

LEVELS AND GAS-PARTICLE PARTITIONING OF POPs IN URBAN AMBIENT AIR

Barbas B, de la Torre A, Sanz P, Navarro I, Artíñano B, Martínez MA

Department of Environment, CIEMAT, Avda. Complutense 40, E-28040 Madrid, Spain

Introduction

Air pollution continues to be a major health, environmental, and economic issue in Europe, because it leads to health problems, premature deaths and damage to ecosystems, crops and buildings¹. Despite progress in reducing air pollution, certain pollutants such as particulate matter (PM) remain a significant threat. PM is a complex and heterogeneous mixture of inorganic and organic substances, and constitutes the greatest risk in terms to harm the human health, especially in urban areas where the majority of the European population lives¹.

Persistent Organic Pollutants (POPs), and emerging pollutants as flame retardants, are some of the wide extent of dangerous chemicals which can be found in the ambient air². They are present in the gas phase and also adsorbed on the suspended particulate matter, depending on ambient temperature and the physico-chemical properties of the chemical. Due to their toxic, bio-accumulative and persistent characteristics these pollutants are matter of great concern for human health and natural ecosystems³. However there are several data gaps related to their fractionation in ambient air. Therefore improving our knowledge of POPs in this matrix remains a challenge.

The aim of this study was to evaluate the presence of several POPs in ambient air samples from the city of Madrid (Spain). Gas phase and airborne particulate matter were studied separately. Levels and fractionation of the following analytes were studied: polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs: (the 2,3,7,8-substituted congeners), polychlorinated biphenyls (PCBs): dioxin-like PCBs (dl-PCBs: CB-81, -77, -123, -118, -114, -105, -126, -167, -156, -157, 169 and -189) and indicator PCBs (i-PCBs: CB-28, -52, -101, -138, -153 and -180), polybrominated diphenyl ethers (PBDEs: tri to deca-BDE) and Dechloranes (Dec 602, Dec 603, Dec 604, Dec 605 also called Dechlorane Plus (DP), Chlordane Plus (CP) and Mirex).

Materials and methods

A total of 6 sampling events were conducted between January and May (winter and spring) 2013 in the weather station located in CIEMAT facilities of Madrid (UTM coordinates: 30T, 0438676 long., 4478881 lat.). Ambient air volumes of 1000 m³ were drawn using high-volume samplers CAV A/M model, at 30 m³/hour flow rate. Particulate matter was collected on glass microfiber filters (GFF) (grade GF/A, 15 cm diameter, Whatman, England), and gases were adsorbed on polyurethane foam (PUF) plugs (0.029 g/cm³) placed downstream of the filter.

Handling and sampling procedures were performed following the guidelines of UNE-EN 12341:1999 and UNE-EN 14907:2006 Norms^{4, 5}. Prior to sampling, GFF were baked at 450 °C for 24h to remove any organic contaminants. GFF were then stabilized in a temperature and humidity controlled chamber (20 °C, 50 % relative humidity) for 48 h before weighing. PUF plugs were pre-cleaned by using milli-Q water, and then Soxhlet extracted with acetone/hexane (1:1 v/v) for 24 h. Finally they were dried at 70 °C. After each sampling, GFF and PUF plugs were re-sealed in their original transport containers and returned to the laboratory. GFF were stabilized again for 48 h and weighing at the same temperature and relative humidity conditions. Then, both GFF and PUF were stored at -20 °C until extraction.

The same analytic procedure was carried out for GFF samples and PUF plugs. They were Soxhlet extracted separately with toluene for 24 h. Prior to extraction samples were spiked with ¹³C₁₂ and ¹³C₁₀ labeled recovery standards (¹³C₁₂-PCDD/Fs, ¹³C₁₂-PCBs, ¹³C₁₂-PBDEs and ¹³C₁₀-DP: *syn*- and *anti*-DP isomers). The obtained extracts were solvent exchanged with hexane and purified firstly in an acid silica column (20 g, 44% sulfuric acid) topped with 2 g of anhydrous sodium sulfate, which was washed with 50 mL hexane and eluted with 150

mL hexane. Then it was executed an automated purification step with a multilayer silica column, an alumina column and a carbon column eluted by pressure (Power Prep™ System, Fluid Management Systems Inc., USA). Two fractions were obtained: Fraction A) containing PCDD/Fs and non-ortho dl-PCB (CB-77, -81, -126 and -169), and Fraction B) containing PBDEs, Dechloranes, i-PCBs and mono-ortho dl-PCBs. Final extracts were concentrated to dryness and redissolved in nonane spiked with injection standards (1613-iSS, WP-ISS, i-PCBs-ISS and BDE-CVE-EISS from Wellington Laboratories Inc.) prior to instrumental analysis.

Instrumental analyses of PCDD/Fs, PCBs and Dechloranes were carried out by high-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC-HRMS), on a Micromass Autospec Ultima NT, operated in electron ionization mode at resolution greater than 10,000 (10 % valley). PBDEs determination was performed by high-resolution gas chromatography coupled to low-resolution mass spectrometry (HRGC-LRMS), on an Agilent 5973 MSD (quadrupole mass spectrometer) connected to an Agilent 6890 GC. Identification and quantification were performed by isotopic dilution for all compounds except for Dec 602, Dec 603, Dec 604, CP and Mirex whose quantification was carried out using ¹³C₁₀-syn DP as the internal standard. Field and laboratory blanks were analyzed and final data were blank corrected.

Results and discussion

Mean total concentrations (gas phase + PM) and standard deviations (SD) of POPs studied for the whole sampling period were (in decreasing order): i-PCBs = 324.5 ± 219.5 pg/Nm³, dl-PCBs = 109.4 ± 77.3 pg/Nm³, PBDEs = 17.1 ± 13.2 pg/Nm³, DP = 1.8 ± 2.0 pg/Nm³ and PCDD/Fs = 0.18 ± 0.14 pg/Nm³. Dec 603, Dec 604 and CP were not found in any of the samples analyzed, and Dec 602 was only detected in gas phase in one of the spring samplings (0.02 pg/Nm³). Mirex was detected in winter gas phase samples (0.05 pg/Nm³; mean n=3), while it was only measured, but at much higher concentration (0.91 pg/Nm³), in one GFF sample of spring sampling events.

Data obtained were used to evaluate the fractionation between gaseous and particulate phases for all analytes studied (Figure 1). I-PCBs and dl-PCBs were present dominantly in gas phase (99 % and 98 % of total concentration, respectively), while PBDEs, PCDD/Fs and DP were mainly bounded to particulate matter (89 %, 85 % and 93 % of total concentration, respectively). However, data evidence an interesting increase of 27 % and 14 % in spring gas-phase levels (with respect to winter) for PCDD/Fs and PBDEs. This fact could be due to the increase of 9 °C in spring (17 °C; mean temperature) compared to winter (8 °C; mean temperature) which could promote the evaporation of compounds bounded to PM. This result correlates well with data reported in other studies⁶.

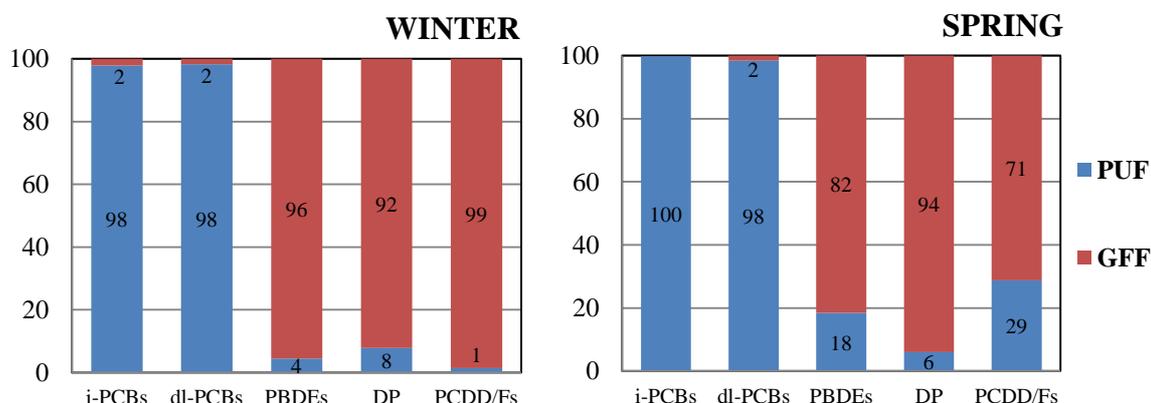


Figure 1. Gas-particle partitioning of POPs per season (%). Mean obtained with data from 6 sampling events.

Total concentration of i-PCBs ranged from 123.7 to 715.9 pg/Nm³. These results are similar to those obtained in Brescia (North Italy) but higher to previously reported in other Spanish cities such as Barcelona^{7,8}. As expected, presence of i-PCBs in filter samples (GFF) was dominated by congeners with high chlorination degree (PCB-138 > PCB-180 > PCB-153; hexa and heptachlorobiphenyls) (Figure 2). On the contrary, tetra (PCB-52; 29 %) and pentachlorobiphenyls (PCB-101; 35 %) were the predominant congeners in the gas-phase.

Levels of dl-PCBs ranged between 24.9 pg/Nm³ (winter) and 184.7 pg/Nm³ (spring). These results are in the same range as those measured by Colombo *et al.* in Brescia (Italy)⁷. DI-PCB congener pattern showed a major contribution of PCB-118 (75 % of dl-PCBs measured in gas-phase), followed by PCB-105 (14 %).

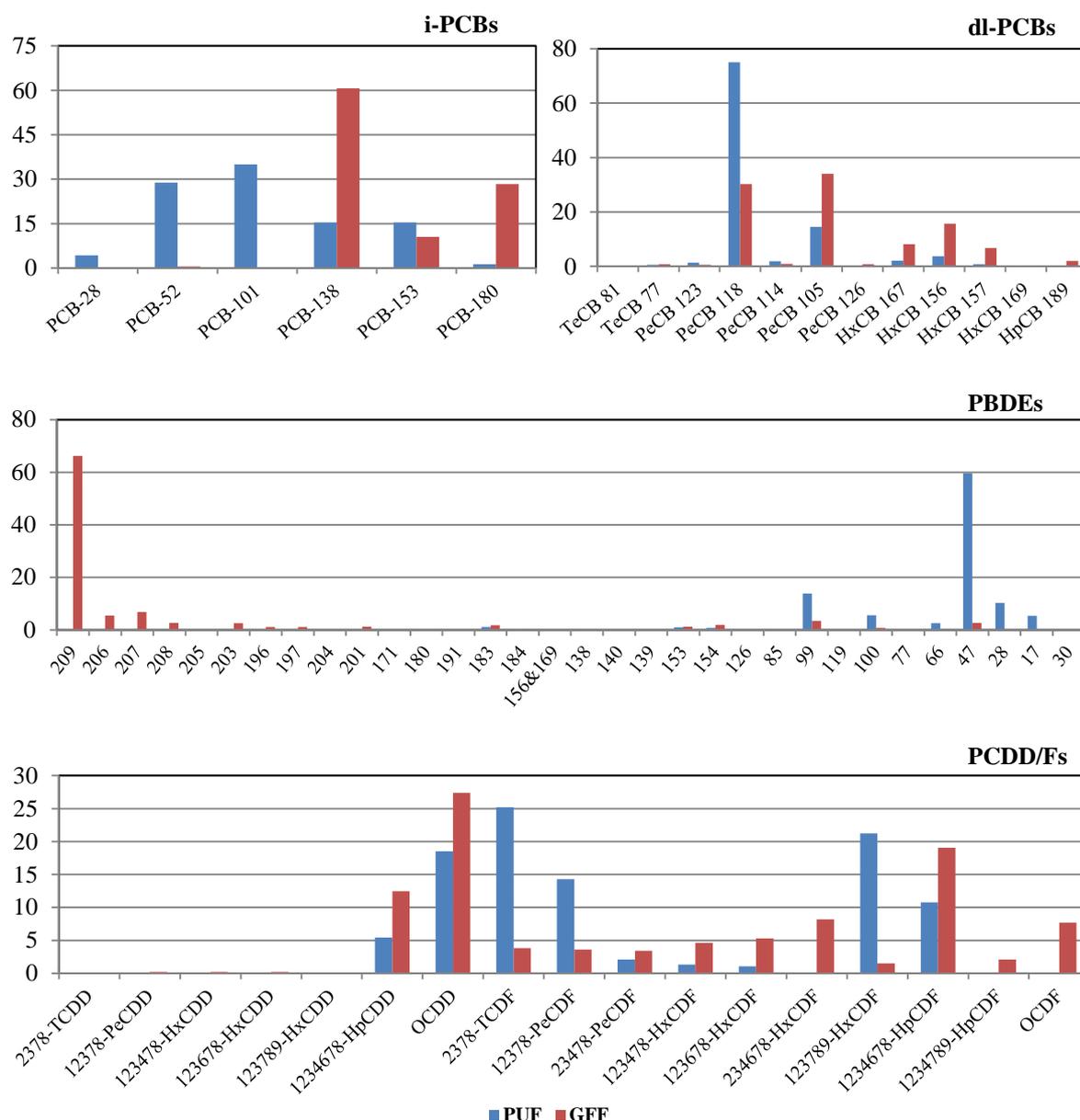


Figure 2. I-PCB dl-PCB, PBDE, and PCDD/F congener patterns (%) of PUF (blue) and GFF (red). Mean obtained with data from 6 sampling events.

Concentrations of PBDEs, varying between 7.2 and 38.9 pg/Nm³, are similar to those reported in other European cities such as Heraklion (Greece) or Birmingham (UK), but lower than levels described in China^{9, 10, 11}. PBDEs showed a distinct fractionation based on their degree of bromination. Deca and nonabromodiphenyl ethers (BDE-209 > BDE-207 > BDE-206) were mainly associated to PM, while gas phase was dominated by PBDEs with low bromination degree (BDE-47 > BDE-99 > BDE-28, penta to tribromodiphenyl ethers), see Figure 2. Considering that the production and use of Deca-BDE commercial mixture is forbidden in Europe since 2008¹², presence of BDE-209 (66 %), BDE-207 (7 %), and BDE-206 (6 %) in PM suggests the use or disposal of items containing Deca-BDE as a potential source of this pollutant into the environment.

Total DP (sum of *syn*- and *anti*-DP isomers) concentrations varied between 0.1 and 5.6 pg/Nm³. These results are in the same range (2-4 pg/m³) than those reported in Chicago and Cleveland (North American Great Lakes Area)¹³. The fraction of the anti-isomer (f_{anti}) was calculated as the ratio of the anti-DP isomer to the total DP concentration. Obtained f_{anti} for this study was 0.71 ± 0.11 (mean ± SD), which is very similar to the American commercial mixture¹³.

Total concentrations of PCDD/Fs ranged from 0.04 pg/Nm³ (spring) to 0.37 pg/Nm³ (winter), which are in the same order of magnitude than those described in Barcelona (Spain)⁸. The averaged PCDD/F profile showed a higher contribution of PCDF compared to PCDD. All PCDF congeners were detected in PM, but only the heaviest PCDD congeners (1234678-HpCDD and OCDD) showed a significant contribution to the total concentration (the other PCDD congeners were lower than 0.02 %). PCDD/Fs with a higher degree of chlorination were mainly found in the particulate-phase. The predominant congeners were: OCDD (27 % in PM), 1234678-HpCDF (19 % in PM), 1234678-HpCDD (12 % in PM) and OCDF (8 % in PM).

In summary, this study reported the total concentrations and fractionation of several POPs in the ambient air of Madrid, Spain. The levels measured were consistent with those reported in other studies. Results evidence that PBDEs, PCDD/Fs and DP were primarily bounded to particle phase, while i-PCBs and dl-PCB were mainly associated to gas-phase. Further investigation will be necessary to evaluate potential seasonal variations.

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