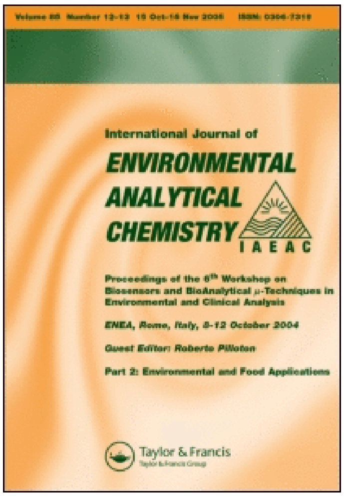

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A FIELD COMPARISON OF 'TOTAL SUSPENDED PARTICLES' AND 'PM_{10}' AIR SAMPLERS IN COLLECTING POLYCYCLIC AROMATIC HYDROCARBONS

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Air concentrations of particulate-phase polycyclic aromatic hydrocarbons (PAHs), collected by three samplers, were compared. Tested instruments were two hi-vol samplers—the one for 'total suspended particles' (TSP) and the other provided with a 10-μm cutoff (PM_{10}) inlet—and a lo-vol portable TSP sampler. Sampling was performed under a variety of ambient conditions, at an urban site where vehicle emissions are the prevailing PAH source. Individual concentrations of PAHs were quantified by high-resolution gas chromatography and ranged 0.05 to 6 ng/m^3. The PM_{10} sampler provided concentrations which were on average 73% to 93% (about 90% for the 5- and 6-ring carcinogenic PAHs) of those provided by the hi-vol TSP sampler; the between-instrument ratios showed a good homogeneity throughout the study. The hi-vol and lo-vol TSP samplers, operating at the same face velocity, showed a very good agreement regarding PAH collection (overall mean ratio lo-vol/hi-vol: 97%), but the observed detection limit in lo-vol samples (ca. 0.3 ng/m^3) may turn out to be too high.

KEY WORDS: Polycyclic aromatic hydrocarbons, sampling, TSP, PM_{10}, urban air.

INTRODUCTION

The determination of polycyclic aromatic hydrocarbons (PAHs) in urban air is becoming a widespread practice in pollution surveillance since many compounds of this class have proven to be experimental carcinogens[1,2].

A previous review[3] has shown that sampling of suspended particulate matter (SPM) for determining PAHs has usually been performed by high-volume (hi-vol) samplers collecting total suspended particles (TSP). PAH determination, however, by samplers collecting only particles with a 50% cutoff at the aerodynamic diameter of 10 μm (the so-called PM_{10}[4] or thoracic[5] fraction) has occasionally been reported in recent years[6–8]. This may be expected to become more diffuse in the future, particularly in monitoring programmes, as a consequence of the use of PM_{10} samplers in air quality surveillance for SPM, since the PM_{10} fraction is recognized to be a more appropriate indicator of health risks associated with ambient particles[4]. In fact, after the non-destructive SPM measurement, a PM_{10} sample can be subjected to analysis for PAHs, as for other

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chemical substances. So, the following question arises: to what extent are PAH concentrations determined in TSP and in PM_{10} samples comparable?

In earlier studies (previously reviewed[3]; see also more recent refs. 9 and 10), distributions of PAHs (benzo[a]pyrene only, in the papers reviewed in ref. 3) were evaluated according to given particle-size fractions, by cascade impactors: most of PAH content was found to be adsorbed on particles with an aerodynamic diameter of less than a few micrometers (the actual cut point of the impactor first-stage varied with different studies, up to 7.6 μm). To our knowledge, however, a direct comparison of PM_{10} and TSP samplers for PAH determination has not been performed so far.

In this paper, we present the measurements of particulate-phase PAH concentrations at an urban site, performed by three different adjacent samplers operating simultaneously: two conventional hi-vol samplers—one PM_{10} and one TSP –, and one TSP low-volume (lo-vol) sampler. The latter (commonly used in Italy in air quality surveillance for SPM) was included as it is employed, on occasion, for PAH determination[11] owing to its ease of transport, despite the disadvantage of lower amounts of collected material.

The aim of this investigation is to evaluate the comparability of PAH concentrations in urban aerosol collected by different samplers, with a view toward method standardization.

Samples were collected in different periods of the year under a variety of ambient conditions, with respect to meteorology, traffic and residential heating. Thirteen PAHs, listed in Table 1 along with the abbreviations used, were selected for analysis, according to the criteria of including 4- to 7-ring compounds as well as the most abundant atmospheric PAHs among those classified by IARC[2] as 'probable' or 'possible' carcinogens for humans. PAHs with less than 4 rings were not included as they are known to be almost exclusively collected as vapour-phase compounds[12].

EXPERIMENTAL

Sampling

The following air samplers were used:

(A) PM_{10} Hi-Vol Air Sampler, Model SAUV-15H (General Metal Works—Sierra Andersen), which includes a PM_{10} Size Selective Inlet (Model SA 1200). The sampler is supplied with a volumetric flow controller (a dimensional Venturi device) and a continuous flow recorder. It operates at a constant flow rate of 1.13 m^3/min.

(B) TSP Hi-Vol Air Sampler, Model SAUV-1360H (also known as GMWL 2000 H; General Metal Works—Sierra Andersen). This is the same instrument as A, but not provided with the PM_{10} inlet.

(C) Lo-Vol Air Sampler, Model Bravo M (Tecora, Milan, Italy), equipped with an open-face stainless steel filter-holder for TSP collection. This is a portable, constant flow sampler. Flow rate was adjusted at ca. 25 l/min, which resulted in the same face velocity (ca. 43 cm/s) as the TSP hi-vol sampler B. The filter-holder faced downwards, protected from rain and direct sunlight exposure.

Particulate matter was collected on pre-weighed glass fiber filters: 20.3 × 25.4 cm (General Metal Works, type G810) for samplers A and B, 47 mm diameter (Gelman, type A) for sampler C.

Table 1 Target PAHs.

Compound[a]	*Abbrev.*	*Mol. wt.*	*No. of rings*	*IARC class.*[d]
Fluoranthene	FA	202	4	3
Pyrene	PY	202	4	3
Benz[a]anthracene	BaA	228	4	2A
Chrysene+triphenylene[b]	CHR+TRI	228	4	3
Benzofluoranthenes sum[b,c]	BFA	252	5	2B
Benzo[a]pyrene	BaP	252	5	2A
Indeno[1,2,3-cd]pyrene	IP	276	6	2B
Benzo[ghi]perylene	BghiP	276	6	3
Anthanthrene	ATR	276	6	3
Coronene	COR	300	7	3

[a] Ranked according to increasing GC retention time.
[b] Determined together as their GC peaks are not resolved.
[c] Isomers 'b', 'j' and 'k'.
[d] Human carcinogenicity according to IARC.[2]
Group 2A: probably carcinogenic; 2B: possibly carcinogenic; 3: not classifiable.

Samplers were operated simultaneously for 24-h periods during week-days.

Three sets of samples, each one including three daily subsets, were collected. The sampling site was located in an urban, not industrialized, area with various public institutions generating rather intense traffic during morning hours. The most important source of PAHs in this area are vehicle emissions, from both gasoline and diesel engines. Fuels for residential heating are gas and oil, and—to a lesser extent—coal. Heating was off during sampling of set I, and on during sampling of set III; it was on for a few days, and only in some of the buildings, during sampling of set II.

The three samplers were located at road level in the courtyard of our Institute, 8 m from the road. Inlets were aligned over a 7-m footboard parallel to the road. Using smoke tubes (Auer, type 5019-701), it was checked that the inlets did not influence one another in operating conditions. Internal surfaces of the TSP hi-vol sampler were cleaned before sampling; the PM_{10} sampler and its inlet were cleaned according to manufacturer's schedule.

Meteorological parameters (Table 2) were measured at a station located on the roof of the Institute, at a height of 35 m.

After sampling and reweighing, filters were stored at −18°C and extracted within one week.

Extraction and clean up

A previously published method[13] was adopted with some minor modifications, as here summarized.

Large filters (hi-vol samplers) were cut into 3-cm size squares and ultrasonically extracted three times for 15 min with 80+50+50 ml cyclohexane (Carlo Erba, HPLC grade); small filters (lo-vol sampler) were extracted as a whole with 30+20+20 ml. After filtration, the combined extracts (one half or the whole, respectively, from large or small filters) were concentrated and subjected to thin-layer chromatography (TLC) on silica gel (20 × 20 cm, 1-mm-thick layer plates, Merck type 13895; plates were pre-washed with

Table 2 Meteorological observations during sampling.

Sample set/ subset	*Date*[a]	*Temp. (°C) range*[b]	*Relative humidity (%) mean*[b]	*Wind velocity (m/s) mean (max.)*[b]	*Rainfall (mm)*
I/1	25 May 93	19–30	59	1.8 (5.0)	0
I/2	28 May 93	19–29	67	2.6 (5.8)	0
I/3	31 May 93	21–33	44	2.7 (6.3)	0
II/4	12 Nov. 93	15–19	92	1.1 (3.1)	53
II/5	15 Nov. 93	11–19	66	4.9 (7.4)	1
II/6	18 Nov. 93	9–14	60	1.8 (3.9)	0
III/7	14 Jan. 94	9–17	82	0.6 (2.1)	0
III/8	3 Feb. 94	12–17	71	4.0 (6.6)	0
III/9	4 March 94	9–22	43	3.5 (7.3)	0

[a] Initial day (24-h sampling starting at 9 a.m.).
[b] Values refer to 24 hourly averages.

redistilled-in-glass acetone). The TLC plate was developed with 1:1 (v/v) n-hexane-toluene to a height of 12 cm and the PAH spot (R_f: ca. 0.8) was detected with 254-nm UV light. The silica gel spot was then scraped off, transferred to a 1-cm i.d. glass tube and eluted with 12 ml (5+5+2 portions) of toluene. Eluate and washings were combined, concentrated to ca. 250 and 50 µl (respectively, hi-vol and lo-vol samples) and analysed.

Analysis

A gas chromatograph (Carlo Erba, Model 5160 Mega) equipped with a cold on-column injector, a 25 m × 0.32 mm × 0.25 µm fused-silica SE-54 column (Nordion) and a flame ionization detector (temp.: 300°C), was employed. The oven temperature was programmed from 90° to 280°C at 8°C/min and then held isothermally; hydrogen was used as carrier gas. A Hewlett-Packard Model 3396 II integrator was used for data acquisition and processing.

PAH identification and quantification were performed by comparing sample chromatograms with a reference solution of standards (pure standards were purchased from Analabs, Fluka and the Community Bureau of Reference of the Commission of European Communities).

RESULTS AND DISCUSSION

Collective measurements of PAH concentrations are presented in Figure 1, along with respective SPM concentrations. PAH levels were in close agreement when measured by the same sampler, in the three sampling days of set I, as expected on the basis of similar meteorological conditions. On the other hand, decreases in PAH concentrations within sample sets II (subset 5) and III (subsets 8 and 9) seem attributable to corresponding increases in wind velocity (traffic intensity was roughly constant within each set).

Results of comparisons are reported in Figures 2 and 3, and in Table 3.

The amounts of SPM collected were in the ranges of 47 to 130 mg (PM_{10} samples), 90 to 205 mg (TSP hi-vol samples) and 1.3 to 4.6 mg (TSP lo-vol samples).

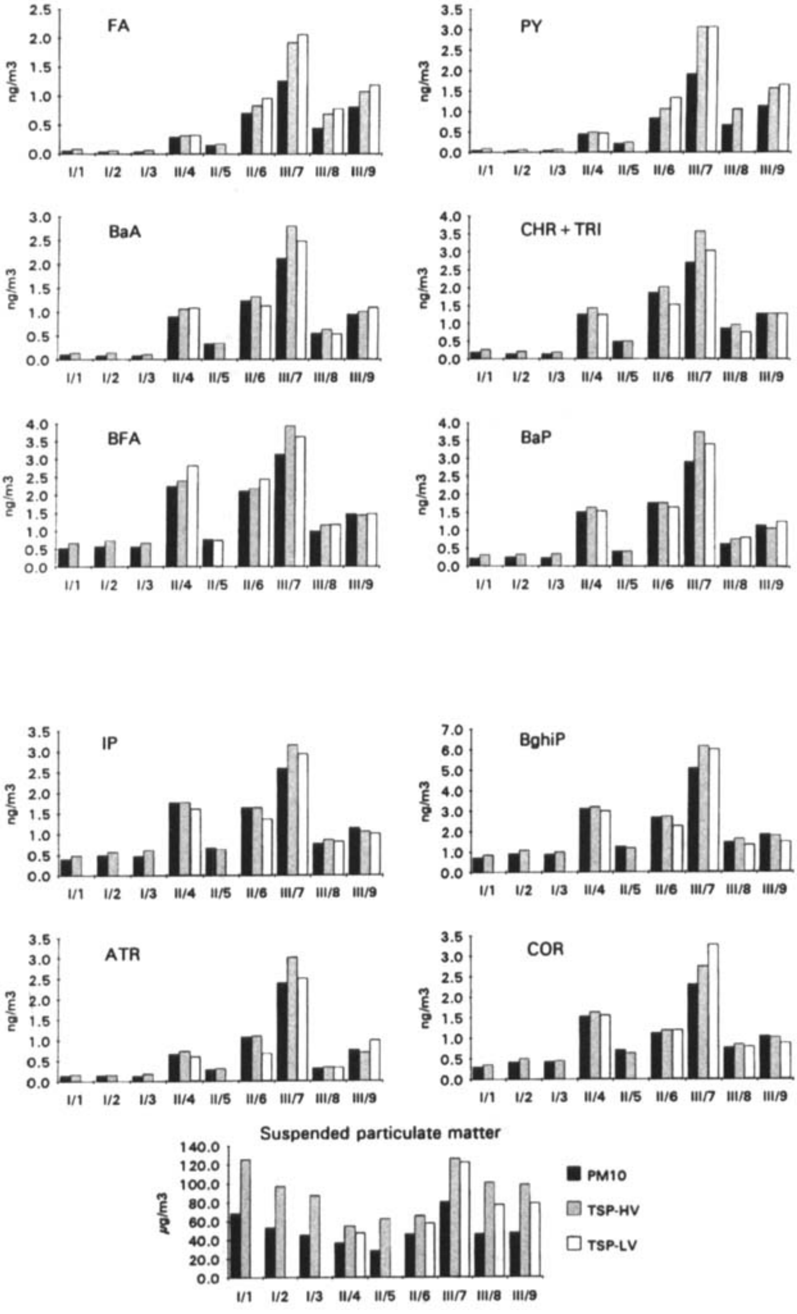

Figure 1 Concentrations of particulate-phase PAHs in air, as determined by the three samplers operating simultaneously. Legend: see 'Suspended particulate matter' histogram. PM_{10}, TSP-HV and TSP-LV are samples collected by, respectively, samplers A, B and C mentioned in "Sampling" section. Lacking of samples TSP-LV is due, in subsets 1–3, to low amounts (near detection limit) of collected PAHs impairing a reliable quantitative comparison and, in subset 5, to sample loss. PY was not determined in sample TSP-LV of subset 8 owing to an interfering peak. Concentrations are uncorrected for recovery efficiency.

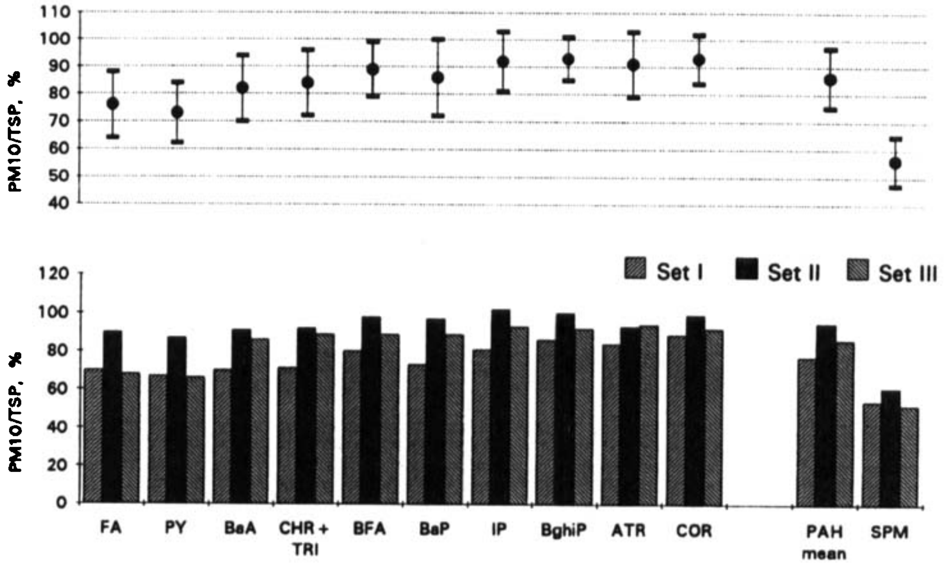

Figure 2 Comparison of PAH concentrations determined by PM_{10} and TSP hi-vol samplers. Top: mean ± 1 SD ratios over all sample subsets (1–9); bottom: mean ratios of each set.

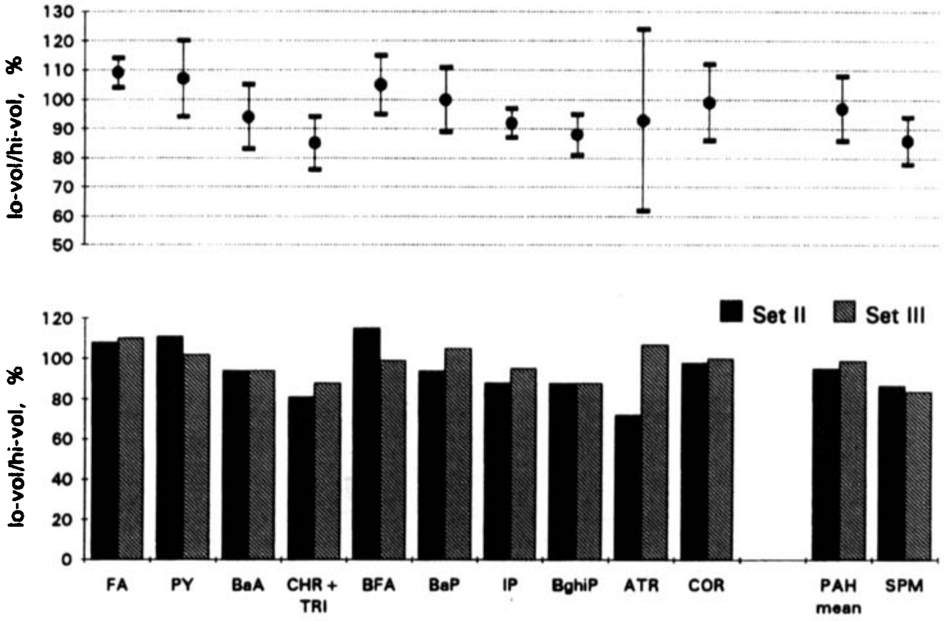

Figure 3 Comparison of PAH concentrations determined by lo-vol and hi-vol TSP samplers. Top: mean ± 1 SD ratios over all pertinent sample subsets (4, 6–9; see note of Figure 1); bottom: mean ratios of each pertinent set.

Table 3 Regression data for sampler comparisons.

Sampler comparison	*n*	*Intercept*	*Slope*	*Correl. coeff.*
PM_{10} vs. TSP-HV				
All target PAHs	90	0.05	0.83	0.98 ($P < 0.001$)
FA and PY excepted	72	0.07	0.84	0.99 ($P < 0.001$)
FA and PY	18	0.05	0.64	0.99 ($P < 0.001$)
TSP-HV vs. TSP-LV				
All target PAHs	49	0.02	1.03	0.98 ($P < 0.001$)

Abbreviations: see Table 1 and Figure 1.

Comparison of PM_{10} and TSP hi-vol samples

PAH concentrations from PM_{10} samples accounted for 73% to 93% (mean: 86%) of those from TSP samples (individual PAH averages from all subsets) (Figure 2). This finding is consistent with the results of previous studies (mentioned in 'Introduction') which involved sampling by cascade impactors.

Mean PM_{10}/TSP ratios (averages over all measured PAHs), as calculated for each subset (not shown in Figure 2) and each set, were appreciably higher than corresponding ratios for SPM concentrations, thus indicating that PAHs are associated predominantly with particles with $d < 10$ μm. This may be explained by the predominant emitting source (vehicle exhaust), whose particulates show mass median diameters in the submicrometric range[14].

The PM_{10}/TSP ratio tends to decrease with decreasing molecular weight, consistent with the previous observations of Aceves and Grimalt[9], who found a relative increase of FA and PY in the size fraction > 7.2 μm of urban aerosol and assumed it may likely reflect contributions to larger size aerosol from street dust, dominated by low-molecular PAHs and particularly by FA and PY[15].

The intersubset variability of ratios (which includes both the analytical variability and the actual differences due to different ambient conditions during sampling) was relatively low (mean intersubset CV: 13%), in light of analytical variability which is known to be associated with various methods for PAH determination in air: reported intralaboratory CVs (mean values for different PAHs; sampling not included) are 8% in urban air analysis[16], 10% in occupational environment[17], 7% (extraction not included) in vehicle emissions[18]. In other terms, the measured PM_{10}/TSP ratios present a good homogeneity in spite of different ambient conditions.

Comparison of hi-vol and lo-vol TSP samples

The two instruments showed a very good agreement, based on an overall mean ratio lo-vol/hi-vol of 97% (Figure 3). Individual mean ratios do not apparently account for any tendency within the PAH class, while deviations from the mean likely reflect a generally poorer accuracy in the analysis of lo-vol samples because of the smaller amounts of collected material: the measured levels of various PAHs in lo-vol samples were not much higher than the limit of detection, which was about 0.3 ng/m^3. (In some cases—see note of Figure 1 –, this limit did not make it possible to estimate a reliable ratio.) The mean intersubset CV was 12%.

CONCLUSIONS

The results indicate that, under the conditions of this study (characterized, in particular, by vehicle emissions as the prevailing source of PAHs), the choice of a PM_{10} or TSP sampler should not play a major role in determining concentrations of carcinogenic PAHs in urban air. In particular, the observed differences may be considered negligible when compared with: (a) the generally high variability of results in PAH investigations, deriving from the complexity of sampling factors and parameters[3]; (b) the uncertainity in the quantitative carcinogenic risk assessment associated with the inhalatory exposure to PAHs[19–21].

From a practical point of view, it would be advisable to use PM_{10} samplers if already present in a monitoring network for SPM surveillance. But using the less expensive TSP samplers in a PAH-dedicated network would allow the number of sampling sites to increase, with the same cost, and hence the representativeness of results for the area under investigation.

The study also indicates that hi-vol and lo-vol TSP samplers, operating at the same face velocity, provide similar PAH measurements, within about ±10%. Lo-vol samplers would be recommended when a temporary arrangement or, more generally, an easy transport from site to site are required, but the higher limits of detection must be taken into account when planning the investigation.

Additional field tests in urban sites with different characteristics, particularly as to PAH sources (e.g., industrial emissions or other prevailing heating fuels), are needed before generally valid conclusions can be drawn.

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