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Influence of traffic on the PM_{10} and $PM_{2.5}$ urban aerosol fractions in Madrid (Spain)

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Abstract

A preliminary assessment carried out in Madrid demonstrates the difficulty of compliance with the new European PM_{10} tolerances. Daily and annual limiting values would be exceeded at almost all the network stations under the terms of the directive's second stage. An experimental study, based on the chemical characterisation of the PM_{10} and $PM_{2.5}$ fractions sampled at a representative urban site, provides the major mass contents of these two fractions. These are mainly related to two different particle sources: combustion processes including traffic emissions and mineral-origin particles. Nonmineral carbon is the major component of particulate matter in this region, mostly in the $PM_{2.5}$ fraction, increasing its contribution in wintertime. The second largest component identified in the PM_{10} mass, is associated with crustal origin particles and is more relevant in summer, whereas the second largest contributor to $PM_{2.5}$ is secondary particles.

In general, PM_{10} and $PM_{2.5}$ concentrations show good agreement with traffic-related pollutants, such as nitrogen oxides and CO, being time-correlated in winter pollution episodes. PM_1 and $PM_{2.5}$ have been simultaneous and continuously measured indicating road transport as the main source of these finer fractions. Mineral contribution has been mainly identified in the coarser particles associated with dust resuspension and some long-range transport events of Saharan dust, although they are also present in the finer $PM_{2.5}$ fraction.

Keywords: Urban aerosols; Particle composition; PM_{10}; $PM_{2.5}$; PM_1; Road transport; Particle monitoring; Madrid; Urban pollution

1. Introduction

As a result of the recently approved European directive on air quality (99/30/CE), new limiting values for several atmospheric pollutants must be met by 2005 and 2010. Particulate matter with aerodynamic diameter < 10 μm (PM_{10}) will be henceforth the parameter used for measuring and controlling atmospheric pollution by airborne particles. In addition, although the reference method for $PM_{2.5}$ (aerodynamic diameter < 2.5 μm) is not yet established and consequently no limiting values have been approved for this fraction, its measurement is at present required in the European Union at representative sites. These sites should coincide, wherever possible, with the PM_{10} sampling points.

The Spanish regulations in force up to 2002, applied to total suspended particles (TSP), which

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resulted in extremely high limits when compared to annual and daily limiting values established by the Directive for PM_{10}, which are to be achieved in the first instance by 2005, and even higher than the more stringent requirements of the second stage in 2010.

In a preliminary assessment, based on 1995–1998 PM_{10} data, the Madrid urban network satisfactorily fulfilled the Spanish regulations at that time, but the situation with respect to the new Directive appeared to be rather critical (Artíñano et al., 2001). Regarding the annual average, 20% of the stations would have exceeded the limit established for the first phase (40 $\mu g\ m^{-3}$), and 80% of the network stations would have been above the upper limit (20 $\mu g\ m^{-3}$) envisaged for the second phase. The situation was even worst in terms of the daily tolerance (50 $\mu g\ m^{-3}$), and 80% of stations would have exceeded the limit for a number of days beyond that allowed by either stage of the directive (35 and 7 days, respectively).

In conclusion, this survey pointed out that severe control measures should be taken to diminish atmospheric particle levels in the urban area. But the emission of atmospheric particles, as recent European reports on air quality reveal (APEG, 1999), seems to be a general problem that not only affects Madrid's citizens, but almost 80% of the European population, who will be exposed to exceedances of the PM_{10} standards (EEA, 2000) in the near future.

Road transport is known to be one of the main sources of urban pollution, although other sources also linked to combustion processes, such as domestic-residential and institutional heating, also contribute to significant pollutant emissions in urban areas. Road transport in the Madrid region is roughly responsible for 80% of CO and NO_x and more than 50% of nonmethane hydrocarbon (NMHC) emissions (MIMAM, 1996).

The car fleet in Madrid came to 2.5 million vehicles in 2000, of which more than 80% were passenger cars. The number of vehicles circulating through the capital's streets and main motorways of the metropolitan area every working day has been estimated to be 1.8×10^6 units. Of these, 83% have petrol engines, whereas the remaining 17% use diesel as fuel (Palacios, 2001). Unlike other European countries, diesel may be used for both private and public transport.

The most recent European and national atmospheric emission figures make great efforts to introduce TSP, PM_{10}, $PM_{2.5}$, or even $PM_{0.1}$ emissions in terms of mass. Although thorough studies and reviews deal with secondary and natural sources (QUARG, 1996; APEG, 1999), most of them only consider primary sources or anthropogenic particles (Berdowski et al., 1996). This is due to the uncertainties and difficulties still associated with emission factors for some source categories, particularly road transport, which cannot be scaled up or are country-specific. Some of the latest and more extensive applied methodologies used to estimate road transport emissions (Ntziachristos and Samaras, 2000) in Europe only consider primary emission of total atmospheric particles, which are commonly assumed to be PM_{10}. As experimental emission figures obtained for diesel powered vehicles are roughly one order of magnitude higher than those for petrol engine vehicles (Berdowski et al., 1996), most figures only consider PM_{10} emissions from diesel engines. This implies neglecting the contribution of the remaining cars, which can significantly contribute to the levels of particles, especially if secondary particles are to be considered. Primary particle emissions from road transport resulting from tyre and brake wear and dust resuspension are often neglected. Emissions are lower when compared to direct vehicle exhausts, but their sum can give rise to an underestimation of PM_{10} emissions from road transport in the current figures. $PM_{2.5}$ emission figures are less frequent and subject to even larger uncertainty.

The absence of reliable and suitable emission figures from road transport in many countries, and other uncertainties associated with road traffic, makes particulate matter an important issue, and this is a matter of concern to air quality managers in most cities of the world. Recent European Community policies, such as unleaded petrol consumption or the use of more efficient vehicles, have been aimed at decreasing emissions due to road transport. However, the continuously increasing number of vehicles, perhaps due to the centralisation of big cities and new social patterns and habits, obscures the efficiency of these technical measures.

This work analyses the average PM_{10} values and seasonal evolution of the Madrid air quality network during the past few years. It summarises the results of the chemical composition of the PM_{10} and $PM_{2.5}$ fractions sampled during an experimental study conducted at a representative traffic-influenced urban site. The main components of these fractions differed and

evolved in different ways, allowing an investigation of the contribution of five main particle sources at the site. Traffic influence on atmospheric particulate matter is relevant but mineral contribution should also be taken into account. The $PM_{2.5}/PM_{10}$ and $PM_1/PM_{2.5}$ ratios are analysed in terms of traffic and the influence of other natural particle sources.

2. Methodology

2.1. The Madrid air quality network

The air quality network of this city consists of 25 stations covering all of the municipal districts and specific areas of main interest. They are all urban and traffic-oriented stations, except for one that is located on the outskirts of the city in a large park. This site is in an open place with no traffic thoroughfares in the vicinity. Thus, from this point of view, it can be considered to be an urban background station, Casa de Campo, #24 (Fig. 1). The other monitoring stations are placed at major junctions, squares, or main roads in the city; the distance to the kerb not being greater than 15 m in all cases.

The height of the inlet (≈ 3 m) is within the range established by the 99/30/EC directive guidelines for microscale location of sampling sites; nevertheless, the measurement could be affected by local aerodynamic and recirculation effects resulting from reduced dispersive and airflow conditions at some measurement sites.

Location criteria for all these stations have been based on human health protection and spatial coverage objectives in order to get air quality information on the whole city and provide it to the population. This study is based on CO, NO_x (NO and NO_2), and PM_{10} data provided by the network stations in the period 1996–2000. These have been obtained by using automated standard reference methods, with

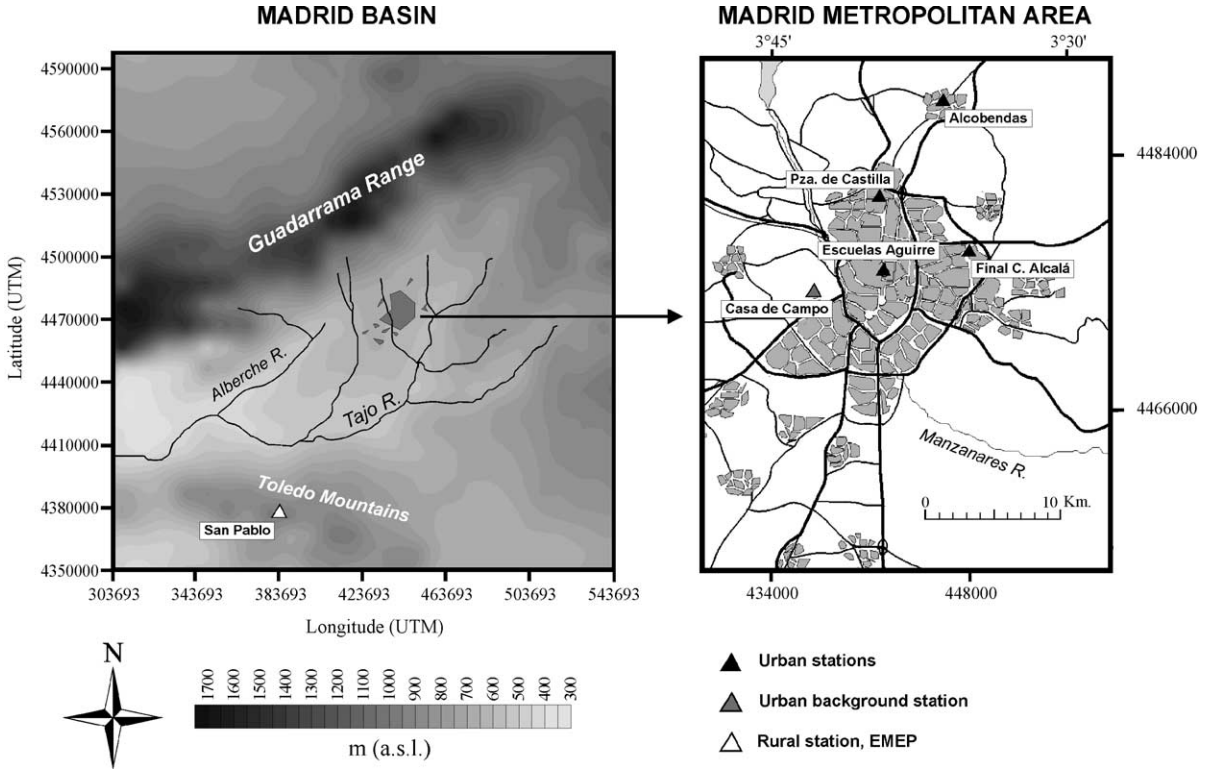

Fig. 1. Two-dimensional topography and location of the Madrid basin. The shaded area delimits the metropolitan area, represented with the main roads on the right. The locations of the monitoring stations referred in the text are depicted.

the exception of the PM_{10} measurement. This parameter has been obtained using TEOM™ (oscillating microbalance) monitors. Thus, a possible underestimation of PM_{10} mass concentration, due to sample heating, with respect to the gravimetric reference method should be taken into account (Allen et al., 1997; Salter and Parsons, 1999). In the absence of consistent experimental data on this subject, no correction factor has been applied to this network PM_{10} data.

Additionally, data from a rural background station (San Pablo) from the EMEP network, located 100 km to the Southwest of Madrid, was used for this study (Fig. 1). This station was included as being representative of the rural nonanthropogenic-influenced levels of particulate matter and as an indicator of long-range transport events of dust on a regional or larger scale. TSP was measured at this station on a daily basis using the reference gravimetric method.

2.2. TSP, PM_{10}, and $PM_{2.5}$ sampling

An experimental study was conducted from July 1999 to May 2000 to characterise the chemical composition of the urban aerosol of these two size fractions. TSP was sampled only for mass concentration determination by gravimetry. Three high-volume samplers (flow rate 30 m^3 h^{-1}, DIGITEL DH-80 PM_{10} and $PM_{2.5}$ cutoff inlets) were installed next to one of the network stations, Escuelas Aguirre (Fig. 1). TSP and PM_{10} were sampled twice per week and $PM_{2.5}$ once a week, on working days. Quartz fibre filters, previously conditioned, were utilised for sampling and subsequently chemically analysed to determine the main components as well as trace elements. Sampling and analytical procedures can be found elsewhere (Querol et al., 2001a,b), and consequently will not be described in detail.

The sampling site was selected at the urban centre on a street junction that experiences heavy traffic influence during the week, pollution levels decreasing at the weekends. No industrial emissions affect this site or the Madrid region in general, as there are no heavy industry or power generation plants in this area. Thus, road transport and heating facilities are the main sources of atmospheric pollution. Domestic coal and oil burning and natural gas combustion, as well as electricity, are the main energy sources in the area.

2.3. PM_{10}, $PM_{2.5}$, and PM_1 continuous measurements

Continuous measurements of PM_{10}, $PM_{2.5}$, and PM_1 were obtained during 2001, using a GRIMM 1107 laser spectrometer. This device performs particulate measurement by 90° laser light scattering. The air sample passes through a flat laser beam, produced by a laser diode, and through an analyser for size classification. The counts for each size are converted to mass by an established equation, providing values averaged every hour. The measurement period covered was from February to December 2001. An urban park located in Alcobendas (Fig. 1), a smaller town 13 Km away from Madrid, was selected as a measurement site. This is an urban background site, although it can be influenced in specific circumstances by emissions from radial motorways and the urban plume of Madrid. At this site, there is an air quality monitoring station belonging to the regional network, which provided additional continuous pollutant measurements.

3. Results and discussion

3.1. PM_{10} annual mean levels and seasonal evolution

As has been previously mentioned, most automatic monitoring stations in the Madrid network are traffic influenced due to the proximity of traffic thoroughfares. NO_2 concentrations can be considered to be an indicator of traffic emissions. Fig. 2 shows mean annual NO_2 and PM_{10} concentrations for all of the stations during 1999–2000. In terms of nitrogen dioxide, all of the stations, including the urban background station in the Casa de Campo that has the lowest value, were above 40 μg m^{-3}. This is the same as the annual limit established by the 99/30/CE directive for PM_{10}, although a limit of 20 μg $m^{-3}PM_{10}$ is envisaged in the second stage for this pollutant. With respect to PM_{10}, most of the stations are in between the limits of the two phases, six of them exceeding both. These stations also exhibit high NO_2 values, although there is not a straightforward relationship between mean annual PM_{10} and NO_2concentrations. When compared with concentrations recorded in other European cities, PM_{10} levels in the Madrid network are higher in general than those from

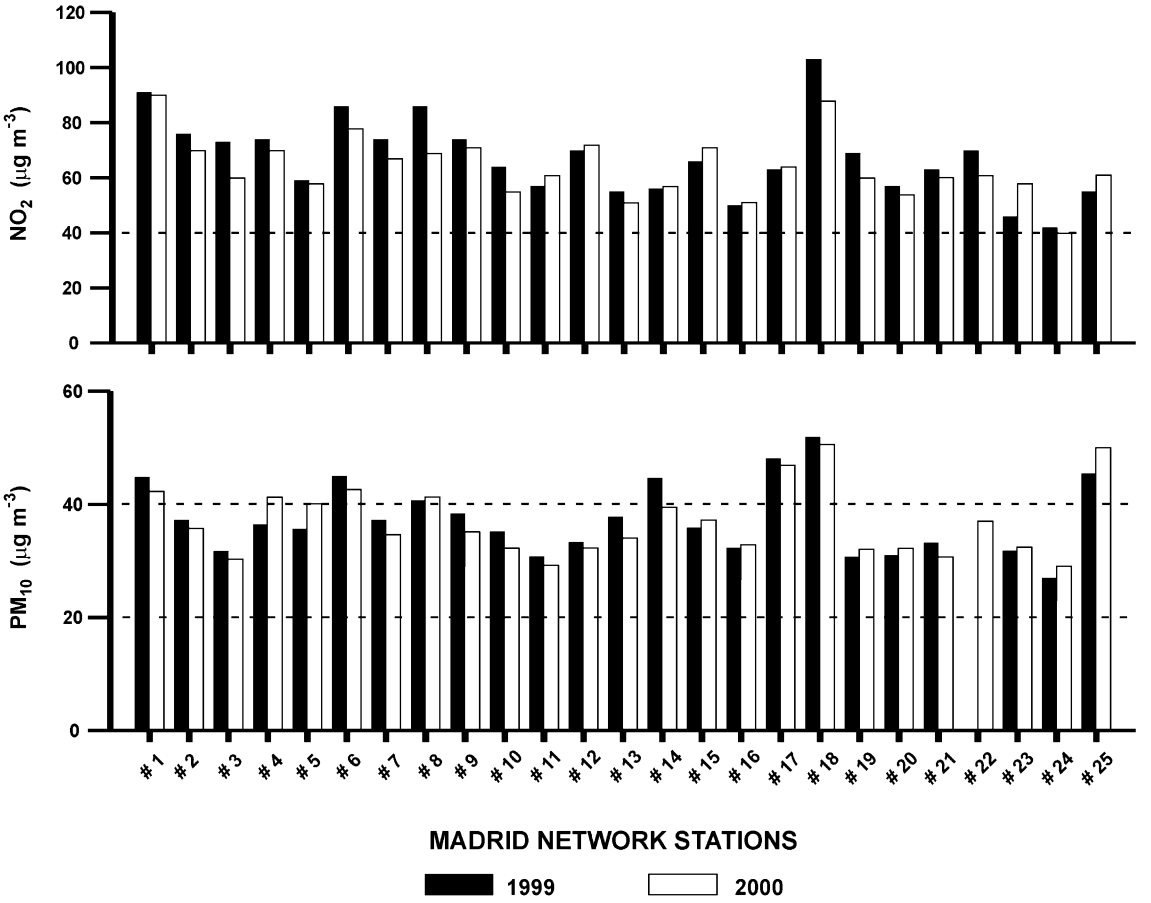

Fig. 2. Madrid air quality monitoring stations NO_2 and PM_{10} annual means, (1999–2000 term). The dotted lines indicate the annual limiting value of 40 μg m^{-3} for NO_2 (top), and the two annual limiting values for PM_{10} (40 μg m^{-3} first stage and 20 μg m^{-3} second stage, bottom), established by the new EU-Directive.

Switzerland (Monn et al., 1995) or UK (APEG, 1999), lower than those from Central and Eastern Europe cities (Houthuijs et al., 2001), and similar to those from other urban (Artíñano et al., 2001) and industrial (Querol et al., 2001b, 2004) areas in Spain.

PM_{10} and nitrogen oxides display quite different seasonal patterns. Fig. 3 shows monthly mean concentrations over 5 years at three stations with a different degree of traffic influence: Pza. de Castilla (station #15) is representative of a heavy traffic area; Final C. Alcalá (station #23) has a medium traffic density; and Casa de Campo (#24) is the urban background station (Fig. 1). NO_x mean levels vary from one to the other according to the degree of traffic influence; nevertheless, in all of them, there is a drop in the NO_x concentration in spring–summer. This is due to the photochemically active nature of this pollutant, which is affected by temperature and radiation indices whose high values in these months trigger the chemical reaction cycle in which ozone and other precursors (i.e., volatile organic compounds) are involved. NO_x maxima are usually recorded in the November–February months. On the other hand, PM_{10} concentrations are not so different between the stations (20% PM_{10} variation from station #15 to #24, as compared to a 70% of variation in NO_x). Maxima may be evenly distributed throughout the year, although they are more frequent in February, March, and the summer months, depending upon the year. The absolute minimum has always been regis-

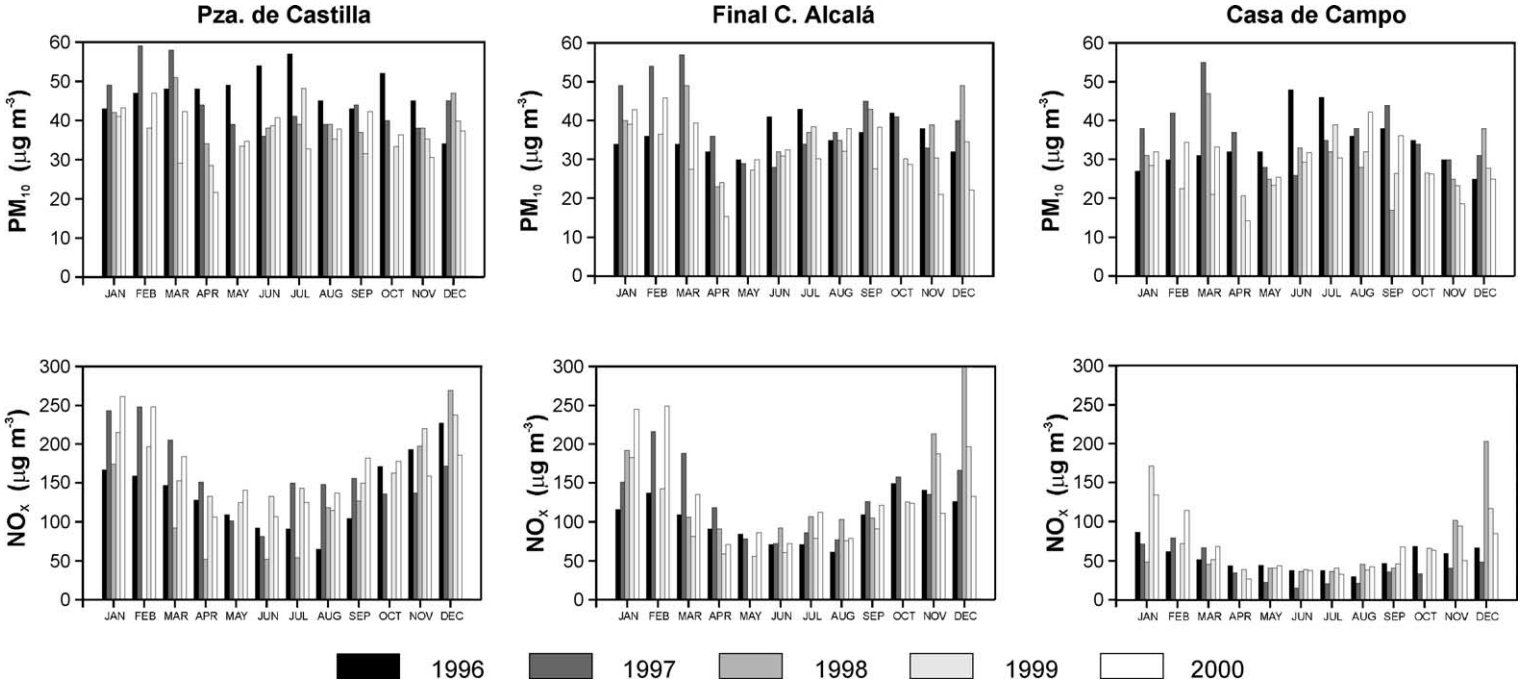

Fig. 3. Monthly averages of PM_{10} and NO_x at three selected stations for the 1996–2000 period. Pza. de Castilla, (urban station influenced by heavy traffic), Final C. Alcalá (urban station in a medium traffic density area) and Casa de Campo (urban background station).

tered in April, clearly attributable to meteorological factors. For the 5-year period considered, this month has experienced the highest annual precipitation rates, which has apparently affected PM_{10} more than the NO_x concentrations.

Comparing the mean annual PM_{10} evolution, different features can be observed depending on the local characteristics of each station. Fig. 4 represents the monthly averages (1996–2000 average) at the same three urban stations as in Fig. 3 and at the rural EMEP station. The heavy-traffic station registers the highest levels during the whole year, with similar values in the winter and summer months. In this season, a slight decrease in August indicates the holiday season. The April minimum, previously mentioned, may also be noted. At stations less influenced by traffic, such as Final C. Alcalá, the April decrease is more pronounced. There, the PM_{10} concentrations are very similar to those of the background station, Casa de Campo, during spring and summer, although they differ in autumn/winter. This urban background station experiences the highest values in March and the summer months, coinciding with the behaviour of the San Pablo rural station. Maximum levels are also recorded in summer at this location, with TSP concentrations very similar to those recorded at the background and light traffic urban sites. This fact suggests that a dust-laden air mass is similarly affecting the urban area and the regional air shed at this time of year. The March increase, simultaneously recorded at the two background stations (urban and rural), also points to an additional external contribution of particulate matter in these months. Geographical features have been found to play a key role in this type of contribution. Dust resuspension and transport processes are favoured by strong ground heating and thermal convection that, among other factors, such as aridity and low rainfall rates, are common in the centre of the Iberian Peninsula in late spring and summer (Font, 1983). Long-range transport events of Saharan dust from North Africa are also frequent throughout these months (Querol et al., 1998; Rodríguez et al., 2001, 2002), although they can also take place in other seasons. Linked to specific synoptic scale conditions, regularly occurring in July, August and also in March Saharan dust outbreaks can affect particulate levels over a large part of the Iberian Peninsula, often reaching the Madrid area (Artíñano et al., 2001). This phenomenon must be considered and characterised in order to quantify its natural contribution to PM_{10} levels in urban areas. To do this, there is an ongoing large national project whose preliminary results can be found in Querol et al. (2004). Chemical characterisation and continuous sampling of different grain sizes are being used for this purpose.

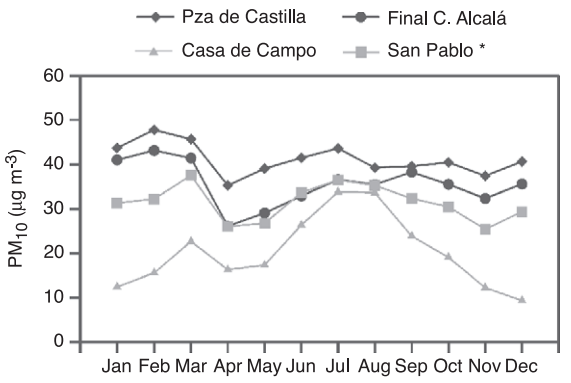

Fig. 4. Monthly averages for the 1996–2000 period at Pza. de Castilla, Final C. Alcalá, Casa de Campo and San Pablo stations. San Pablo is a rural background EMEP station, located 100 Km away from Madrid, free of any anthropogenic emission or influence. * Particle concentrations at this station are referred as total suspended particles (TSP).

3.2. Chemical composition of PM_{10} and $PM_{2.5}$ fractions

PM_{10} and $PM_{2.5}$ chemical characterisation is a powerful tool to support atmospheric particle source apportionment studies. Emission figures usually require chemical profiles of sources that are often neither available nor can be extrapolated from one place to another as there are large variations between similar source categories. Even within the same geographical area, local features can be rather different, affecting physicochemical properties of particulate matter in different ways. In this experimental study, the mean annual PM_{10} value obtained (69 daily samples) was 47 µg m^{-3}, slightly higher than that obtained at the monitoring station for the same period (42.3 µg m^{-3}). This difference may be due to the known underestimation of the continuous method when compared to the gravimetric standard method, and the fact that no sampling was performed at

weekends. The mean $PM_{2.5}$ fraction concentration (38 samples) was 34 μg m^{-3}, with no reference value from the network station, as it did not measure this parameter at the time. The mean PM_{10}/TSP ratio in this period was 0.54. The $PM_{2.5}/PM_{10}$ ratio ranged from 0.46 to 1.00, having a mean value of 0.72. The sum of the particle mass obtained by chemical analyses accounted on average for 85% of the total mass found by gravimetry. Thus, most of the particulate mass composition was characterised.

To perform a source contribution study, the different compounds and elements analysed were grouped into the following well-known main sources (Chow et al., 1996; Harrison et al., 1997a,b; Querol et al., 2001a,b): nonmineral carbon, secondary (nitrates, sulphates, and ammonia), heavy metals (Pb, Zn, Cu, Cr, Ni, V, Mn), crustal or mineral origin compounds (CO_3^2, SiO_2, Al_2O_3, Ca, K, Fe, Mg, Ti, P, Ba, Sr), and marine (Cl^-, Na, and SO_4^{2-} marine). The major component of the PM_{10} and $PM_{2.5}$fractions was nonmineral carbon, generated by combustion processes, which accounted for 39% and 53% of the bulk mass concentration, respectively (Fig. 5). Crustal-origin components were found mostly in the PM_{10} fraction (38%) and in a lesser proportion in the finer fraction (20%). Secondary compounds contributed to 20% and 24% of the particle mass in both fractions, whereas heavy metals and the marine aerosol were only present in minor quantities. The most abundant heavy metal present in both fractions was Pb ranging from 44 to 388 ng m^{-3} in PM_{10}, and 40 to 330 in $PM_{2.5}$, below the limit established by the 99/30/CE Directive (500 ng m^{-3}). The mean values were 118 and 99 ng m^{-3}, respectively.

This average source contribution varied throughout the year, significantly in certain cases. Fig. 6 illustrates the evolution of two main contents, crustal and nonmineral carbon in the PM_{10} and $PM_{2.5}$ fractions during the sampling period. In summer, the crustal origin components account for a high proportion of the PM_{10} mass; in contrast, the main

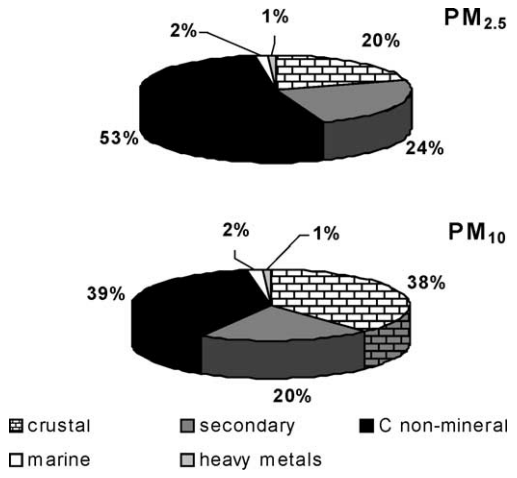

Fig. 5. Mean source contribution analysis for the PM_{10} and $PM_{2.5}$ samples obtained at Escuelas Aguirre site from June 1999 to June 2000.

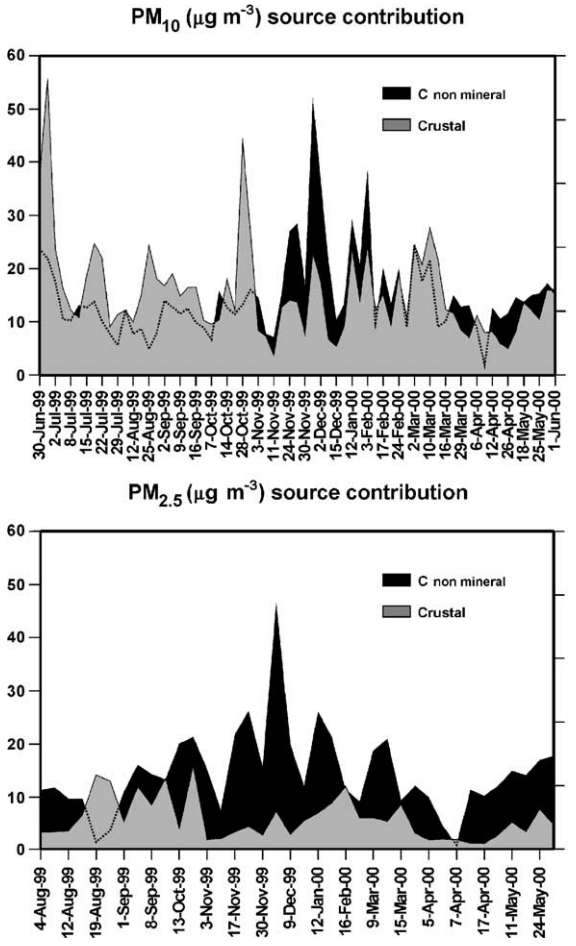

Fig. 6. Time series of the PM_{10} and $PM_{2.5}$ crustal and nonmineral carbon source contribution analysis at Escuelas Aguirre from June 1999 to June 2000.

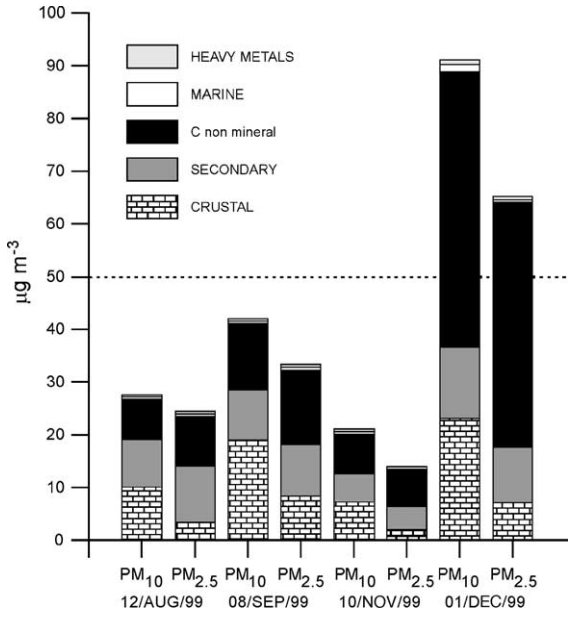

Fig. 7. Source contribution of PM_{10} and $PM_{2.5}$ selected samples on specific days in summer and winter.

contributor in winter is nonmineral carbon. Nevertheless, during the period of study, specific episodes involving high proportions of crustal origin components have been detected throughout the year that have been mostly associated with Saharan dust outbreaks (Rodríguez et al., 2001; Querol et al., 2004). The nonmineral carbon content experiences a marked increase in winter in both fractions but is particularly significant in the $PM_{2.5}$, where it can increase values to as high as those obtained for PM_{10}. Fig. 7 shows the chemical composition of PM_{10} and $PM_{2.5}$ samples on specific days in summer and winter. A low-traffic day in summer was selected in August, a typical vacation month in Madrid, with minor activity as confirmed by the lowest values of mean CO and NO_x concentrations recorded during the sampling period included in Table 1. As can be seen in this Table, in September, the traffic density was once again reestablished. Two days with minimal (November 10) and high traffic (December 1) were selected from the winter period. The relative contribution of the crustal compounds is higher in the PM_{10} fraction on summer days. Nonmineral carbon and secondary particles are the main components of the finer fraction $PM_{2.5}$, although there are no great variations in the secondary contribution throughout the year. Perhaps the most noticeable contribution is due to the increase in nonmineral carbon during specific episodic events, such as the one that took place at the beginning of December 1999. Daily PM_{10} and $PM_{2.5}$ concentrations exceeded the 50 $\mu g\ m^{-3}$ limit of the EU-Directive. The $PM_{2.5}/PM_{10}$ ratio was 0.75. Although crustal compounds also increased during the episode in both fractions, indicating an influence of traffic on the local resuspension processes, the most significant contribution was due to nonmineral carbon, whose concentration reached 52.27 and 46.25 $\mu g\ m^{-3}$ in the PM_{10} and the $PM_{2.5}$ fractions, respectively, whereas the secondary fraction did not exceed the concentrations of the summer months. It seems that the main components affected by traffic density are therefore the nonmineral carbon and crustal species affecting both particle sizes.

Fig. 8 shows the evolution of traffic-related pollutants during the above episode at the experimental site (Escuelas Aguirre) and at the urban background station, Casa de Campo. A high-pressure system

Table 1
Total Suspended Particles (TSP), PM_{10}, $PM_{2.5}$, CO and NO_x daily air concentrations on specific days in summer and winter at the Escuelas Aguirre urban traffic station in Madrid

Sampling dates		Summer						Winter					
		12/AUG/99			08/SEP/99			10/NOV/99			01/DEC/99		
		TSP	PM_{10}	$PM_{2.5}$	TSP	PM_{10}	$PM_{2.5}$	TSP	PM_{10}	$PM_{2.5}$	TSP	PM_{10}	$PM_{2.5}$
PM	$\mu g\ m^{-3}$	63	31	28	97	41	31	55	34	25	175	107	81
CO	$mg\ m^{-3}$	0.52			1.65			1.07			4.62		
NO_x	$\mu g\ m^{-3}$	91.9			255.7			146.1			620.7		

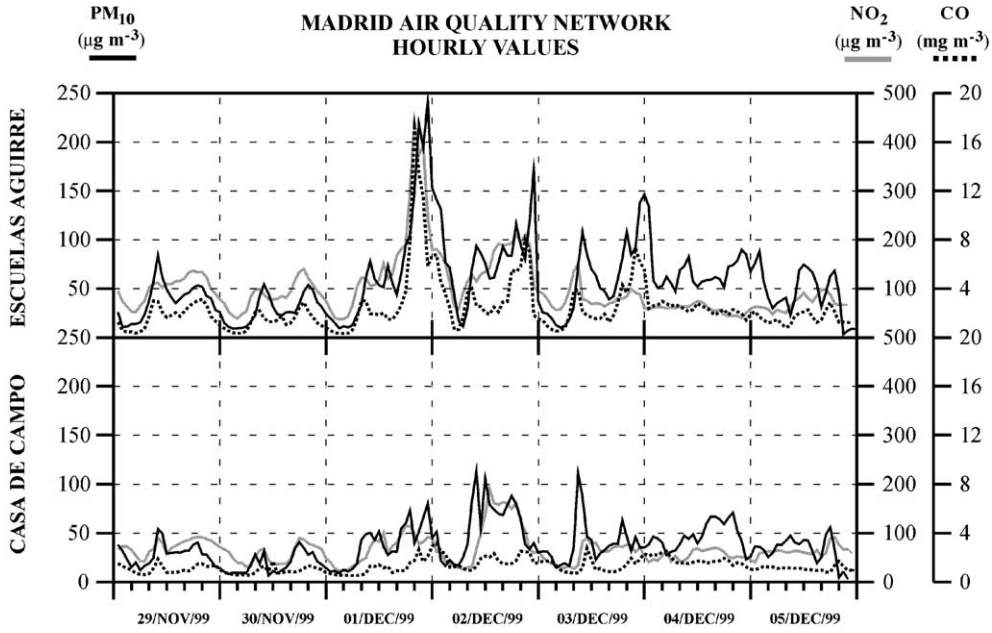

Fig. 8. Hourly values of PM_{10}, NO_2 and CO recorded at Escuelas Aguirre (top) and the urban background station of Casa de Campo (bottom) during a pollution episode that occurred on December 1999 in Madrid.

remained over the Madrid air shed in the first week of December giving rise to a high degree of atmospheric stability and poor airflow conditions. This is a typical autumn/winter episode, which frequently occurs in the Madrid air basin (Artíñano et al., 1994; Pujadas et al., 2000). During these days, air concentration levels of NO, NO_2, and CO were high, reaching hourly values of up to 1300 μg NO_x m^{-3} and 13 mg CO m^{-3} on December 1–2. Atmospheric concentrations of all pollutants also increased in the Casa de Campo. Although the most affected were PM_{10} and NO_x, CO values rose slightly as well. On 29th and 30th of November, these three pollutants followed the daily cycle associated with traffic flow, having clear maxima during the morning and afternoon rush hours. On December 1, NO_x and PM_{10} concentrations increased during the day, reaching the daily maxima at midnight. Next day, the NO_x and PM_{10} levels remained rather high, whereas over the following days, a declining trend, slower in the PM_{10} case, indicated the end of the episode, with two days of very low traffic emissions coinciding with three nonworking days in Madrid (December 4–6). Although traffic emissions were much lower during these days, atmospheric PM_{10} concentrations still remained at high levels (>50 μg m^{-3}) for two more days.

3.3. PM_{10}, $PM_{2.5}$, and PM_1 time series analysis

Road transport affects both PM_{10} and $PM_{2.5}$ concentrations; although traffic emissions seem to mostly concentrate on the finer fraction. In NO- and NO_2-enriched air masses, for example during winter pollution episodes, this fraction of particle concentrations can exceeded the EU-directive limit. Fig. 9 depicts the time series (1-h resolution) of the two particle sizes and nitrogen oxides (NO and NO_2) at a regional urban background site (Alcobendas) near Madrid (Fig. 1) in December 2000. During this month, several pollution episodes took place in the metropolitan area, and air concentrations experienced severe increases for all pollutants at all the stations. PM_{10} and $PM_{2.5}$ recorded similar values at this site, being very closely correlated to the evolution of nitrogen oxides. NO concentrations were really high during the whole month, corresponding to recent emissions that had not yet reacted because of the low photochemical activity at this time of the year. The highest annual levels of PM_{10}, $PM_{2.5}$, and

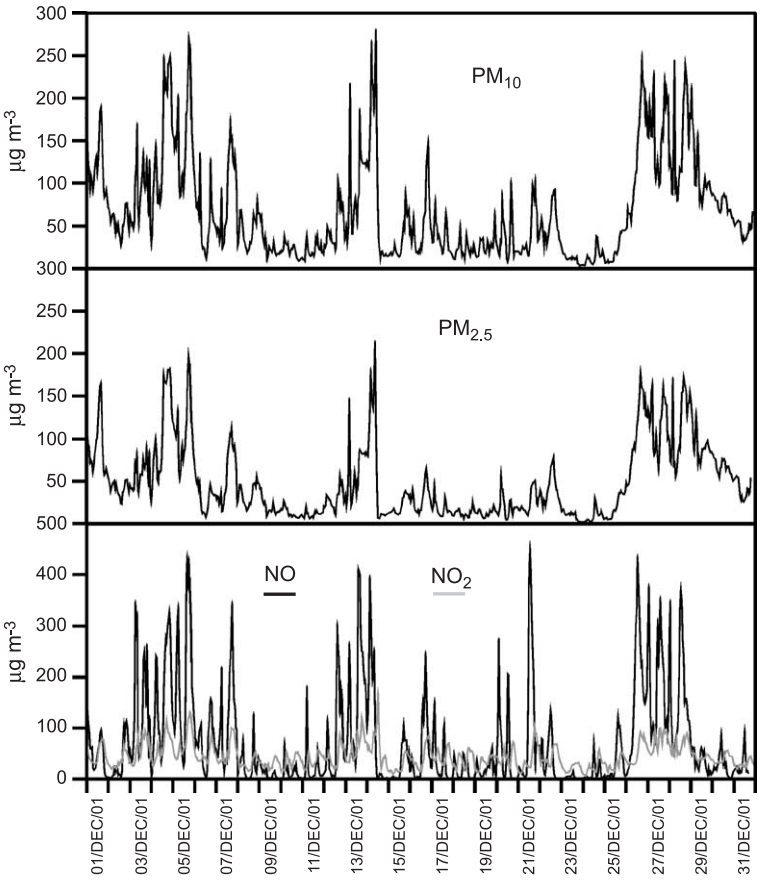

Fig. 9. Hourly values of PM_{10}, $PM_{2.5}$, NO and NO_2 recorded at Alcobendas site during December 2001.

PM_1(not shown in the figure) particles were recorded during this month, the contribution of these two finest fractions to PM_{10}being around 80–90%. In this case, as an urban background station with no direct influence from local traffic, the coarse fraction seemed to not be affected by local traffic resuspension processes. Annual averages, maxima and minima for the whole year at this site, are shown in Table 2. The $PM_{2.5}/PM_{10}$ and $PM_1/PM_{2.5}$ ratios are also included. Fig. 10 shows the annual evolution of these two parameters. The $PM_{2.5}/PM_{10}$ ratio exhibits a clear seasonal behaviour. Maxima were recorded in autumn/winter, whereas in spring and mainly in the summer months, this ratio falls to around 0.40. This seems to be predominantly due to the nature of the particulate matter, which has a larger crustal/mineral content in summer mainly allocated to the PM_{10} fraction, whereas the larger relative contribution in winter of nonmineral carbon is mainly allocated to the finer fraction. This is in agreement with Harrison et al. (1997b), although a larger winter/summer variation has been observed at this site. On the other hand, the PM_1 content in the $PM_{2.5}$ size remains around 80% throughout the whole year, pointing to the importance of the

Table 2
Mean annual values, daily maximum and minimum of PM_{10}, $PM_{2.5}$, PM_1, and $PM_{2.5}/PM_{10}$, $PM_1/PM_{2.5}$ ratios recorded at Alcobendas (Madrid) during the year 2001

	Min.	Mean	Max.
PM_{10} (µg m^{-3})	3	33	180
$PM_{2.5}$ (µg m^{-3})	2	21	156
PM_1 (µg m^{-3})	1	18	143
$PM_{2.5}/PM_{10}$ (%)	21	62	99
$PM_1/PM_{2.5}$ (%)	51	80	96

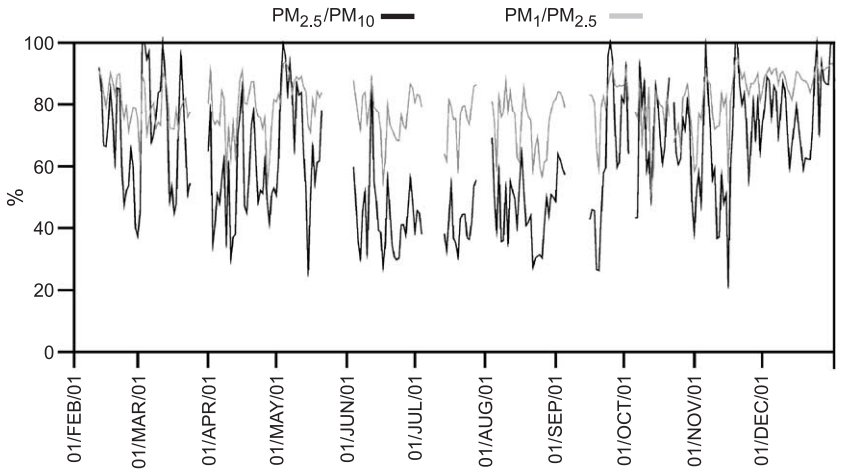

Fig. 10. $PM_{2.5}$/ PM_{10} and $PM_1/PM_{2.5}$ daily ratios computed at Alcobendas from February to December 2001.

contribution of these fine particles to the urban aerosol, considering their high capacity for penetration into the respiratory system and corresponding health effects.

4. Conclusions

Analysis of the Madrid monitoring network data recorded in the period 1999–2000 revealed that PM_{10} and NO_2 environmental air concentration levels exceeded the annual limits established by the 99/30/CE European Directive. The annual limit of nitrogen dioxide has been exceeded at all of the network stations, highlighting the influence of traffic emissions on the urban stations. NO_2 and PM_{10} exhibit a different seasonal behaviour, associated in the former with its photochemical nature, having the lowest concentrations in spring and summer. PM_{10} maxima are recorded either in summer or winter and are associated with different atmospheric processes and sources.

The chemical characterisation of around 85% of the PM_{10} and $PM_{2.5}$ bulk masses at an urban traffic-influenced site concludes that nonmineral carbon is the major component of these two particle fractions, accounting for 39% and 53% of the total mass, respectively, increasing in winter. Crustal contribution is mostly found in the PM_{10} size (38%), increasing in the spring/summer months. Secondary particles contributed to 20% and 24% of the total PM_{10} and $PM_{2.5}$ mass analysed. No seasonal variation was observed in this component.

The $PM_{2.5}$/ PM_{10} ratio experiences a marked decrease in summer at an urban background site, mainly due to the major crustal particles content mostly affecting the coarser fraction. In winter, and especially during pollution events, the $PM_{2.5}$/ PM_{10} ratio experiences a marked increase. PM_1 and $PM_{2.5}$ mass fractions may contribute to >90% of the total PM_{10} mass in these cases. Roughly 80% of the $PM_{2.5}$ fraction is composed of PM_1 particles. The short-term (1 h) evolution of these finer fractions is closely linked to traffic emissions, showing a good correlation with nitrogen oxides.

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