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

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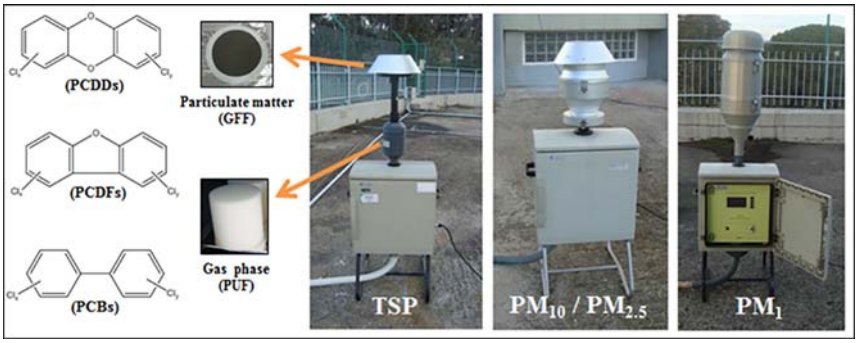
HIGHLIGHTS

- 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 log*Kp* vs logP_L and log$K_{OA,}$ and human respiratory risk assessment were used to evaluate local or long-distance transport sources, gas-particle partitioning sorption mechanisms, and implications for health. 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-