Particle Size Distribution of Toxic Organic Compounds in airborne urban particulate matter

P. Di Filippo, C. Riccardi, A. Busca, S. Spicaglia, D. Pomata, F. Incoronato
ISPESL/DIPIA
Via di Fontana Candida, 1 00040 Monteporzio Catone (Rome)

Aerosol mass distributions measured in emissions from combustion sources show peaks at very low particle diameters, about 0.4 μm, therefore it's expected that the products of incomplete combustion are almost entirely distributed into the smaller size fractions.
Most air pollution in urban atmosphere is caused by combustion products and particulate organic matter released by incomplete combustion is suspected to contribute to the etiologic factors in the development of lung cancer.
Ultrafine particles (<0.1μm) penetrate cellular membranes and their distribution within tissues of target organs have been demonstrated.
We studied the distribution of two classes of compounds known for their toxicity in thirteen size-fractions of urban airborne particulate matter, including ultrafine and coarse particles (from 0.03 μm to 10 μm), in order to facilitate an assessment of the carcinogenic potency of the particles known to penetrate into lungs, liver, hearth and nervous system.
Polycyclic aromatic hydrocarbon and their nitro derivative distribution and their concentration profile provided helpful information to compare the toxicity of each fraction.
For the first time the concentrations of the up mentioned classes of compounds were measured in the ultrafine particles.
The pollutant distributions of all the two classes of compounds were unimodal and centrated at 0.4 μm size fraction in winter and 0.1 μm size fraction in summer. Nevertheless the ultrafine particles contained a percentage of 12% in summer and 35% in winter of the cancerogenic compounds we analyzed.
To date the toxicity of ultrafine particles (<0.1 μm) was attributed to their capability to penetrate into all major tissue compartments and cells, and to their high number in atmosphere. This study suggests that it can be attributed even to their content in carcinogenic compounds.

1. Experimental

A low-pressure impactor (DLPI, Dekati Ltd) was used to collect aerosol samples during two sampling campaigns.
The cascade low pressure impactor classifies airborne particles into 13 size fractions. The size classification was from 30 nm up to 10 μm. The impactor sampling flow rate was 10 l/min. The particles were collected on PTFE filters (25 mm diameter and 0.45 μm porosity; ALBET srl) that were weighed before and after the measurement to obtain gravimetric size distribution of the particles. The filters were conditioned for twenty-

four hours in a chamber maintained at 40% relative humidity and 20 degrees Centigrade prior to weighing.
The first sampling campaign took place in July 2007 (9th–23th) during a period characterized by typical summer weather conditions: insulation and extreme hot temperatures; the second one in January 2007 (9th–23th) during winter: a period characterized by low temperature, low turbulence and higher atmospheric stability.
In order to collect enough amount of sample to reach the detection threshold of the chemical analysis, each sampling duration was 2 weeks.
The sampling campaigns were carried out downtown Rome, in a site not directly affected by emissions.
Particle-associated PAHs and nitro-PAHs extraction and analysis are described in detail elsewhere (Di Filippo et al., 2007).

2. Results And Discussion

2.1 Airborne Particulate Matter concentrations

The size-resolved mass distributions derived from the thirteen stage impactor were studied. The seasonal characteristics of the different modes of aerosols were additionally investigated.
The distributions are shown for each season in Fig. 1. In the winter case (9–23 Jenuary 2007), a higher particle loading is observed with two distinct modes at 0.4 and 6.8 μm, respectively, however enhanced concentration is found at the 0.4 μm mode. In the summer case (9–23 July 2006), two main modes are again observed, but the fine mode is shifted on the left (0.26 μm) and with more mass contained in the coarse one.
Briefly, particles from 0.03 to 0.17 μm are more abundant in summer (11%) than in winter (10%); particles from 0.26 to 1.0 μm are more abundant in winter (47%) than in summer (19%) and particles from 1.6 to 10 μm are more abundant in summer (70%) than in winter (43%). This behaviour can be explained as follows.

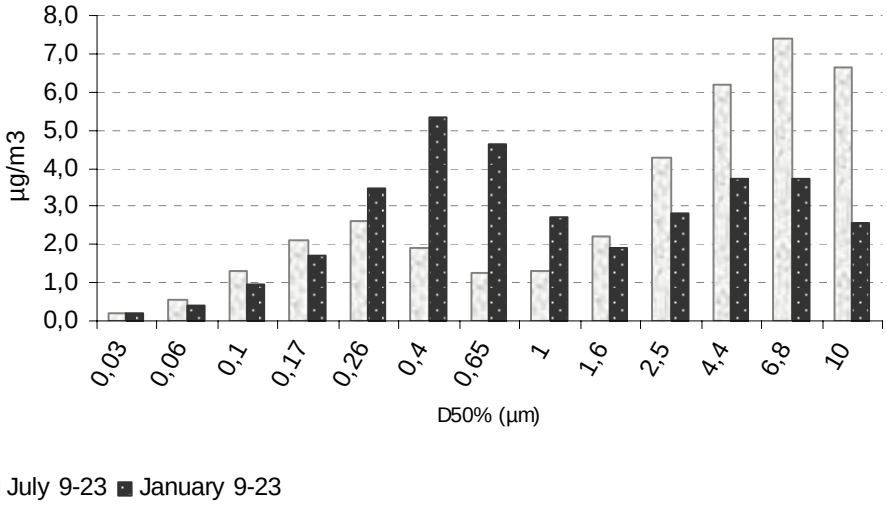


Fig. 1 Seasonal size-resolved mass distributions of atmospheric particulate matter in Rome

The submicron part of the mass distributions mainly come from the coagulation of particles after the primary pollutant emission and after photochemical reactions in the atmosphere; while the coarse particles mainly depend on the resuspension phenomena and on the Saharan dust.
In winter the primary emissions are higher, moreover low temperature and stable atmospheric conditions yield a lower dispersion of air pollutants. Therefore the concentrations of fine particles are higher than in summer. But the ultrafine particles have a different behaviour: they are slightly higher in summer, probably due to the higher temperature and the lower humidity that don't favour the growing toward the accumulation range at higher diameters.
The greater amount of coarse particles in summer can be attributed to the larger particle resuspension due to the higher wind speed and the lower relative humidity. In addition lidar observations collected at Rome in 2001 found 27–31% of days characterized by the advection of Saharan dust over the city; these events peaked in summer (Gobbi et al. 2007).

2.2 PAH concentrations

The particle-bound composition of polycyclic aromatic hydrocarbons (PAHs) associated with size distribution is showed in Fig. 2. In winter the highest PAH concentrations were found in the 0.4 μm size fraction corresponding to the most abundant mass fraction. Unlike winter, in summer the highest amount of PAHs were found in the third fraction, 0.1 μm, although in this season the most abundant mass concentration occurred in correspondence of the fifth fraction (0.26 μm). As displayed in Fig. 3, in winter, the smaller the particles sizes are, the richer the PAH amount is. In summer the PAHs can be instead found at higher percentage in the first three fractions. That means that the ultrafine fraction has in both the seasons a percentage of PAHs higher than the other fractions.

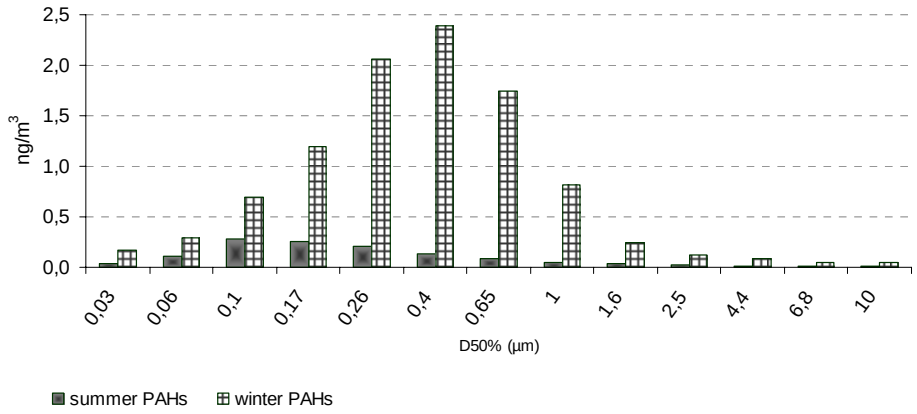


Fig. 2 Seasonal PAHs distributions in size-resolved atmospheric particulate matter in Rome

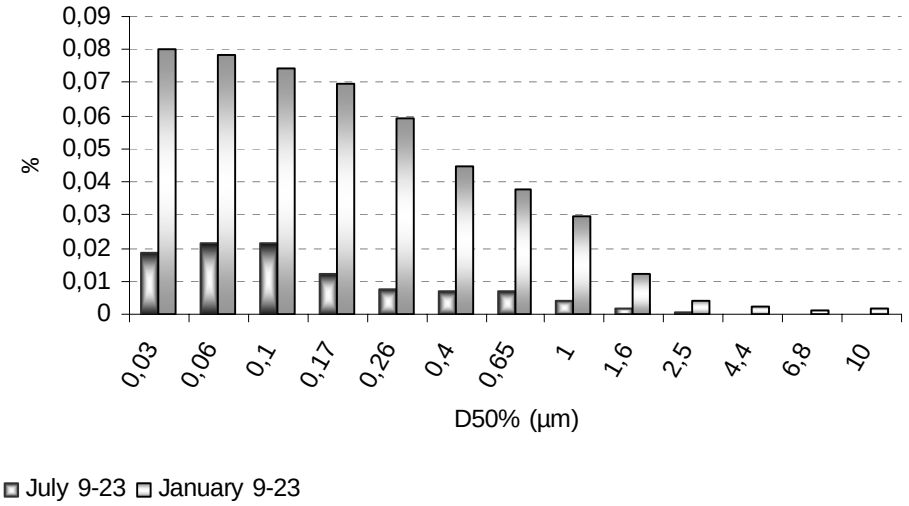


Fig. 3 Percentage distributions of PAHs in size-resolved atmospheric particulate matter in Rome

2.3 nitro-PAH concentrations

For what concern particle-bound nitro-PAHs, the behaviour of this class of compounds is similar to that of PAHs both in winter and in summer (fig. 4) and the highest percentage is in the ultrafine fraction both in winter and in summer, as shown in fig 5.

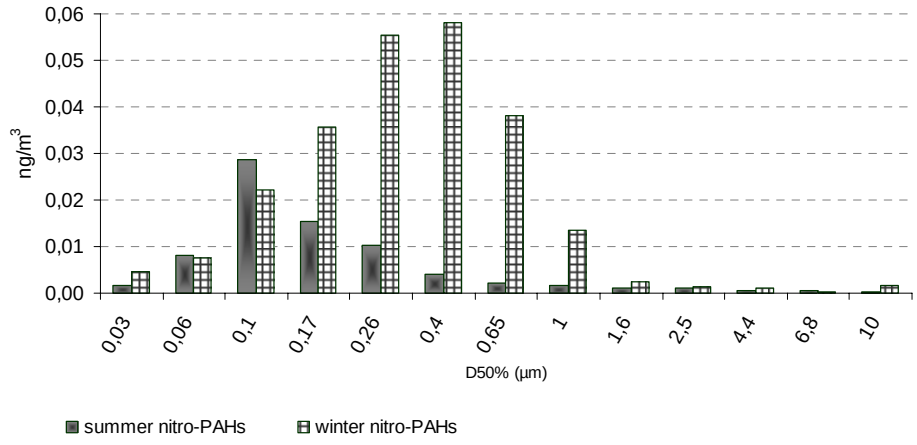


Fig. 4 Seasonal nitro-PAHs distributions in size-resolved atmospheric particulate matter in Rome

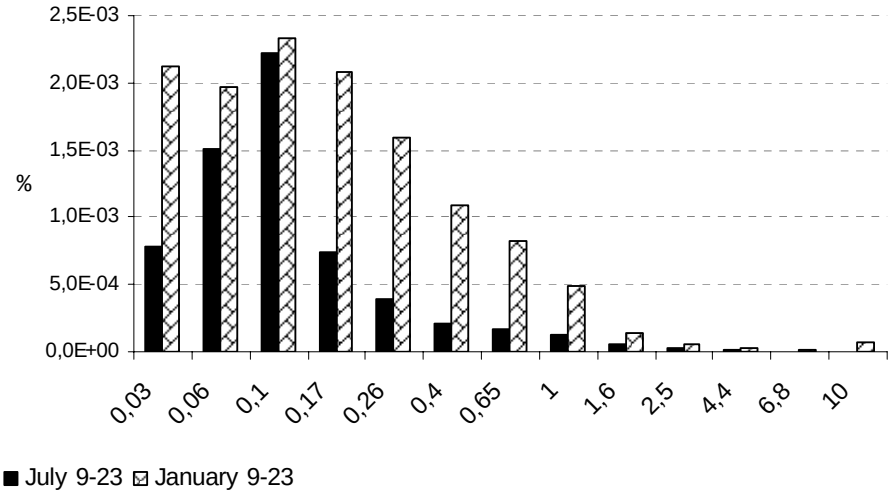


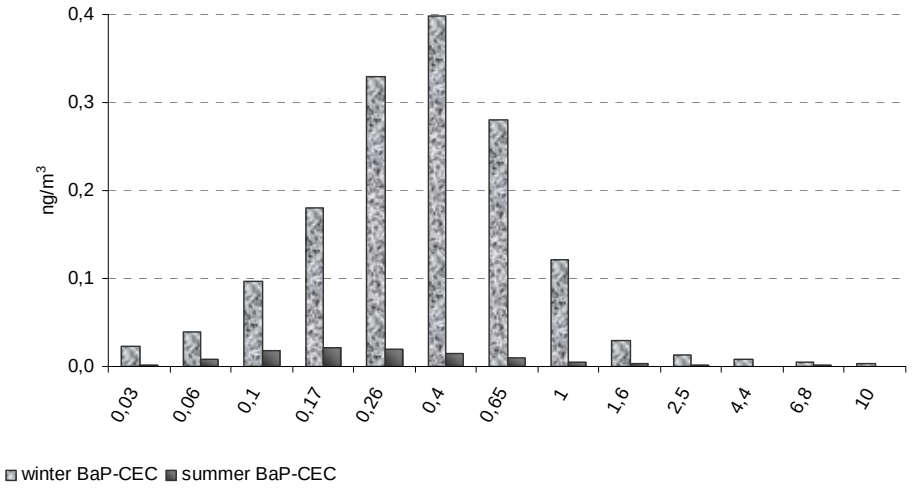
Fig. 5 Percentage distributions of nitro-PAHs in size-resolved atmospheric particulate matter in Rome

3. Toxicity

3.1 Carcinogenic Equivalence Concentration

In order to compare the toxicity of the particle-size fractions in both the seasons, the Benzo(a)Pyrene - Carcinogenic Equivalence Concentration (BaP-CEC) was calculated, multiplying the estimates of Cancer Potencies compared to benzo(a)pyrene provided by Nisbet and Lagoy (1992) for six PAHs and by OEHHA (2002) for five nitro-PAHs and multiplying those for the concentration of the individual PAHs and nitro-PAHs found in each fraction of the two seasonal field campaigns.

The results shown in Figure 6 individuate a higher risk situation in winter with a BaP-CEC concentration of 0.4 ng/m^3 in the 6th fraction and with a concentration of 0.16 ng/m^3 as the total of the first three fractions, that is the ultrafine fraction.



4. Conclusions

We studied the distribution of PAHs and nitro-PAHs known for their toxicity in thirteen airborne particle size-fractions during two seasons in an urban atmosphere.

In order to facilitate an assessment of the carcinogenic potency of the particles known to penetrate into lungs, liver, hearth and nervous system, the Benzo(a)Pyrene - Carcinogenic Equivalence Concentration was calculated.

While the size-resolved mass distributions were bimodal in both the seasons, the pollutant distributions of the two classes of compounds were unimodal and centrated at 0.4 μm size fraction in winter and 0.1 μm size fraction in summer. The ultrafine particles showed a mean percent content of 35% in winter and 12% in summer of the cancerogenic compounds we analyzed.

Concerning toxicity results, in winter 10% and in summer 27%of the BaP-CEC was in the ultrafine fraction. To date the toxicity of ultrafine particles (<0.1 μm) was attributed to their capability to penetrate into all major tissue compartments and cells, and to their high number in atmosphere. This study suggests that it can be attributed even to their content in carcinogenic compounds.

5. References

Di Filippo P., Riccardi C., Gariazzo C., Incoronato F., Pomata D., Spicaglia S., Cecinato A., 2007, Air pollutants and the characterization of the organic content of aerosol particles in a mixed industrial/semi-rural area in central Italy, Journal of Environmental Monitoring, 9, 3, 275-282.

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