

PAHs, nitroPAHs and oxiPAHs in atmospheric particle samples

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INTRODUCTION

PAHs have been monitored in atmospheric particle samples (PM₁₀, PM_{2.5}, PM₁, six stage cascade impactor up to $d_{ac} < 0.5 \mu\text{m}$) for the urban area of Milan (as the biggest urban area of the highly anthropised Lombardy Region in the North of Italy) for a long-time (since 2001). PAHs atmospheric distribution (gas-particle phase as well particle-size distribution), sources, seasonal trends and vertical profiles of the Milan urban atmosphere are studied.

PAHs derivatives in atmospheric particle samples are also analysed, like nitroPAHs and oxiPAHs. Such compounds are monitored to investigate both primary sources (e.g. 1-nitropyrene) as well PAHs atmospheric reactivity.

NitroPAHs and oxiPAHs are very important from a toxicological point of view, and some of them can have an higher toxicological power (mutagenic action), even if their concentrations are lower than their parent PAHs.

METHODS

A method for a simple and rapid PAHs extraction from atmospheric particulate samples has been developed by using sonication technique: for low volume gravimetric samples (47 mm \varnothing filters) 3 minutes time extraction with 2 ml of organic solvent, without any post concentration step required. Analysis are performed by HPLC-RF or GC-MS, and a method was developed for simultaneous extraction and analysis of nitroPAHs. For HPLC-RF analysis of nitroPAHs, a pre-reaction of reduction to amino-PAHs (fluorescent compounds) is necessary and is performed off-line by reacting the extract with Zn (MacCrehan W.A., 1998), with a % of reaction of $84 \pm 4\%$ for 1-nitroPy and $72 \pm 5\%$ for 6-nitroCHR. No reaction is required for analysis of nitroPAHs by GC-MS, but lower detection limit could be reached by HPLC-FD method (0.1-0.2 pg/ μl for HPLC-FD, compared with 0.4-0.8 pg/ μl for GC-MS method).

For oxiPAHs a method has been developed by LC-MS, by using an LC-APCI-MS single quadrupole (Shimadzu). In this case the samples require a preconcentration step, and an analytical method has been developed for 7 oxiPAHs: 1,6 benzo[a]pirene-dione (1,6 BaPQ); 3,6 benzo[a]pirene-dione (3,6 BaPQ); 6,12 benzo[a]pirene-dione (6,12 BaPQ);

anthraquinone, benzo[a]anthracene-7,13-dione and phenanthraquinone.

RESULTS

The traffic source is estimated to be one of the main PAHs source for the Milan urban area. By comparing two different Milan urban sites, a background and a kerbside site primarily influenced by traffic source, the second one shows daily PAHs concentrations about 5-6 times higher, and the relative PAHs content in atmospheric particles (ngPAHs/ μgPM) is over 2-3 times more than background urban site. Despite different quantitative values, daily trends of PAHs pollution are strictly correlated for the all highly anthropised Lombardy Region (Perrone M.G., 2004), and PAHs are also uniformly distributed on the vertical profile of the Milan urban area, with ground concentrations less than 20% higher than 100 m height. In all urban cities of the North of Italy, a strong seasonal trend is observed for relative PAHs content in atmospheric particles, with maximum values during December-January ($0.45 \pm 0.18 \text{ ng } \Sigma_9\text{-PAHs} / \mu\text{g PM}_{2.5}$, Milan) and minimum quite constant values between April and August ($0.03 \pm 0.02 \text{ ng } \Sigma_9\text{-PAHs} / \mu\text{g PM}_{2.5}$, Milan). Opposite trends have been observed in an urban area of the South of Italy (Catania), and this is very important as it determines a "different toxicological quality of PM".

One of the main reasons for very low PAHs content in atmospheric particles during summer is attributed to PAHs photochemistry reactivity, even if atmospheric degradation pathways for particle-bound PAHs are not yet well known. PAHs photochemistry reactivity is investigated by analyzing main degradation products like oxiPAHs (Koeber R., 1999). Summer and winter samples, as well daytime and night samples are analysed for main BaP oxidation products like 1,6 BaPQ, 3,6 BaPQ, and 6,12 BaPQ.

Between nitroPAHs, 1-nitroPY is known to be from primary source, in particular from diesel vehicles. 1-nitroPY has been analysed in PM samples from the Milan urban area, with concentrations ranging from 0.021-0.087 ng/ m^3 during winter months and 0.004-0.15 ng/ m^3 during summer. Mean mass concentrations in PM_{2.5} samples for 1-nitroPY was $0.74 \pm 0.13 \text{ ng/mg}$, more than 1 order of magnitude lower than single PAHs for the same days.

Keywords: PAHs, nitroPAHs, oxiPAHs

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