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Particulate matter and black smoke concentration levels in central Athens, Greece

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Abstract

This study presents the statistical analysis of PM_{10} and $PM_{2.5}$ concentrations (measured at a central site, in the Athens area), along with black smoke (BS) data, for a 2-year period. The biennial average concentrations of PM_{10} and $PM_{2.5}$ were 75 and 40 $\mu g\ m^{-3}$. The respective average concentration of BS, as estimated by the OECD method, was 108 $\mu g\ m^{-3}$. Severe exceedances of the PM_{10} air quality standards were recorded. The seasonal variation of PM_{10} and BS was less pronounced than the variation of $PM_{2.5}$, which concentration was elevated by 14.2% during the cold period. Concentrations of all three pollutants were significantly lower during weekends; however, $PM_{2.5}$ and BS displayed a more uniform weekly distribution pattern. PM_{10} particles were found to be almost equally comprised by $PM_{2.5}$ and $PM_{10-2.5}$ particles ($PM_{2.5}/PM_{10}$ ratio=0.53 ± 0.09 $\mu g/m^3$). The average PM_{10}/BS value was found lower than unity revealing the inappropriateness of the used reflectance conversion method, for the estimation of mass-equivalent BS concentrations, in the study area, where diesel-powered vehicles mainly control emissions of light-absorbing substances. Important reductions in concentrations were observed during days when drivers of diesel-powered taxies and transportation buses went on strike (reaching 40% for BS). Calm wind conditions were found to have an incremental effect on particle concentrations and were also associated with the appearance of persistent episodic events. Increased PM levels were also observed during southern–southwestern wind flows while significantly lower-than-average concentrations were measured during precipitation events. Separate regression analyses were performed for PM_{10}, $PM_{2.5}$ with BS and NO_x as independent variables, in an attempt to estimate the relative contribution of specific source types (diesel-powered vehicles) to measured particle levels. The contribution of the diesel-exhaust component to PM_{10} mass was estimated at 49.9%, while the corresponding contributions to $PM_{2.5}$ mass concentrations was 53.8%. These results may have important implications with the oncoming decision of national authorities to allow the purchase of diesel-powered private cars to the residents of the Greater Athens Area, which was forbidden up to this day.

Keywords: Black smoke; Particulate matter; Greater Athens Area

1. Introduction

Over the last two decades, a large number of epidemiological studies have been conducted around the world to highlight the health significance of ambient particulate matter (Dockery and Pope, 1994; Boezen et al., 1999; Samet et al., 2000). Considering the detrimental impact of increased particle levels on public health, the European Union has promulgated an air quality standard for PM_{10}. However, uncertainty exists as to the exact physical properties and chemical components responsible for the adverse health effects, with many studies implicating that exposure to fine and ultrafine particles poses the greater risk (Schwartz et al., 1996; Harrison and Yin, 2000). In order to address these issues, the USEPA has set up air quality standards for $PM_{2.5}$ since 1997. On the contrary, the EU was reluctant to establish limit values for $PM_{2.5}$ in the 1st Daughter Directive 1999/30/EC. Instead, there is a sugges-

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tion to the Member States to install and operate measurement stations of $PM_{2.5}$, and report their measurement results annually (EC, 1999). The recent position paper of the expert working group on Particulate Matter of the Clean Air for Europe (CAFE) programme includes the recommendation for replacing PM_{10} with $PM_{2.5}$ as the principle measure. However, there is still not a specific proposal for a $PM_{2.5}$ limit value and, in any case, the provisional attainment date would be after 2010 (CAFE, 2004). Up to this date, Greece as a member state has not done much to contribute to the assessment of the fine particle levels in Europe, with the installation of $PM_{2.5}$ monitoring stations still pending.

In addition, Greece is one of the member states still using black smoke (BS) as a surrogate for PM concentrations and especially for concentrations of fine particles. The black smoke method is based on the conversion of filter reflectance into mass concentration expressed in micrograms of black smoke per squared centimeter of the stained surface area of filters, using a standard calibration curve (OECD, 1964). With particles of elemental carbon and their agglomerations being the principal light absorbing substances in the atmosphere (Hamilton and Mansfield, 1991; Horvath, 1995), it is clear that the conversion method is dependant on the characteristics of the dominant carbon emitting combustion sources. At the time of the development of the black smoke method, the production of soot particles was primarily controlled by coal combustion. During the last decades, the type of used fuels has changed. It has been estimated that up to 90% of elemental carbon emissions, in Western Europe and the USA, are related to diesel exhaust particles (Chow, 1995). This gradual shift in the importance of elemental carbon emission sources has undermined the adequacy of the BS calibration curve to calculate particle mass concentrations. The obvious question that emerges is about the use of BS monitoring nowadays and of the potential use of the BS concentration data accumulated over the years.

Particles of the finer size fractions are mainly associated to combustion processes and soot particles are probably the most characteristic emissions deriving from use of fossil fuels. Given that fact, the measurement of reflectance on filters used for collection of ambient PM comprises an expeditious and economic mode for the investigation of combustion-related particulate matter (Pentinnen et al., 2000). In our case, where a typical traffic-impacted urban location is examined, the major contributor to soot particles are diesel-powered vehicles. As a result, the statistical treatment of PM and BS concentration data could provide a first, rough, estimate on the contribution of diesel-powered vehicles to measured PM levels. This should be useful since the Greek authorities are planning to allow the circulation of private diesel cars in the Greater Athens Area. This shall be a decision of great importance, given the already aggravated air pollution conditions.

Another possibility is the use of PM–BS relationships for retrospective epidemiological studies. Numerous epidemiological studies, carried out mainly in European countries, utilized black smoke concentrations, for many years acknowledging their linkage to specific emission sources, since gravimetric methods used for the determination of particulate mater levels, do not allow a direct insight to the causal processes of the health effects (Clancy et al., 2002). Nonetheless, few published data are available on PM_{10}–$PM_{2.5}$ and BS relationships and assumed PM_{10}/BS, $PM_{2.5}$/BS ratios are often used for comparison needs between different studies referred to the health risk of particles (Dockery and Pope, 1994).

The present work analyses 2-year simultaneous measurements of PM_{10}, $PM_{2.5}$ and BS concentrations in Athens, Greece. The data used comprise the sole and longest parallel time series of PM_{10} and $PM_{2.5}$ concentrations available in the Greater Athens Area. The results can provide an indication about the feasibility of attainment of the 2005 PM_{10} limit value for urban-traffic locations and should comprise important reference material for authorities for $PM_{2.5}$ assessment and monitoring design. The time series of gravimetric PM concentrations along with BS and gaseous pollutants concentrations are statistically examined at different temporal scales in order to identify common emission patterns. Additionally, the impact of meteorology on measured concentrations and the frequency and persistence of PM episodes is assessed. The relationships of PM with BS concentrations are explored and comparison is made with PM/BS ratios reported in previous studies. Finally, a first attempt is made to quantify the contribution of light absorbing particles and their specific sources to the gravimetrically measured particle size fractions, and also to compare the contribution of diesel-powered vehicles versus that of the overall vehicular traffic using specific regression approaches.

2. Study area and methods

PM_{10} and $PM_{2.5}$ sampling was conducted in central Athens, at Aristotelous Str., a busy roadway. Samplers were placed in a station of the National Air Pollution Monitoring Network, located on the first floor balcony of the Ministry of Public Health building. The corner of the building, where the station is sited, faces a three-roadway junction (traffic is controlled by street lights). Both the building where the samplers were installed and the surrounding buildings are multistory constructions (over 20 m of height). The sampling location is characterized by heavy vehicular traffic and frequent congestion of the neighbouring roads, as well as intense commercial and human activity.

Regarding the size and composition of vehicular fleet, it has been documented that the total number of vehicles circulating over the Greater Athens Area exceeds 2 million (including 180,000 LDV, 50,000 HDV, 7000 buses and 20,000 taxies) and is rising at a rate of 7% per year. The vast majority of HDV and taxies as well as a large proportion of

LDV is diesel-powered. It also has to be noted that the average yearly mileage covered by taxies is estimated at approximately 10 times the respective average mileage of a private car (data and information were made available from published reports of the Greek Ministry of Environment).

The height of the sampler inlets was 6.7 m above ground and the distance from the street was less than 5 m. Twenty-four-hour particle samples (midnight to midnight) were collected daily during the period of June 1, 1999 through May 31, 2001. PM_{10} and $PM_{2.5}$ filter samples were collected simultaneously using two low-volume reference-equivalent samplers (US EPA-approved Partisol Model 2000, Rupprecht and Patashnick). The sampling flow rate was the same for both samplers—16.7 l min^{-1} and particles were collected on 47 mm Pallflex TX40 filters (Teflon-coated glass fiber filters). Particle concentrations were determined gravimetrically using an electronic microbalance (Mettler Toledo AT201), with 0.01-mg resolution. Both blank and field filter samples were conditioned at constant temperature (22 ± 3 °C) and relative humidity (40 ± 5%), for at least 24 h prior to weighting, before and after sampling. The precision of the measurements was determined with parallel sampling and was found equal to 2.5%. The limit of detection (LOD) was estimated at three times the standard deviation of field blank filters collected (Burton et al., 1996) and was found 5.4 μg m^{-3} for PM_{10} and 6.3 μg m^{-3} for $PM_{2.5}$.

Black smoke concentrations were measured by the Ministry of Environment, using the method of the Organization for Economic Cooperation and Development (OECD, 1964). Particles were collected using a Filtromat black smoke sampler (Environnement SA), on Whatman 1 paper filters. Reflectance of filters was measured using a smoke stain reflectometer (EEL 043 DM, Diffusion Systems), calibrated with white and gray tiles. The reflectance (%) of exposed filters (R) was converted in μg cm^{-2} of filter surface (S), according to the formula (Christolis et al., 1992):

$$S = 602.40365 - 21.894125R + 0.32603453R^2 - 2.3214402 \times 10^{-3}R^3 + 6.4810413 \times 10^{-6}R^4$$

The BS concentration (μg m^{-3}) was subsequently calculated taking into account the sampled air volume.

Data for other gaseous pollutants, wind speed, wind direction, temperature and relative humidity monitored at the same location, were provided by the National Air Pollution Monitoring Network. Concentrations of CO, nitrogen oxides and SO_2 were determined using NDIR, chemiluminescence and fluorescence techniques, respectively. Data for precipitation and solar radiation were measured at a meteorological station (2 km to the north of the sampling site) in the premises of the National Technical University of Athens.

PM_{10} and $PM_{2.5}$ concentrations were found to be log-normally distributed; therefore, hypothesis testing was conducted using t-tests and ANOVA procedures on log-transformed PM_{10} and $PM_{2.5}$ values. In contrast, BS concentrations displayed asymmetric distribution, deviating from normality, and therefore non-parametric tests were used for the statistical analysis (Mann–Whitney and median tests for two samples, Kruskal–Wallis H-tests for multiple samples). The statistical software package SPSS 11.0 for Windows was used for the statistical calculations.

3. Results and discussion

3.1. Concentration levels

A first remark emerging from the summary statistics presented in Table 1 is the high levels of measured PM_{10} and $PM_{2.5}$ average and maximum concentrations. Specifically, PM_{10} average concentration for the 2-year period exceeds the air quality standard promulgated by the EU Directive (40 μg m^{-3}, to be met by January 2005). A slight inter-annual decrease of PM_{10} levels is noted; for the first year, the mean concentration is 75.5 μg m^{-3}, which declined to 74.5 μg m^{-3} for the second year. The difference is not statistically significant (t-test, p=0.20), while the decrement of 1.0 μg m^{-3} is even lower than the annual decrease of the tolerance limit value (1.6 μg m^{-3}), as proposed by the EU air quality standard. The daily PM_{10} standard, to be achieved by January 2005, is 50 μg m^{-3} not to be exceeded over 35 days/year (9.6%). The percentage of the days with PM_{10} concentrations higher than the 24-h limit value declined from 87% on the first year to 74% on the second. The results for PM_{10} concentrations are similar with those reported in previous research studies conducted at the present site (Chaloulakou et al., 2003a,b; Grivas et al., 2004).

Given the fact that the European Union has not promulgated an air quality standard for $PM_{2.5}$, an evaluation of the measured fine particle levels could be attempted in comparison with the USEPA standards. The average $PM_{2.5}$ concentration for the 2-year period is 39.7 μg m^{-3}, a value considerably higher than the USEPA annual standard of 15 μg m^{-3} (one should note though that the standard presumes more than one monitoring stations over an urban area). The working group on Particulate Matter from the CAFE programme on its recent position paper makes a clear suggestion that, if an average limit value for $PM_{2.5}$ was to be adopted, it should not exceed 20 μg/m^3. It is evident that, for this traffic-oriented site, compliance with such a limit value would be difficult, in present terms.

The average biennial $PM_{2.5}$ concentration is comparable in magnitude to that reported in an earlier short-term study (35.6 μg m^{-3}), conducted during 96–98, including sporadic measurements in Athens (Gotschi et al., 2002). The 2-year average of the 98th percentile of daily $PM_{2.5}$ concentrations was calculated at 88 μg m^{-3}, exceeding the USEPA limit value of 65 μg m^{-3} (which however, refers to 3-year monitoring periods).

Table 1
Descriptive statistics of daily average PM_{10}, $PM_{2.5}$ and BS concentrations for the 2-year period

	PM_{10}	$PM_{2.5}$	$PM_{10-2.5}$	BS
Mean	75 (76–74)	40 (40–39)	36 (35–36)	108 (95–123)
S.D.	31 (28–34)	18 (17–20)	17 (14–20)	59 (46–69)
Minimum	25 (25–26)	8.0 (13–8.0)	8.0 (8.0–10)	11 (11–11)
25th percentile	52 (56–48)	26 (27–24)	24 (25–23)	60 (57–60)
Median	68 (69–66)	36 (37–34)	32 (33–31)	103 (93–119)
75th percentile	92 (91–92)	49 (49–48)	43 (42–43)	150 (130–180)
Maximum	208 (184–208)	135 (124–135)	123 (102–123)	329 (225–329)

Separate values for each year of measurements listed in parentheses. All values expressed in $\mu g\ m^{-3}$.

The high levels of PM and BS concentrations measured are partly attributed to the character of the sampling site, which is a roadside site, in a heavily trafficked location. Although the observed concentration levels are not characteristic of the general population exposure in Athens, they provide an indication of the magnitude of the particle atmospheric pollution problem in the area.

3.2. Temporal variation

The 2-year study period was divided in cold and warm periods, ranging between October 16 and April 15, and between April 16 and October 15, respectively. This was made in an effort to examine the seasonal variation of pollutants and the seasonal importance of specific particle sources. The definition of warm and cold periods was done with respect to regional meteorological considerations (Argyriou et al., 2004). As a consequence, the "cold period" also covers the largest part of the time period when the space-heating appliances of buildings are operating. It appears from the results presented in Table 2 that mean PM_{10}, $PM_{2.5}$ and BS concentrations are higher during the cold period. The difference, expressed as a percentage, is 7.2% for PM_{10}, 14.6% for $PM_{2.5}$ and 4.5% for BS. The seasonal differences were found significant for $PM_{2.5}$ (t-test, $p<0.01$) and non-significant for PM_{10} (t-test, $p=0.14$) and BS concentrations (Mann–Whitney U-test, sig.=0.74). The existence of additional emission sources contributes to the higher particle concentrations observed during the cold period. The levels of $PM_{2.5}$ are directly influenced by emissions derived over the winter months from domestic heating, which also explains the elevation of PM_{10} levels. The cold-start of engines is an additional parameter contributing to the increment of particle concentrations, during the cold period. In addition during the summer months, prevailing winds, which are due to thermal circulations, are stronger and the mixing height is deeper, aiding the slight attenuation of observed pollutant levels, during the warm period (Kassomenos et al., 1995). The insignificant seasonal variation of BS concentrations could support the initial hypothesis that the use of diesel for heating purposes (coal or wood is rarely used in central areas of Athens) does not reflect much on light-absorbing particles (at least for the present site) and diesel exhaust particles (DEP) emissions should be considered as the major BS source.

To further assess the importance of DEP as a source of particulate matter, the BS and PM levels during the absence of taxies and public transportation buses were examined. During the study period 21 days for which the taxi driver or public bus driver unions have gone on full daily strikes were recorded. The average concentrations of PM_{10}, $PM_{2.5}$ and BS for these days were 66.7, 34.5 and 63.8 $\mu g\ m^{-3}$, respectively. Reductions in comparison to the values of Table 1 are apparent (12.1% for PM_{10}, 13.1 for $PM_{2.5}$ and 40.9% for BS) and statistically significant (Mann–Whitney U-test: sig.<0.01 for BS; t-test: $p<0.05$ for PM_{10}, $PM_{2.5}$). Each event was isolated and the measured concentration was compared to the concentrations 3 days before and 3 days after the event. Days for which special meteorological conditions (stagnation of air masses, extreme temperatures, extreme rainfall) were observed were excluded. The average of differences in strike–nonstrike days was as high as 48% for BS concentrations. This is a rather high percentage taking in mind the remaining diesel-powered HDV and LDV in circulation.

Table 2
Seasonal variation of PM_{10}, $PM_{2.5}$ and BS concentrations ($\mu g\ m^{-3}$)

	Cold period[a]				Warm period[b]			
	PM_{10}	$PM_{2.5}$	$PM_{10-2.5}$	BS	PM_{10}	$PM_{2.5}$	$PM_{10-2.5}$	BS
Mean	77	42	35	111	72	37	35	106
S.D.	34	21	20	61	27	14	15	56
Minimum	25	13	8.0	11	26	8.0	12	11
Median	67	36	31	103	68	36	33	98
Maximum	208	135	112	266	186	91	123	329

[a] Cold period: October 16th–April 15th.

[b] Warm period: April 16th–October 15th.

Weekday average concentrations were found to be significantly higher than the corresponding values for weekends, as it can be seen in Table 3. This is reasonable since traffic- and other human-related particle generating activities are reduced during Saturdays and to a greater extent during Sundays. When tested by one-way ANOVA and Tukey HSD procedures, concentrations of PM_{10} vary significantly by day of week and are discerned in two homogenous subgroups (weekdays and weekends). In the case of $PM_{2.5}$, uniformity is observed for concentrations from Monday to Saturday, with only concentrations on Sunday being significantly lower. Bearing in mind that particles of the fine fraction have longer residence times in the atmosphere and are more resistant to removal, due to physical processes (Raes et al., 2000), this fact is not unexpected. The day-to-day variation of BS concentrations was found statistically insignificant by the non-parametric Kruskal–Wallis *H*-test. A possible explanation for this is that the main source controlling black smoke levels is the emission of diesel exhaust particles, which is associated with public transportation vehicles and taxies and thus is characterized by a more stable temporal pattern, on a weekly scale.

3.3. Concentration ratios of PM_{10}, $PM_{2.5}$ and BS

The median values of the daily average $PM_{2.5}/PM_{10}$, PM_{10}/BS and $PM_{2.5}$/BS ratios are displayed in Table 4. Fine particles have a marginally higher contribution to PM_{10} mass concentrations, in comparison to coarse particles. This contribution is more intense during the cold period of the year, while in the warm period the participation of fine and coarse fraction is similar. Higher $PM_{10}/PM_{2.5}$ ratios are generally reported in studies carried out in countries of Northern and Western Europe (Van Dingenen et al., 2004). PM_{10} concentrations measured in Southern Europe urban areas are frequently characterized by higher coarse particle abundances (Manoli et al., 2002; Querol et al., 2004). This fact might suggest the increased importance of crustal materials and soil resuspension, as factors influencing particulate levels at areas of temperate or dry climatic conditions.

While PM_{10}/BS median values up to 3.67 have been reported in Central and West European areas (Hoek et al., 1997a), in the present study, the median PM_{10}/BS value is lower than unity, a fact suggesting the significant contribution of diesel-powered vehicles to elemental carbon (EC) emissions and consequently to calculated BS concentrations (Janssen et al., 1997). A PM_{10}/BS median value lower than unity (0.88) has also been reported by Hoek et al. (1997a), for an urban location in Athens, for the winter of 1993/1994. Kassomenos et al. (1999) also report a PM_{10}/BS ratio of 0.83 for central Athens. PM_{10}/BS ratios below one are frequently reported for traffic impacted locations (Keary et al., 1998; Ruellan and Cachier, 2001).

Table 3
Weekly variation of average PM and BS concentrations (μg m^{-3})

	PM_{10}	$PM_{2.5}$	BS
Weekday	78	41	111
Weekend	67	36	100
Saturday	71	37	108
Sunday	62	34	92

Table 4
Arithmetic mean values of daily PM_{10}/BS and $PM_{2.5}$/BS concentration ratios (median values in parentheses)

	Full period	Cold period	Warm period
$PM_{2.5}/PM_{10}$	0.53 (0.53)	0.56 (0.54)	0.51 (0.51)
PM_{10}/BS	0.89 (0.74)	0.93 (0.74)	0.85 (0.70)
$PM_{2.5}$/BS	0.46 (0.39)	0.51 (0.41)	0.41 (0.37)

Taking into account that the 50% cut-off diameter of the BS sampler is below 5 μm (Hoek et al., 1997b) and the major fraction of elemental carbon particles is expected to be present in the fine particle fraction, a PM_{10}/BS ratio greater than unity should be expected. However, the unsuitability of the old BS curve in the modern environment has been indicated by various studies examining the relationships between PM_{10} and BS. Aerosols derived from vehicles and especially diesel exhaust particles, which nowadays largely control elemental carbon emissions, have different light absorbing properties than particles from coal combustion. The mass absorption coefficient of elemental carbon depends on the size of particles. It has been reported that the ratio of the mass absorption coefficient between particles with a diameter of 0.2 μm and particles with a diameter of 1 μm has a value higher than 5 (Horvath, 1996). Diesel particles originating from fresh exhaust emissions near roads are expected to be present mainly in the submicron range, thus having relatively high mass absorption coefficients. Diesel particles have a darkness index of 3, in relation to coal combustion particles (Turnbull and Harrison, 2000). In our study, which involves a roadside sampling location in the Greater Athens Area, it is expected that the OECD method will overestimate BS concentrations. Recent studies use an absorption coefficient-derived from reflectance measurements using a simpler formula (ISO 9835)—as a more appropriate proxy for elemental carbon (Roorda-Knape et al., 1998; Hoek et al., 2002).

3.4. Correlations within the pollutant dataset

Pearson correlation coefficients for pair-wise comparison between PM_{10}, $PM_{2.5}$, $PM_{10-2.5}$ and BS are displayed in Table 5. Correlations between PM_{10} and $PM_{2.5}$ as well as between PM_{10} and $PM_{10-2.5}$ are very high throughout the sampling period. Strong correlations were found between particle concentrations and BS for the study periods (in the range of 0.65–0.68), which indicate important parts of PM_{10} and $PM_{2.5}$ having the same sources as black smoke. Keary et al. (1998) report a correlation coefficient of 0.69 between PM_{10} and BS for an urban site adjacent to a major road in Dublin. The estimated value of the Spearman correlation

Table 5
Pearson correlation coefficients between PM_{10}, $PM_{2.5}$ daily average concentrations and BS daily average concentrations. All correlations significant at the 0.01 level

		PM_{10}	$PM_{2.5}$	BS	CO	NO	NO_2	SO_2	WS
PM_{10}	Full period		0.89	0.66	0.72	0.70	0.60	0.40	−0.61
	Cold period		0.91	0.67	0.80	0.73	0.59	0.43	−0.58
	Warm period		0.86	0.65	0.71	0.70	0.66	0.36	−0.62
$PM_{2.5}$	Full period	0.89		0.67	0.76	0.74	0.58	0.47	−0.65
	Cold period	0.91		0.68	0.83	0.76	0.58	0.50	−0.59
	Warm period	0.86		0.66	0.75	0.69	0.67	0.43	−0.68
BS	Full period	0.66	0.67		0.65	0.67	0.56	0.44	−0.56
	Cold period	0.67	0.68		0.60	0.70	0.49	0.45	−0.52
	Warm period	0.65	0.66		0.68	0.63	0.62	0.43	−0.56

coefficient between PM_{10} and BS (0.67) during the cold period is lower than the one reported by Hoek et al. (1997a), for the urban location in Athens (0.89). However, the highly uneven number of measurements in the two cases (since the previous study covers only 2 months) as well as the different sampling equipment used do not permit a direct comparison. The differences in correlations between the cold (heating) period and the warm period are very subtle. This provides another indication that the common sources that explain the strong statistical relationship between PM and BS should be sought to emissions of DEP rather than the use of oil for heating appliances.

The impact of traffic-related emissions, on particulate matter concentrations, is outlined by the strong correlation coefficients between PM_{10}, $PM_{2.5}$, BS and primary gaseous pollutants (Table 5). The correlation involving CO with BS was lower than those with PM_{10} and $PM_{2.5}$, reasonably enough since diesel-powered vehicles comprise a negligible CO source in comparison to gasoline vehicles. Associations of PM and BS with SO_2 concentrations were comparable as expressed by the correlation coefficient for the whole sampling period. However, when examined by period of the year, they display a dissimilar character. While correlations of PM_{10} and $PM_{2.5}$ with SO_2 are significantly higher during the cold period, the correlation coefficient between BS and SO_2 is similar in both cold and warm periods (0.45 and 0.43, respectively). Given the major role that domestic heating plays as a SO_2 emission source (Monn et al., 1995), the insignificant difference observed supports the assumption already made regarding the less important contribution of domestic heating as a BS source.

3.5. Effects of meteorology on observed concentration levels

Significant negative correlations were obtained between concentrations of PM_{10}, $PM_{2.5}$ and BS, and daily average wind speed values (Table 5). The prevalence of stagnant or weak flow regimes favors the suspension and accumulation of particles produced locally, resulting at the elevation of PM levels. Average concentrations during days of calm wind conditions (wind speed below 1 m/s) were 170, 68 and 232 $\mu g\ m^{-3}$ for PM_{10}, $PM_{2.5}$ and BS, respectively. PM and BS concentrations of such magnitude most often appear during prolonged episodic events characterized by stagnant wind conditions (Chaloulakou et al., 2003b; Grivas et al., 2004). The multi-day character of particulate matter episodes on the atmosphere is partially reflected in the autocorrelation functions displayed in Fig. 1. Correlation with the previous day concentrations are over 0.5 for all three pollutants, while the autocorrelation coefficient is also statistically significant for the 2-day lag. The preponderance of low-wind conditions is closely related to the occurrence of multi-day PM episodes. The 86% of the days when the daily average wind velocity remained under 2 m/s, PM_{10} concentrations exceeded 100 $\mu g\ m^{-3}$ and the 72% of these high concentration events were part of multi-day episodes. The respective percentages for $PM_{2.5}$ concentrations over 50 $\mu g\ m^{-3}$ were 86% and 80%.

The influence of the wind direction is shown in Fig. 2. It can be seen that higher concentrations are observed during winds of the S–SW sectors. It has been documented that the appearance of weak southern atmospheric flow inhibits the dispersion of particulate matter and consequently lags their removal, while the appearance of stronger southern–south-

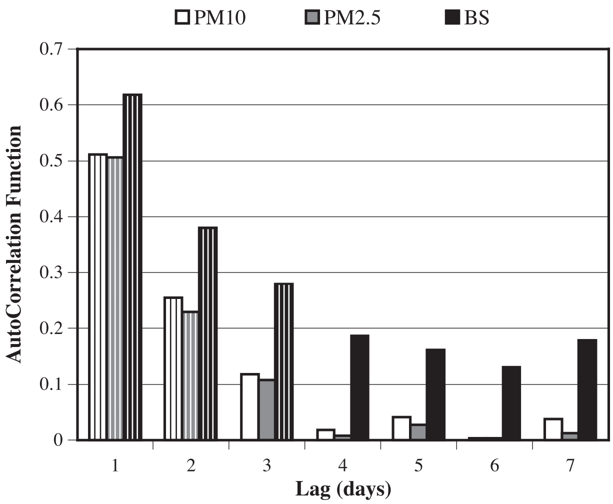

Fig. 1. Plots of the autocorrelation functions for PM_{10}, $PM_{2.5}$ and BS daily average concentrations. Striped columns denote statistically significant autocorrelations.

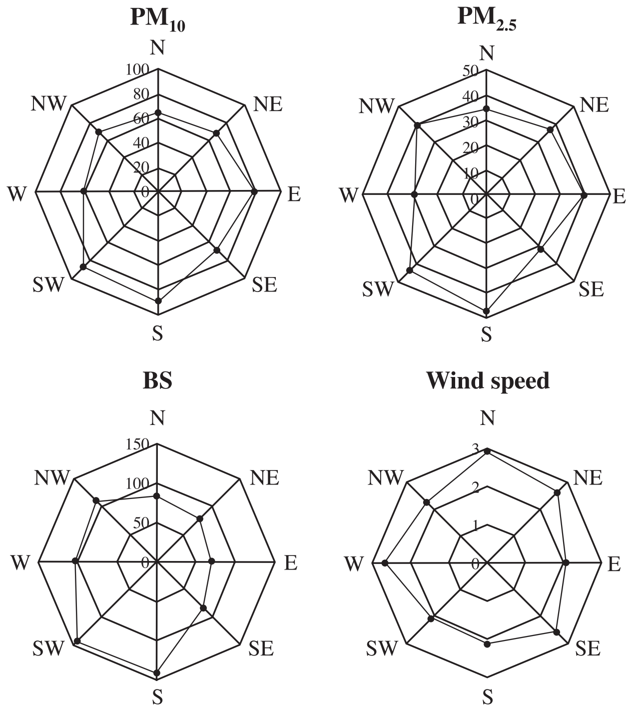

Fig. 2. Daily average PM_{10}, $PM_{2.5}$ and BS concentrations (μg m^{-3}) and wind velocity (m s^{-1}) during prevailing wind directions.

western flows is responsible for the transport of particles originating from the industrial zones of Piraeus and Elaionas or from the sea (Chaloulakou et al., 2000). In addition, winds of the southern sector often favor the appearance of inversions, because of the transfer of warm air masses from the southern part of the Mediterranean (Kassomenos et al., 1995).

Regarding associations with temperature, significant correlations were not found. However, it should be mentioned that the correlation coefficient between BS concentrations and daily average temperature (as well as with the daily minimum temperature) had a positive value (0.33 and 0.30) for the cold period. Research studies frequently report negative correlation between BS concentrations and minimum temperature values during the cold months of the years and attribute this fact to the excessive use of domestic heating during low temperature events (Branis and Domasova, 2003). In the present case, a completely different association is observed providing a further indication that central heating is not an important factor in the determination of BS levels. Associations with solar radiation and relative humidity were very loose and will not be further discussed.

The impact of precipitation on particulate matter and BS was also examined and the difference of average concentrations between dry and rainy days (which had a frequency of 24%) was found significant for PM_{10}, $PM_{2.5}$ and BS at the 0.01 level and at the 0.05 level for $PM_{10-2.5}$. Concentrations were lower during rainy days for PM_{10}, $PM_{2.5}$, $PM_{10-2.5}$ and BS by 17.7%, 20.3%, 13.9% and 17.9%, respectively. The daily average amount of rainfall (mm) was categorized at three ranges (0–3, 3–10 and >10 mm) and the variation of concentrations was examined with ANOVA and Tukey post-hoc tests. The variation was not found significant with the exception of $PM_{10-2.5}$ concentrations, which are significantly lower ($p<0.05$) during heavy rainfall events. This is due to the increased wash out of large particles from the atmosphere (Chate et al., 2003) and also by the increase of moisture of the surfaces, which hinders the resuspension processes.

3.6. Assessment of vehicular contribution to PM concentrations

Regression analysis using BS as an independent variable has been implemented in many studies for the assessment of the contribution of diesel combustion sources and DEP mobile sources to PM concentrations (Clarke et al., 1996; Stedman, 1998; Turnbull and Harrison, 2000). It has been mentioned already in several occasions that the influence of central heating on BS concentrations should be considered not significant for the present site, in comparison to the contribution of diesel vehicles. This is also verified by earlier emission inventories, which estimate the relative contribution of diesel-powered vehicles and domestic heating on BS emissions, to be approximately 4:1 for central locations within the Greater Athens Area, while the contribution of gasoline vehicles to overall BS emissions is estimated at only 6% (Scheff and Valiozis, 1990; Economopoulos, 1997). On this basis, it is assumed that the regression analysis of PM concentrations with BS can provide a crude estimate of the component of PM_{10} and $PM_{2.5}$ derived from diesel vehicles.

PM_{10} and $PM_{2.5}$ concentrations were regressed at first with BS concentrations for the warm period when central heating is not an active particle source. The ordinary least squares equations are displayed in Table 6a. The contribution of diesel vehicles to PM_{10} and $PM_{2.5}$ was calculated at 47.2% and 48.2%, respectively (taking into account the difference of the mean PM values and the intercepts). The analysis is repeated for the entire sampling period. The calculated contributions are slightly higher (49.9% for PM_{10} and 53.8% for $PM_{2.5}$), while standard error overlap also exists. In both cases, the calculated correlation coefficients were between 0.65 and 0.67. Various studies report correlation coefficients between PM and BS, being in a range between

Table 6a
Intercepts, slopes and correlation coefficients (*r*) of ordinary least-square equations of particle concentrations (μg m^{-3}) vs. black smoke concentrations (μg m^{-3})

		Intercept (μg m^{-3})	Slope	*r*
Full period	PM_{10} vs. BS	37.10 (2.01)	0.35 (0.02)	0.66
	$PM_{2.5}$ vs. BS	18.62 (1.12)	0.19 (0.01)	0.67
Warm period	PM_{10} vs. BS	37.89 (1.55)	0.31 (0.01)	0.65
	$PM_{2.5}$ vs. BS	18.21 (1.31)	0.18 (0.01)	0.66

Table 6b
Intercepts, slopes and correlation coefficients (r) of ordinary least-square equations of particle concentrations ($\mu g\ m^{-3}$) vs. NO_x concentrations ($\mu g\ m^{-3}$)

		Intercept ($\mu g\ m^{-3}$)	Slope	r
Full period	PM_{10} vs. NO_x	25.35 (2.02)	0.45 (0.02)	0.74
	$PM_{2.5}$ vs. NO_x	9.73 (1.17)	0.27 (0.01)	0.75

0.58 and 0.86, depending on the sampling site characteristics and the length of the examined time series (Keary et al., 1998; Ruellan and Cachier, 2001; Branis and Domasova, 2003).

Contributions to PM_{10} mass seem disproportional as compared the ones for fine particles, at first sight, since the overwhelming majority of elemental carbon particles are categorized in the fine fraction. However, it should be considered that the circulation of diesel-powered vehicles also affects coarse particle concentrations. This can be done by the soil resuspension caused by vehicle movement and the thermal turbulence related to vehicle exhausts (Ruellan and Cachier, 2001). It has also been suggested that a significant proportion of coarse elemental carbon at roadside monitoring sites is derived by tire wear (Ulrich and Israel, 1992).

Regression analysis between particulate matter and NO_x concentrations has also been used for the quantitative estimation of vehicular traffic's contribution to particle concentrations (Harrison et al., 1997; Fuller et al., 2002; Harrison et al., 2003; Grivas et al., 2004). The results are presented in Table 6b. The overall traffic-related component comprises 65.9% of the PM_{10} and 75.5% of the $PM_{2.5}$ mass average. The calculated contribution to PM_{10} is comparable to the one derived from the chemical mass balance source apportionment of PM_{10} at traffic-impacted locations in the city of Thessaloniki, northern Greece (63–65%, Samara et al., 2003). The development of the separate regression models for the estimation of source contributions was attempted for comparative reasons and was conducted in an empirical manner. However, the estimated contributions indicate that diesel-powered vehicles strongly influence the observed levels of both PM_{10} and $PM_{2.5}$ particles, in a typical central traffic-oriented sampling location.

4. Conclusions

The results of the first biennial PM_{10}, $PM_{2.5}$ parallel measurement campaign, conducted in Athens, reveal the intensity of the particle-related atmospheric pollution problem, especially highlighted at a central monitoring site. The observed level of exceedances of the PM_{10} limit values indicates that unless robust abatement measures are implemented, attainment with the EU standard will be difficult to be achieved on January 2005. Levels of $PM_{2.5}$ are also a cause of concern and since this particle fraction is linked with adverse health effects the systematic monitoring of fine particle concentrations by national authorities should commence without any further delay. The average ratios between PM and BS concentrations were found below unity, being comparable to relevant ratios reported previously for central Athens and urban locations of the same type in Europe.

The examination of the relationships between PM concentrations and concentrations of gaseous pollutants reveals the importance of fuel combustion processes and especially of vehicular sources to particle emissions. Calm wind conditions were found to have an incremental effect on particle concentrations and were also associated with the appearance of persistent episodic events. Increased PM levels were also observed during southern–southwestern wind flows while significantly lower- than-average concentrations levels were measured during precipitation events.

Black smoke was used, as an adequate proxy for elemental carbon concentrations, (in the absence of data available through chemical analysis) giving useful information for particulate matter specific source types. A large contribution of diesel vehicles to ambient levels of PM was estimated through regression analysis, and it was also confirmed by the significant reduction of PM and BS concentrations during days when drivers of diesel-powered taxies and transportation buses went on strike.

The important contribution of emission from diesel vehicles to PM_{10} and even more $PM_{2.5}$ concentrations should be regarded with respect to the planned opening of the diesel-car market for the population residing in the Greater Athens Area. The large difference between the prices of diesel and gasoline might be a decisive factor for the appearance of a burst of new diesel-powered private cars. Although new-technology diesel vehicles are expected to have reduced particle emissions, it is necessary that stringent measures for the control of emissions and maintenance of the diesel-vehicle fleet be undertaken, in order to safeguard air quality regarding particulate matter, in Athens for the years to come.

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