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Spatial and temporal variations in PM10 and PM2.5 across Madrid metropolitan area in 1999-2008

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Abstract

This paper presents a summary of the results obtained from the particulate matter (PM) data collected over the 1999-2008 period from representative sites of the Madrid air basin (an urban traffic site, an urban background site and a rural site) which is located in the centre of Spain. A number of PM10 and PM2.5 filters were obtained with high volume samplers and cut-off inlets and chemically analyzed. Pollutants recorded in this area at the Air Quality monitoring stations were also analyzed. The influence of the atmospheric transport scenarios on the levels of PM was investigated by means of atmospheric back-trajectories, satellite imagery and meteorological synoptic charts. Source apportionment studies were performed to characterize the main PM sources whenever was possible. Their contributions to bulk PM levels showed clear spatial patterns, linked to characteristic meteorological scenarios.

Keywords: PM10; PM2.5; Source apportionment; Road traffic; African dust;

1. Introduction

Atmospheric pollution has become a matter of concern as result of the dramatic consequences on population of several severe pollution episodes that took place in US and Europe in the middle of the last century. These episodes were rapidly known by the immediate effect on human health that were associated to those pollutants more known or documented at the time, particulate matter (PM) and sulphur dioxide. As a consequence of the increasing deterioration of air quality in industrial and urban areas, the European legislation developed standards for a number of gaseous pollutants and for total suspended particles (TSP) [1].

The improvement of the measurement techniques in the last 15 years have made possible the study of a great variety of different properties related to atmospheric aerosol. In the field of air quality, one of the key properties related with health effects is the aerosol size, directly related to dust capacity of penetration in the human respiratory

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system. Results from epidemiological studies in the last decades [2] contributed to demonstrate that PM10 (particle matter with aerodynamic diameter < 10 µm) was a parameter most appropriated for air quality purposes regulation than the existing one TSP, not taking into account the aerosol size. This lead to a new battery of European Directives that made PM10 and the smaller size range PM2.5 (particle matter with aerodynamic diameter < 2.5 µm), be the control parameters for particulated matter pollution [3]. More recent studies are pointing at more acute effects associated to finer particles, promoting therefore a research line of measurements and studies on the aerosol properties at the sub-micrometric range.

Chemical composition is also a property subject to certain controversy that has piled up a lot of research effort. Despite this is not routine information in air quality networks, only obtained through research projects, knowing the major components and several trace elements of the particle mass can provide invaluable information on the emission sources as well as some transformation processes that the aerosol has experienced once in the atmosphere. Results shown in this work are an example of the important insights on the characteristics of the aerosol, obtained from the characterization of some of these relevant properties collected from a wide range of sites across the Madrid air basin.

2. Methodology

Different data sets were obtained during experimental studies performed in the Madrid air basin. The sampling campaigns were carried out to characterize mean PM10 and PM2.5 concentration levels and their chemical composition at three representative sites of this area (Figure 1).

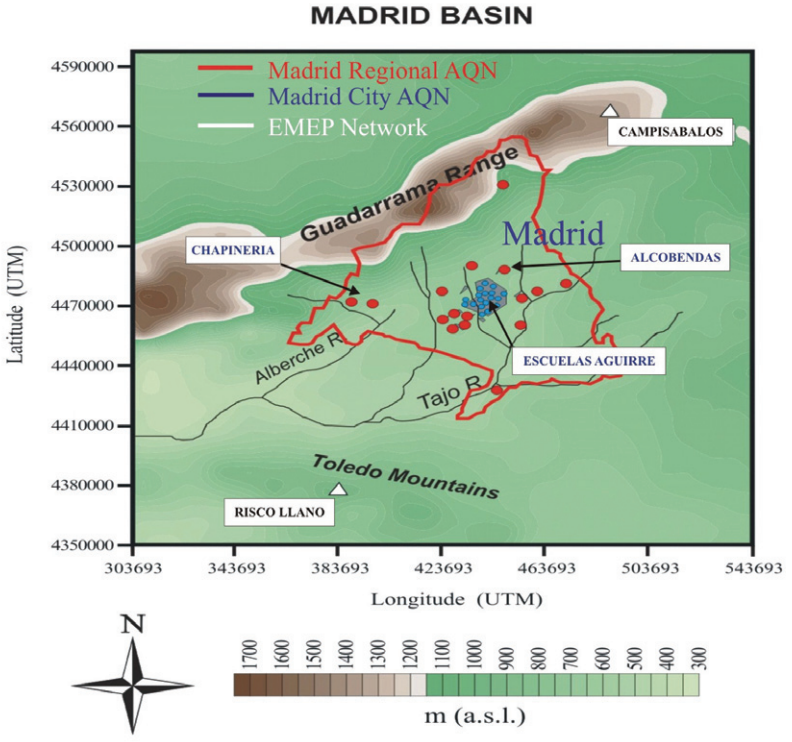

Figure 1. Geographical location of the Madrid air basin, the PM collection sites (Escuelas Aguirre, Alcobendas and Chapinería) and the Air Quality monitoring stations (blue ovals - Madrid City AQN stations; red ovals - Madrid Regional AQN stations; white triangles - EMEP stations).

The first study was conducted from June 1999 to June 2000 at an urban traffic site (Escuelas Aguirre-EA) in the Madrid city downtown. The second study was conducted throughout the year 2001 at an urban park located in

Alcobendas (ALC), a smaller town 13 Km away from Madrid city. The third one was carried out from May 2004 to April 2005 at the outskirts of Chapinería (CHA), a small village 25 Km southwest from Madrid City located in a rural area (Figure 1). ALC site can be considered as urban-background, whereas the CHA site can be representative of the air basin background. Finally a new study was carried out at EA from January 2007 to April 2008, with the aim to analyze the temporal variations produced in the PM levels and composition at this representative urban site, during the last decade.

At each site, 24-h sampling was carried out by means of a PM10 Graseby-Andersen high volume sampler (68 m3/h), which is an EN12341 reference instrument, and a MCV high volume sampler (30 m^3/h) equipped with a PM2.5 inlet and quartz micro-fibre filters (QF20 Schleicher and Schuell). Manual sampling was carried out at a rate of 3 moving days per week. It should be noted that in the first two studies, only two PM10 and one PM2.5 samples were selected for chemical analysis. A number of PM10 and PM2.5 filters were collected at the EA urban (67 and 38 in 1999-2000 and 95 and 104 in 2007-2008), ALC urban background (84 and 34 in 2001) and CHA rural (98 and 96 in 2004-2005) sites. Following sampling and standard gravimetric determination of the PM mass concentration levels, major and trace elements and compounds were analysed in PM10 and PM2.5 filters, with a total of 57 determinations per sample (for specific conditions see [4]). During this study the chemical components were grouped as: (a) crustal component (sum of elements typically found in rock-forming minerals, including Al_2O_3, SiO_2, CO_3^{2-}, Ca, Fe, K, Mg, Mn, Ti and P); (b) marine component (sum of Cl^-, Na^+ and marine sulphate); (c) OM+EC or organic matter plus elemental carbon (value obtained after applying a 1.2 factor to the OC+EC concentrations for urban sites and 1.4 for regional background sites considering the different possible values of OC and EC at these sites, [5]); (d) secondary inorganic compounds (SIC, as the sum of the non-marine SO_4^{2-}, NO_3^- and NH_4^+ concentrations) and (e) metals..

The main pollutants recorded at the stations of the Air Quality Networks (AQN) operating in the Madrid air basin were also analysed for these studies. During the period 1999-2008 there were two different AQN that covered the Madrid province territory taken as work domain in this study (Figure 1). The network managed by the Madrid municipality (Madrid City AQN) consisted of 27 stations (blue ovals in Figure 1) located in almost all the districts of the city (~3.2 million inhabitants). The regional network (Madrid Regional AQN) contributed with 18 stations (red ovals in Figure 1) distributed throughout the province as follows: 5 stations in the Eastern zone, 5 stations in the Southern zone, 2 stations in the Western zone, 2 stations in the Northern zone, 2 stations in the Southwestern zone and 2 stations in the Southeastern zone.

All the stations of the Madrid City AQN were urban ones, and most of them traffic oriented. Only one of them could be classified as urban background station. For the Madrid Regional AQN 11 out of the 18 stations were located in urban nuclei affected by traffic and no-heavy industrial activity and 2 stations were located in areas being representative of urban background conditions. Those remaining were located at rural sites in the region being representative of the regional background. However these rural stations were not prepared for PM sampling. For this reason two regional background monitoring sites included in the AQN of the UNECE/LRTAP/EMEP (European Monitoring and Evaluation Programme) were utilized. These sites were located on the far Northeastern (Campisabalos) and Southwestern (Risco Llano) limits of the Madrid air basin, respectively (white triangles in Figure 1).

Madrid City AQN stations measured PM10 and PM2.5 concentration levels on a daily basis since 1999 and 2004, respectively. Most of the Madrid Regional AQN stations started to measure regularly PM10 and PM2.5 concentration levels in 2000 and 2006, respectively, whereas EMEP stations provide them since 2001. The PM measuring instrumentation of the Madrid City and Madrid Regional AQN stations was automatic, based on the Tapered Element Oscillating Microbalance (TEOM) and beta attenuation method, respectively. Standardised gravimetric manual instruments were only used at the EMEP stations.

First, the ranges of mean annual PM10 and PM2.5 concentration levels were obtained for the study period (1999-2008) at urban-traffic, urban background and rural background AQN stations.

Next, seasonally adjusted non-parametric methods were used to determine trends in air pollutants time series. Seasonal Kendall Slope Estimator (SKSE) was calculated to quantify the magnitude of the trend. It is expressed as a slope (pollutant concentration per unit time). Positive slopes result from an overall increase in the values of the pollutants, while negative slopes result from an overall decrease. In order to quantify whether the trends in concentrations of pollutants are statistically significant, a seasonal Mann-Kendall test has been applied [6]. It is a

non-parametric test, insensitive to the existence of seasonality that can be applied to data that are not normally distributed and where there are missing data.

Then the influence of atmospheric transport scenarios on the levels of PM was investigated by means of atmospheric back-trajectory analysis using the Hysplit [7] and the Flextra [8] models and synoptic charts. A cluster analysis was performed to group air mass back-trajectories (7-day backward) arriving over the Madrid air basin in 1999-2005 [9]. Meteorological scenarios associated to them were obtained and interpreted.

The occurrence of African dust outbreaks over the Madrid air basin, were studied on the basis of the meteorological analysis carried out to estimate the origin of the air masses and information obtained from satellite imagery and numerical models (TOMS-NASA, NRL, SKIRON, and ICoD-DREAM aerosol and dust maps (TOMS, http://www.jwocky.gsfc.nasa.gov; NRL, http://www.nrlmry.navy.mil/aerosol; SKIRON: http://www.forecast.uoa.gr; DREAM: http://www.bsc.es/projects/earthscience/DREAM), and satellite images provided by the NASA SeaWIFS project (http://seawifs.gsfc.nasa.gov/SEAWIFS.html)).

It should be noted that 2008/50/EC European directive on air quality takes specifically into account the potential exceedence of the PM10 daily limit value - DLV (50 $\mu g/m^3$), due to the influence of natural sources, including "the transport of natural particles from arid regions" (article 2.15). In these cases the exceedences caused by natural episodes may be discounted by the Member States after careful justification of their natural origin. A procedure for the quantification of the net African dust load transported initially proposed by [10] was applied to estimate the impact of the African dust contributions, on the PM10 DLV exceedences registered at Madrid monitoring stations during days with African dust transport. This methodology built on the identification of days with African dust transport and statistical analyses based on the calculation of the 30 days moving 40^{th} percentile for regional background PM time series. This percentile is an indicator of the non-African regional background to be subtracted from the daily PM levels during African dust outbreaks, and thus allows calculating the daily net African dust contribution. This methodology became in the year 2004, the Spanish and Portuguese reference method to identify and quantify African dust contributions to PM levels.

Next, chemical composition of PM10 and PM2.5 fractions were analysed at the different monitoring sites. A non-parametric technique known as the Kruskal Wallis test was used to test the significance of inter-site variation in PM concentration. If the test leads to the rejection of the null hypothesis, it means that PM levels are influenced by the sampling site. Thus, the Dunn test for multiple sample comparison could be used to find out which sites are significantly different from which others in terms of PM levels and composition.

Finally, source apportionment studies were performed to characterise the main PM sources whenever was possible, using Positive Matrix Factorization (PMF [11])). Uncertainties used in the receptor modelling analysis were calculated based on [12]. Source contributions to PM10 and PM2.5 concentrations were estimated on an annual and daily basis.

3. Results and discussion

3.1 PM mean levels

For this study we have analysed only the time series of pollutants from those AQN stations with the best data coverage, which were not re-located in the 1999-2008 period. Finally, the mean levels for PM10 presented were obtained from 20 urban stations, from which 7 were located at hot spots strongly affected by road traffic, 1 urban background station and 2 rural background stations. Mean levels for PM2.5 were recovered from 9 urban (5 hot spots), 2 urban background and 2 rural background sites

According to the character of each AQN monitoring site in the Madrid air basin, the ranges of PM10 mean annual value (average +/- standard deviation) were approximately 39.6 ± 6.0 $\mu gPM10/m^3$ in heavy traffic hotspots sites, 31.8 ± 4.2 $\mu gPM10/m^3$ in urban sites, 27.8 ± 2.9 $\mu gPM10/m^3$ in urban background sites and 13.1 ± 2.7 $\mu gPM10/m^3$ at regional background sites.

On average mean annual PM2.5 concentration levels reached 19.4 ± 3.2 $\mu gPM2.5/m^3$ at heavy traffic hotspots and 16.6 ± 2.4 at urban sites. At urban background sites 12.5 ± 1.8 $\mu gPM2.5/m^3$ were determined whereas at regional background sites 8.5 ± 1.8 $\mu gPM2.5/m^3$ were obtained during the 1999-2008 period.

These values are within the average ranges of PM10 and PM2.5 concentrations obtained from the PM pollution data collected by [5] from a wide range of sites across Spain, covering all main types of different climatic conditions and anthropogenic activities but also in many European cities [13].

During the experimental studies mean PM concentrations reached 32 µgPM10/m^3 and 25 µgPM2.5/m^3 at ALC urban background site, and 32 µgPM10/m^3 and 17 µgPM2.5/m^3 at CHA rural site. At the EA urban site PM concentrations decreased from 48 µgPM10/m^3 and 34 µgPM2.5/m^3 in 1999-2000 to 41 µgPM10/m^3 and 21 µgPM2.5/m^3 in 2007-2008. The high reduction in the PM2.5 concentrations registered at the urban site during this period, should be mentioned as one of the most relevant results. However the drop in the concentrations of PM10 concentrations at the urban site was much less dramatic. PM10 mean levels at ALC and CHA were equal (32 µgPM10/m^3). However mean PM2.5 levels were 32% lower at CHA than at ALC. It should be attributed to relevant contributions of coarse PM from different origins at rural and urban sites in the Madrid air basin.

3.2 Trend analysis of atmospheric pollutants

Trends in the concentration of the main pollutants recorded in the Madrid AQN monitoring sites were calculated and analysed. Figure 2 shows the monthly mean evolution in CO, NO_x, SO_2, O_3, PM10 and PM2.5 averaged for all monitoring sites in the Madrid city AQN. A 12 month moving averaged trend was fitted to all the datasets.

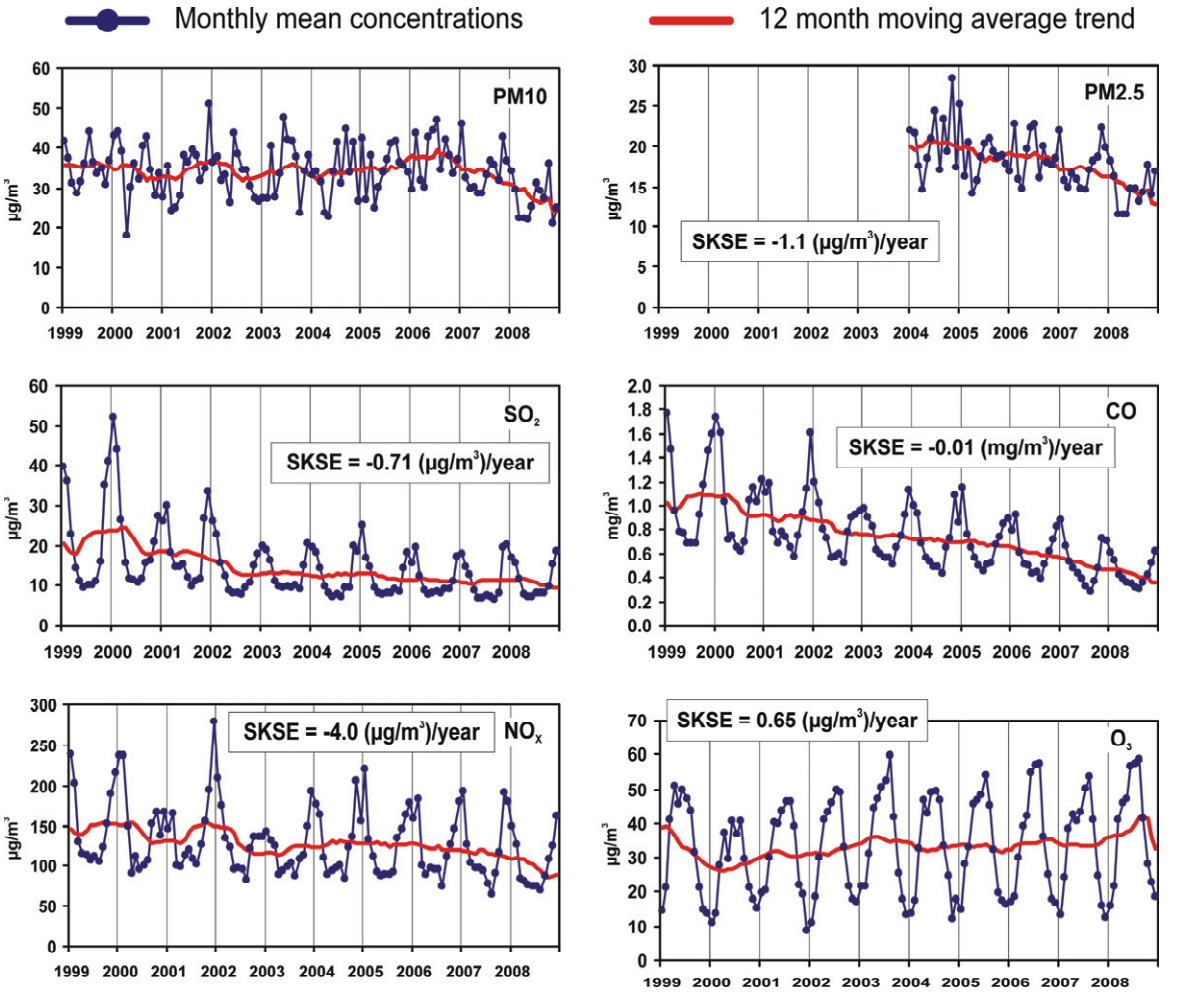

Figure 2. Trends in monthly mean concentrations of the main pollutants registered in the Madrid City AQN, averaged across all the monitoring sites for the 1999-2008 period. SKSE*: Seasonal Kendall Slope Estimator.

Except for O_3, the highest values of all these pollutants were recorded in January and February, although high levels were registered during the whole autumn and winter period. Traffic emissions and central domestic and administrative installations, usually coal or fuel-oil fed during the official heating season (November-March), were the predominant sources contributing to these winter maxima. The highest values for these pollutants were recorded during typical autumn-winter pollution episodes, linked to stagnant meteorological conditions as described by [14]. PM10 and PM2.5 also exhibited an elevated monthly maximum for the period June-September. Atmospheric conditions produced in this period favoured lower air mass renovation capacity, higher soil dust resuspension by wind and convective processes and higher formation capacity of secondary inorganic and organic aerosols by photochemical activity [15].

The seasonal Mann-Kendall test was applied to the data averaged across all monitoring sites in Madrid city (Network Average) during 1999 – 2008 but also for any single station. Figure 2 shows the results obtained for the Network Average. The tests show that there was a statistically significant downward trend in SO_2, NO_x, CO and PM2.5 concentrations at the 99% confidence level. No statistically significant trend was detected in PM10 and NO_2 whereas O_3 concentrations showed a statistically significant upward trend at the 99% confidence level. This was the more common behaviour obtained for the trends of the pollutants registered in most of the urban and urban background stations operating in the Madrid AQN. No statistically significant trend was detected in PM10 and PM2.5 concentrations in the EMEP Risco Llano and Campisábalos rural background stations.

The reductions may be attributed to a reduction in the coal fed domestic heating devices in Madrid City during this period, with a significant effect on PM concentrations, especially in the fine fraction.

3.3 Atmospheric transport scenarios over Madrid air basin

Eight different clusters were obtained as the best number for describing significantly different air-flow patterns, depending on their direction and speed (Figure 3). Slow (cluster 1) and moderate (cluster 8) air flows were produced in the summer as a consequence of the quasi-persistent influence of the Azores high over the Iberian Peninsula. During the day, the formation of a low pressure loop that evolves to form a thermal low was often observed over the central plateau, being associated with the development of regional wind flows.

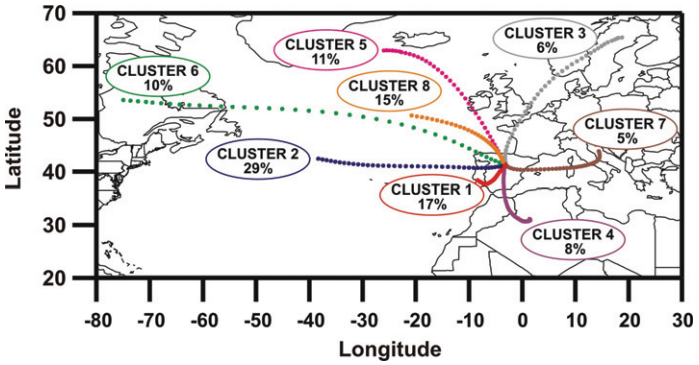

Figure 3. Cluster centres (average of the members of each cluster). The percentage of trajectories occurred in each cluster is also included.

The fastest air flows (clusters 3 and 6) were more frequent during the winter, being generated by strong baric gradients. The transition period between the occurrence of the longest trajectories in winter and the shortest one in summer was characterized by the advection of moderate flows from Atlantic Western and Northern regions (clusters 2 and 5). They occurred more frequently during the spring and autumn months and less during the summer. No clear seasonal trends were found for the occurrence of clusters 4 and 7. Cluster 4 contained trajectories of air mass

coming from the North-African regions of Morocco, Algeria, Tunisia, Libya and Mauritania. Cluster 7 was characterised by an ensemble of trajectories coming from South Europe and the western Mediterranean area.

3.4 African dust episodes

Long-range transport of dust by African flows was the most significant natural event contributing to PM10 levels registered at the Madrid air basin. African flows were registered throughout the year although during some months they could be more probable. On average, during the period 1999-2005 North-African flows (cluster 4) were more frequently produced in March, August, October and December. Different synoptic situations were identified depending on the season (Figure 4). The winter meteorological scenario was identified by a high pressure system centered over Argelia and extended from Western Sahara to Libya. The spring transport scenario was characterised by a deep low, centred west of the Portuguese coast. In the summer, the intense heating of the Northern-Africa surface generated the development of a thermal low. A compensatory high pressure system was formed in the upper atmospheric levels (850 hPa), frequently over Northern Argelia. During the autumn, the African high was shifted to the North and a trough was observed southwest of the Portuguese coast.

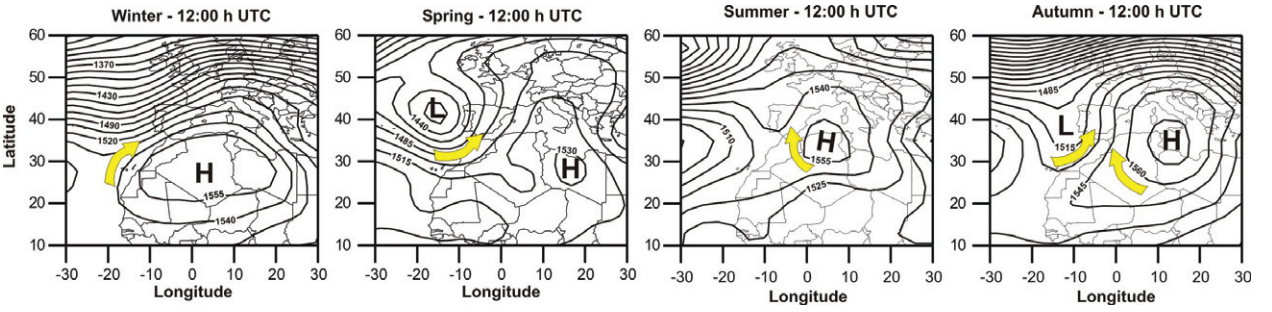

Figure 4. Composite 850 mb geopotential height (m) for the African flows arriving over the Madrid air basin.

On the basis of the meteorological analysis carried out to estimate the origin of the air masses and the detection of African dust outbreaks using satellite imagery and numerical models, 17 African dust episodes per year were identified on average (59 days/year) in the period 1999-2008, influencing the PM levels recorded in the Madrid air basin monitoring stations. The effect of the dust outbreaks was clearly detectable in the PM10 values determined at the EMEP rural background stations. Figure 5 shows how the main peaks of these PM10 time series coincide with dust events. There is a clear trend towards a higher frequency of African dust episodes during summer and in the February-March months.

With the aim to qualitatively estimate the impact of the African dust contributions, the PM10 DLV (50 $\mu g/m^3$) exceedences registered at Madrid monitoring stations during days with African dust transport, were calculated during the 2001 – 2006 period. On average, 34%, 42% and 54% of the total PM10 DLV exceedences registered at Madrid hot-spots, urban and urban-background stations respectively, were detected during African dust outbreaks. At the Risco Llano and Campisabalos rural-background stations, 30 out of 31 and 20 out of 21 PM10 DLV exceedences were registered respectively, during African dust outbreaks. Thus, there is a positive relationship between the number of African dust outbreaks and the number of PM10 DLV exceedences.

However this methodology is only qualitative and did not allow for the quantification of the net African dust contributions to PM levels. For this reason the procedure proposed by [10] for the quantification of the net African dust load transported was applied. Thus, on average during the 2001 – 2006 period, 18%, 28% and 45% of the total PM10 daily limit value (50 $\mu g/m^3$) exceedences registered at Madrid hot-spots, urban and urban-background stations respectively, were exclusively attributed to African dust.

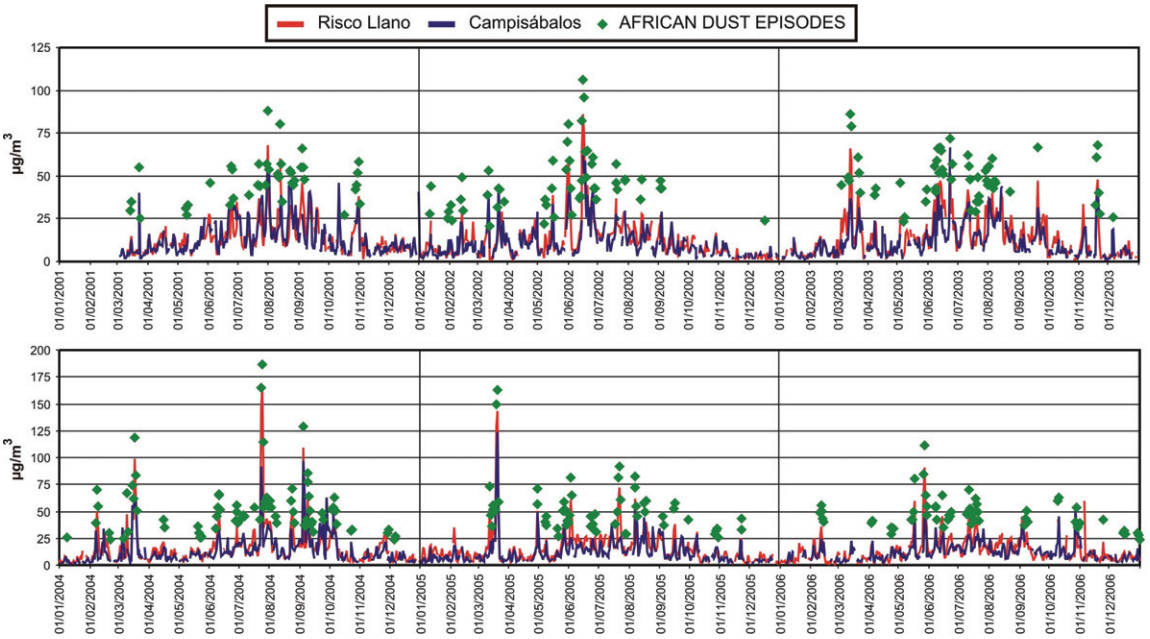

Figure 5. Daily mean PM10 values registered at EMEP rural-background sites in 2001-2006. African dust episodes are highlighted.

3.5 Chemical characterization

Table 1 summarises mean concentration values of major and trace elements of PM10 and PM2.5 at EA, ALC and CHA. The sum of ions determined accounted for 78-95% and 87-100% % on average, of the PM10 and PM2.5 bulk mass, respectively. Kruskal-Wallis non-parametric tests indicated statistically significant differences in PM concentrations (crustal, marine, carbonaceous, SIC and metals content) among sites in PM10 and PM2.5, at the 95% confidence level. This means that significant differences in receptor PM concentrations were observed between the sites. Except for marine content, the Dunn test for multiple sample comparison results shown that PM mean concentrations registered in EA were significantly higher compared with those registered in ALC and CHA. In this urban site, the test shown that PM mean concentrations were significantly higher in the period 1999-2000 than in the 2007-2008, with the exception of the crustal and the SIC mean content in the PM10 fraction.

Carbonaceous material was the most abundant component of the aerosol mass in the two fractions, increasing from the rural site (24 and 35 % in PM10 and PM2.5) to the traffic one (47 and 63 % in PM10 and PM2.5). The fine fraction was specially enriched in this component reaching up to 63% of the PM2.5 mass at the EA traffic site in the 1999-2000 period.

Crustal material, mainly present in the coarse fraction, was more abundant in the traffic site. This can be explained by the effect of local dust re-suspension due to road traffic and wind blown but also to African dust.

Secondary inorganic compounds (SIC) were the third major component group of the aerosol mass, with a significant contribution in the fine fraction and at the rural site, where it can reach 22.5 % of the PM2.5 mass, exhibiting the secondary (gas-particle conversion from precursors) characteristics of the regional background aerosol.

Marine aerosol was also present in low levels, mainly in the coarse fraction.

Only Zn, Ti, Ba, Cr, Pb and Mn concentrations exceeded 10 ng/m^3. Highest levels of Zn were associated to a small smelter in ALC and those of Pb in EA to traffic exhausts as leaded gasoline was in use for the first measurement period at that site. Cu, Zn and Ba levels were associated to brake and tyre abrasion. In any case limit

or target values established in 1999/30/CE Directive for Pb or As, Cd and Ni in 2004/107/CE Directive were exceeded.

At EA, carbonaceous particle concentrations for both coarser and finer fractions, significantly decreased from 1999-2000 to 2007-2008 (43% in PM10 and 54% in PM2.5). The reduction in the concentrations of other major group of components from 1999-2000 to 2007-2008 was much lower especially for the coarse fraction. Crustal and SIC content reduced 13% and 8% in PM10 and 55% and 18% in PM2.5 respectively. Marine aerosol and metals content did not suffer significant variations. It should be a consequence of the reduction in the emissions of pollutants from local anthropogenic sources (mainly traffic and heating devices), as it was depicted in the trend analysis (Section 3.2 and Figure 2). The lower drop in the concentrations of PM10 concentrations at the urban site should be attributed to relevant contributions of crustal and secondary aerosol throughout the whole basin.

Table 1. Mean concentrations (in $\mu g/m^3$) of major and trace elements of PM10 and PM2.5 registered at representative sites of the Madrid air basin (Escuelas Aguirre urban site-EA; Alcobendas urban-background site-ALC; Chapinería rural site-CHA). Standard deviations are shown between brackets.

PM10	PM	Crustal components	Marine components	OM+EC	SIC	Metals	Unknown
EA 1999-2000	47.7 (20.8)	14.6 (8.2)	0.8 (0.4)	22.2 (12.2)	7.6 (3.6)	0.34 (0.17)	2.2 (3.4)
EA 2007-2008	41.4 (19.4)	12.7 (6.9)	1.2 (0.8)	12.7 (6.9)	7.0 (3.7)	0.40 (0.20)	7.2 (3.9)
ALC 2001	32.2 (19.2)	8.6 (6.5)	1.2 (0.7)	12.9 (6.9)	6.4 (4.7)	0.25 (0.27)	3.0 (2.0)
CHA 2004-2005	31.6 (21.7)	11.0 (11.1)	0.46 (0.53)	7.6 (4.5)	5.2 (4.6)	0.08 (0.04)	7.0 (8.1)

PM2.5	PM	Crustal components	Marine components	OM+EC	SIC	Metals	Unknown
EA 1999-2000	34.1 (13.3)	5.6 (3.6)	0.5 (0.3)	21.3 (11.9)	6.5 (3.1)	0.21 (0.11)	0.4 (7.8)
EA 2007-2008	20.7 (9.2)	2.5 (1.5)	0.6 (0.3)	9.8 (5.0)	5.3 (2.9)	0.19 (0.09)	2.3 (3.1)
ALC 2001	24.9 (15.3)	2.7 (1.8)	0.6 (0.2)	13.8 (9.2)	5.4 (6.0)	0.13 (0.07)	2.3 (1.2)
CHA 2004-2005	16.8 (10.7)	4.8 (4.1)	0.13 (0.08)	5.7 (3.8)	3.7 (3.9)	0.08 (0.03)	2.2 (3.0)

3.6 Source apportionment study

Receptor modelling analysis agrees with the identification of four main sources for PM10 and PM2.5 at all the sampling sites: Emissions from **vehicular traffic** (with C, Fe, Sb, Cu as main tracers), **mineral dust** (Al, Ca, K, Ti, Mn,...), **secondary sulfate** (SO_4^{2-}, V and NH_4^+) and **secondary nitrate** (NO_3^-, and NH_4^+). In the coarse fraction, **marine aerosol** (Cl^-, Na and Mg) was also identified everywhere. **Industrial** (Cr, Ni, Pb,..) and **biomass burning** (P, C,...) were sources identified exclusively at the urban-background and rural-background sites, respectively.

During the second sampling period carried out at the urban site (2007-2008), **residential coal combustion** (As, Se,...) and **African dust** (Al, Ti, K, Mn, Sr...) were discriminated as individual sources. The use of a more complete data base and a higher number of samples in comparison with that obtained during the first sampling period (1999-2000) allowed identifying these PM sources. The contributions of all these sources to bulk PM levels are shown in Table 2.

Table 2. Source contributions to gravimetric PM10 and PM2.5 mass (in µg/m^3) resulting from the PMF analysis at representative sites of the Madrid air basin (Escuelas Aguirre urban site-EA; Alcobendas urban-background site-ALC; Chapinería rural site-CHA).

PM10	Crustal	African dust	Traffic	Secondary nitrate	Secondary sulfate	Marine	Industrial	Coal Combustion	Biomass burning
EA 1999-2000	10.8	-	20.0	9.2	5.0	2.0	-	-	-
EA 2007-2008	7.8	4.9	14.6	7.3 **		2.8	-	3.9	-
ALC 2001	8.0	-	8.4	4.4	4.4	2.4	4.2	-	-
CHA 2004-2005	12.8	-	4.2	4.4	4.2	1.8	-	-	3.6

PM2.5	Crustal	African dust	Traffic	Secondary nitrate	Secondary sulfate	Marine	Industrial	Coal Combustion	Biomass burning
EA 1999-2000	ND*	ND	ND	ND	ND	ND	ND	ND	ND
EA 2007-2008	1.5	2.0	8.0	5.0 **		-	-	3.9	-
ALC 2001	ND	ND	ND	ND	ND	ND	ND	ND	ND
CHA 2004-2005	4.6	-	1.5	2.1	4.2	-	-	-	3.2

* ND: Not Determined due to the low number of samples of the data sets.
** Both sources were grouped in a single one "Secondary Inorganic" at this site

4. Conclusions

During the 1999-2008 term a statistically significant downward trend in the concentrations of SO_2, CO and NO_x was produced in the city of Madrid. The reduction in these emissions typically attributed to anthropogenic sources, had a significant effect on PM2.5 concentrations recorded in the Madrid City AQN. Measurements obtained at an urban-traffic site in two different periods, showed an outstanding reduction in PM2.5 mean concentration (from 34 µg/m^3 in 1999-2000 to 21 µg/m^3 in 2007-2008). This is a consequence of the abatement in its carbonaceous content (from 21.3 µg(OM+EC)/m^3 in 1999-2000 to 9.8 µg(OM+EC)/m^3 in 2007-2008). It is attributed to a reduction in the emissions from residential coal burning and in a lesser extent from traffic. Changes in the Madrid vehicle fleet due to the replacement of old vehicles with new ones which incorporate new transport emissions control technologies, such as particle filters [16], have probably contributed to this decrease.

The drop in the concentrations of PM10 at the urban-traffic site was less dramatic (from 48 to 41 µg/m^3), which is attributed essentially to relevant contributions of secondary inorganic aerosol and mineral matter from local and regional sources but also from long-range transport episodes of African dust. For this reason mean PM10 concentrations at urban-background and rural-background sites reached relative high levels (around 32 µg/m^3) in comparison with the urban-traffic sites.

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