; Oberdörster et al., 2005). Recent studies reporting gas-particle partitioning and particle size distribution of PCDD/Fs (Zhang et al., 2016a, 2016b, 2015) and PCBs (Zhu et al., 2017) were conducted in Beijing, China, where pollutants levels are generally higher than those described in Europe or America.

In order to better understand the concentrations and distribution of PCDD/Fs and PCBs in 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. PCB-118 is both an i-PCB and a dioxin-like PCB, so in this study it has been included among dl-PCBs in order to take it into account to assess the toxicity of the samples, in terms of total toxic equivalency WHO-TEQ 2005 (Van den Berg et al., 2006). High-volume air samplers were used to study the concentrations in gas phase and several size particle fractions: total suspended particulates (TSP), and PM

with an aerodynamic diameter (d_{ae}) <10, 2.5 and 1 μm (PM_{10}, $PM_{2.5}$ and PM_1). Meteorological conditions (temperature, humidity, atmospheric pressure, wind speed and direction and solar radiation) were also measured to assess their influence on the ambient air levels of PCDD/Fs and PCBs, and to establish seasonal trends. Finally, data were used to estimate toxicity to human health.

2. Materials and methods

2.1. Sample collection

Sixty-eight ambient air samples (N = 68) were collected in the city of Madrid during fifteen sampling campaigns, from January to December 2013 (Winter, N = 3; Spring, N = 3; Summer, N = 5; Autumn, N = 4). Sampling was carried out at the Center for Energy, Environmental and Technological Research (CIEMAT, 40° 27′ 27″ N, 3° 43′ 23″ W), which is one of the 23 sampling stations belonging to the National Environmental Monitoring Network of POPs, within the National Plan of Implementation of the Stockholm Convention and the Global Monitoring Plan of POPs (UNEP, 2015). This site can be classified as an urban background station (EEA, 1999), as (i) it is located >50 m from the traffic emission sources, with not >2500 vehicles per day within a radius of 50 m, (ii) there are no industrial point sources in the area, and (iii) sources of small scale domestic heating with coal, fuel, oil or wood, or small boiler houses are >50 m away from the measurement point. The weather station of CIEMAT monitors at this site meteorological parameters such as air temperature, atmospheric pressure, relative humidity, wet precipitation, solar irradiance and wind speed and direction, and records the averaged data every ten minutes. Meteorological data from the fifteen sampling campaigns are summarized in Table S1. All samples were taken on days with a stable weather forecast, without precipitation.

Gas and particle phases were collected simultaneously using four high-volume active samplers (HVS, CAV A/m model; MCV Spain) working at 30 m^3 h^{-1} flow rate (1020 m^3 per sample). Polyurethane foam cylinders (PUF, 10 cm diameter, 10 cm height, and 0.03 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 PM_{10} and $PM_{2.5}$ cutoff inlets (PM1025-CAV model; MCV Spain), and a PM_1 cutoff inlet (DIGITEL DPM01/30/00), to collect particulate matter with an aerodynamic diameter equal or <10, 2.5 and 1 μm, respectively. A silicone spray (Dow Corning, USA) was applied to the impaction plate placed after the cutoff nozzles, to prevent the bouncing of coarse particles, which may cause their re-introduction into the air flow and collection in the GFF. Prior to use GFFs were wrapped in aluminum foil and heated at 450 °C for 24 h to remove any organic contaminant. They were weighed and stored in a controlled temperature (20 ± 1 °C; mean ± SD) and humidity (50 ± 5%) weighing chamber until sampling, following the reference standards for the gravimetric determination of particulate matter in ambient air (EN 12341:1999; EN 14907:2006). PUFs were pre-cleaned by Soxhlet extraction with acetone and diethyl ether for 24 h, wrapped in aluminum foil and stored in polyethylene bags at −20 °C until deployment. After sampling, GFFs were stabilized into the weighing chamber and weighed back to determine their particle mass.

2.2. Chemical analysis

The analytical procedure was carried out in accordance with the US EPA 1613B and the 1668A Methods for PCDD/Fs and PCBs. Complete details about chemical analysis have been previously reported (de la Torre et al., 2016). Briefly, samples were spiked with a known amount of ^{13}C-

labelled surrogate standards including PCDD/Fs and PCBs congeners (Table S2), and then they were Soxhlet extracted with toluene for 24 h. Extract obtained was solvent exchanged into hexane prior to cleanup. The cleanup was performed in two steps. First a manual purification was conducted, by solid-liquid adsorption chromatography on an open column (20 g acidic SiO_2, 44% H_2SO_4), eluted with 150 mL of hexane. The extract was concentrated in a rotary evaporator and purified in an automated Power Prep™ System (FMS, Inc., USA) including silica, alumina and carbon columns. Two fractions were obtained: Fraction A, containing i-PCBs and mo-PCBs, eluted from the carbon column; Fraction B, contained PCDD/Fs and no-PCBs, back flushed from the same column. Both fractions were concentrated to incipient dryness under a flow of nitrogen and redisolved in nonane spiked with the injection standards (ISS; see Table S2). 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). Complete details are shown in Table S3. Quantification was carried out using isotopic dilution method.

2.3. Quality assurance/quality control

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. Deviations from nominal flow rate were <3% in all cases. 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. In all cases concentrations in the blanks were below 5% than those obtained in the samples. Instrumental blanks as injections of nonane were run between samples to verify that there was no memory effect. Influence of the silicone spray applied on the inlets was also evaluated. No significant differences were found between the concentration levels of blanks with or without silicone spray. Dioxin and PCB break through the PUF was also evaluated by spiking the PUF with sampling standards (2,3,7,8-[$^{37}Cl_4$]-TCDD, PCB-30 and PCB-198) before sampling. Recoveries for these pollutants were above 70%, complying with EN-1948:2006. Correct identification and quantification of analytes were ensured with three criteria: i) ± 3 s retention time between the analyte and the standard, ii) the ratio of quantifier and qualifier ions within ± 15% of the theoretical values and iii) a signal to noise ratio >3:1. Average recoveries of surrogates were between 63 and 78% for PCDD/Fs, 83–100% for i-PCBs and 79–95% for dl-PCBs. These recoveries are within the ranges accepted in the US EPA Methods considered (1613B and 1668A). The limits of detection of the method (LOD) were established by assessing the amount of analyte with a signal-noise ratio ≥ 3. Congener concentrations below LOD were assigned a concentration of LOD.

2.4. Data analysis

Statistical analyses were performed with Statgraphics Centurion™ XVII and IBM SPSS Statistics 24.0 software. In order to find statistically significant differences, the following tests were applied: ANOVA, Kruskal-Wallis, Mood median, Pearson correlations (Tables S4 to S9) and Fisher's Least Significant Difference test (LSD). Clausius-Clapeyron equation (Table S10), gas-particle partition coefficient (K_p), octanol-air partition coefficient (K_{OA}) and human respiratory risk assessment were used to evaluate local or long-distance transport sources, gas-particle partitioning sorption mechanisms, and implications for health, respectively.

3. Results and discussion

Dioxins, furans and PCBs levels were quantified in all matrices (PUF and PM filters including TSP, PM_{10}, $PM_{2.5}$ and PM_1; N = 14, 15, 12, 13 and 8, respectively). Then, total air concentrations (sum of PUF and TSP; Fig. 1 and Table S11) were calculated to establish a first POP pattern. As can be seen, levels of TPCBs (437 pg m^{-3}; median) were orders of magnitude higher than TPCDD/Fs (0.07 pg m^{-3}). Besides, PCB pattern ranked ($p < 0.01$) as follows: i-PCBs (309 pg m^{-3}) > mo-PCBs (110 pg m^{-3}) ≫ no-PCBs (0.81 pg m^{-3}), with no seasonal variability.

3.1. PCBs

Comparisons of POP concentration in ambient air have to be done with special care, because variations in concentration from pg m^{-3} to ng m^{-3} may be due to changes of location of the sampling point, season sampled or number of congeners analyzed. Assuming this variability, PCB levels (PUF + TSP) found in this study (433 ± 255 pg m^{-3}, average ± SD) were similar to those reported in other European cities such as Roma (553 pg m^{-3}, Menichini et al., 2007), Athens (from 80.5 to 348.6 pg m^{-3}, Mandalakis et al., 2002) or Birminghan (252 ± 156 pg m^{-3}, average ± SD, Halsall et al., 1995; Harrad and Mao, 2004). Higher values have been reported in areas of Asia such as India, where measurements in 2006 and 2007 in several cities yielded results up to 8496 pg m^{-3} (Chakraborty et al., 2013) or China, with PCB levels between 172 and 2720 pg m^{-3} in Guangzhou, one of the most developed and populated cities in the south of the country (Chen et al., 2009). As expected, considering the higher PCB production and/or use in USA (Monsanto Chemical Company supplied 99% of PCBs consumed in the USA and 48% of the world total production before their ban in 1979; Breivik et al., 2002), the concentrations obtained in this study were lower than most of described in USA cities, where levels up to 14.2 and 3.36 ng m^{-3}, the latter only in the gas phase, have been reported in Chicago and Baltimore (Offenberg et al., 1999; Simcik et al., 1997). There are also other studies carried out in these cities, which presented total concentrations more similar to those measured in Madrid, such as those performed by Harner and Bidleman in Chicago with concentrations between 143 and 621 pg m^{-3} (350 ± 144 pg m^{-3}, average ± SD; Harner and Bidleman, 1998), which reflect the great data variability even when obtained in the same locations.

TPCBs showed significantly ($p < 0.05$) higher levels in warm seasons (spring and summer) than in autumn and winter (Fig. 1). Similar results have been described in the literature in relation to locations with similar climates (Castro-Jiménez et al., 2012; Min et al., 2013) and are corroborated by positive correlations between TPCBs and temperature ($r = 0.635$, $p < 0.05$, Table S4). In addition, TPCB content is correlated with humidity ($r = -0.732$, $p < 0.01$) and solar radiation ($r = 0.623$, $p < 0.05$). The production of PCBs in Spain ceased in 1984 and their use was banned two years later (Directive 85/467/EEC, 1985; RD 14061/1989, 1989), so their presence in ambient air can only be linked to the evaporation from materials containing them and to short, medium or long-distance atmospheric transport. A very strong relationship with temperature will indicate a greater weight of evaporation in atmospheric levels, while a greater influence of wind speed ($r = 0.576$, $p < 0.05$) would indicate the entry into the sampling area of air masses from other contaminated areas. In the present study Tno-PCB showed a highly significant correlation with temperature ($r = 0.903$, $p < 0.01$, Table S4), which was stronger than their correlation with wind speed ($r = 0.662$, $p < 0.05$). In addition it was also detected a positive correlation between Ti-PCB and temperature ($r = 0.648$, $p < 0.05$). On the contrary, the concentrations of Tmo-PCBs did not show significant correlation with ambient temperature, but showed a moderate positive correlation with wind speed ($r = 0.632$, $p < 0.05$). It has been observed in other studies that wind speed has great importance in the dependence of PCBs with temperature, decreasing or even disappearing this dependence at higher wind speeds (Halsall et al., 1999). Currado and
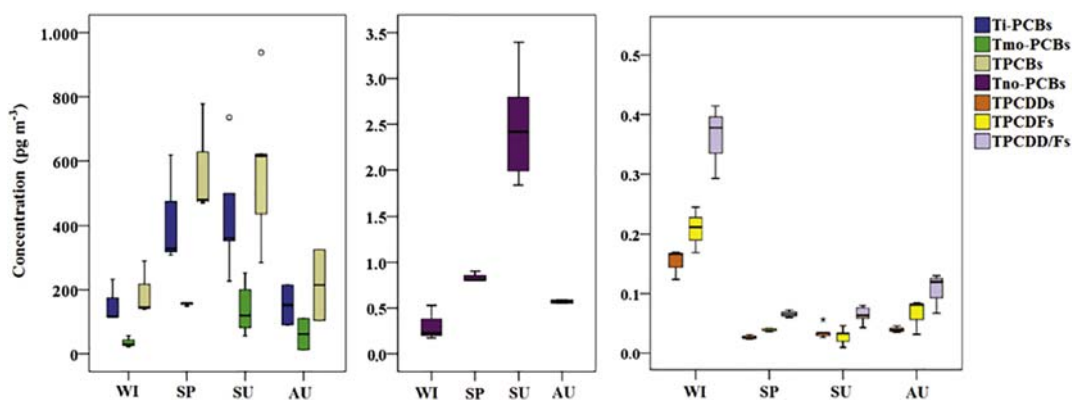
Fig. 1. Box and whiskers plots of concentration in air (pg m^{-3}; PUF + TSP) of TPCBs, Ti-PCBs, Tmo-PCBs, Tno-PCBs, TPCDDs, TPCDFs and TPCDD/Fs, seasonal clustered (WI = Winter; SP = Spring; SU = Summer; AU = Autumn). Upper edge of the box, line within the box and lower edge of the box, represent the 75th, 50th, and 25th percentiles. Vertical lines extend from the minimum to the maximum value, excluding outliers (circles) and extreme (asterisks) values.
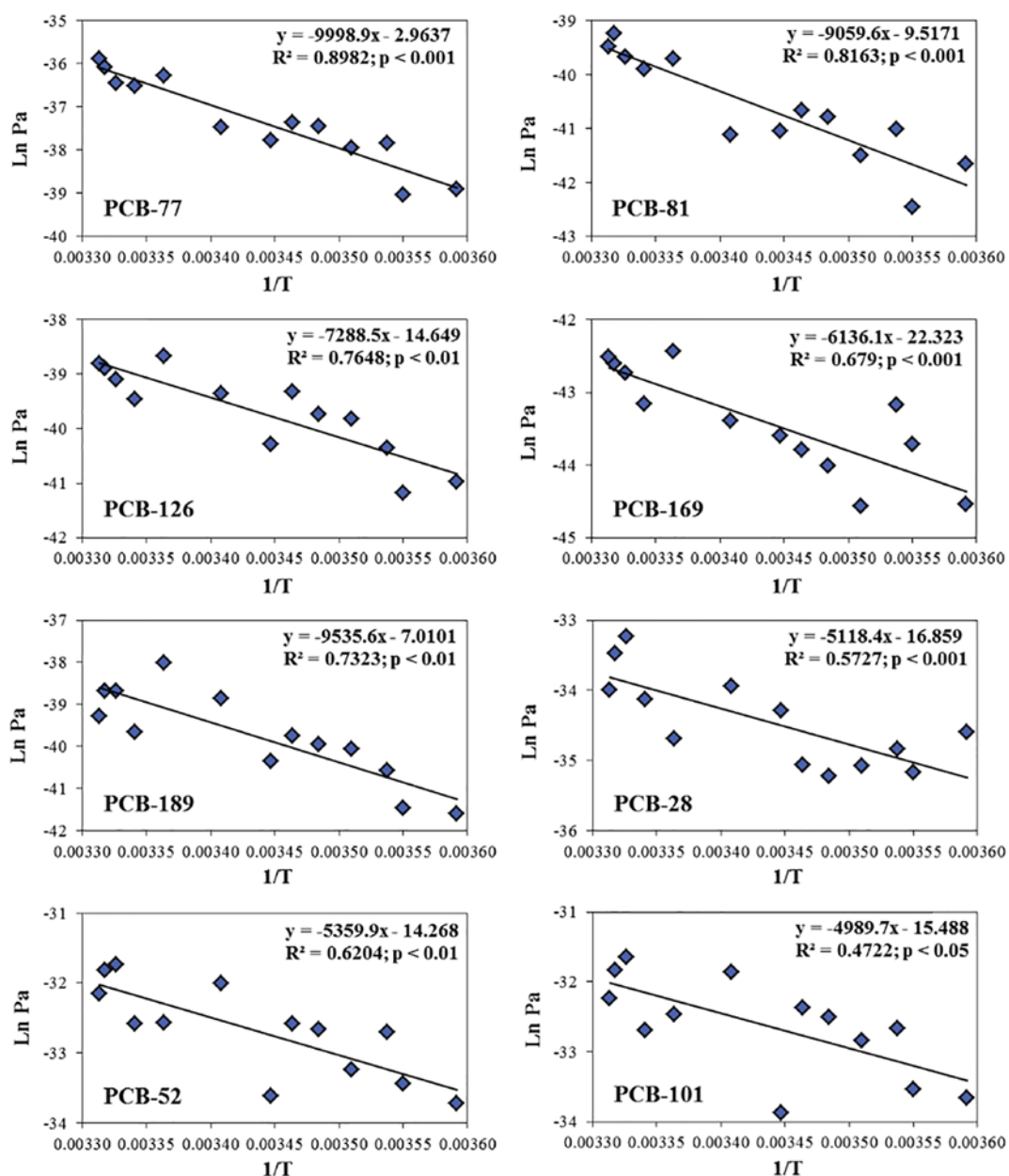

Fig. 2. Plot of the natural logarithm of the calculated partial barpessure (P_a) of PCB-77, PCB-81, PCB-126, PCB-169, PCB-189, PCB-28, PCB-52 and PCB-101 concentrations in air versus reciprocal absolute temperature (Clausius-Clapeyron equation).

Harrad observed in a PCB study in ambient air in Birmingham that for wind speeds higher than 4.4 m/s PCB dependence with temperature disappeared completely (Currado and Harrad, 2000). In the present study the average summer wind speed was 4.4 ± 0.6 m s^{-1}, which could have influenced the absence of correlation between mo-PCB levels and ambient temperature.

In order to better analyze the influence of temperature on the levels of PCBs in ambient air, the Clausius-Clapeyron equation was used (Eq. (1)). The regression of the natural logarithm of the partial pressure (P_a, atm) of the congener to the reciprocal absolute temperature (T^{-1}, K) is shown in Fig. 2 (only congeners with significant temperature dependence ($p < 0.05$) are shown). Both the slope (m) and the coefficient of determination (R^2) obtained from this regression are good indicators of whether pollutants are more affected by long-range atmospheric transport or by evaporation of sources in the study area. The regression parameters are summarized in Table S10.

$$Ln\, P_a = m \left(\frac{1}{T} \right) + b \qquad (1)$$

All the no-PCBs showed a very significant dependence on temperature, with gradients between -6136 and -9999 K, and R^2 between 52% and 73%. PCB-189 was the only mo-PCB that showed significant temperature dependence, with a slope of -9536 K and $R^2 = 52\%$. Among the i-PCBs there were also several congeners with significant dependence: PCB-28, PCB-52 and PCB-101. The congener with the strongest dependence on temperature (with the steepest slope -9999 K, and $R^2 = 73\%$) was PCB-77, indicating that small changes in temperature have a great effect on its gas phase concentration. All these values are in the range of slopes found in urban areas, from -2800 to $-13,500$ K (Harrad and Mao, 2004). The significant temperature dependence observed for these PCB congeners reveals that evaporation from local sources is more important than long-distance transport. The fact that temperature dependence with other congeners has not been found, may indicate a masking of this relationship due to other influential meteorological variables, such as relative humidity, pressure or wind speed (Currado and Harrad, 2000; Halsall et al., 1999).

The study of gas-particle partitioning and size particle distribution provided very interesting results. 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 (Fig. 3a, b and c). 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$_1$), 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 (Fig. S1), that is dominated by PCB-101 (35%, penta-CB) and PCB-52 (30%, tetra-CB), followed by PCB- $138 \approx$ PCB-153 (14%), PCB-28 (5%) and PCB-180 (2%). The gas-particle fractionation of the semi-volatile compounds is controlled by their vapor pressure, which is inversely proportional to the chlorination degree (Biterna and Voutsa, 2005; Harner and Bidleman, 1998). Therefore, it is not strange that TSP pattern is dominated by PCB-138 (41%, hexa-CB) and PCB-180 (22%, hepta-CB).

Although source identification was not considered among this study objectives, a first attempt can be formulated. 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%, Takasuga et al., 2006). As mentioned before, 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. Combustion processes associated with residential heating and motor vehicles are recognized sources of PCBs into
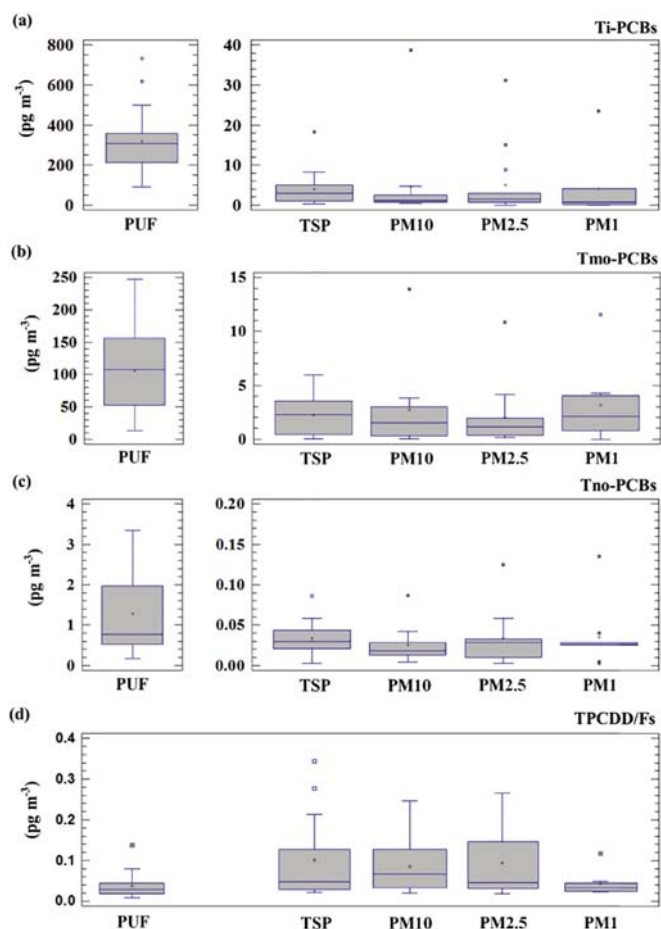

Fig. 3. Box and whisker plots of Ti-PCB (a), Tmo-PCB (b), Tno-PCB (c) and TPCDD/Fs (d) concentrations (pg m^{-3}; PUF + TSP) in gas phase (PUF) and particles (PST, PM$_{10}$, PM$_{2.5}$ and PM$_1$).

ambient air. Biterna and Voutsa analyzed the i-PCB pattern in the TSP of the emissions from these sources and concluded that, in the case of heating, the pattern is dominated almost equally by PCB-180 and PCB-101 (Biterna and Voutsa, 2005). However, if the contribution of this source was high it would reflect a greater content of these two congeners in the particulate material obtained during winter and autumn samplings, a result that does not occur. On the other hand, TSP emissions from diesel and gasoline engines are dominated by PCB-101 (45%), PCB-180 (25–40%) and PCB-118 (15–20%). Therefore, 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 (Breivik et al., 2002). Interestingly, higher PCB-118 levels were obtained during winter in the PUF (Fig. S1), which presence in urban air has been attributed to vehicle emissions (Biterna and Voutsa, 2005).

3.2. PCDD/Fs

The total concentration (PUF + TSP) obtained for TPCDD/Fs varied between 0.04 and 0.41 pg m^{-3}, with an annual average of 0.14 ± 0.13 pg m^{-3} (average ± SD), see Table S11. These levels are comparable to those described for another urban background area in Athens, 0.17 pg m^{-3}, (Mandalakis et al., 2002), however they are lower than the concentrations found in urban center zones, with levels up to 18 pg m^{-3} (Li et al., 2014; Lohmann et al., 2000). Although TPCDD/F

concentrations were lower than those for PCBs throughout the year, they showed statistically significant seasonal differences ($p < 0.05$, Fig. 1). In contrast to PCBs, dioxins and furans exhibit maximum concentrations during the winter. Concentrations of TPCDD/Fs (PUF + TSP) showed negative correlations with ambient temperature ($r = -0.730$, $p < 0.01$, Table S4) 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. There are several factors that can directly influence the achievement of the highest concentrations of dioxins and furans in winter. This period is characterized by an increase in the combustion processes (which are related to the emission of dioxins and furans) associated with heating. The special winter ambient conditions favor nocturnal thermal inversion phenomena, and very stable atmospheres due to high pressure systems. Moreover, the lower height of the mixture layer at this time of the year inhibits the pollutant dispersion, and can accumulate their concentration levels in some areas (Saral et al., 2015). In the present study, temperature differences between the upper and the lower temperature sensors of the meteorological station were up to 7 times higher than the expected differences, in relation to the ambient thermal gradient. This increase in temperature with height, along with high atmospheric pressures at the ground level and stable weather, confirms the existence of thermal inversions during these samplings favoring the accumulation of contaminants in the air at surface level. In addition, it should be pointed out that in situations of increased solar radiation, certain processes could contribute to decrease the amount of PCDD/F in ambient air, such as OH radicals reactions and photodegradation processes (Lohmann and Jones, 1998). In the present study, TPCDDs and TPCDFs showed a negative correlation with solar radiation ($r < -0.560$, $p < 0.05$, Table S4), especially in the TSP ($r < -0.728$, $p < 0.01$, Table S6), that would support this hypothesis.

The concentrations of dioxins and furans were studied in each of the matrices analyzed (Fig. 3d.). Levels of PCDD/F in the gas phase (0.004–0.14 pg m^{-3}, range Table S11) were significantly ($p < 0.05$) lower than those found in the particulate phase (0.02–0.34 pg m^{-3}). At a first glance, it appears that the TPCDF content in PM$_1$ particles is lower than that in PM$_{2.5}$, however this result lacks statistical significance. 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$_1$). This result agrees with those obtained in other studies. Kaupp et al., 1994 estimated that 90% of PCDD/Fs were associated with particles <1.35 μm. Kurokawa et al., 1998 reached a similar conclusion, finding 68–80% PCDD/Fs in particles <2 μm. In this study, TPCDFs in PM$_1$ represent 89 ± 10% (average ± SD) of TSP.

Gas-particle partitioning of semivolatile organic compounds is often studied by the gas-particle partition coefficient, (K_p; m^{-3} μg^{-1}) defined in Eq. (2), where $_i$ is the particle size fraction, PM is the particulate matter concentration (μg m^{-3}), and F and A are the concentrations (pg m^{-3}) in the particle and gas phase (Zhang et al., 2016a).

$$K_p = \left(\frac{F_i}{PM_i}\right)/A \tag{2}$$

The gas-particle partition coefficient (K_p) can be described by two theoretical models, which allow to identify the main sorption mechanism in particulate matter (adsorption or absorption). They are based on the linear relationship between K_p and (i) the subcooled liquid vapor pressure (P_L, adsorption model, Eq. (3)); (Yamasaki et al., 1982), and (ii) the octanol-air partition coefficient (K_{OA}, absorption model, Eq. (4)); (Harner and Bidleman, 1998). The slopes (m_r and m_o) and the intercepts (b_r and b_o) are fitting constants. The values of regression coefficients (m_r and m_o) are important parameters to determine the dominant sorption mechanism onto particles. P_L was calculated from the Eq. (5) (Zhang et al., 2016a), in which T and RI are the absolute

temperature (K) and the gas chromatographic retention index of the compound. The logarithm of K_{OA} was calculated following the procedure described by Harner et al. ($\log K_{OA} = a' + b'$ (RI); where a' and b' are temperature dependent parameters), with Tom Harner's template (Harner, 2017).

$$\log K_p = m_r \log P_L + b_r \tag{3}$$

$$\log K_P = m_O \log K_{OA} + b_O \tag{4}$$

$$\log P_L = \frac{-1.34(RI)}{T} + 1.67 \times 10^{-3} (RI) - \frac{1320}{T} + 8.807 \tag{5}$$

In the present study both models were applied to PCDD/F concentrations in particulate matter (Fig. 4). The logarithm of the coefficient K_p was calculated for all samplings and then plotted against $\log K_{OA}$ or $\log P_L$. Significant relationships ($p < 0.001$) were detected in all size particle fractions, however the determination coefficient (R^2) was in a low range (13%–21% for $\log K_p$- $\log P_L$ regressions, and 11%–18% for $\log K_p$-$\log K_{OA}$), and thus it explains only a small part of variability. The slopes for both models deviate significantly from $|1|$. According to Goss and Schwarzenbach (1998), slopes significantly steeper than -1 are indicative of adsorption, while slopes shallower than -0.6 point to absorption. Intermediate values, between -0.6 and -1, reflect a mixed sorption mechanism. In this study, m_r ranged from -0.21 to -0.36, and m_o from 0.20 to 0.37, therefore these results do not allow identifying the main sorption process. Such deviations may be attributed to: (i) non-equilibrium conditions, (ii) sampling artifacts, (iii) changes in PM$_i$ or PCDD/Fs concentrations (or in ambient temperature) during sampling events, (iv) non-exchangeability, (v) varying activity coefficients in organic matter within a compound class, and/or (vi) different sorbing properties of atmospheric particles from those of the octanol (Finizio et al., 1997; Goss and Schwarzenbach, 1998; Simcik et al., 1998). Moreover, this result could also reflect that there are other variables, such as the organic carbon in particulate matter, that are not considered by the applied equations and could influence gas-particle partitioning. Unfortunately, organic or elemental carbon data were not available because PCDD/F chemical analyses required complete samples to avoid being below LOD. Therefore, fraction partitioned onto particles (φ) was estimated with three empirical organic matter fractions (f_{om}) of 10%, 20% and 30%, according to Eqs. (6) and (7) (Harner and Bidleman, 1998). The curves obtained are shown in Fig. S2. The fraction of PCDD/Fs partitioned onto PM increased with organic matter content.

$$\varphi = \frac{K_p PM_i}{1 + K_p PM_i} \tag{6}$$

$$\log K_P = \log K_{OA} + \log f_{om} - 11.91 \tag{7}$$

The levels of dioxins and furans in TSP, PM$_{10}$ and PM$_{2.5}$ showed significant seasonal differences ($p < 0.001$; number of samples in winter, spring, summer, autumn = 9, 7, 13, 11, respectively), with higher levels in winter. Interesting relationships were obtained between the pollutant content and some meteorological parameters for all particle sizes studied. All totals (TPCDDs, TPCDFs and TPCDD/Fs) in TSP showed positive correlations with pressure and relative humidity ($r > 0.780$ and 0.753, respectively for TPCDD/Fs, $p < 0.01$; Table S6), reflecting higher concentrations in situations of higher atmospheric pressure and relative humidity (winter). On the other hand, significant negative correlations were obtained with solar radiation, temperature, and wind speed ($r < -0.646/-0.750/-0.621$; $p < 0.01/0.01/0.05$) that are due to lower levels of dioxins, furans and sum of both during spring and summer. Although the higher levels obtained during the winter in this study can be related to specific emission processes during this period, the lower concentrations described in summer may not only be conditioned by the decrease of these sources, but also by the greater contribution of
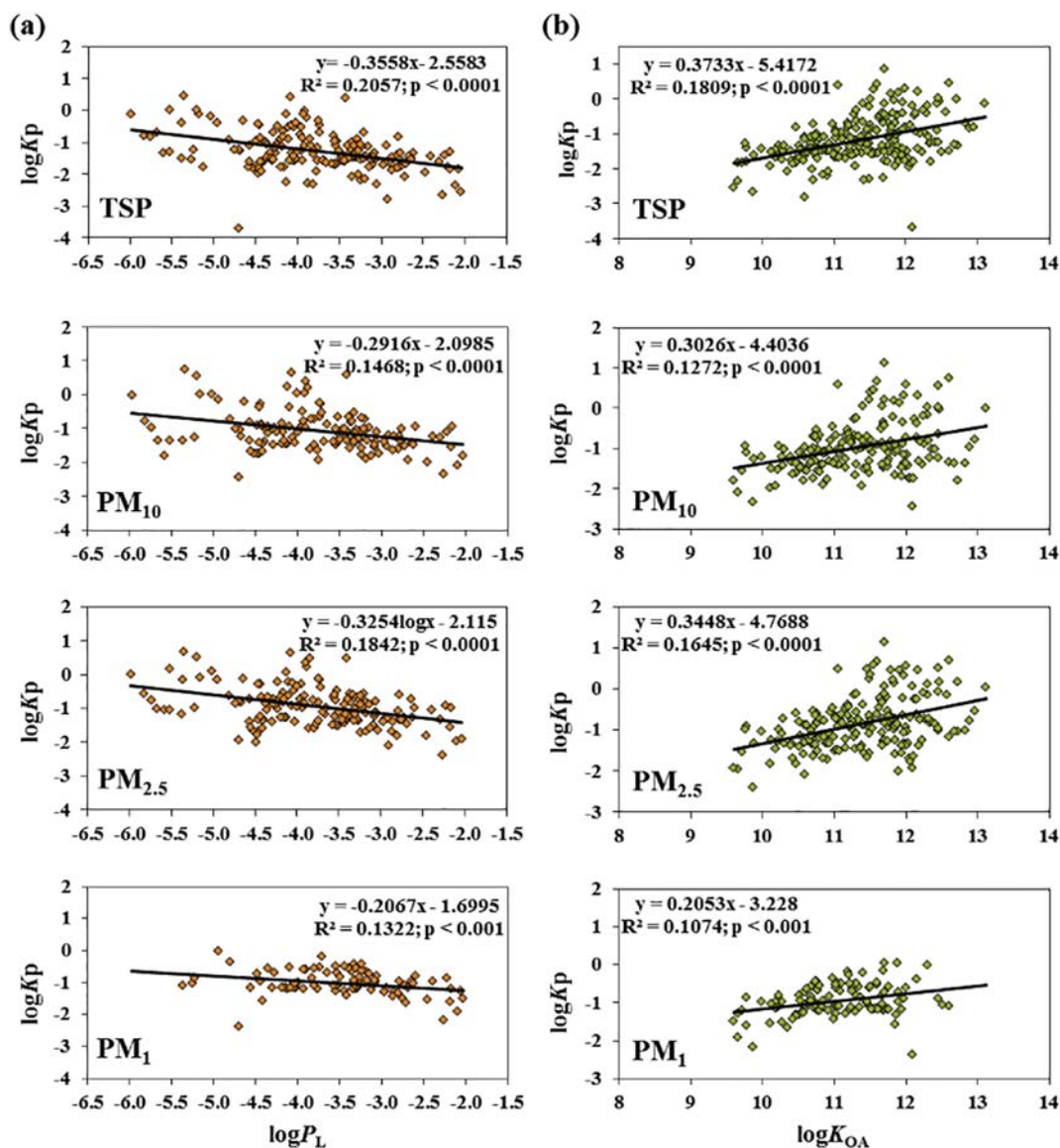
Fig. 4. Plot of the logarithm of (a) the subcooled liquid vapor pressure (P_L) and the (b) octanol-air partition coefficient (K_{OA}) of PCDD/Fs in TSP, PM$_{10}$, PM$_{2.5}$ and PM$_1$ versus the logarithm of the gas-particle partition coefficient (K_p).

degradation/decomposition phenomena that may have more weight during the summer. 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 (Castro-Jiménez et al., 2012; Mandalakis et al., 2002; Saral et al., 2015).

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 (Chang et al., 2004; Li et al., 2014; Martínez et al., 2010) and have been widely attributed in the literature to road traffic emissions. Regardless of the type of vehicle, engine, operating regime and fuel (gasoline or diesel), PCDD/F congener patterns from fueled vehicles are dominated by the presence of OCDD (70–90%), which is mainly emitted in gaseous form due to the high temperature of the exhaust (Chang et al., 2004; Geueke et al., 1999; Kim et al., 2003; Rey et al., 2014). However, studies conducted by Deng et al., 2011, revealed important seasonal differences for vehicle emissions. In that study, authors not only described much higher PCDD/F vehicles emissions during

winter, associated to elevate incomplete combustion process and presence of particle-bond chlorine in the aerosol, but also described an OCDF contribution increase in the emission profile to the detriment of OCDD during winter. This result agrees with the TPCDD/F profile obtained in the PUF (5–39% and 12–10%, summer-winter OCDF and OCDD contributions; Fig. S1) and suggests that the winter effect is not only influenced by meteorological factors (thermal inversions, high surface pressures and stable weather), but also to higher PCDD/F formation rates of fossil fuels combustion processes during winter (Deng et al., 2011). At this point, consideration must also be given to the existence of sources associated with industrial activities in which combustion processes are developed: metal recovery, incinerators of municipal solid waste, hospital waste and production of cement, electric arc furnaces (EAFs), secondary aluminum smelters (ALSs), and sinter plants (SP) among others, which may contribute to the PCDD/F levels detected in this study. However, when comparing PCDD/F congener profiles reported in the literature for these combustion sources (Ames et al., 2012; Lee et al., 2004; Rovira et al., 2014; Wegiel et al., 2014) only unleaded gas-fueled and diesel vehicles together with municipal solid and medical waste incineration produced similar data.

3.3. Toxic contents and inhalation risk assessment

Finally, toxicity to human health was assessed. Toxicity attributable to dl-PCBs was higher (68% of total TEQ, in PUF + TSP) than that obtained for TPCDD/F. Although the latter are more toxic on an individual basis, most toxic congeners (TCDD/Fs and PeCDD/Fs) were found below LOD in most of the samples, and thus with a minor contribution to the total TEQ. In contrast, the most toxic congener of dl-PCBs (PCB-126) was detected in all samples. As expected, gas phase toxicity was mainly due to dl-PCBs (12.6 and 1.82 fg-TEQ_{05} m^{-3}; median values for dl-PCBs and PCDD/Fs; Table S12), while in particulate matter the main contributors to total TEQ were PCDD/Fs (0.80 and 3.01 fg-TEQ_{05} m^{-3}). No significant differences were detected between TEQ of PCDD/Fs in gas (2.96 fg-TEQ_{05} m^{-3}; median) and particulate phase (3.01 fg-TEQ_{05} m^{-3}). There were also no significant differences between toxicity of the different sizes of particulate matter, being mainly attributable to the smaller particle sizes (PM_1). PCBs are mostly associated with the gas-phase, resulting in much higher levels of toxic content in the PUF samples than in the particulate matter filters: 9.95/0.69 fg-TEQ_{05} m^{-3} for no-PCBs and 3.23/0.07 fg-TEQ_{05} m^{-3} for mo-PCBs (median, PUF/TSP, respectively). As happened for PCDD/Fs no statistically significant differences were detected among the evaluated fractions of PM, indicating that the toxic content of dl-PCBs in the particulate phase is mainly due to the smaller particles (PM_1). The toxicity pattern did not change throughout the year for PCBs, resulting the PCB-126 the main contributor to toxic content (75% in gas-phase and 87 $\pm$ 2% in PM, annual average $\pm$ SD of TSP, PM_{10}, $PM_{2.5}$ and PM_1), followed to a lesser extent by PCB-118 (17% in gas-phase and 5 $\pm$ 1% in PM). This result is common in most environmental samples, including ambient air (Choi et al., 2008; Kerst et al., 2003; Kim et al., 2011; Li et al., 2010; Martínez et al., 2010).

The toxic concentrations of PCDD/Fs and dl-PCBs (fg-TEQ_{05} m^{-3}; PUF + TSP) measured in ambient air were used to assess inhalation risk in the studied area, as described in the literature (Aries et al., 2008; Li et al., 2014). Daily intakes of PCDD/Fs and dl-PCBs were estimated by the Daily Inhalation Dose (DID, pg-TEQ_{05} kg^{-1} day^{-1}, Eq. (8)), in which C (pg-TEQ_{05} m^{-3}) is the ambient air concentrations (PCDD/Fs + dl-PCBs), IR is the average daily inhalation rate (1.3 m^{-3} h^{-1}, US EPA, 1997), ET is the average exposure time (ET = 24 h^{-1} day^{-1}, worst possible scenario), BW is the mean body weight (70 kg for an adult), and an inhalation absorption factor (A) of 100% was assumed.

$$DID = \frac{(C \times IR \times A \times ET)}{BW} \qquad (8)$$

The results obtained ranged from 0.004 to 0.02 pg-TEQ_{05} kg^{-1} day^{-1}, which are two and three orders of magnitude lower than the recommended tolerable daily intakes (TDI) of 1–4 pg-WHO-TEQ kg^{-1} day^{-1} (including PCDD/Fs and 12 dl-PCBs) proposed by the WHO European Centre for Environment and Health (WHO, 1998), and 2 pg-WHO-TEQ kg^{-1} day^{-1} recommended by the UK Committee on the Toxicity of Chemical in Food, Consumer Products and the Environment (COT, 2001). These daily inhalation doses are similar to those reported in background (0.002 pg I-TEQ kg^{-1} day^{-1}) and living areas (0.02–0.03 pg I-TEQ kg^{-1} day^{-1}, Tianjing, China) (Ding et al., 2013) and lower than those found in occupational exposure assessment studies. Li et al. calculated a daily inhalation dose between 0.113 and 0.227 and 0.099–0.199 pg I-TEQ kg^{-1} day^{-1} for female and male workers, respectively, in vehicle parking lots in China (Li et al., 2014). In UK, Aries et al. measured daily intakes of workers at an electric arc furnace steelmaking plant. Daily intakes for melting shop workers ranged between 0.15 and 0.41 pg-WHO TEQ kg^{-1} day^{-1}, while in a control room they measured 0.06 pg-WHO TEQ kg^{-1} day^{-1} (Aries et al., 2008). In addition to the daily intakes estimated for inhalation, cancer risk for a whole life exposure (average 70 years) was also calculated by multiplying the inhalation dose by the inhalation cancer

potency factor established for the most toxic congener considered (2,3,7,8-TCDD, 1.3 $\times$ 10^{-5} (kg day mg^{-1})). 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 (US EPA, 1997), reflecting a cancer risk (0.5–2 cancer cases per million people) by inhalation of PCDD/Fs and dl-PCBs in the studied area one order of magnitude lower compared to occupational data from China (12 to 21 cancer cases per million people in Guangzhou; Li et al., 2014).

4. Conclusions

Urban ambient air levels of TPCBs were orders of magnitude higher than TPCDD/Fs. PCB pattern ranked as follows: i-PCBs > mo-PCBs ≫ no-PCBs, with no seasonal variability. Dioxins and furans showed higher concentrations in winter samplings in all matrices considered, whereas PCBs displayed maximum levels in warm seasons (spring and summer). In the case of PCDD/Fs, the atmospheric levels in cold months could be related to the road traffic and home heating sources, together with special weather conditions that make the dispersion of pollutants difficult and favor the concentration of contaminants at the ground level. PCB maximum levels in spring and summer are linked to the increase in the rate of evaporation of these compounds from materials containing them. PCDD/Fs were mainly bounded to PM with increasing gas phase contributions in warmer seasons. In contrasts, PCBs were mainly detected in gas phase regardless of weather conditions. No significant differences in PCDD/F and PCB concentrations were detected between the different matrices considered (TSP, PM_{10}, $PM_{2.5}$ and PM_1). This result evidences that both PCDD/Fs and the lesser fraction of PCBs associated to PM are mainly bounded to PM_1, The analysis of PCDD/F congener profile showed a higher contribution in gas-phase of congeners with lower degree of halogenation.

The toxic content of samples was also evaluated. Total toxicity (PUF + TSP) attributable to dl-PCBs was higher than the reported for PCDD/Fs. The toxic concentrations of PCDD/Fs and dl-PCBs (fg-TEQ_{05} m^{-3}) measured in ambient air were used to assess the inhalation risk. The results reflect that the ambient air concentrations of PCDD/Fs and PCBs in the studied area pose a low cancer risk through inhalation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.12.114.

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