

LEVELS OF POPs IN AIRBORNE PM10 AND PM2.5: PRELIMINARY RESULTS

Quintana JB¹, Fernández-Villarrenaga V², López-Mahía P^{1,3*}, Muniategui Lorenzo S³, Prada Rodríguez D^{1,3}

¹ IUMA - University Institute of Environment, University of A Coruña, Pazo da Lóngora, Liáns, 15179 Oleiros (A Coruña), Spain.

² Scientific Research Support Services, University of A Coruña, Edificio SCI, Campus de Elviña s/n, 15071 A Coruña, Spain.

³ Department of Analytical Chemistry, Faculty of Sciences, University of A Coruña, Campus A Zapateira 15071 A Coruña, Spain.

* E-mail: purmahia@udc.es

Introduction

Airborne particulate matter (PM) comprises a complex mixture of inorganic and organic substances and also a broad range of sizes. Among these PM, the larger ones (ca. > 30 μm) have mainly their origin on re-suspended soils and dusts from roads and industries, remaining in the air for a short period of time. On the other hand, smaller particles remain suspended for larger periods of time and have primarily an anthropogenic origin, due to combustions and also to secondary sources, like e.g. re-condensation of organic vapours and gas-phase reactions. Moreover, the smaller the particle size, the easiest they can penetrate in the respiratory system. For these reasons, the actual European Union legislation¹ has established limit values for PM10 (particulate matter < 10 μm) in order to avoid human health risks. However, this regulation will be soon replaced by PM2.5² (particulate matter < 2.5 μm) because of their harmful potential.

Thus, this work presents a preliminary study of several classes persistent organic pollutants (POPs) in both PM10 and PM2.5 collected from an urban area, aiming to identify them and their relative concentrations in both kinds of samples and to study the implications of this regulation change. This work will be further extended as a part of a project that aims to characterise airborne PM from urban, industrial and rural environments in a long term study.

Materials and Methods

Parallel 24 h samples of PM2.5 and PM10 were collected on an urban area in the city of A Coruña (Galicia, NW Spain, Fig. 1) influenced by a main traffic road (ca. 20 000 vehicles / day) with some potential contribution from petroleum, metallurgy industries and a coal power plant located at ca. 5-15 km. Collection was made through quartz fibre filters (UNE-EN 12341) with a sampling flow of 2.3 and 68 m^3/h for both PM10 and PM2.5, respectively (Fig. 1). Field filter blanks were also collected.



Figure 1. Sampling point location and PM samplers. A Coruña, 43°22'04''N & 08°25'08''W.

Total Organic Carbon (TOC) was determined by elemental analysis with a Flash EA 1112 (Carlo Erba, Milan, Italy). Polycyclic Aromatic Hydrocarbons (PAHs) were analysed by microwave assisted extraction and liquid chromatography-fluorescence detection as described elsewhere³. Polychlorodibenzodioxins/polychlorodibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) were determined by isotope dilution gas chromatography-high resolution mass spectrometry (GC-HRMS) after Soxhlet extraction and a fractionation on a Power Prep FMS system based on a previously published method for PCDD/Fs only⁴. In brief, this fractionation was adapted to the determination of 'dioxin-like PCBs' and was done over disposable columns: multilayer silica columns, basic alumina columns and PX-21 carbon columns. Two extracts were recovered, the first containing the mono-ortho PCB and the second containing the non-ortho PCBs and the PCDDs/Fs. This first extract was also employed for the GC-HRMS quantification of polybromodiphenylethers (PBDEs) by the external standard procedure and the identification of chlorinated phenols (CPs) and polychloronaphthalenes (PCNs).

Results and Discussion

The total concentration of four POP classes (PAHs, PCDD/Fs, 'dioxin-like PCBs' and PBDEs) that were quantified in this study is presented in Fig. 2. The first thing that may be observed from that figure is that the concentration of PM₁₀ is above the EU daily limit¹ of 50 $\mu\text{g}/\text{m}^3$, that may be surpassed a maximum of seven times per year. It must be kept on mind however, that Fig. 2 corresponds to a single sampling day and also that the location of the sampling point may be regarded as a hot spot in very close to a main traffic road and it does not represent human exposure. Also, Fig. 2 (left) shows that the concentration of most POPs is higher in PM_{2.5} than PM₁₀, with the exception of PAHs. This ratio increases by looking at the PM mass related concentration (Fig. 2 right), pointing out that POPs may be preferentially associated to lower size particles, due to their different original sources and to their higher specific surface area. Obviously, this hypothesis needs to be confirmed by a long term study.

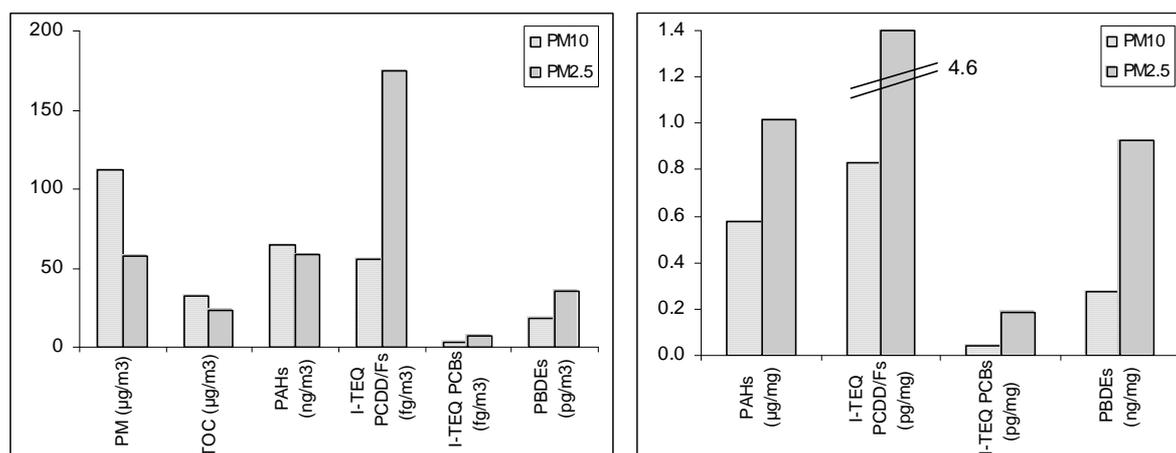


Figure 2. Total concentration of the different POPs in PM, related to sampled volume (left) and to mass of PM (right).

A closer look at the different POPs is depicted in Fig. 3. Again, this figure shows a relatively high concentrations of PAHs is and, in particular, the concentration of benzo(a)pyrene (BaP) would surpass the EU average annual limit⁵ of 1 ng/m^3 , which may be due to the sampling location and needs to be studied in a long term basis. Regarding the distribution of PAHs in PM₁₀ and PM_{2.5}, no significant differences can be observed, either in the profile or concentration of the different compounds. On the other hand, PCDD/Fs and 'dioxin-like' PCBs, although both PM₁₀ and PM_{2.5} show a similar profile, indicating a same source, but being at higher levels in the PM_{2.5} fraction. In the

case of PBDEs, two trends are observed, for PBDE-47, PBDE-100 and PBDE-99 the concentration is higher in the lower particle size fraction, while for PBDE-209 there is not significant difference. This may represent a different origin, as the first three PBDEs are representative of the Penta-BDE mix, whereas PBDE-209 constitutes ca. 98 % of the Deca-BDE.

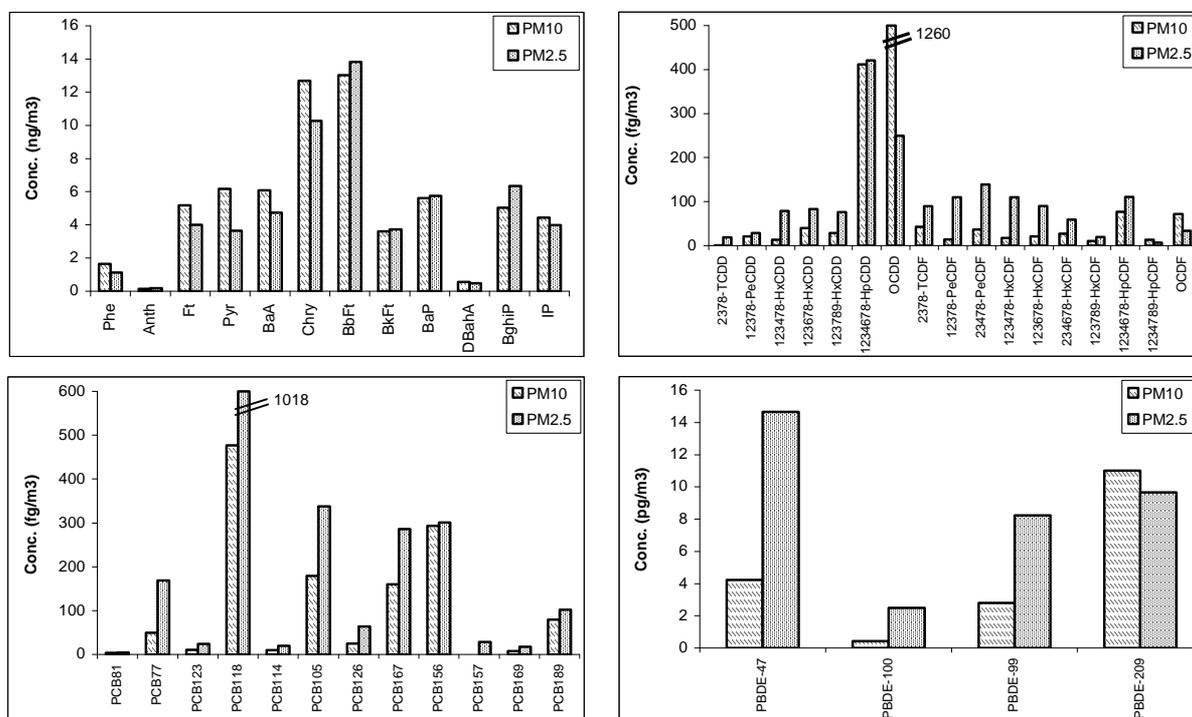


Figure 3. Concentration of different POPs in PM10 and PM2.5.

A further screening for other POP classes was carried out by analyzing the first extract fraction by GC-HRMS. It revealed the presence of several CPs (data not shown) and some PCNs (Fig. 4) in both PM samples, which were not yet quantified due to the lack of standards in the laboratory. Nevertheless, they could be tentatively identified by monitoring three exact m/z values for each compound and their relative abundance, and comparing their relative retention time with literature values.

Thus, it can be concluded from these preliminary set of experiments that several classes of POPs can be found both in PM10 and PM2.5, but their concentration in both fractions can be rather different. This contrasts e.g. with the observations of Martínez et al.⁶ from the concentrations of PCDD/Fs in PM10 and total suspended particles, where not significant difference is observed. Obviously this preliminary results need to be confirmed by a long term study that is being done at the moment and considers not only urban samples, but also industrial and rural ones.

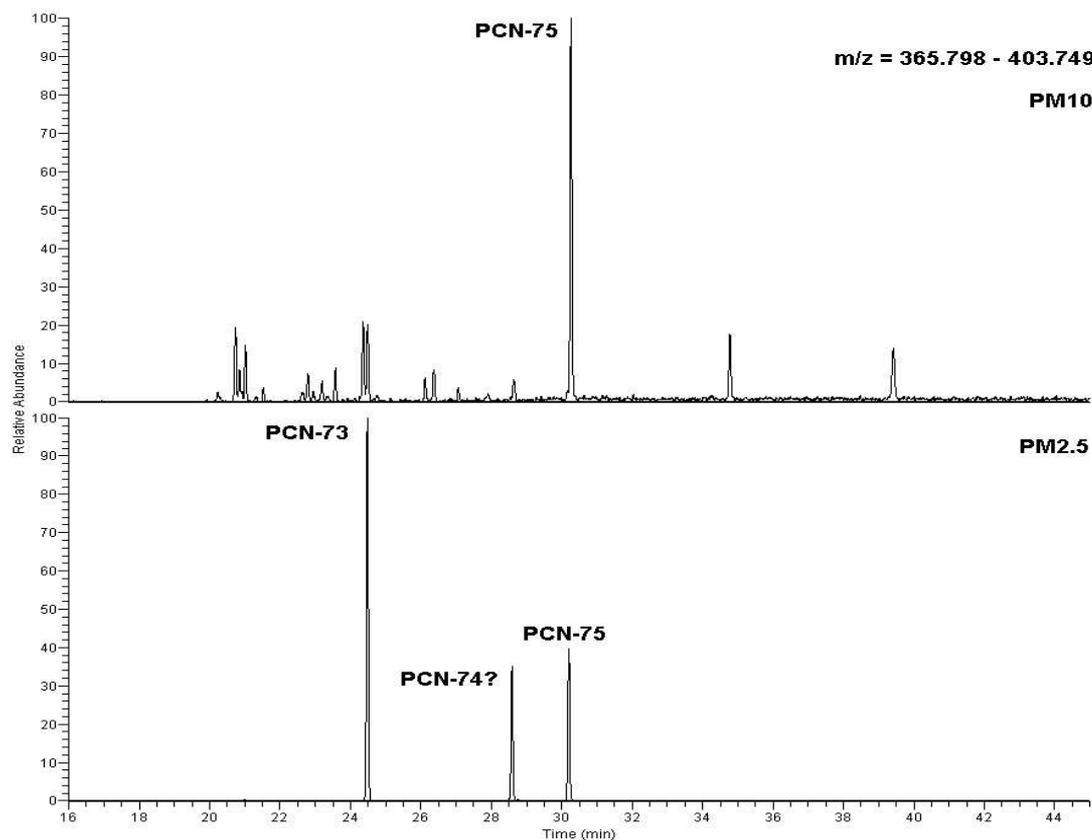


Figure 4. GC-HRMS chromatogram and tentative identification of three PCNs in PM10 and PM2.5 samples.

Acknowledgments

This work was financially supported by 'Ministerio de Educación y Ciencia' (Project no. REN2003-08603-C04-01). We are indebted to the University's Scientific Research Support Services (SAI) for sample analysis. JBQ acknowledges 'Xunta de Galicia' for his contract sponsorship through the 'Isidro Parga Pondal' program.

References

1. Council Directive 1999/30/EC. *Official J. Eur. Communities* 1999, L163: 41.
2. Commission Decision 2004/470/EC. *Official J. Eur. Communities* 2004, L160: 51.
3. López Mahía P, Muniategui Lorenzo S, López Moure M, Piñeiro Iglesias M, Prada Rodríguez D. *Environ. Sci. Pollut. Res.* 2003, 10:98.
4. Fernández Martínez G, López Vilariño JM, López Mahía P, Muniategui Lorenzo S, Prada Rodríguez D, Abad E, Rivera J. *Chemosphere* 2004, 57:67.
5. Directive 2004/107/EC. *Official J. Eur. Communities* 2004, L23: 3.
6. Martínez K, Abad E, Gustems L, Manich A, Gómez R, Guinart X, Hernández I, Rivera J. *Atmos. Environ.* 2006, 46: 576.