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Distribution of *n*-alkanes, polynuclear aromatic hydrocarbons and nitrated polynuclear aromatic hydrocarbons between the fine and coarse fractions of inhalable atmospheric particulates

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Abstract

The distribution ratios of *n*-alkanes, polynuclear aromatic hydrocarbons (PAHs) and nitrated PAH components between fine and coarse fractions of soot has been investigated in downtown Rome through three field campaigns carried out at different times of the year. The preferential accumulation of almost all species investigated onto fine particles has been observed in all field experiments performed. Moreover, nitrated PAHs had varied distributions, according to the origin of their occurrence in the atmosphere; in fact, congeners of photochemical origin accumulated more in fine particles than those released by primary sources. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is well known that organic compounds, including toxic species, are important components of atmospheric soot (consisting of small carbonaceous particles) where they are mostly adsorbed onto *thoracic* particles (up to 10 μm aerometric diameter) [1,2]. Therefore, national and international guidelines for air quality nowadays have to be modified in order to stress the $\text{PM}_{2.5}$ assessment in the air, i.e., the evaluation of the aerial content of particles whose diameters range from 0.1 to 2.5 μm ($\text{PM}_{2.5}$) [3]. In fact, if we look at the human respiratory system, we observe that: (a) particles with diameters larger than 10 μm do not reach the thorax; (b) particles ranging

from 2.1 to 10 μm are preferentially retained by pharynx, trachea and bronchi; and finally, (c) particles below 2.1 μm can reach terminal bronchi and alveoli. Therefore, a *physical* detrimental action of inhalable particles (i.e., the development of pulmonary emphysema) is observed along with the chemical impact due to their toxicity [4]. In spite of that, only a few investigations focussed onto the *fine* distribution of organic components in the soot have carried out [5,6], although such a knowledge should be of great concern.

In that context, the IIA-CNR and ISPESL carried out three field experiments in October 1996, July 1997 and March 1998 in downtown Rome. These months were selected as indicative of three different climatic and anthropic activities situations, that characterise middle autumn, summer and late winter. In fact, during summer and autumn vehicle exhausts are

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the predominant anthropic source of pollutants in downtown Rome, while in March the contribution of domestic heating has to be taken into account. On the other hand, the weather is sunny in summer but often rainy in spring, while in winter a marked atmospheric stability easily occurs.

2. Experimental

2.1. Particulate sample collection

Airborne particles were collected at the top of the ISPESL building, located in a financial district of the city, about 20 m above ground level. The location of sampling device was selected in order to prevent any direct exposition to near sources of soot, like traffic or stacks.

A preliminary field experiment was carried out in December 1994, in order to verify the suitability of the sampling site selected for our investigation. For this purpose, two sets of soot samples were collected by means of high-volume instruments (both supplied by Graseby Sierra Andersen, Village of Cleves, OH, USA). The former was run to sample “total” suspended particulates (TSPs), the latter (PM_{10}), collected only *thoracic* particles, because it was equipped with an inlet device preventing large particles (i.e., larger than 10 μm) to reach the collecting filter.

In the core experiment, *fine* and *coarse* fractions of particulates (consisting of particles which aerometric diameters ranged from 0.01 to 2.5 μm , and from 2.5 to 10 μm , respectively) were collected separately, by using a cascade impactor device equipped with two filter membranes, located in front of the aspirating pump. Particles were collected onto inert membranes (Teflo type, diameter=47 mm, pore size is 0.45 μm , supplied by Pall Gelman, Ann Arbor, MI, USA) by pumping air at mean-flow conditions (16.7 l/min).

In both campaigns, the collection time of soot was fixed at 24 h, starting every day at 07.00 h.

2.2. Method of analysis

The chemical evaluation of particulate organic matter (POM) in a preliminary field experiment was

carried out by using a method previously standardised at IIA-CNR [8]. For the core experiment, this procedure was shortly modified, accounting for the reduced amounts of soot subjected to analysis. In both cases, *n*-alkanes, polynuclear aromatic hydrocarbons (PAHs) and nitrated-PAHs (N-PAHs) were investigated and their respective distribution ratios between fine and coarse fractions of soot were determined. As ancillary information, data about seasonal variations of soot content were gained.

Briefly, particle samples were extracted by refluxing with a mixture of dichloromethane–acetone (3:1, v/v) in a Soxhlet apparatus for 16 h (six cycles per hour). Solvent was reduced to low volume by means of a Kuderna–Danish device and transferred onto a neutral Alumina column (3.0 g, Brockmann activity I), then POM was partitioned into three fractions, by eluting with *n*-hexane, dichloromethane and methanol. Aliphatic components, comprising *n*-alkanes, were eluted into the first fraction (F-1); aromatic and meanly-polar components were in F-2 and very polar species eluted in the last fraction (F-3). The second fraction evaporated and was further separated into three sub-fractions, comprised of PAHs (F-2A), N-PAHs (F-2B) and oxygen-containing species (F-2C). For this purpose, the F-2 residue was back-dissolved with dichloromethane and eluted through a high-performance liquid chromatography (HPLC) silica column (Erbasil 10 μm silica, Carlo Erba, Milan, Italy), by using a solvent gradient from pure *n*-hexane to dichloromethane. Finally, *n*-alkanes and F-2 sub-fractions were run by capillary gas chromatography (GC), by using flame ionisation (FID) or mass spectrometry (MS) operated in selected-ion monitoring (SIM) mode, respectively. In the former case, a HRGC-5160 system was used, equipped with a FID system 50 and a FID-580 electrometer all purchased from Fisons Carlo Erba, a split–splitless injector and a methylphenyl silicone capillary column (SP-20 purchased from Supelco, Bellefonte, PA, USA; 30 m \times 320 μm I.D., phase thickness=0.25 μm) capillary column. Analytes were eluted by operating a temperature programmed from 40 up to 280°C. To determine PAHs, molecular ion currents were recorded together with [M–1], [M+1] and [M/2] traces; four ion currents were detected for N-PAHs (i.e., [M], [M–30], [M–46], [M–58]). For this purpose, a HP 5890 gas chromatograph coupled

with a 5971A mass spectrometric detector was used (Hewlett-Packard Italiana, Cernusco sul Naviglio, Italy). The mass spectrometer was equipped with a split–splitless injector and a DB-5 type column (25 m×0.20 µm I.D., phase thickness=0.33 µm, purchased from J&W Scientific, Folsom, CA, USA) and chromatographic runs were developed by increasing the oven temperature from 80 up to 280°C. All PAHs and N-PAHs investigated were separated at baseline, except benz[*j*]-, benz[*b*]-, benz[*k*]fluoranthene, and benz[*a*]anthracene/chrysene, which were partly overlapping). *n*-Alkanoic acid methyl esters and oxygen-containing components (like phthalate esters, keto-PAH or PAH-quinones) were not determined at this stage, but they will be taken in concern in our future investigations.

In order to reduce any artefact due to sample losses or analyte decomposition, internal standards were added to sample extracts: 1-bromodocosane for the *n*-alkane fraction, *ortho*-terphenyl and *meta*-triphenylbenzene for PAHs, perdeuterated 1-nitropyrene for N-PAHs. Blank controls demonstrated that interfering compounds did not affect analyses.

At the core experiment step, the only difference concerned POM extraction from particles, which was performed by sonication (three times for 20 min) instead of Soxhlet refluxing. Besides that, all samples collected at each weekly campaign were pooled; in that way we could get enough soot material to

perform qualitative and quantitative determinations at a low uncertainty level, and on the other hand, by replacing the filters everyday we could reduce artefacts due to decomposition processes of analytes or to stream volatilisation from particles.

Our concern was focussed onto those organic components of airborne particles relevant to urban air quality (i.e., PAHs and N-PAHs) or source identification (i.e., *n*-alkanes and N-PAHs). In fact, PAHs are released by any combustion process and several of them are carcinogenic and indirectly mutagenic [9,10]; N-PAHs are strong direct mutagens [11], and their occurrence in the atmosphere is related to both direct emission and photochemical pollution [8,12,13]; *n*-alkanes allow one to assess the relative contribution of biogenic sources to global content of POM in the air [14–16].

3. Results and discussion

3.1. Quantitative results

The preliminary campaign confirmed that the site was not exposed to close sources releasing organic components (see Table 1 for PAH and N-PAH data). In fact, benzonaphthothiophene and benzonaphthofuran levels were below the detection limit of our method (i.e., 0.1 ng/m³), and PAH concen-

Table 1
Mean concentrations (in ng/m³ units) of selected PAHs and N-PAHs in both total (TSP) and thoracic (PM₁₀) particulates^a

Species	Particle symbol	Total (TSP)	Thoracic (PM ₁₀)	Large (TSP-PM ₁₀)	R _v (PM ₁₀ /TSP)
Fluoranthene	Fa	1.17	0.93	0.24	0.79
Pyrene	Py	1.33	1.05	0.28	0.79
Benz[<i>a</i>]anthracene	BaAn	1.27	1.21	0.06	0.95
Chrysene	Chr	2.79	2.54	0.25	0.91
Benz[<i>b</i>]fluoranthene	BbFa	4.49	4.25	0.24	0.95
Benz[<i>k</i>]fluoranthene	BkFa	1.19	1.06	0.13	0.89
Benz[<i>e</i>]pyrene	BePy	2.80	2.70	0.10	0.96
Benz[<i>a</i>]pyrene	BaPy	1.73	1.56	0.17	0.90
Indeno[1,2,3- <i>cd</i>]pyrene	InPy	2.98	2.65	0.33	0.89
Dibenz[<i>ah</i>]anthracene	DBAn	0.35	0.32	0.03	0.91
Benz[<i>ghi</i>]perylene	BPer	5.04	4.73	0.31	0.94
Total PAHs		32.55	29.10	3.45	0.89
2-Nitrofluoranthene	2-NFa	0.38	0.35	0.03	0.92
1-Nitropyrene	1-NPy	0.12	0.10	0.02	0.83

^a Rome, Via Urbana (ISPESL Building), December 1994.

trations were typical of a residential area; in addition, the benz[*a*]pyrene/benz[*e*]pyrene ratio (close to 0.7) and the 2-nitrofluoranthene/1-nitropyrene ratio (close to 3) were not in agreement with values currently observed at street level or at chimneys of industrial plants [7,17].

Regarding the core experiment, Table 2 reports the mean concentrations of soot fractions in the air and the whole contents of *n*-alkanes, PAHs and N-PAHs recorded in October 1996, July 1997 and March 1998; symbols used for PAHs are listed in Table 1. The data reported in all tables and figures and further discussed refer to *mean aerial concentrations* of compounds, recorded over all the periods investigated. In Table 2 volume and mass distribution ratios for all classes are shown. In October 1996 and July 1997 the coarse particles content in the air was more abundant than that of the fine ones, while the reverse occurred in March 1998; the total concentration of soot in March 1998 was quite low, as a consequence of frequent rain episodes which occurred in that period; nevertheless, this did not duty affect the aerial abundance of organic components. The POM components investigated seemed to follow different temporal evolutions of volume and mass distribution. In fact, aerometric concentrations of all classes achieved their minimum values in July and the maximum ones in March, whereas soot composition was richer in *n*-alkanes and N-PAHs in October, and in PAHs in March. In general, the accumulation of

compounds onto the *fine* fraction of particles was more pronounced in October 1996.

Finally, looking at the volume and mass distribution ratios (see Table 2), R_v and R_m of all the classes of components investigated were similar, according to aerometric concentrations of *fine* and *coarse* fractions of soot.

3.2. *n*-Alkane fraction

The percent abundance of congeners among the *n*-alkane fraction in aerosols is determined by the typology of sampling site, and in particular by the relative impact of anthropogenic and biogenic emission [16]. In fact, the *n*-alkane concentration profile versus carbon number, typical of a canyon street, fits with a monomodal distribution, with its maximum centred around C_{23} – C_{24} ; instead, a saw-tooth distribution with a preferential presence of odd-carbon numbered congeners and absolute maxima centred around C_{29} – C_{31} is representative of biogenic emission and can be observed in forest areas. Fig. 1 shows the typical *n*-alkane profiles we have observed during two field experiments performed in Italy at a canyon street (downtown Naples, December 1993) and in a forest site (Castelporziano, February 1994).

Fig. 2a–c shows the *n*-alkane content of suspended particles collected during the three periods investigated. The figure reports not only the aerometric concentrations of compounds (in ng/m^3 units),

Table 2

Volume and mass concentrations of organic components of coarse and fine fraction of soot (distribution ratios R between fine and coarse particles are also reported) (Rome, ISPESL building)

	Sampling time								
	October 1996			July 1997			March 1998		
	Soot fraction			Soot fraction			Soot fraction		
	Coarse	Fine	R	Coarse	Fine	R	Coarse	Fine	R
SPM ($\mu g/m^3$)	55	49	0.89	29	18	0.62	15.6	17.4	1.12
<i>n</i> -Alkanes (ng/m^3)	9.4	69.7	7.4	11.3	11.1	1.0	22.1	52.9	2.4
PAHs (ng/m^3)	0.4	3.6	8.1	0.3	1.0	3.4	3.0	14.3	4.8
N-PAHs (ng/m^3)	0.09	0.17	1.8	0.01	0.03	2.5	0.07	0.37	5.0
<i>n</i> -Alkanes ($\mu g/g$)	169	1416	8.4	383	615	1.6	236	506	2.1
PAHs ($\mu g/g$)	8.0	73.4	9.2	13.0	64.5	5.0	40.4	159.1	3.9
N-PAHs ($\mu g/g$)	1.7	3.5	2.1	0.4	1.6	4.1	0.8	3.5	4.5

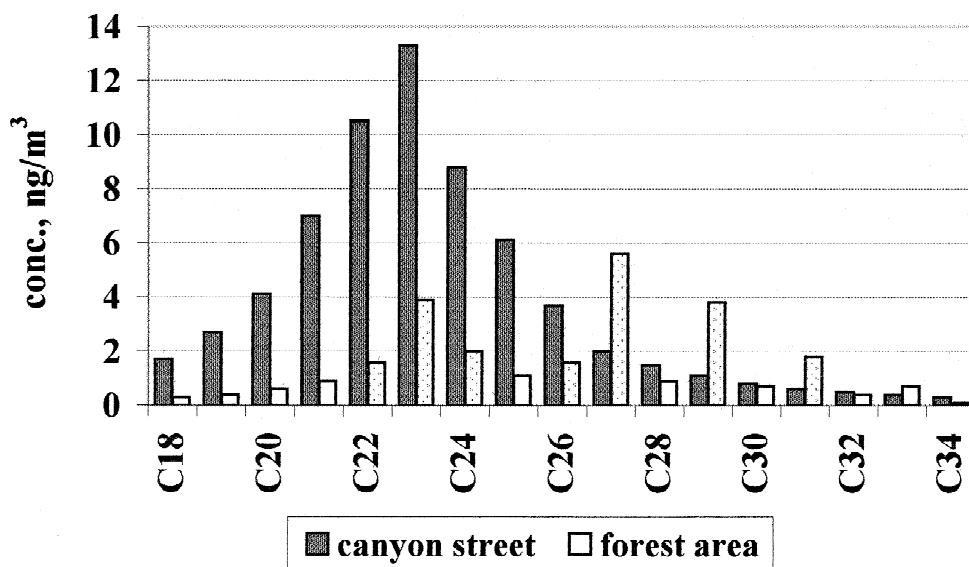


Fig. 1. *n*-Alkane concentration profile versus carbon number observed in a canyon street and forest area soot samples. The former sample was collected in downtown Naples, the latter in the Castelporziano Estate, 20 km SW of Rome.

but also the volumetric distribution ratio R_v , given by the formula: $R_v = [X_{\text{fine}}, \text{ng/m}^3] / [X_{\text{coarse}}, \text{ng/m}^3]$. In all samples a combination of anthropic and biogenic sources determined the distribution of the congeners and the biogenic contribution to the global budget appeared to be similar in October and March but reached the maximum in July; the relative abundance of semivolatile or heavier congeners was influenced by temperature. Concerning the distribution ratios peculiar for all compounds at different seasons, R_v values were at the minimum (i.e., close to 1) in July 1997, and peaked in October 1996. At that time, values larger than 7 were found, probably determined by appreciable washout, preferentially involving *coarse* or *large* particles. All these observations seem to suggest that biogenic soot, containing odd-numbered *n*-alkanes, is comprised of *coarse* particles to a significant extent.

3.3. PAH fraction

Fig. 3a–c reports the PAH content in the soot fractions during the three above field experiments. Data are relative to selected PAH congeners, i.e., fluoranthene and pyrene (as precursors of N-PAHs investigated), and those recognised as displaying

carcinogenic properties. The actual concentrations of PAHs were maximum in March and minimum in July, and the less volatile congeners were relatively more abundant in October 1996. In July 1997 accumulation of some species, especially benz[*a*]pyrene, benz[*a*]anthracene and dibenz[*a,h*]anthracene was prevented by peculiar sinks like oxidation processes because of their strong reactivity [18,19]. Unlike *n*-alkanes, PAHs accumulated anytime in *fine* particles; that behaviour was in agreement with the expected anthropic origin of these components, i.e., their release from vehicle exhaust, that is recognised as the most important source in Rome. Fig. 4 shows that the highest R_v ratios relative to PAHs were observed in October 1996, and the lowest in July 1997 for all the compounds; they usually increased concurrently with molecular mass and decreased with volatility of compounds.

3.4. N-PAH fraction

Before discussing Fig. 4a–c which shows the aerometric content of N-PAH components in soot, it is necessary to introduce the possible sources of the eight possible nitrofluoranthene and nitropyrene isomers, that have been found in particulates [12,13].

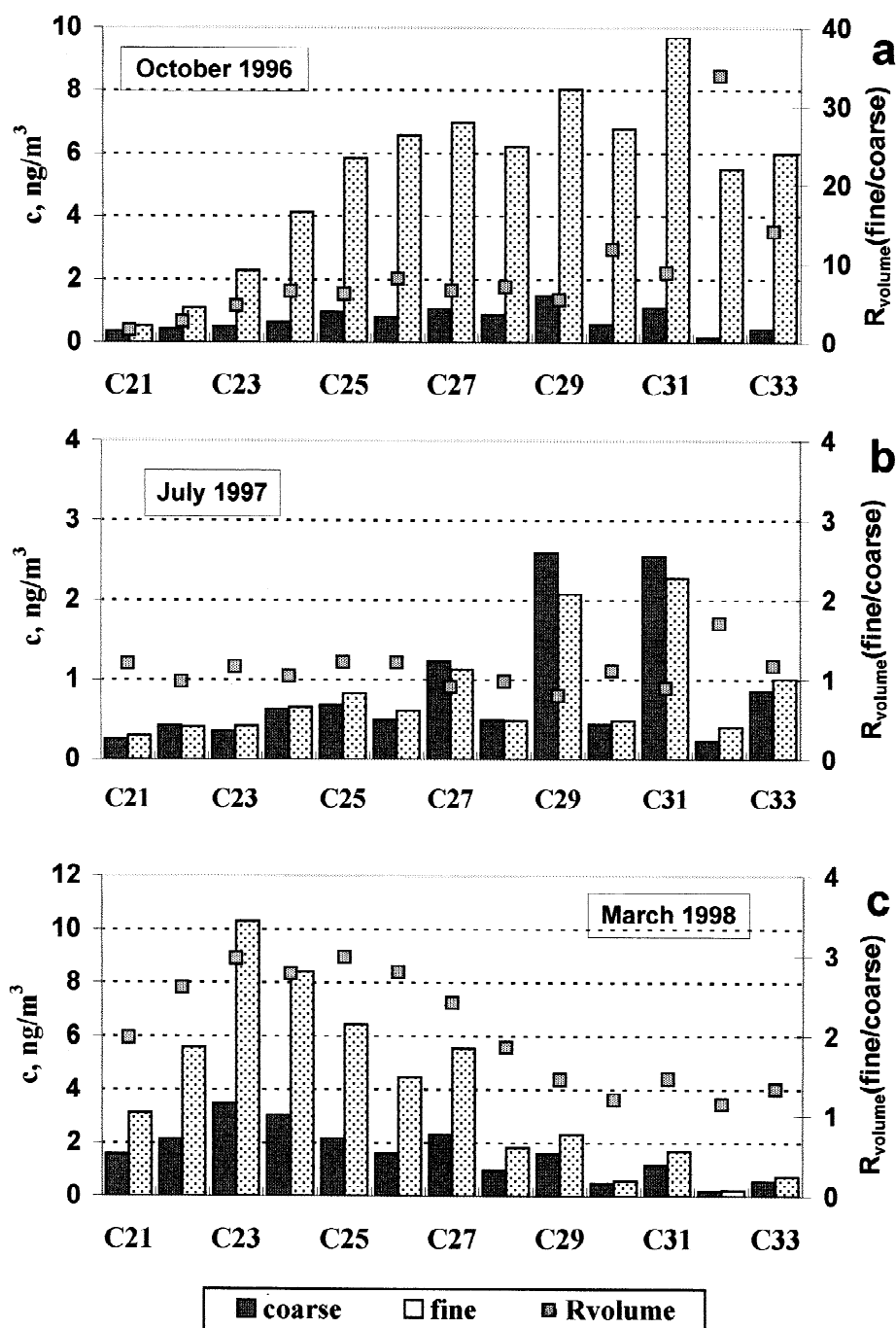


Fig. 2. *n*-Alkane content in both *fine* and *coarse* particles collected in downtown Rome, at the three field experiments. The distribution ratio R_v is also reported for each compound. Data refer to: (a) October 1996; (b) July 1997; and (c) March 1998.

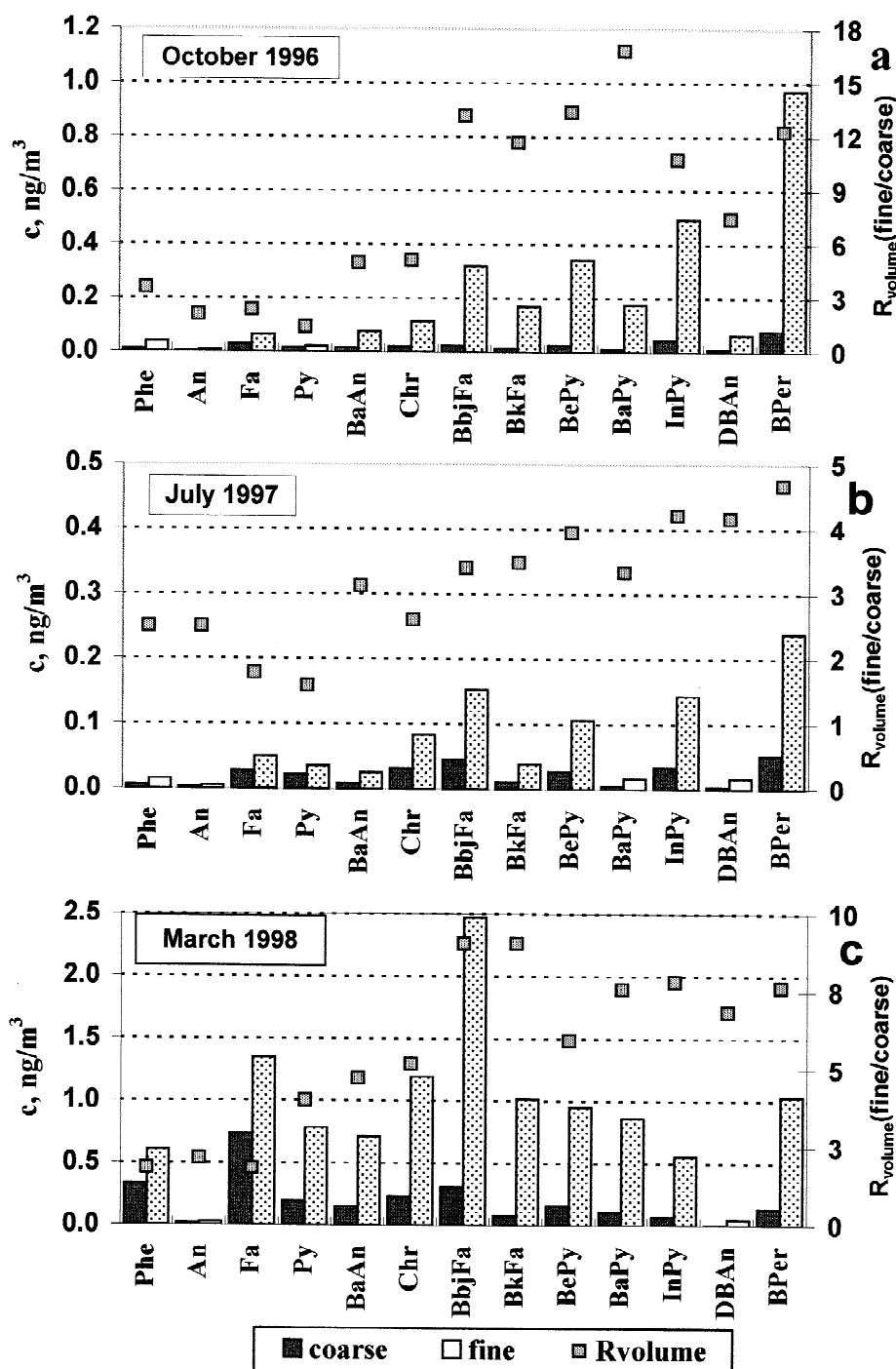


Fig. 3. PAH content in both fine and coarse particles collected in downtown Rome, at the three field experiments. The distribution ratio R_v is also reported for each compound. Data refer to: (a) October 1996; (b) July 1997; and (c) March 1998.

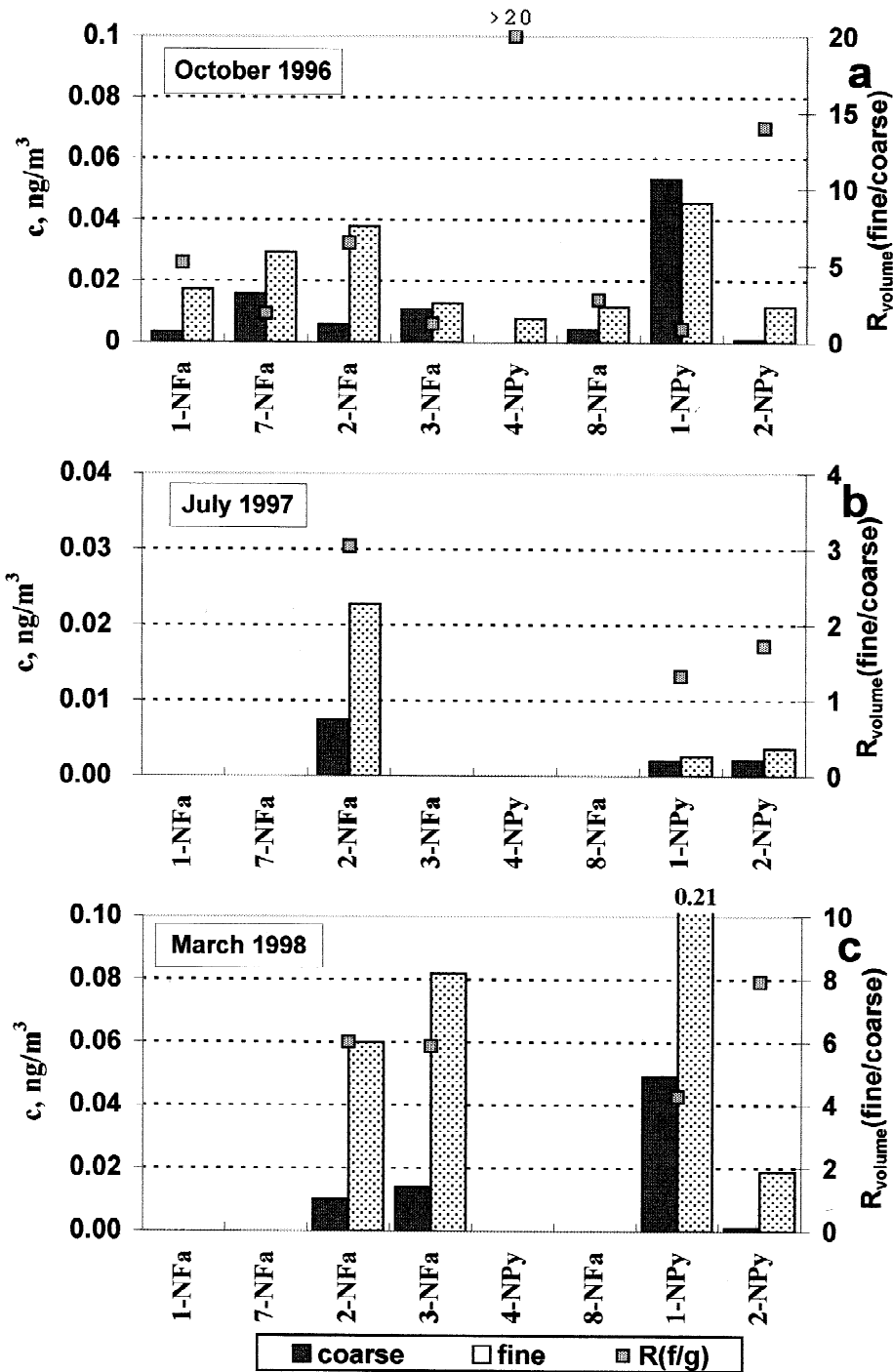


Fig. 4. N-PAH content in both fine and coarse particles collected in downtown Rome, at the three field experiments. The distribution ratio R_v is also reported for each compound. Data refer to: (a) October 1996; (b) July 1997; and (c) March 1998.

The reason of our concern for these compounds is related to their strong mutagenicity, that yields N-PAHs as active partners in toxicity of soot [11,13]. The preliminary experiment (see Table 1) suggested that N-PAHs are usually present in both *fine* and *coarse* particles. We classified N-PAHs into two groups [8,12,20], the former consisting of the directly emitted species (N-PAHs_{em}), the latter formed by secondary pollutants (N-PAHs_{phot}). In fact, the former group (consisted by 1-NPy and, to a lesser extent, 3-, 8-, 7- and 1-NFa) is usually present in vehicle exhausts, whereas congeners belonging to the latter group are generated in the atmosphere by reactions induced by photochemical oxidants. In fact: (i) 2-NFa and 2-NPy come from the gas-phase reaction of parent PAHs with OH radicals and NO₂, in the daytime; (ii) the night-time interaction of fluoranthene and pyrene with NO₃ radical leads to formation of 2-NFa (with 7-NFa as a minor product), or 4-NPy, respectively; and finally (iii) 3-, 8-, 7- and 1-NFa and 1-NPy are produced through heterogeneous reaction of parent PAHs adsorbed onto particles with the nitrating agents [20,21]. Fig. 4 shows that the simplest situation occurred in July, when a quite low direct emission (represented by the sole 1-NPy) was concurrent with the daily generation of 2-NFa and 2-NPy. In March 1998, the contribution of direct emission was predominant (1-NPy > 2-NFa; presence of 3-NFa). In October 1996, all isomers were detected, indicating a concurrence of the following processes: (i) direct emission (1-NPy); (ii) day-time gas-phase reaction (2-NFa, 2-NPy); (iii) night time gas-phase generation (2- and 7-NFa, 1- and 4-NPy); and (iv) gas-particle interaction (3-, 8-, 7- and 1-NFa, 1-NPy). The nitrated components appeared to be less abundant in July, because of a more extensive dispersion of emissions through the atmosphere occurring on sunny days, which are more frequent in that season. N-PAHs usually accumulated in the *fine* fraction of particulates; nevertheless, surprisingly distribution ratios relative to different components appeared to depend upon the respective sources. In fact, by looking at the large differences observed between R_v values, 2-NFa, 4-NPy and 2-NPy behaviour was different from that of the remaining congeners. We suppose it was a consequence of heterogeneous reactions preferentially taking place onto *coarse* particles, because they usually contain some percent of metal oxides or salts

acting as catalysers. On the other hand, *fine* carbon particles easily capture organic gaseous compounds produced in the atmosphere. The most abundant congeners (i.e., 2-NFa, 1-NPy and 2-NPy) reached maximum concentrations during the March 1998 experiment. Whereas photochemically-originated 2-NFa and 2-NPy accumulated anytime in *fine* particles, 1-NPy was almost equally distributed in October and in July. This should be determined by the concurrence of a bigger direct emission and some heterogeneous reaction, that at the March experiment time were favoured by meteorological conditions (i.e., low temperature and frequency of stability of the atmosphere).

4. Conclusions

All concentration data recorded during the field experiments seem to demonstrate that the main portion of organic components is always adsorbed onto the *fine* fraction of particulates; nevertheless, the relative content in *fine* particles modulates with molecular mass, nature of compounds, and time of the year. In fact, the relative content in *fine* fraction increases according to the molecular mass of species but it decreases with temperature.

The fraction comprising N-PAH components seems to be of the highest concern, because differences were observed not only about its composition but also with respect to the relative content of directly emitted and photochemically-originated congeners. In particular, 1-nitropyrene, a marker compound indicative of direct emission, is significantly present also in the *coarse* fraction, whereas 2-nitrofluoranthene, of photochemical origin, is mostly in *fine* particles. Since *fine* particles result to be carriers of most of the mutagenic and carcinogenic organic components in humans, the impact of soot on human health seems to be increased; in fact, the ability of *fine* particles to be inhaled and retained by pulmonary alveoli results to be concurrent with the large residence times they have in the atmosphere.

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