PAHs AND ALKANES IN THE ATMOSPHERIC PARTICULATE MATTER: TRAFFIC AND BIOGENIC SOURCE

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Polycyclic aromatic hydrocarbons (PAHs)

PAHs are investigated as they are mutagenic compounds and they are known to be amongst the most harmful compounds in determining adverse health effects associated to atmospheric particle pollution in urban areas (Hanningan M., 1998).
9 PAHs are constantly monitored for the background urban atmosphere of Milan (Italy), that is BaA, CHR, BbF, BkF, BeP, BaP, BghiP, dBahA and IcdP. Such compounds are found in the atmosphere quite exclusively in the particulate phase (particle/gas distribution =96-100%), where they are completely distributed in the fine fraction ([PAHs]PM2.5 >95%[PAHs]PM10). A strong seasonal trend is observed for relative PAHs content in atmospheric particles, with maximum values during December-January (0.45±0.18 ngΣ9-PAHs/μgPM2.5, that means about 0.04 % of total PM mass) and minimum quite constant values between April-August (0.03±0.02 ngΣ9-PAHs/μgPM2.5).This indicates a different"quality" of particulate matter, with important implications for its toxicological properties (particles more than ten times richer in PAHs during winter months) (Perrone, M.G., 2004).

The **traffic source** is estimated to be **one of the main PAHs source for urban areas** (Harrison R.M., 1996).
A campaign was done by analyzing PAHs concentrations in PM10 samples from two different sites of Milan: a background urban site (near the city center, but not directly influenced by point sources: more than 100 m from roads) and a kerbside site, primarily influenced by traffic source (≈ 10m away from a busy road). The **traffic site** shows [PAHs] about 5-6 times higher (FIG 1), and the relative **PAHs content in atmospheric particles** (ngΣ9-PAHs/mgPM) is **over 2-3 times more than the background urban site**.
The relative PAH profile is different for the two sites, and for the kerbside urban site is the same as that for traffic source (road traffic tunnel), with higher concentrations for lighter PAHs like PY, while for the background urban site BghiP is the most abundant one (FIG 2)

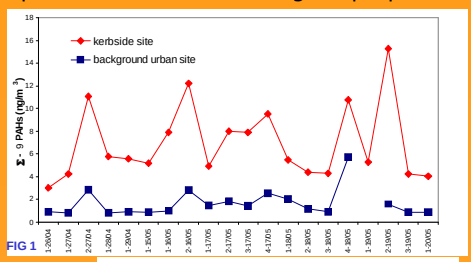

FIG 1

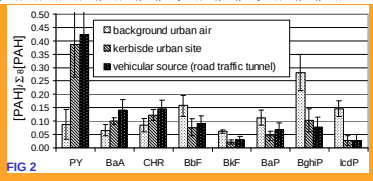

FIG 2

FIG 1. PAHs concentrations (ng/m3) at a kerbside site and a background urban site in Milan (Italy).

FIG 2. PAHs relative profile in PM10 samples from a kerbside site and a background urban site in Milan (Italy), compared with vehicular source (road traffic tunnel, Milan).

Alkanes

Linear alkanes (C14-C32) have been analysed in PM10 samples as they give information about the different relative contribution of **anthropogenic and natural (biogenic) sources**. Molecular diagnostic ratios, as **CPI** (*carbon preference index:=[alkanes Cn(odd)] / [alkanes Cn(even)] are used for the reconciliation of compounds sources. Biogenic contribution leads to a predominance of n-C25-n-C33 congeners with odd-even predominance: the biogenic source can be quantitatively estimated by calculating ***waxCn** (Simoneit B.R.T., 1991)

$$*CPI = 0.5 \times [(\sum_{n=10}^{n=15} C_{2n+1} / \sum_{n=10}^{n=15} C_{2n}) + (\sum_{n=10}^{n=15} C_{2n+1} / \sum_{n=11}^{n=16} C_{2n})]$$

CPI = 1 Anthropic source
CPI = 1-3 Mixed sources
CPI > 3 Biogenic source

$$*waxCn\ \% = \frac{\sum n\ (Cn - [Cn+1 + Cn-1]/2)}{\sum m\ Cm} \times 100 \quad (m=14\text{-}32;\ n=25,27,29,31)$$

	CPI	% biogenic source
Road traffic tunnel	1.1±0.04	4% ± 1% (n=5)
Milan (summer)	2.9 ± 0.7	38% ± 9% (n=5)
Milan (winter)	1.3 ± 0.1	12% ± 2% (n=6)

TAB 1

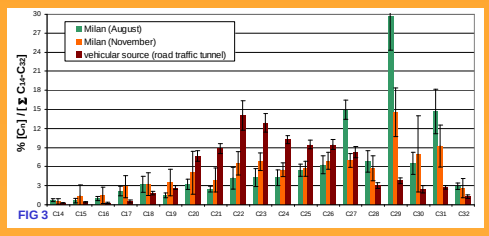

FIG 3

For the vehicular source (road traffic tunnel) a CP1≈1 is calculated, which indicates pure anthropogenic source. In the background urban area of Milan, biogenic source is estimated to contribute to about 38 % during summer (CPI= 2.9±0.7), while during winter 12 % (CPI=1.3±0.1%) (TAB 1).

TAB 1. CPI and waxCn% (% biogenic source) for linear alkanes C14-C32 in PM10 samples.

FIG 3. Alkanes relative profile in PM10 samples from a background urban site in Milan (Italy), during summer (August) and winter (November), compared to vehicular source (road traffic tunnel, Milan).

PAHs and alkanes in the first 90 m of the urban atmosphere of Milan

Atmospheric vertical mixing in the first 90 m height of the urban atmosphere of Milan was studied by parallel sampling of PM10 at the ground (4m height) and at altitude (86 m height). PM10 was been analyzed for both PAHs and alkanes during a sampling campaign in March 2005 (24-28/03/05; sampling time h 00-04(night); h 04-08(night); h 08-00(day)).

PM10 sampling (low volume gravimetric samplers, 38.3 l/min) at two different altitude (Torre Branca, 108 m, an open panoramic tower in the city center of Milan).

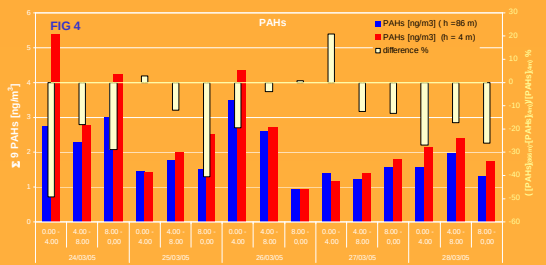

FIG 4

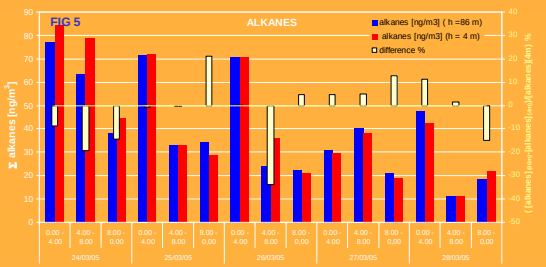

FIG 5

By comparing concentrations and trends at the ground and at altitude, PAHs (FIG 4) and alkanes (FIG 5) show a good correlation, during night as well as day time. It indicates a good mixing in the first 90 m of the urban atmosphere for both PAHs and alkanes, which are both associated to the fine fraction of PM10. Such good correlation is not always seen also for PM10, in particular during some night events when, because of a higher atmospheric stability, the coarse fraction tends to sediment at the ground (FIG 6).

For PAHs, higher concentrations are usually measured at the ground than at altitude, with a % reduction of about 20 % (mean value),indicating a general major contribution of local sources at the ground (e.g. traffic source).
Dislike PAHs, alkanes don't show this clear trend of reduction with altitude.

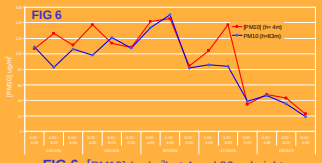

FIG 6

FIG 6. [PM10] (μg/m³) at 4 and 86 m height.

FIG 4 and **FIG 5.** PAHs concentrations (Σ 9PAHs ng/m³) and alkanes concentrations (ΣC14-C32, ng/m³) at 4 m and 86 m height in the urban atmosphere of Milan, and difference % between the two altitude.

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NOTE. PAHs nomenclature = PY(pyrene), BaA (benzo[a]anthracene), CHR (chrysene), BeP (benzo[e]pyrene), BbF (benzo[b]fluoranthene), BkF (benzo[k]fluoranthene), BaP (benzo[a]pirene), DBhA (dibenzo[ah]anthracene), IcdP (indeno[1,2,3-c,d]pyrene), BghiP (benzo[g,h,i]perylene).

REFERENCES

Hanningan M. (1998). "Bioassay-direct chemical analysis of Los Angeles Airborne Particulate Matter Using a Human Cell Mutagenicity Assay"; Env.Sci.Techn., 32, 3502-3514,1998
Perrone M.G. (2004) "Polycyclic aromatic hydrocarbons in the urban aerosol"; EAC2004, 6-10 Sept2004, Budapest (Hungary)
Harrison R.M. (1996). "Source Apportionment of Atmospheric PAHs Collected from an Urban Location in Birmingham, U.K."; *Env. Sci. Techn., 30, 825-832, 1996*
Simoneit B.R.T. (1991): "Molecular marker study of extractable organic matter in aerosols from urban areas of China" Atm. Env. Vol.25A, N.10, pp.2111-2129, 1991