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RESEARCH PAPER

A Study of $PM_{2.5}$ and $PM_{2.5}$-Associated Polycyclic Aromatic Hydrocarbons at an Urban Site in the Po Valley (Bologna, Italy)

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Abstract $PM_{2.5}$ and PAHs bound to $PM_{2.5}$ were investigated in downtown Bologna, from January to June 2003, in order to determine the burden of the fine fraction in the aerosol of a typical urban environment of the Po Valley, a critical area in Northern Italy in terms of atmospheric pollution. The sampling campaign was divided into three parts: a winter sub-campaign, an intermediate campaign where $PM_{2.5}$ and PM_{10} were simultaneously sampled and which identified $PM_{2.5}$ as the major component of PM_{10}, and a summer sub-campaign. Critical concentrations of both $PM_{2.5}$ and PAHs were observed in winter time; for example, in January 2003 the mean value for the 24-h average $PM_{2.5}$ concentration was 58 $\mu g/m^3$, much higher than the annual arithmetic mean of 15 $\mu g/m^3$ established by the US ambient air quality standard (NAAQS). Correspondingly, the mean value for benzo[a]pyrene (BAP) in $PM_{2.5}$ was 1.79 ng/m^3, again higher than the annual mean of 1 ng/m^3, required by European regulations for BAP in PM_{10}. In summer time the BAP concentration considerably decreases to 0.10 ng/m^3 as the likely effect of photolysis and dilution on a higher boundary layer; $PM_{2.5}$ decreases too, but the mean concentration (22 $\mu g/m^3$) is still higher than the NAAQS value. Further analysis included TEM microscopy of collected particles and correlations between $PM_{2.5}$, PAHs and gases (benzene, O_3, CO, NO_2, SO_2). All these observations identified on-road mobile sources as the main source of emissions and, in general, of the poor air quality level in the city of Bologna.

Keywords $PM_{2.5}$ · polycyclic aromatic hydrocarbons · air pollution · urban environment · on-road mobile pollution sources

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1 Introduction

Evidence from epidemiological and toxicological studies on the health effects of airborne particulate matter (Englert, 2004) has been the object of a series of review articles, dealing, for instance, with prenatal and early childhood health effects (Lacasana, Esplugues, & Ballester, 2005), asthma and other paediatric morbidities (Trasande & Thurston, 2005), respiratory health effects (Donaldson et al., 2004), adverse chronic cardiopulmonary effects (Heinrich & Wichmann, 2004; Lippmann, Gordon, & Chen, 2005), and carcinogenicity (Harrison, Smith, & Kibble, 2004).

In 1998, the World Health Organization (WHO), European Centre for Environment and Health – Rome Division, was asked by the Italian Ministry of

Environment to carry out a health impact assessment study for the eight largest cities in Italy: Turin, Milan, Bologna, Genoa, Florence, Rome, Naples and Palermo. The overall population in 1991 in these cities was 8.3 million, 15% of the total national population. In this study motor vehicle traffic was identified as the main source of particulate matter (PM) in Italian cities; in the 1998–1999 period, WHO estimated a two-year average PM_{10} concentration of 51.2 μg/m^3 in Bologna, and, among the eight cities examined, Bologna experienced the highest percent of premature deaths attributable to air pollution in the same period (Martuzzi, Galassi, Ostro, Forastiere, & Bertollini, 2002).

The EC Council Directive enacted in 1999 (European Union, 1999), regulates the atmospheric daily mean mass concentration of PM_{10} to a maximum value of 50 μg/m^3, with a yearly mean value of 40 μg/m^3, and an allowed number of exceedances for the maximum value limited to 35 per year. From 2010 these regulations will be tightened up to a yearly mean of 20 μg/m^3, with the number of allowed exceedances of 50 μg/m^3 reduced to seven days per year. Nowadays, the planned PM_{10} limits are seldom met, particularly in two critical European areas, central Europe (Spindler, Müller, Brüggemann, Gnauk, & Herrmann, 2004) and the Po River Valley in Northern Italy (Decesari et al., 2001; Petritoli et al., 2004; Spirig, Neftel, Kleinman, & Hjorth, 2002).

$PM_{2.5}$, the respirable particles capable of being deposited in the deep lung and the most harmful fraction of total suspended matter (see Schwartz, Laden, & Zanobetti, 2002 for concentrations/response relationships between $PM_{2.5}$ and daily deaths in US cities), is not regulated yet by the EU. However, the proposal for a directive of the European Parliament and of the Council on Ambient Air Quality and Cleaner Air for Europe, (CAFE; Commission of the European Communities, 2005) establishes that the $PM_{2.5}$ annual average concentration threshold of 25 μg/m^3 should be attained within 2010/01/01.

In the US (US EPA, 1997), the EPA promulgated the National Ambient Air Quality Standards for Fine Particles, which fixed the annual standard for $PM_{2.5}$ at 15 μg/m^3, based on the 3-year average of annual mean $PM_{2.5}$ concentrations, and the 24-h standard at 65 μg/m^3, based on the 3-year average of the 98th percentile of 24-h concentrations.

The present study was carried out in the city of Bologna, and was centred on $PM_{2.5}$ and polycyclic aromatic hydrocarbons (PAHs) associated with it. The aim was to verify the air quality of the respirable fraction of particulate matter and to trace the main emission sources in a typical urban site of the Po Valley.

2 Materials and Methods

2.1 Sampling location

The city of Bologna (380,000 inhabitants) is located in the southern border of the Po River Valley, a flat region surrounded by the Alpine chain in the north and northwest, by the Apennine Hills in the south and by the Adriatic Sea on the eastern boundary, as shown in Figure 1. The whole basin is densely populated and heavily industrialized; both the amphitheater-like land

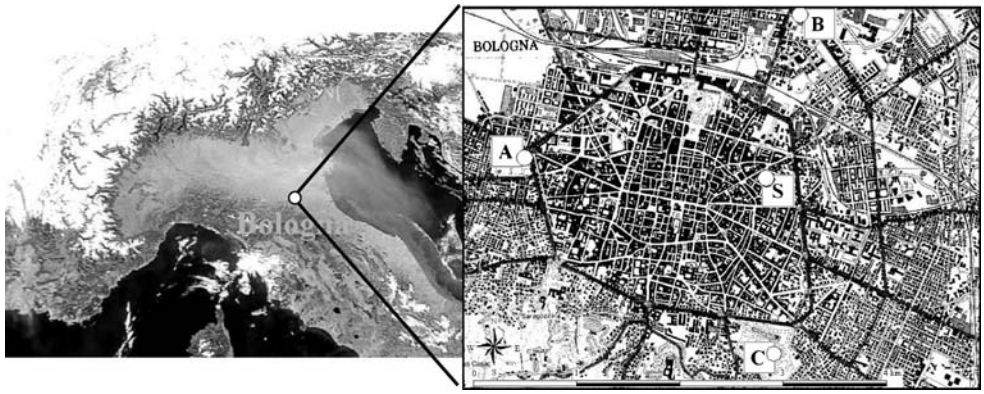

Figure 1 A layer of smog covers the Po River plain and spreads up to northern and medium Adriatic Sea. Satellite picture taken on February 14, 2000. The map of Bologna, showing the sampling location S and the network of the ARPA stations A–C.

morphology which protects the valley from winds that might otherwise disperse air pollution, and socioeconomic conditions which render this area the most vibrant and developed in Italy, are ideal to promote intense winter and summer-smog pollution episodes during frequently occurring air stagnation conditions (Ancellet & Ravetta, 2003; Bonasoni et al., 2004; Decesari et al., 2001; Petritoli et al., 2004; Schaap, Van Loon, Ten Brink, Dentener, & Builtjes, 2004; Spirig et al., 2002). The Bologna district does not host heavy industries, power plants, petrochemical industries, steel mills, coke ovens, or other polluting facilities, however it hosts one of the most important and congested motorways junction in Northern Italy as well as an international airport, 5 km away from the city centre. Thus, residential combustion, mainly based on methane as feedstock, and vehicle exhausts are the main sources of primary and secondary atmospheric aerosol.

The sampling site S (Figure 1) selected for this study is located in a yard of the University district (44°29′47″N and 11°21′14″E); the yard opens onto a road with restricted traffic, however two main axis of heavy traffic are only 300 and 500 m far from S. Three to five floor buildings shield the yard from these traffic-congested roads.

This sampling site S was selected on the basis of two criteria: (1) S is almost at the centre of the three air quality control stations of ARPA-Bologna, labelled as A (S. Felice), B (Fiera), C (Giardini Margherita), and shown in Figure 2. Sites A and B correspond to two typical street canyons, while station C is located in a public park close to the city ring road; (2) S is representative of the city centre, where traffic is restricted, but which receives smog from the busy ring road, the outskirts and, at a longer distance (~5 km), from the motorway network.

2.2 $PM_{2.5}$ sampling and sampling strategy

$PM_{2.5}$ samples were collected on Quartz Fiber Filters (QFF; QF 20 Schleicher & Schuell) with a Bravo PM Tecora instrument equipped with $PM_{2.5}$ size selective inlet complying with the European norm EN 12341 (flow = 2.3 m^3/h). $PM_{2.5}$ concentrations, expressed as $\mu g/m^3$ of air, were obtained by gravimetric analysis. QFF were pre-conditioned for 24 h in a dessicator (silica gel) at room temperature (T ~ 20–25 °C) and constant humidity (RH ~ 20%–45%) and weighed. After sampling, the QFF was conditioned for 24 h at the same initial conditions, weighed, and stored in a glass container at −22 °C before PAH extraction. The uncertainties of $PM_{2.5}$ determinations were the result of the error propagation of weight uncertainty (standard deviation of five measures) and total air volume collected (precision 2%).

The campaign was carried out in 2003 and consisted of 53 samples (24 h each, from 10 A.M. to 10 A.M.), divided in three periods: sampling campaign # 1 (SC1), 29 consecutive $PM_{2.5}$ samples (24 h each) from 2003/01/08 to 2003/02/05; (SC2), 10 parallel random samples (8 h each) of $PM_{2.5}$ and of PM_{10} (high volume Thermo Environmental Instruments Inc., sampler, 600 model) from 2003/02/06 to 2003/06/12; and (SC3), 14 consecutive $PM_{2.5}$ samples (24 h each) from 2003/06/13 to 2003/06/26 (the international standard date notation, Year-Month-Day, is used across the text, according to ISO 8601).

2.3 Analytical Methods

A set of eight PAHs, phenanthrene (PHE, $C_{14}H_{10}$), pyrene (PYR, $C_{16}H_{10}$), benz[a]anthracene (BAA, $C_{18}H_{12}$), chrysene (CHR, $C_{18}H_{12}$), benzo[b]fluoranthene (BBF, $C_{20}H_{12}$), benzo[k]fluoranthene (BKF, $C_{20}H_{12}$), benzo[a]pyrene (BAP, $C_{20}H_{12}$) and benzo[ghi]perylene (BGP, $C_{22}H_{12}$), were analysed. Filter-absorbent collectors are known to be subjected to sampling artifacts (Bidleman & Harner, 2000), however the use of a low volume with respect to high volume samplers reduces: (1) adsorption on the filter matrix, which overestimates particle-bound PAHs and which is more relevant in the case of the heaviest PAHs, and (2) the blow out of PAHs from the filter, (more severe in the case of the lightest PAHs) which gives rise to an underestimation of particle-phase concentrations (Simcik, Eisenreich, Franz, & Zhang, 1998).

PAHs were extracted from $PM_{2.5}$ loaded QFF filters in a Soxhlet apparatus for 8 h (~6–7 cycles per hour) with dicloromethane (DCM). The sample extracts were concentrated in a rotary evaporator system to ~1 ml and subjected to silica gel clean-up, according to US EPA (1999). In detail, a slurry of activated silica gel (10 g) in DCM (40 ml, JT Baker, Ultra-Resi Analyzed Reagent) was poured in a chromatographic column (10 mm ID, 25 cm height); after solvent elution, anhydrous sodium sulfate (1 g)

was put on the top of the column. The column was then pre-eluted with hexane (40 ml) and the sample charged on the column. Aliphatic hydrocarbons are first separated by elution with hexane (25 ml), then the PAH containing fraction was collected using a dicloromethane/hexane solution (4/6 v/v, 35 ml). The latter eluate was vacuum evaporated to ~1 ml, then further concentrated under a gentle nitrogen flow. The residue was dissolved in 0.2 ml of acetonitrile and analysed by HPLC (Perkin-Elmer LC250) equipped with a fluorescence detector (Perkin-Elmer LC240). It is interesting to note that the highly sensitive analytical technique adopted, HPLC/fluorimetry, allows the determination of this set of PAHs using a low-volume $PM_{2.5}$ sampler which filters about 50 m^3 of air in 24 h, with respect to the ~2,000 m^3 filtered by high volume samplers.

The HPLC analytical conditions, wavelength program and PAH retention times (min) have been reported in previous work (Stracquadanio, Bergamini, Massaroli, & Trombini, 2005). The HPLC system was calibrated for quantification using standard solutions (10 ng/μl each, in acetonitrile, Dr. Ehrenstorfer GmbH cat. n. LS20950900) of the 16 US EPA PAH priority pollutants at five different concentration levels in the range 100 up to 2,000 pg, injecting 20 μl.

2.4 Quality assurance

Blank QFFs handled in the same way of the sampled filters were analysed and the PAH concentrations were below the limit of the detection for every one.

In order to obtain the recovery efficiency, 1/2 QFF of three $PM_{2.5}$ samples were spiked with 25 ng of each PAH, using 0.2 ml of the above quoted PAH standard solution diluted to 50 ng/ml with acetonitrile.

Both spiked and original QFFs half-filters were subjected to the same analytical procedure. PAH concentrations measured in the no-spike filters were subtracted from the concentrations of the spiked filters. The following PAH recoveries were determined: PHE 75%, PYR 87%, CHR 87%, BAA 88%, BBF 90%, BKF 85%, BAP 70%, BGP 100%. PAH concentrations were corrected on the basis of the reported recoveries.

A certified reference material (SRM1649a, Urban Dust), was also used to compare the method efficiency to the consensus value; heavier PAHs were recovered with a 85%–100% efficiency, while for the more volatile PHE and PYR recoveries were 75%–85%.

Reproducibility for PAHs as relative standard deviations (RSD) were calculated on triplicate analyses (three aliquots of the same filter) and resulted in: PHE 10%, PYR 8%, CHR 12%, BAA 8%, BBF 5%, BKF 5%, BAP 5%, BGP 5%.

Detection limits (DL), defined as the mean plus three times the standard deviation of the blank values, varied between 0.005 and 0.02 ng/m^3.

3 Results and Discussion

3.1 Sampling site

Traffic congestion problems are common issues in Bologna as a consequence of both local and geographical grounds. The town-plan, basically conditioned by its origin in the Middle Ages, causes daily traffic jams particularly along the ring road and in the converging road network connecting Bologna to its neighbourhoods. Diesel vehicles make the most important contribution to the overall pollution, accompanied by a huge number of two-stroke motorcycles in warmer months (Martuzzi et al., 2002).

Moreover, owing to its geographic position, Bologna neighbourhoods host the second most congested motorway junctions in Northern Italy, including the two main north–south connections A1 and A14, as well as the international ‘G. Marconi Airport’, 5 km away from the city centre.

3.2 $PM_{2.5}$ monitoring

$PM_{2.5}$ mass concentrations relative to the 52 samples are presented in Appendix. Table I reports the minimum, median and maximum value for each sub-sampling campaign; winter (SC1) and summer (SC3) sub-samples are also presented as histograms in Figures 2 and 3.

Figure 2 includes the *mean* and the *median* concentration values, the 24-h US EPA $PM_{2.5}$ limit (65 μg/m^3), and the succession of $PM_{2.5}$ concentrations, which displays a rough weekly trend, observed both in urban (Chaloulakou, Kassomenos, Grivas, & Spyrellis, 2005) and in rural environments

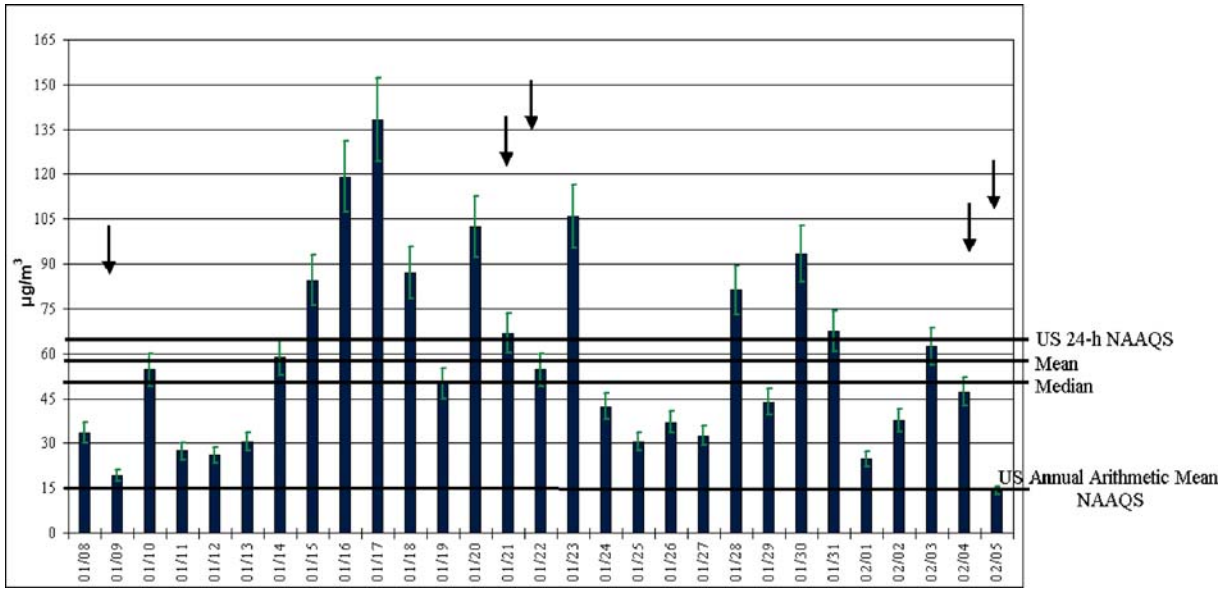

Figure 2 $PM_{2.5}$ concentrations in the winter sub-campaign SC1.

(Spindler et al., 2004). In winter time, in most of the cities of northern Italy, traffic on Tuesday was halved through the so-called odd/even number-plate measures; however this effect was negligible on $PM_{2.5}$ in comparison to the weekend effect, when traffic considerably drops down for two consecutive days. Meteorological conditions play a fundamental role in determining critical pollution events: for example, high pressure, low wind velocity and an exceptional stability of the boundary layer were found in 01/16 and 01/17. The diurnal boundary layer height was less than 400 m, and 200 m was the nocturnal height (Natali & Bollini, 2003). Correspondingly, $PM_{2.5}$ concentrations reached the highest values ever observed in our campaign, and, in particular, from Monday 13 to Friday 17 January, its concentration constantly increased about 30 µg/m^3 every 24 h, reaching the top value of 138 µg/m^3.

Figure 2 also locates five rain episodes (arrows) when an appreciable decrease in $PM_{2.5}$ concentrations was observed. In the whole winter period examined the extreme (max–min) concentration values were 138 and 14 µg/m^3, $PM_{2.5}$ covering a range of more than 100 µg/m^3.

The concentrations for the summer campaign (SC3), shown in Figure 3, reflect the turbulence and the height (800–1,000 m) of the boundary layer in during this time (Natali & Bollini, 2003), when an efficient mixing in the air column considerably reduces $PM_{2.5}$ concentrations. However, the $PM_{2.5}$ mean value is still higher than the US annual threshold limit. No appreciable weekly trend is apparent and the difference between extreme values is limited to 14.5 µg/m^3.

For the parallel sampling campaign (SC2) consisting of a limited dataset of nine samples, a regression analysis of PM_{10} vs $PM_{2.5}$ was checked and a linear correlation Equation (1) was found:

$$PM_{2.5} = (0.9 \pm 0.2)PM_{10} + (-4 \pm 9) \quad (1)$$

The slope 0.9 could suggest that the most important mass contribution to PM_{10}, at location S,

Table I Minimum, mean and maximum $PM_{2.5}$ concentrations value for each sub-campaign

Sub-Campaign	Samples Number	$PM_{2.5}$ (µg/m^3)		
		Min	Mean	Max
SC1 (03/01/08 ÷ 03/02/05)	29	14 ± 2	58	138 ± 2
SC2 (03/02/10 ÷ 03/05/05)	8	9 ± 2	36	52 ± 3
SC3 (03/06/13 ÷ 03/06/26)	14	17 ± 2	22	32 ± 1

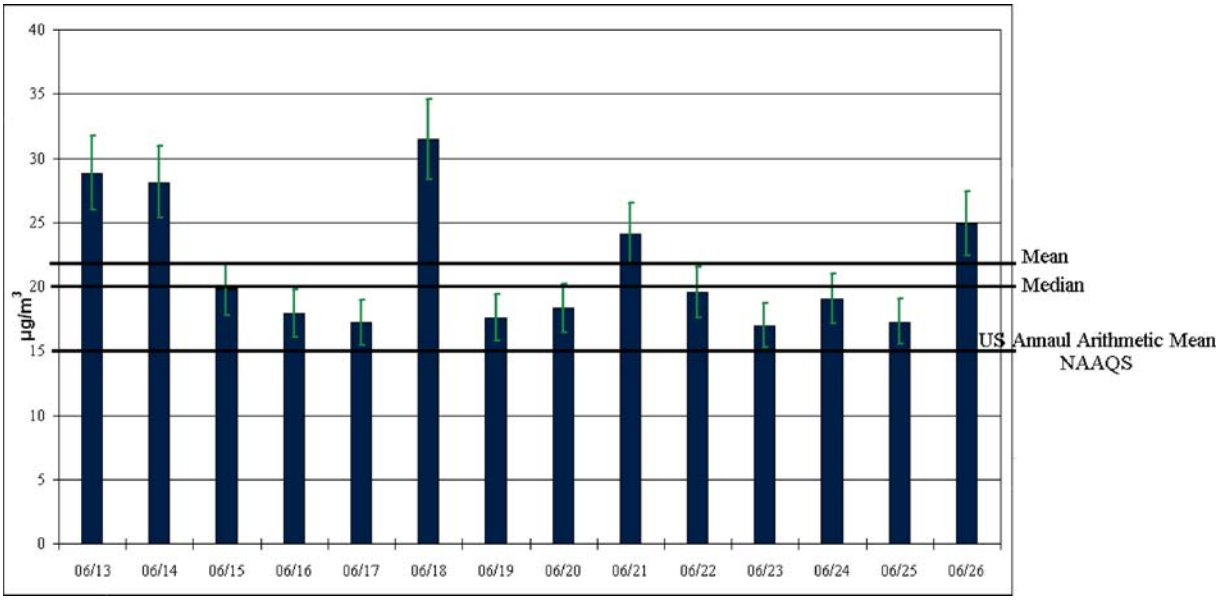

Figure 3 $PM_{2.5}$ concentrations in the summer sub-campaign SC3.

is given by $PM_{2.5}$, and that pollution episodes by coarse particulate matter (PM_{10}–$PM_{2.5}$), are occasional. Moreover, correlation is good ($r^2 = 0.77$, $P < 0.01$) considering the dataset size and the inclusion of data collected over five months, from January to June, under a wide spectrum of meteorological conditions. It is known, indeed, that the correlation of atmospheric aerosol components can heavily depend on seasonal parameters when different pollution sources are present (Berner et al., 2004; Gehrig & Buchmann, 2003).

3.3 $PM_{2.5}$-bound PAHs

$PM_{2.5}$ particles adsorb on their surface a number of organic compounds, often referred to as Organic Carbon (OC), during their transport through the troposphere (physical and chemical ageing of the particle).

We focused our attention on a defined fraction of the organic compounds adsorbed in $PM_{2.5}$ collected in our sampling site, namely polycyclic aromatic hydrocarbons (PAHs), well known for their toxicological properties (US EPA, 1993; WHO, 1983). A set of PAHs were analysed from a limited number (27) of $PM_{2.5}$-coated filters. In particular, in winter SC1, PAHs were analysed on 11 filters out of overall 29 QFF, selecting one sample every four days. In SC2 all filters collected were analysed for PAHs. In the summer (SC3) PAHs were analysed every two days, for a total of seven out of 14 $PM_{2.5}$ filter samples. Collective data for the whole campaign are reported in Table II.

The general trend of PAH concentrations parallel that of $PM_{2.5}$, going from high values in winter to values close to the detection limit in summer time.

The EU regulates ambient concentrations of BAP, the most studied carcinogenic member of the PAH family, at the target value of 1.0 ng/m^3 in PM_{10}, as an annual mean (European Commission, 2001). Moreover, the EU shall adopt, by 2010, an air quality limit of between 0.5 and 1.0 ng BAP/m^3, annual mean, measured in the PM_{10} fraction and expressed at ambient conditions.

In Table II the mean and median values of PAH concentrations are also calculated for the each sub-campaign. To evaluate the status of air quality in terms of BAP concentration, we can compare BAP to the EU limit of 1.0 ng/m^3 (annual mean) just as a reference value: in winter time (SC1) the mean BAP concentration is 1.73 ng/m^3, while in summer (SC3) the BAP mean concentration decreases to 0.10 ng/m^3, a tenth of the EU limit.

3.4 Pollution source apportionment

The analysis of PAHs profiles provides a first clue about vehicular traffic as the main source of PAHs

Table II Concentrations of PAHs ($PM_{2.5}$ size fraction), expressed in ng/m^3

	Sampling Number	PHE	PYR	CHR	BAA	BBF	BKF	BAP	BGP
SC1	1	1.0	1.5	2.2	1.11	2.6	0.96	1.79	3.1
	2	1.3	1.4	1.7	0.75	1.82	0.66	1.07	2.0
	6	1.8	1.4	1.9	1.10	1.69	0.65	1.19	1.75
	10	0.58	1.16	2.3	1.04	2.7	0.96	1.62	3.2
	14	0.53	0.95	2.2	1.17	2.6	0.96	2.4	3.2
	15	0.60	1.6	2.8	1.7	3.2	1.13	2.5	3.6
	17	0.59	1.4	2.4	1.16	2.8	0.98	2.1	2.9
	18	0.74	1.00	1.4	0.78	1.97	0.74	1.28	2.2
	22	0.80	1.7	2.7	1.6	2.9	1.00	1.92	3.4
	26	1.1	1.8	2.3	1.3	2.3	0.91	1.79	2.9
	27	1.2	2.4	3.8	1.4	3.9	1.36	2.31	3.6
	30	0.83	0.84	1.0	0.58	0.97	0.37	0.75	1.29
	Mean	0.93	1.4	2.2	1.14	2.5	0.89	1.73	2.7
	Median	0.81	1.4	2.3	1.13	2.6	0.96	1.79	3.0
SC2	31	0.76	0.96	1.7	0.70	1.92	0.68	1.06	2.1
	32	0.93	1.21	1.9	0.88	2.1	0.78	1.33	2.4
	33	1.3	1.12	1.6	0.75	1.81	0.64	1.18	1.87
	34	0.48	0.51	0.78	0.26	0.79	0.29	0.48	1.07
	35	0.30	0.42	0.67	0.26	0.74	0.224	0.34	0.91
	36	0.37	0.40	0.9	0.50	0.88	0.34	0.56	0.99
	37	0.57	0.71	0.69	0.31	0.83	0.27	0.38	0.91
	38	0.40	0.16	0.22	0.021	0.176	0.052	0.087	0.23
	39	0.24	0.13	0.16	0.076	0.146	0.045	<0.005	0.24
	Mean	0.59	0.62	1.0	0.42	1.05	0.37	0.60	1.18
	Median	0.48	0.51	0.78	0.31	0.83	0.29	0.48	0.99
SC3	40	1.9	0.29	0.18	0.76	0.36	0.29	0.251	0.47
	42	1.8	0.51	0.11	0.84	0.26	0.26	0.228	0.147
	44	0.29	0.12	0.10	0.094	0.148	0.06	0.074	0.181
	46	0.125	0.058	0.055	0.043	0.085	0.036	0.038	0.138
	48	0.16	0.049	0.042	0.037	0.065	0.040	0.030	0.086
	50	0.16	0.056	0.038	0.030	0.059	0.021	0.031	0.084
	52	0.19	0.010	0.059	0.049	0.113	0.044	0.049	0.140
	Mean	0.67	0.16	0.084	0.26	0.16	0.107	0.10	0.178
	Median	0.19	0.058	0.06	0.05	0.11	0.044	0.049	0.140

in downtown Bologna. Indeed, hints for PAH apportionment can be derived by comparing ratios of selected pairs of particulate phase PAHs with the same ratios reported in the literature to be characteristic of different sources. In Table III we compare the ratio BAP/BGP (column 1, calculated as geometric means ±SD from the PAH concentration data reported in Table II), with typical ratios found in the literature (Simcik et al., 1999). The resulting value of 0.45 ± 0.25 clearly indicates vehicular traffic as the main source of particulate-bound PAHs at site **S**.

Additional information about on-road mobile sources as the main emission source of air pollutant in downtown Bologna was gathered from an electron microscopy inspection of several $PM_{2.5}$ samples. In particular, a series of grids for trans-

Table III Comparison of geometric means of diagnostic BAP/BGP ratios in $PM_{2.5}$ collected in Bologna (this work), and values reported by Simcik et al. (1999)

$PM_{2.5}$	Vehicles	Gasoline Exhaust	Diesel	Coal	Coke Oven	Oil Burning Power Plant	Petroleum Refineries
0.45 ± 0.25	0.3 – 0.78	0.3 – 0.4	0.46 – 0.81	0.9 – 6.6	5.1	>2	0.65 – 1.7

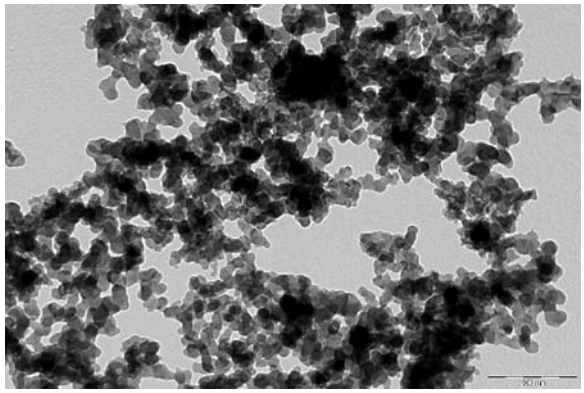

Figure 4 Transmission electron microscopy (TEM) image of a particle collected on a grid placed on the QFF in sampling location S.

mission electron microscopy (TEM) were put onto quartz filters and $PM_{2.5}$ was collected as usual in 10 different sampling days. A careful analysis of the TEM images revealed the almost exclusive presence of nanostructured particles consisting of random combinations of elemental units whose diameters were in the range 20 – 40 nm. A detailed image analysis of more than hundred pictures will be published in due course. A typical particle collected in site S (05/05) is shown in Figure 4, displaying an apparent analogy with the so called 'diesel-exhausts particles' (Park, Cao, Kittelson, & MacMurry, 2003; Park, Kittelson, & MacMurry, 2004).

Diesel-exhaust aerosols consist of chain aggregates of roughly spherical nuclei composed largely of elemental carbon (EC). Diesel-exhausts particles have large surface areas, ranging from 30 to 100 m^2/g, on which a wide range of organic compounds are adsorbed (WHO, 1996). Nearly all diesel-exhaust particles fall within the $PM_{2.5}$ size range, with mass median diameters ranging from 0.05 to 0.3 μm (Godlee, 1993).

Further evidence on the role played by traffic on the air quality of the urban environment of Bologna was gathered from a linear correlation analysis of $PM_{2.5}$ and PAHs concentrations and PM_{10}, criteria pollutant gases (O_3, CO, benzene) and reactive gases (NO_2, SO_2) monitored by the ARPA stations A– C.

The results of the linear correlation analysis (LCA) in the form of correlation coefficients are presented in Table IV.

Besides to the excellent correlations between each pair of higher PAH (CHR, BAA, BBF, BKF, BAP and BGP) with *r* ranging from 0.87 to 0.99, we pointed the attention to the good correlations between $PM_{2.5}$ vs PM_{10} (station A) and between higher PAH on one hand and benzene, CO and ozone on the other. Aware that 52 measurements represent a relatively small dataset, we believe the afore-mentioned correlations confirm that PAH and criteria pollutant gases share a main common emission source.

Table IV Matrix of Pearson correlation coefficients[a]

	$PM_{2.5}$	PHE	PYR	CHR	BAA	BBF	BKF	BAP	BGP	PM_{10} (A)	Benzene (A)	CO (A)	PM_{10} (B)	NO_2 (B)	CO (B)	SO_2 (B)	O_3 (C)
$PM_{2.5}$	1	−0.093	0.39	**0.055**	0.42	**0.58**	**0.57**	**0.52**	**0.60**	**0.85**	**0.63**	**0.50**	**0.65**	0.33	0.34	**0.55**	−0.40
PHE		1	0.33	0.11	0.42	0.09	0.20	0.080	0.055	−0.083	0.00	−0.07	0.12	0.22	0.13	0.03	0.16
PYR			1	**0.94**	**0.88**	**0.92**	**0.92**	**0.87**	**0.90**	**0.50**	**0.55**	**0.68**	**0.58**	**0.55**	**0.83**	**0.79**	**−0.78**
CHR				1	**0.87**	**0.99**	**0.98**	**0.96**	**0.99**	**0.66**	**0.72**	**0.77**	**0.65**	**0.50**	**0.83**	**0.82**	**−0.86**
BAA					1	**0.88**	**0.92**	**0.89**	**0.87**	**0.48**	**0.56**	**0.60**	**0.56**	**0.46**	**0.78**	**0.59**	**−0.57**
BBF						1	**0.99**	**0.97**	**0.99**	**0.68**	**0.72**	**0.76**	**0.62**	**0.43**	**0.79**	**0.78**	**−0.84**
BKF							1	**0.97**	**0.98**	**0.66**	**0.72**	**0.72**	**0.61**	0.41	**0.77**	**0.73**	**−0.79**
BAP								1	**0.97**	**0.63**	**0.74**	**0.74**	**0.57**	0.34	**0.78**	**0.70**	**−0.80**
BGP									1	**0.72**	**0.73**	**0.78**	**0.66**	**0.46**	**0.80**	**0.78**	**−0.85**
PM_{10} (A)										1	**0.71**	**0.62**	**0.84**	0.39	**0.42**	**0.63**	**−0.57**
Benzene (A)											1	**0.58**	**0.52**	0.22	**0.46**	**0.59**	**−0.68**
CO (A)												1	**0.47**	0.42	**0.72**	**0.81**	**−0.75**
PM_{10} (B)													1	**0.71**	**0.59**	**0.67**	**−0.48**
NO_2 (B)														1	**0.72**	**0.66**	−0.32
CO (B)															1	**0.77**	**−0.69**
SO_2 (B)																1	**−0.84**
O_3 (C)																	1

[a] Coefficients in bold refer to $P < 0.05$.

The last correlation analysis joined to the values of the BAP/BGP ratio and to the inspection of the TEM images of the collected particulate matter converge on identifying traffic as the main emission source of $PM_{2.5}$ and PAHs in Bologna.

4 Conclusions

This investigation on $PM_{2.5}$ and PAHs in downtown Bologna reinforces the conclusions of the previous study by WHO (Martuzzi et al., 2002) on air pollution in Bologna and points out the difficulty of complying with the new European air quality guidelines in this area. Indeed, critical concentrations of both $PM_{2.5}$ and PAHs are regularly observed during the winter time; for example, in January 2003 the mean value for $PM_{2.5}$ was 58 $\mu g/m^3$, significantly higher than the annual arithmetic mean of 15 $\mu g/m^3$ established by the US ambient air quality standard (US EPA, 1997), and the mean value for BAP in $PM_{2.5}$ was 1.79 ng/m^3, again higher than 1 ng/m^3, required by the European directive for BAP in PM_{10} (European Union, 2005).

Agreement between $PM_{2.5}$ and PAHs and gaseous pollutants was investigated using LCA. Particulate matter, PAHs and primary gaseous pollutants emitted by engine exhausts (e.g., SO_2, CO and benzene) display significant correlations with each other, indicating the major role of vehicular traffic emissions in determining the air quality of this urban environment, particularly, in acute winter smog episodes. The role of on-road mobile sources was further on confirmed by the analysis of PAHs profiles and by TEM analysis of collected particulate matter.

Pollution abatement strategies in the area of Bologna, have mainly focused, so far, on traffic control actions in the urban area. The ordinance in force in 2003 relative to the odd/even number-plate vehicle circulation on Tuesday, seems to have been uneffective in improving air quality. Nowadays, even though controls on vehicle emissions (use of catalytic converters, 'smog check' maintenance programs with regular vehicle inspections) have become much more strict and new traffic limiting measures (automatic access control gates to the city centre and traffic limited on Thursday to EURO 4 vehicles adopting the Exhaust Gas Recirculation technology) have been established, air quality standards are still hardly met. To comply with pollution control requirements, actions towards other likely sources of air pollution, namely the traffic in the second most congested motorways junction in Northern Italy, the international airport and vehicular traffic related to it, both at 5 km only away from the city centre, are desirable.

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Appendix

$PM_{2.5}$ concentrations in the whole campaign (53 samples), ordered in sub-campaigns SC1, SC2 and SC3.

SC1

Sample Number (T_{Mean}, °C)	Date	Day	$PM_{2.5}$ ($\mu g/m^3$)
1 (1.8)	03/01/08	Wednesday	34 ± 3
2 (1.1)	03/01/09	Thursday	19 ± 2
3 (1.1)	03/01/10	Friday	55 ± 5
4 (0.7)	03/01/11	Saturday	27 ± 2
5 (−0.3)	03/01/12	Sunday	26 ± 1
6 (−0.3)	03/01/13	Monday	30 ± 1
7 (1.2)	03/01/14	Tuesday	59 ± 3
8 (2.9)	03/01/15	Wednesday	85 ± 2
9 (3.8)	03/01/16	Thursday	119 ± 2
10 (4.5)	03/01/17	Friday	138 ± 2
11 (4.5)	03/01/18	Saturday	87 ± 1
12 (4.5)	03/01/19	Sunday	50 ± 2
13 (5.3)	03/01/20	Monday	103 ± 1
14 (5.6)	03/01/21	Tuesday	67 ± 1
15 (6.1)	03/01/22	Wednesday	55 ± 1
16 (5.1)	03/01/23	Thursday	106 ± 3
17 (5.6)	03/01/24	Friday	42 ±1
18 (6.1)	03/01/25	Saturday	31 ± 1
19 (5.9)	03/01/26	Sunday	37 ± 2
20 (6.5)	03/01/27	Monday	32 ± 1
21 (7.3)	03/01/28	Tuesday	81 ± 2
22 (6.2)	03/01/29	Wednesday	44 ± 2
23 (5.0)	03/01/30	Thursday	93 ± 2
24 (3.8)	03/01/31	Friday	67 ± 1
25 (3.7)	03/02/01	Saturday	25 ± 2
26 (3.1)	03/02/02	Sunday	38 ± 2
27 (3.2)	03/02/03	Monday	62 ± 2
28 (2.6)	03/02/04	Tuesday	47 ± 1

Sample Number (T_{Mean}, °C)	Date	Day	$PM_{2.5}$ ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)
SC1				
29 (4.5)	03/02/05	Wednesday	14 ± 2	
30 (6.1)	03/02/06	Thursday	–	
	Mean		58	
	Median		50	
SC2				
31 (5.3)	03/02/10	Monday	46 ± 3	61 ± 6
32 (4.7)	03/02/11	Tuesday	37 ± 2	49 ± 5
33 (4.1)	03/02/12	Wednesday	46 ± 2	43 ± 4
34 (14)	03/03/21	Friday	44 ± 3	46 ± 5
35 (20)	03/03/26	Wednesday	52 ± 3	61 ± 6
36 (6.6)	03/04/03	Friday	9 ± 2	12 ± 1
37 (20)	03/04/14	Monday	41 ± 2	46 ± 5
38 (28)	03/05/05	Monday	12 ± 2	35 ± 3
39 (24)	03/05/15	Thursday	–	16 ± 2
	Mean		36	44
	Median		41	46
SC3				
40 (34)	03/06/13	Friday	29 ± 3	
41 (34)	03/06/14	Saturday	28 ± 3	
42 (32)	03/06/15	Sunday	20 ± 1	
43 (30)	03/06/16	Monday	18 ± 1	
44 (25)	03/06/17	Tuesday	17 ± 2	
45 (28)	03/06/18	Wednesday	32 ± 2	
46 (30)	03/06/19	Thursday	18 ± 3	
47 (32)	03/06/20	Friday	18 ± 3	
48 (31)	03/06/21	Saturday	24 ± 2	
49 (32)	03/06/22	Sunday	20 ± 3	
50 (34)	03/06/23	Monday	17 ± 2	
51 (33)	03/06/24	Tuesday	19 ± 2	
52 (34)	03/06/25	Wednesday	17 ± 2	
53 (29)	03/06/26	Thursday	25 ± 2	
	Mean		22	
	Median		20	

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