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A combined analysis of backward trajectories and aerosol chemistry to characterise long-range transport episodes of particulate matter: The Madrid air basin, a case study

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ABSTRACT

This study has investigated the influence of synoptic weather patterns and long-range transport episodes on the concentration levels of airborne particulate matter (TSP, PM10 and PM2.5) and some major ions (SO_4^{2-}, NO_3^- and NH_4^+) at a background rural station in central Spain. Air mass back-trajectories arriving at the site in 1999–2005 have been analysed by statistical methods. First, cluster analysis was used to group trajectories into 8 clusters depending on their direction and speed. Meteorological scenarios associated to each cluster have been obtained and interpreted. Then, the incidence of different air mass transport patterns on particle concentrations and composition recorded at this station was evaluated. This evaluation included PM10 and PM2.5 concentrations and chemical composition data, obtained at three representative sites of the Madrid air basin during sampling campaigns carried out in the course of the 1999–2005 period. Finally, a residence time analysis of trajectories was also performed to detect remote sources and transport pathways. Significantly elevated concentrations of TSP and PM10 were observed for Northern African flows as a consequence of the transport of mineral dust. Significant inter-cluster differences were also observed for PM2.5 and secondary inorganic compounds, with the highest concentrations associated with low baric gradient situations and Southern European flows. The residence time analysis confirmed that current TSP and PM10 concentrations in central Spain are likely to be influenced significantly by long-range transport of desert dust from different desert regions in North Africa. Furthermore, emissions from continental Europe with a high time of residence in the western and central areas of the Mediterranean basin, seem to significantly influence PM2.5 and secondary inorganic aerosol concentrations in this region.

1. Introduction

Particulate matter (PM) concentrations recorded at a specific site may vary on time scales from minutes to days. This variability is closely related to the immediate history of the air before arriving at the sampling point. For this reason, a classification of the air mass origins can be used to categorise PM concentration data for further interpretation. It should be pointed out that once airborne, particles evolve in size and composition through condensation, coagulation or chemical reactions and can be eventually removed by wet and dry deposition processes. Furthermore, natural and anthropogenic aerosol components can be released at one location and travel long distances in the atmosphere with the prevailing

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winds. Thus, PM can affect air quality locally and at a long distance away.

There is evidence that long-range transport of PM with diameters under 10 and 2.5 μm, (PM10 and PM2.5 respectively) over distances exceeding natural borders, may affect air quality in urban and rural areas in Europe (Beverland et al., 2000; Abdalmogith and Harrison, 2005; Escudero, 2006). Furthermore, PM10 and PM2.5 are widely recognised to cause a number of different problems to human health and the environment (climate, visibility and biogeochemical cycles) (IPCC, 2001; WHO, 2003). International actions and collaboration are required to control their levels and effects, as local authorities have little control over pollution from outside their regional area. In this sense, the analysis of time series of pollutants registered at rural background sites located at some distance from anthropogenic PM sources and urban nuclei can help to identify contributions to surface PM levels via long-range transport processes (Escudero, 2006). As a result of this, the assessment of the synoptic meteorological scenarios which give rise to the highest daily PM concentration data at the rural background sites, as well as the identification of transboundary sources of PM, can be important factors in addressing air pollution concerns at specific regions.

With this aim the present study uses a classification technique, cluster analysis (CA), which considers the wind speed and direction of air masses back-trajectories in the preceding 5 days over 7 years to assess dominant flow patterns. This technique has worked very well for discriminating distinct flow patterns and large-scale circulation features (Harris and Kahl, 1990; Dorling et al., 1992; Jorba et al., 2004). One of the advantages of CA applied to trajectories is that it allows characterizing the main atmospheric circulation features of every cluster pattern by mean composite pressure and geopotential height maps (Dorling et al., 1992). This information can be applied for establishing PM reduction strategies in specific areas since the daily analysis of the weather forecast reports, supplied by the meteorological institutions, will provide indications on the generation of the meteorological scenarios that result in long-range transport episodes.

Nevertheless, CA does not provide any information on the geographical location of these external sources. For this reason, a residence time analysis (RTA) has also been carried out in this work (Ashbaugh et al., 1985). Both of these techniques, CA and RTA, have been separately applied to air mass trajectories in many air pollution studies (Ashbaugh et al., 1985; Moody and Galloway, 1988; Dorling et al., 1992; Brankov et al., 1998; Beverland et al., 2000; Cape et al., 2000; Gebhart et al., 2001; Salvador et al., 2004; Abdalmogith and Harrison, 2005). However, Sirois and Bottenheim (1995) have been so far the only ones to show that when utilised in combination, these techniques provide information that is not available when only one of them is used. To date, as far as we know, no one has applied both analyses in combination to interpret a large set of PM concentrations and chemical composition data as the one used in this work for any region of the Iberian Peninsula. It should be noted that the use of statistical techniques employing large trajectory ensembles is recommended to reduce the errors of analysing single trajectories (Stohl, 1998).

This work is primarily concerned with characterizing the meteorological scenarios and source regions that give rise to long-range transport episodes which contribute to the daily levels of PM in the Madrid air basin. This case study has been designed to illustrate the usefulness of back-trajectories statistical techniques for detecting and predicting these episodes elsewhere in the world. First, the main large-scale atmospheric circulation features that influence the air masses flowing over the center of the Iberian Peninsula throughout the 1999–2005 period have been identified by CA. Next, an analysis of the meteorological scenarios associated to each cluster has also been carried out. Then, the influence of the different meteorological scenarios on observed PM levels and composition at representative sites of the Madrid air basin has been examined. Finally, a RTA has also been carried out to determine the most probable origin of air parcels containing the highest 10% of PM concentration values observed at the study site.

2. Methodology

CA is a statistical method used to examine data and group it into sets of similar data known as clusters. It is a useful method for organizing large data sets into smaller, similar groups. In this work we have used air masses trajectory coordinates (endpoints or time steps) as the clustering variables. A non-hierarchical method known as the k-means procedure has been used in this study. This is an iterative algorithm that uses a specified number of clusters, k, to partition the data by comparing each object to the mean of the members of each of the k clusters (cluster centers). This procedure is comprehensively described in Owen (2003). The selection of the optimal number of clusters that best describes the different air-flow patterns, was done by computing the percentage change in within-cluster variance, V_w, as a function of the number of clusters. V_w is calculated as the sum of the root-mean-square deviations of each trajectory from its cluster center (Owen, 2003). This statistic increases abruptly as clusters of trajectories which are significantly different in terms of wind directions and speeds are joined (Dorling et al., 1992). A threshold of 5% change in the V_w has been adopted (Dorling et al., 1992; Brankov et al., 1998; Jorba et al., 2004) which, when exceeded at some step in the reduction of clusters, signifies a possible number of clusters to be retained.

In this study 7-day backward air trajectories arriving over Campisabalos monitoring site were utilised. Campisabalos is a regional background monitoring site included in the air quality network of the UNECE/LRTAP/EMEP (European Monitoring and Evaluation Programme). This site is located at the center of the Iberian Peninsula (41° 17′N, 3° 09′W, 1360 m ASL), on the far northeastern limit of the Madrid air basin (Fig. 1).

For each day, four trajectories ending at 00:00, 06:00, 12:00 and 18:00 h UTC have been computed by the Norwegian Institute for Air Research NILU using the FLEXTRA model (Stohl et al., 1995). In all, 10,204 complete trajectories were available for analysis, each with 56 endpoints. Only the last 5 days of transport to Campisabalos were considered to reduce the uncertainty of the trajectory (Sirois and Bottenheim, 1995;

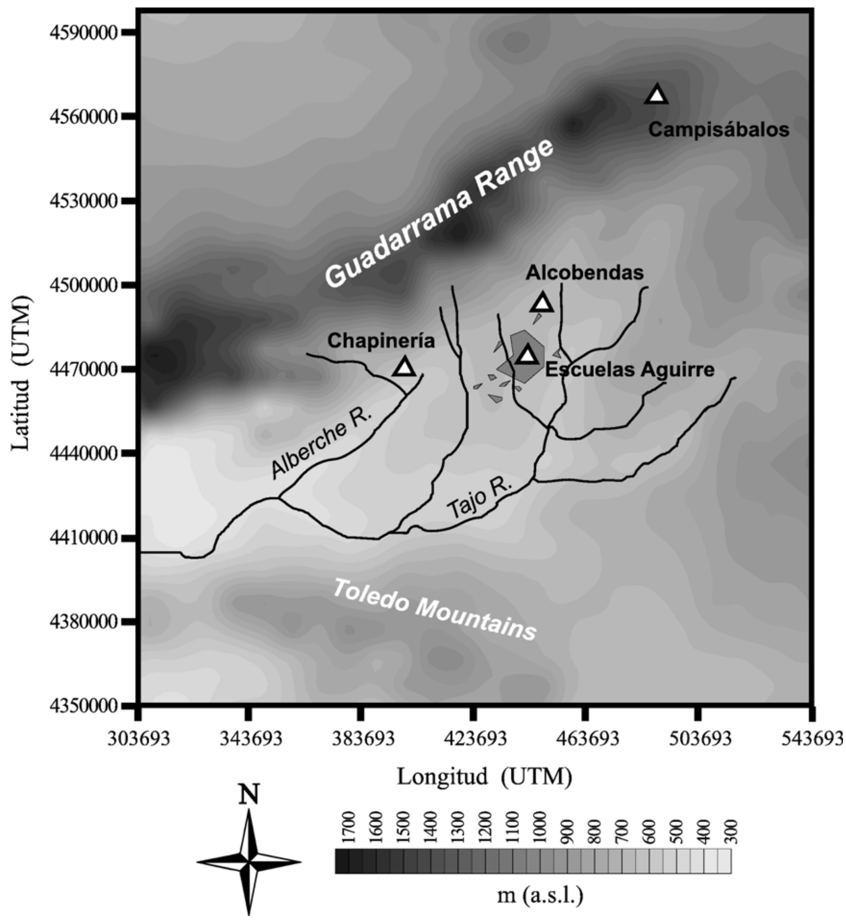

Fig. 1 – Bi-dimensional topography and location of the Madrid air basin. The locations of Campisabalos, Escuelas Aguirre, Alcobendas and Chapinería monitoring sites are shown. The metropolitan area, represented by the city of Madrid and satellite towns has been shaded.

Cape et al., 2000). The meteorological data used for trajectory calculations were provided from ECMWF (European Centre for Medium-Range Weather Forecasts). These are so-called analysis data, which are a combination of observations and numerical calculations. The spatial resolution is T106, which corresponds with a resolution of about 1.125° in latitude and longitude. The temporal resolution is 6 h, and 60 levels are available in the vertical direction. 3-D trajectories were calculated using the vertical wind provided by ECMWF. A fixed height of 1400 m asl was chosen as the arrival level. At this height, surface artifacts can be avoided and it can be considered as a representative height of the mean transport wind at a synoptic scale, within the upper boundary layer (Stohl, 1998).

Once the CA were performed, composite synoptic maps have been obtained by averaging the sea level pressure and the geopotential height at the 850 hPa topography, using the data corresponding to all days in which back-trajectories were assigned to a particular cluster. The meteorological variables used were obtained from the NCEP/NCAR Reanalysis datasets files (Kalnay et al., 1996), provided by the NOAA/OAR/ESRL PSD, USA.

Next, mean TSP, PM10, PM2.5, SO_4^{2-}, NO_3^- and NH_4^+ concentrations were obtained for all trajectory clusters arriving at Campisabalos. PM was measured at this station on a daily basis using high-volume samplers. During the period 1999–2005, TSP samples were obtained from January 1999 to December 2002. PM10 and PM2.5 simultaneous sampling started in March 2001. TSP, PM10 and PM2.5 concentrations were obtained by standard gravimetric methods. Levels of SO_4^{2-} and NH_4^+ in TSP samples were chemically obtained by ion chromatography (EMEP, 2001) during the 1999–2002 and 1999–2000 periods, respectively. Levels of SO_4^{2-} and NO_3^- in PM10 samples were also determined from 2003 to 2005 by ion chromatography (EMEP, 2001). The number of samples and mean values are summarised in Table 1. For each PM sample, the 12:00 h UTC trajectory was assigned as the one best representing the sampling period.

A non-parametric technique known as the Kruskal–Wallis test was used to test the significance of inter-cluster variation in PM concentration. This technique tests the null hypothesis that several samples have been drawn from the same population. If the test leads to the rejection of the null hypothesis, it is interpreted as follows: PM levels sampled at Campisabalos are influenced by the transport paths of air masses arriving at this site, which are represented by the clusters (Moody and Galloway, 1988). In this case it is appropriate to use a multiple sample comparison to find out

Table 1 – Mean TSP, PM10, PM2.5, SO_4^{2-}, NO_3^- and NH_4^+ concentrations (μg/m^3) for 1999–2005 and by trajectory cluster at Campisabalos

	TSP	PM10	PM2.5	SO_4^{2-} (TSP)	SO_4^{2-} (PM10)	NO_3^- (PM10)	NH_4^+ (TSP)
Mean	18.5	12.3	7.8	2.07	1.68	1.11	0.36
N	1305	1590	1469	1303	1001	970	690
Cluster 1	27.6	17.7	10.9	2.91	2.22	1.37	0.61
Cluster 2	14.7	9.2	6.0	1.53	1.23	0.93	0.26
Cluster 3	9.5	8.1	6.3	1.80	1.56	1.06	0.22
Cluster 4	35.1	22.9	9.6	1.83	1.83	1.06	0.24
Cluster 5	12.0	7.2	5.1	1.47	1.14	0.84	0.21
Cluster 6	9.1	6.2	4.6	1.29	1.08	0.84	0.17
Cluster 7	26.7	19.2	10.4	2.67	2.58	1.51	0.41
Cluster 8	23.9	14.5	9.6	2.70	1.98	1.11	0.50

N, number of samples.

which clusters are significantly different from which others. In these cases, the Dunn test for multiple sample comparison was used (Brankov et al., 1998; Beverland et al., 2000).

With the aim of demonstrating that the meteorological scenarios which give rise to long-range transport episodes contribute to PM level and composition everywhere in this airshed, additional data registered during experimental studies were also analysed. These sampling campaigns were carried out to characterise mean PM10 and PM2.5 concentration levels and chemical composition at other representative sites of the Madrid air basin (Fig. 1). Part of these data was published in prior studies (Artíñano et al., 2004; Querol et al., 2004b). 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 from Madrid city. The third was carried out from May 2004 to April 2005 at the outskirts of Chapinería (CHA), a small village 25 km southwest of Madrid city. The second place can be considered as an urban background site, whereas the CHA site is more isolated from anthropogenic sources of PM than the ALC site and can be representative of the airshed background. A number of PM10 and PM2.5 filters were obtained and analysed at the EA (67 and 38), ALC (84 and 34) and CHA (98 and 96) sites. PM measurements were carried out with gravimetric high-volume samplers. Quartz fibre filters, previously conditioned, were utilised for sampling and subsequently chemically analysed to determine the levels of major and trace components. Sampling and analytical procedures can be found elsewhere (Querol et al., 2004b) and consequently will not be described in detail. The chemical components were grouped as: a) crustal component (sum of elements typically found in rock-forming minerals, including Al and Si oxides, CO_3^{2-}, Ca , Mg, P, Fe, K, Mn and Ti); b) marine component (sum of Cl^-, Na^+ and $SO_4^{2-}{}_{marine}$); c) total carbon; d) secondary inorganic compounds (SIC, as the sum of the $SO_4^{2-}{}_{non\text{-}marine}$, NO_3^- and NH_4^+ concentrations) and e) sum of heavy metals. The mean concentration levels registered at each site are summarised in Table 2.

Finally, a RTA has been performed for every year of the period 1999–2005, to determine the geographic origin and transport pathways of air masses that arrive at a site under any given pollution scenario. This work uses the conditional probability function (CPF) (Ashbaugh et al., 1985). A 2° longitude × 2° latitude cell grid was superimposed over the region defined by 18°N–62°N and 27°W–21°E. The CPF for the *ij*-th grid cell represents the probability that an air mass arrives at the receptor site when the pollutant concentration is higher than a specified value, after having been observed to reside in this specific geographical cell. Areas with high CPF can be considered as source regions or preferred air mass pathways of the pollutant under study. To check the statistical significance of every grid cell CPF value, a statistical test based on the binomial distribution has been applied (Vasconcelos et al., 1996). CPF has been computed at each grid cell for TSP, PM10, PM2.5, SO_4^{2-}, NO_3^- and NH_4^+ concentration values higher than the 90th percentile.

3. Results and discussion

3.1. CA results

A large increase in the V_w statistic appeared when reducing the number of clusters from 13 to 12 and from 8 to 7. A percentage change of 6.9 and 7.2% was respectively produced. This suggested that 13 or 8 clusters could be retained as the best number for describing significantly different air-flow patterns in this study. 13 clusters were considered too many, since the composite synoptic maps (sea level pressure and geopotential height at the 850 hPa topography) obtained for some of these clusters were very similar (Brankov et al., 1998). For this reason, 8 clusters have been retained for use in this analysis.

Fig. 2 shows the eight final cluster centers after the last iteration in the clustering procedure. Cluster 1 represents low

Table 2 – Mean PM, crustal, SIC, C, marine aerosol and metals concentrations (μg/m^3) for the PM10 and PM2.5 samples registered at Escuelas Aguirre – EA (1999–2000), Alcobendas – ALC (2001) and Chapinería – CHA (2004–2005)

	N	PM	Crustal	SIC	C	Marine	Metals
EA							
PM10	67	47.7	14.6	7.6	15.7	0.72	0.34
PM2.5	38	34.1	5.3	6.5	14.6	0.47	0.21
ALC							
PM10	84	32.2	8.7	6.4	9.1	1.20	0.25
PM2.5	34	24.9	2.7	5.4	9.4	0.58	0.13
CHA							
PM10	98	31.6	5.4	5.2	5.5	0.46	0.08
PM2.5	96	16.8	1.8	3.7	4.0	0.13	0.08

N, number of samples.

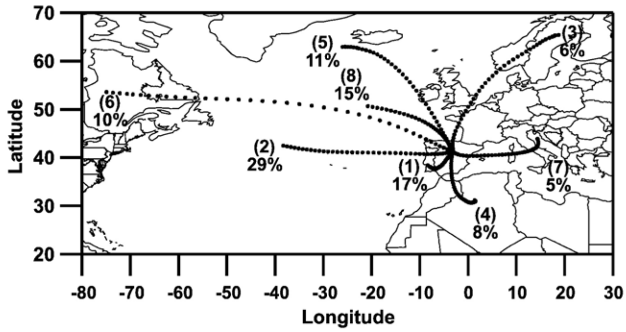

Fig. 2 – The 8 cluster centers resulting of the analysis, identified by the number between parentheses, are shown. The percentage of trajectories occurring in each cluster is also included.

speed air circulation or regional transport. It contains short trajectories of air mass recirculating within the Iberian Peninsula. Cluster 2 gathers westerly trajectories moderately moving from the mid Atlantic Ocean. Cluster 3 represents north-easterly flows moving fast along the North European coastal corridor. Cluster 4 is characterised by trajectories from the North-African regions of Morocco, Algeria, Tunisia, Libya, Western Sahara and Mauritania. Cluster 5 indicates a moderate flow moving to central Spain from the northwestern regions close to Iceland. The fastest-moving trajectories from the west are grouped in Cluster 6. Cluster 7 is characterised by an ensemble of trajectories coming from Southern Europe and the western Mediterranean area. Finally, a slow moving north-westerly flow is represented by cluster 8.

In sum, the Atlantic advection flows accounted for 66% of the data. They have been grouped into fast westerly flows (cluster 6) with a 10% of occurrence, moderate westerly and north-westerly flows (clusters 2 and 5) representing 29% and 11% of the data respectively, and slow north-westerly flows (cluster 8) which accounted for 15% of the trajectories. The slowest trajectories cluster accounted for 17% of the data (cluster 1). The transport regimes that have less frequently occurred were the North-African (cluster 4), the north-easterly (cluster 3), and the Southern European flows (cluster 7). They represented 8%, 6% and 5% of the data respectively.

The meteorological scenarios represented by the shortest trajectories (cluster 1) and the slow north-westerly trajectories (cluster 8) occurred predominantly in the summer and early autumn months (Fig. 3a). During this period, the quasi-persistent influence of the Azores high over the Iberian Peninsula generates a low baric gradient situation. Consequently, moderate and slow air flows are produced. During the day, the formation of a low pressure loop that evolves to form a thermal low is often observed over the central plateau. The formation process has a marked diurnal cycle, being produced by the strong ground heating of some dry areas at the center of the Iberian Peninsula in the summer (Millán et al., 1997). The formation of this so-called Iberian thermal low is usually associated with the development of regional wind flows (sea breezes, up-slope and down-slope winds or valley-channeled winds). In the central air basin of the Iberian Peninsula characteristic regional flows are induced during the summer, by the daily cycle of slope heating and cooling of the Guadarrama mountain range (Plaza et al., 1997). This results in the recirculation of the air masses in the airshed, from the NE and E areas in the morning to the S and SW areas in the afternoon.

The fastest air flows, represented by clusters 3 and 6, have been more frequent during the winter months (Fig. 3b). The most common scenarios causing these flows in the winter season are described as follows. The first one is characterised by a north-easterly flow over the Madrid air basin (cluster 3)

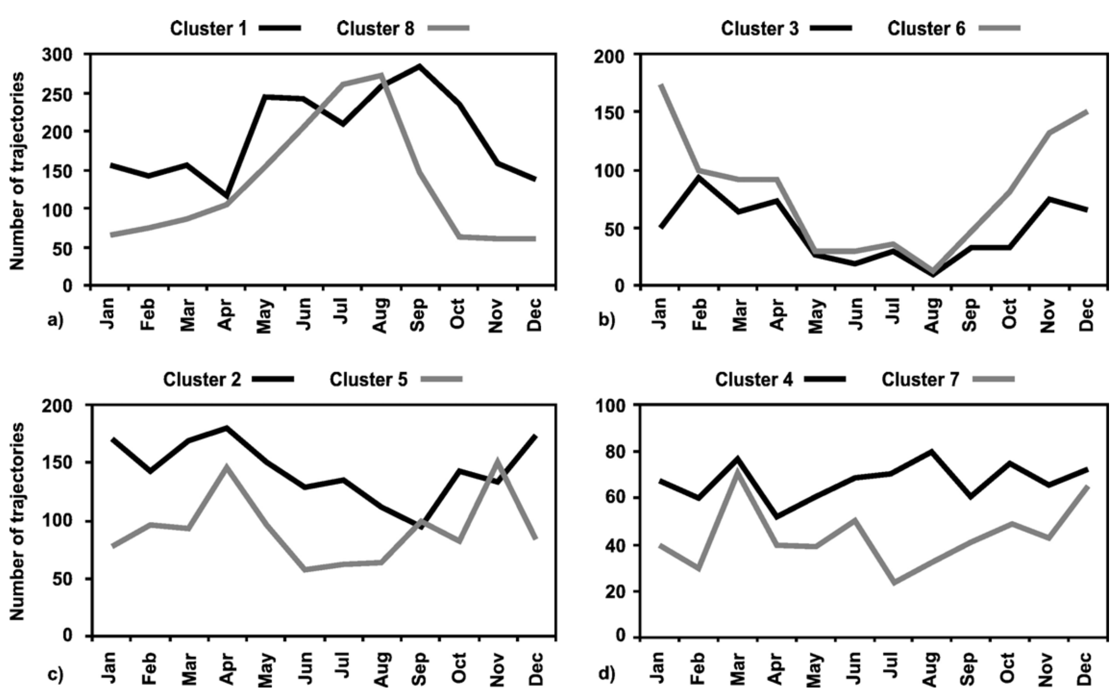

Fig. 3 – Monthly number of trajectories analysed for each cluster.

produced by the combination of the Azores high, shifted to the north to be placed west of the British Islands coast, while a surface level low stays over the central Mediterranean. The fast westerly flows that characterise cluster 6 have been generated by a strong longitudinal baric gradient, caused when the Azores high is lightly shifted to the south of its normal position. This cluster includes the longest trajectories analysed.

The transition period between the occurrence of the longest trajectories in winter and the shortest ones in summer is characterised by the advection of moderate flows from Atlantic Western and Northern regions (clusters 2 and 5, respectively). They have occurred more frequently during the spring and autumn months and less during the summer (Fig. 3c). Moderate longitudinal flows (cluster 2) typically occur from October to April by the combination of two pressure systems at the synoptic scale. On the one hand, the Azores high is slightly shifted to the south. On the other, a deep low is centered northwest of the British Islands coast. This meteorological scenario favours the advection of Atlantic air masses towards the Iberian Peninsula. In addition to this, northeasterly moderate flows (cluster 5) have been more frequently observed in April and November (Fig. 3c). Two types of synoptic meteorological scenarios causing these flows have been observed. The first scenario has been associated with a shift of the Azores high towards the north and the presence of a trough that can be observed over Italy. In the second scenario, the most outstanding feature has been a low pressure system centered over the UK.

No clear seasonal trends were found for the occurrence of clusters 4 and 7 (Fig. 3d). These flows have been registered throughout the year, although they can be more likely in certain months. On average, during the period 1999–2005 North-African flows (cluster 4) have been more frequently produced in March, August, October and December. Different synoptic situations have been identified depending on the season. The winter meteorological scenario has been identified by a high pressure system centered over Argelia and extending from Western Sahara to Lybia (Fig. 4a). The spring transport scenario is characterised by a deep low centered west of the Portuguese coast (Fig. 4b). In the summer, the intense heating of the North-African surface generates the development of a thermal low. A compensatory high pressure system is formed in the upper atmospheric levels (850 hPa), frequently over Northern Argelia (Fig. 4c). During the autumn, the African high is shifted to the north and a trough is observed southwest of the Portuguese coast (Fig. 4d). Cluster 7 represents the transport of air masses from the European Continent towards the Iberian Peninsula, through the Mediterranean Sea. On average March, June and December were the months with a higher occurrence of this transport pattern, observed during the 1999–2005 period. The composite 850 hPa

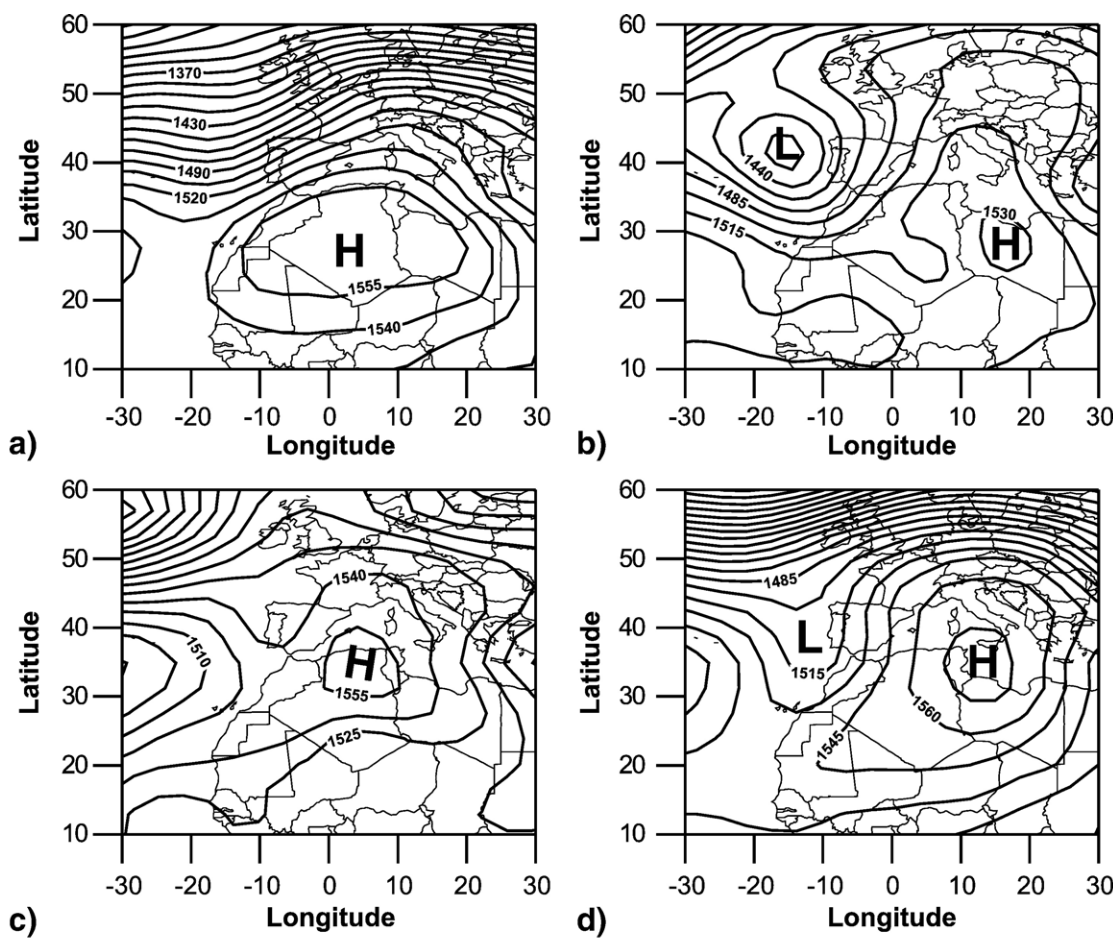

Fig. 4 – Composite 850 mb geopotential height (m) for the trajectories of the cluster 4 during the winter (a), spring (b), summer (c) and autumn (d) at 12:00 h UTC.

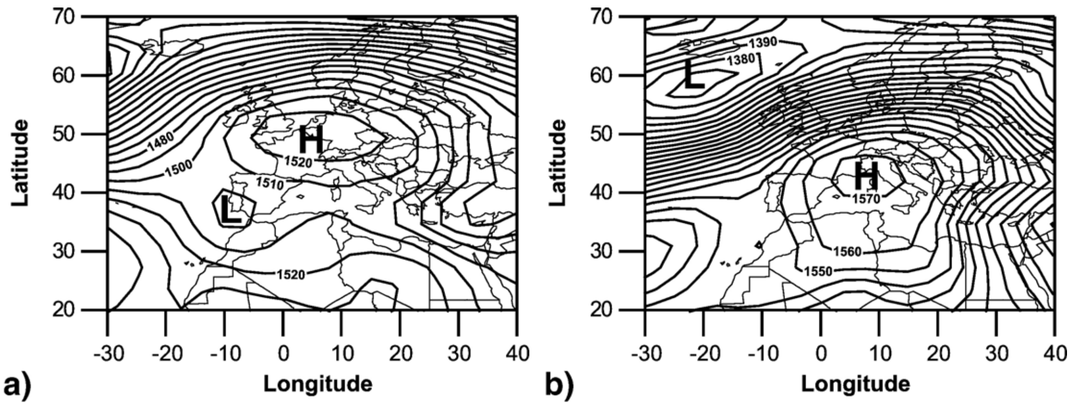

Fig. 5 – Composite 850 mb geopotential height (m) for the trajectories of the cluster 7 during the spring (a) and summer (b) at 12:00 h UTC.

geopotential height maps obtained for the winter and spring seasons show that it was produced by the presence of a strong high pressure system over the center of the European mainland (Fig. 5a). The typical summer meteorological scenario is similar to that which explains these atmospheric flows in winter and spring, but with a shift of the high pressure system towards the Mediterranean Sea (Fig. 5b).

3.2. *PM levels*

Table 1 shows the mean TSP, PM10, PM2.5, SO_4^{2-}, NO_3^- and NH_4^+ concentrations for all trajectory clusters arriving at Campisabalos. Kruskal–Wallis non-parametric tests indicated statistically significant differences in TSP, PM10, PM2.5, SO_4^{2-}, NO_3^- and NH_4^+ concentrations among clusters, at the 95% confidence level. This means that significant differences in receptor PM concentrations were observed between the air mass transport patterns.

TSP and PM10 concentrations associated with North-African air flows (Cluster 4) were significantly higher compared to the other clusters. This meteorological scenario can give rise to the transport of highly dust loaded air masses from North Africa desert regions to the Iberian Peninsula. It is well known that the Sahel and Sahara regions in North and West Africa respectively are important sources of dust particles that are transported in the troposphere to various distant areas. Previous studies have highlighted the incidence of these episodes, which are known as African dust outbreaks, on the surface PM levels recorded in different areas of the Iberian Peninsula (Querol et al., 2004a,b).

In marked contrast with the coarser fractions, mean PM2.5 concentrations levels associated with clusters 1 and 7 were significantly higher than in any of the other patterns. The mean nitrate and sulphate concentrations in PM10 associated with these clusters were significantly higher compared to those associated with maritime air masses and even with North-African flows. Similarly, sulphate and ammonium mean concentrations in TSP, associated with slow and moderate moving flows (clusters 1, 7 and 8) were significantly higher than mean concentrations observed for the other trajectory categories.

As stated above, cluster 1 and cluster 8 are characterised by a lack of significant air mass advection and the prevalence of recirculation of air masses. Taking this into consideration, the persistence of these scenarios has given rise to an increase in PM concentration levels with a local and regional origin. The high solar insolation degree usually associated with these events favours the formation of secondary inorganic compounds (SIC) by photochemical conversion. These are the main reasons why higher mean PM2.5, nitrate, sulphate and ammonium concentrations were registered during weak baric gradient situations at this rural background site in central Spain.

The fact that cluster 7 seems to influence PM2.5 and SIC concentrations suggests that a long-range transport of these compounds from highly-polluted European urban and industrial regions could contribute to increase the concentration values obtained in Campisabalos in these periods.

Overall, the Dunn test results have shown that PM mean concentrations associated with moderate and fast moving maritime air masses (clusters 2, 5 and 6) were significantly lower compared to those observed for other clusters (Table 1). Advections of Atlantic air masses are usually linked to frontal systems crossing the Iberian Peninsula from west to east. These atmospheric transport scenarios favour scavenging processes, such as high precipitation rates and strong winds, producing a drop in surface PM concentration levels. As for maritime air flows, the north-eastern air masses (cluster 3) were found to have significantly lower mean concentrations for most of the components. This atmospheric transport scenario gives rise to fast blowing winds that advect cold air mass from Northeastern European areas. The low PM concentration levels associated to this cluster suggests that long-range transport processes from European regions have no impact on surface PM levels under this meteorological scenario, or maybe that the strong winds reduce the PM levels by dispersion and dilution processes during the transport.

3.3. *Sampling campaigns*

Kruskal–Wallis tests have indicated significant differences between the clusters in receptor concentrations registered at EA, ALC and CHA for PM, crustal and SIC concentrations. The tests have not found statistically significant differences for the concentrations of carbonaceous aerosol (C) and most of the metals analysed at any location. This is interpreted as follows:

emissions of these compounds from local anthropogenic sources, mainly traffic and other combustion processes, have a stronger influence on their concentration levels than the origin of the air masses. Hence, it is not expected that long-range transport episodes will contribute to them. In the case of marine aerosol concentrations, the tests only found significant differences between clusters for CHA. The highest concentrations were associated with the fast and moderate maritime air flows (clusters 2, 5 and 6). The fact that these flows seem not to influence the marine aerosol concentrations in both urban EA and sub-urban ALC suggests that at these locations there are additional emissions of Cl^- and Na from local sources, such as motor vehicle exhaust or resuspended dust (Salvador et al., 2004) that are higher than at CHA.

Fig. 6 shows the mean PM, crustal and SIC levels for the PM10 and PM2.5 samples obtained at EA, ALC and CHA for the eight clusters. It can be clearly observed that the highest PM10 and crustal mean concentration values are associated with cluster 4, for EA, ALC and CHA. This means that during African dust outbreaks, PM10 concentration levels increase abruptly as a consequence of the transport of substantial amounts of mineral particles. The crustal load in the PM2.5 fraction also increased in these episodes. Nevertheless, this did not lead to a significant increase in the PM2.5 concentration mean value. This is a consequence of the dominant grain size mode in the coarse (PM10-2.5) range of elements typically associated with African dust (Alfaro et al., 1998). In addition to this, the regional recirculation meteorological scenario (cluster 1) was found to have the highest mean PM2.5 and SIC concentrations measured at ALC and CHA. This fact highlights the incidence of local and regional sources of fine particles and SIC precursors in the PM2.5 and SIC levels during regional episodes. However, very high mean PM2.5 and SIC values were also detected associated with air mass flows from the European mainland (cluster 7), the highest being registered at EA.

Another important consideration concerns the relationship of long-range transport episodes with exceedances of the PM10 daily limit value (50 μg/m^3) established by the European Air Quality Directive 1999/30/EC. At the urban monitoring site EA, the PM10 daily limit value was exceeded on 33% of the sampling days. The percentage of exceedances at the suburban and regional sites, ALC and CHA, ranged from 13% to 16% of the sampling days, respectively. The majority of the PM10 exceedances in the three monitoring sites (56% in CHA, 73% in ALC and 77% in EA) were attributed to local and regional sources. Most of these were caused during meteorological scenarios represented by trajectories associated with slow and moderate moving flows (clusters 1 and 8). However, exceedances registered during North-African transport scenarios were not infrequent, representing 38%, 18% and 14% of the total number of exceedances in CHA, ALC and EA, respectively. European transport scenarios accounted for a lower proportion of the PM10 daily exceedances, 6% in CHA, 9% in ALC and 9% in EA. From March 2001 to December 2005, 19 exceedances of the PM10 daily limit value were registered at Campisabalos. Most of these, 18 out of 19, occurred during African dust outbreaks. Only 1 exceedance was attributed to emissions of PM from local and regional sources.

3.4. *RTA results*

Figs. 7 and 8 show the maps with the CPF values for extreme concentrations (higher than the 90th percentile) of TSP, PM10, PM2.5, SO_4^{2-}, NO_3^- and NH_4^+, recorded in Campisabalos. This analysis has been carried out for every single year of the study

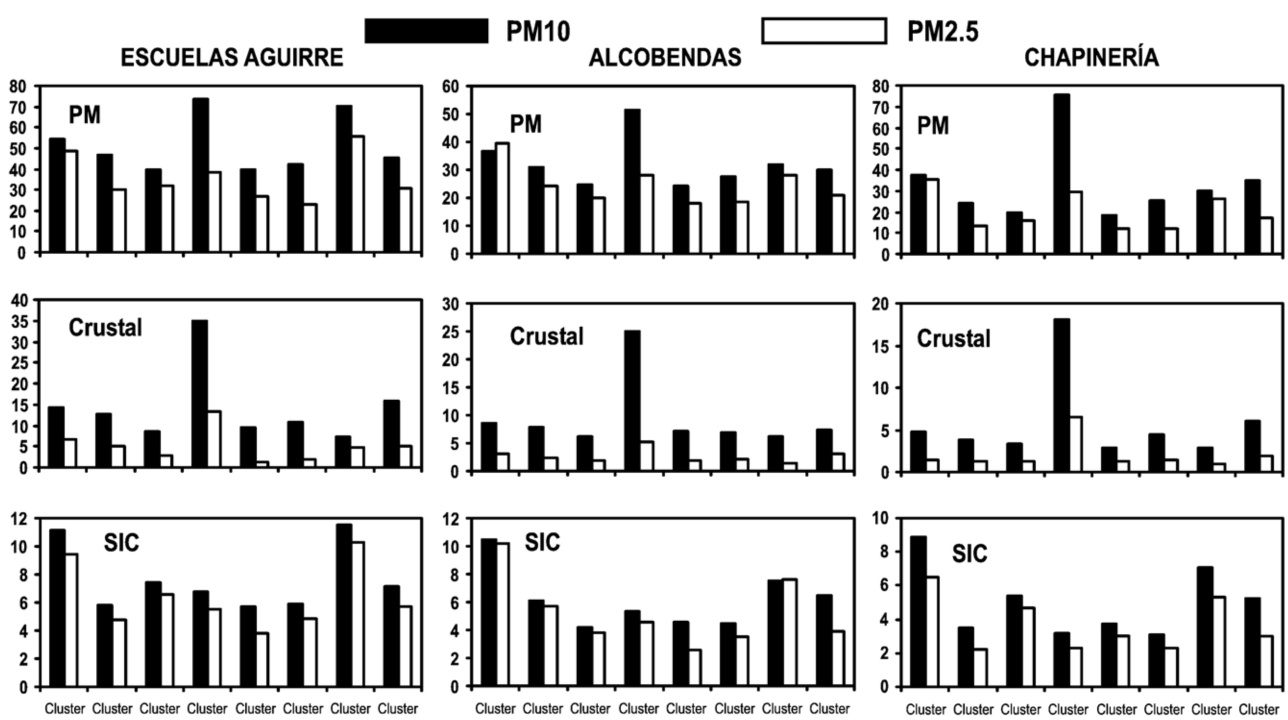

Fig. 6 – Mean PM, crustal and SIC concentration levels (in μg/m^3) for the PM10 and PM2.5 samples by cluster, registered at EA, ALC and CHA monitoring sites.

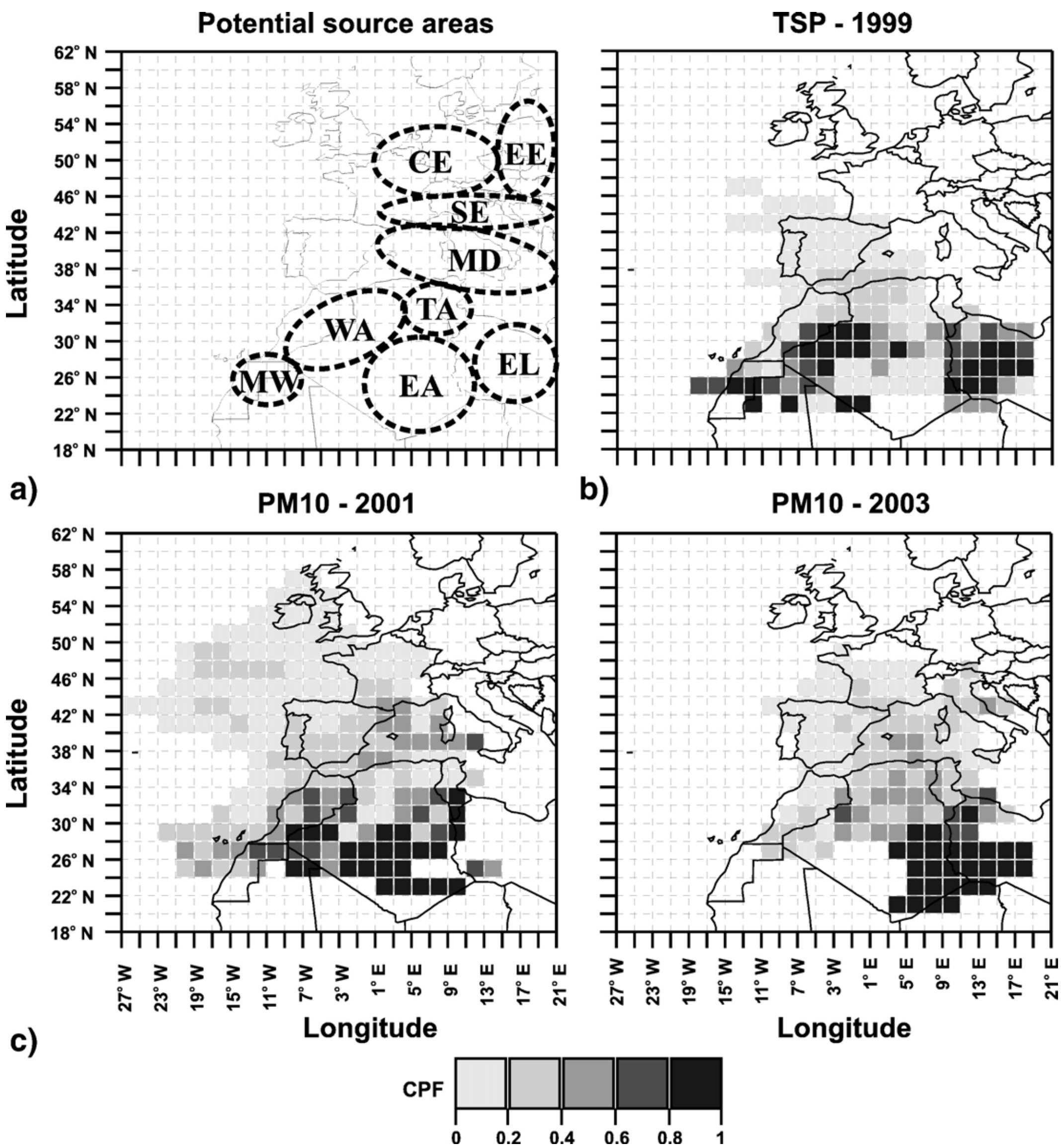

Fig. 7 – Predefined source areas of PM considered in the RTA. CE, central Europe; EE, Eastern Europe; SE, Southern Europe; MD, western and central Mediterranean; TA, Tunisia and Northeast Algeria; WA, Western Algeria; EA, Eastern Algeria; EL, Eastern Libyan desert; MW, Mauritania and Western Sahara (a). CPF values for extreme values of TSP for the year 1999 (b) and PM10 for the years 2001 and 2003 (c). Only significant CPF values at the 95% confidence levels are displayed.

period, since external source regions may change from one year to another. Different geographic areas have been considered as potential source areas of PM (Fig. 7a). The most significant results have been displayed in these figures.

Moderate to high CPF values (>0.4) for TSP and PM10 were found in different North-African regions depending on the year (Fig. 7b and c, respectively). In this work the regions determined by Prospero et al. (2002) and Escudero (2006) have been considered as the main potential source areas of dust over North Africa (Fig. 7a). Among these, the greatest potential contributions to PM concentration were located in Tunisia and Northeast Algeria – TA (years 2001 to 2005), Eastern Libyan desert – EL (years 1999, 2003, 2004 and 2005), Mauritania and Western Sahara – MW (years 1999, 2001, 2004 and 2005), Western Algeria – WA (years 1999, 2000, 2001, 2002 and 2003) and Eastern Algeria – EA (years 2001, 2003 and 2004).

In the case of PM2.5 and the SIC, the following regions have been considered as the main potential source areas (Fig. 7a): the western and central Mediterranean – MD, Southern Europe (regions of southern France, Italy and the Balkan Peninsula) – SE, central Europe (regions of France, Germany, Holland, Belgium, Swiss and Austria) – CE and Eastern Europe (regions of Poland, the Czech Republic and Hungary) – EE.

Cells with significant moderate to high CPF values were found in the following potential source areas, for the years or periods specified in parentheses (Fig. 8): SE has been identified as a potential source area of PM2.5 (2002, 2003 and 2005), NH_4^+ (1999–2000), SO_4^{2-} (1999–2000, 2003–2005) and NO_3^- (2005); CE has been considered as a potential source area of PM2.5 (2004), NH_4^+ (1999), SO_4^{2-} (1999, 2003–2004) and NO_3^- (2003–2004); and EE has been recognised as a potential source area of SO_4^{2-} (2003 and 2005) and NO_3^- (2003 and 2005). MD has also been identified

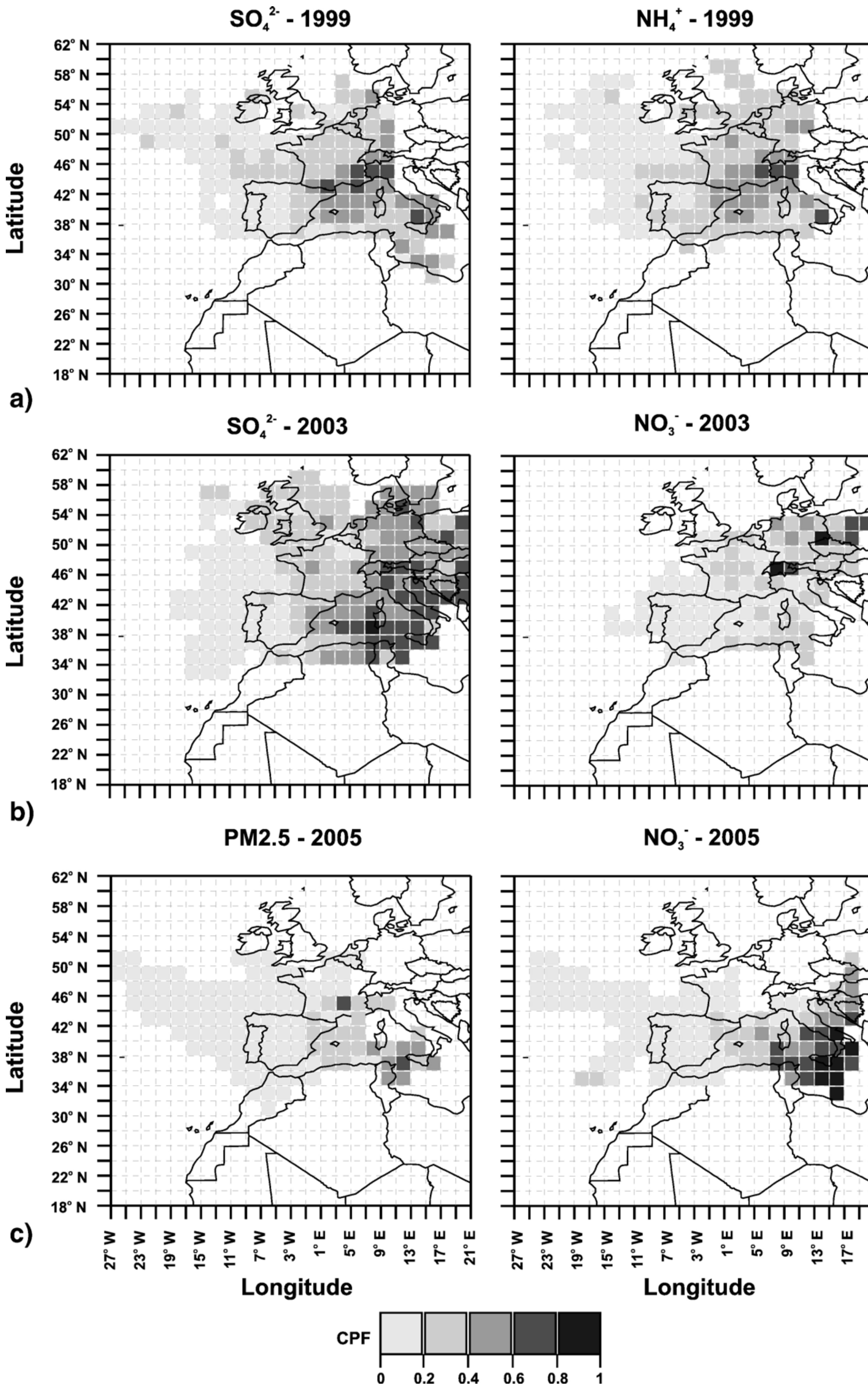

Fig. 8 – CPF values for extreme values of SO_4^{2-} and NH_4^+ obtained in TSP samples for the year 1999 (a), SO_4^{2-} and NO_3^- obtained in PM10 samples for the year 2003 (b) and PM2.5 and NO_3^- obtained in PM10 samples for the year 2005 (c). Only significant CPF values at the 95% confidence levels are displayed.

as a potential source area of PM2.5 (period 2001–2005), NH_4^+ (year 1999), SO_4^{2-} (1999–2005) and NO_3^- (2004–2005). This can be explained by the transport of polluted air masses with a high content of fine particles and SIC, originating in European source areas and moving southward over the Mediterranean Sea. As a result of re-circulations within the western Mediterranean basin, they may remain there for some days before reaching the Iberian Peninsula. There are experimental evidences that, during the warm season, there is a persistent southward flow of European pollution into the western and central Mediterranean basin at the lower troposphere (Millán et al., 1997; Gangoiti et al., 2001). European emissions together with fresh local emissions are trapped into atmospheric recirculation flows, giving rise to the formation of tropospheric O_3 reservoir layers. Air mass re-circulations lasting more than 5 days have been documented in previous works for trajectories entering the western Mediterranean basin at the Gulf of Lyon (Gangoiti et al., 2001). This is the reason why 5-day back-trajectories cannot describe the complete process of transport from the source areas and the recirculation flows within the Mediterranean basin.

This confirms the results obtained by CA, which suggested that under specific meteorological scenarios a transport of fine particles of continental European origin with a high content of SIC takes place. Beverland et al. (2000) and Abdalmogith and Harrison (2005) have reported evidences of the influence of this phenomenon on the PM10 and SIC surface levels recorded at different points of the UK. In addition, modelling studies have shown that emissions from Southern Europe can be transported to the tropical Atlantic and America following several pathways (Gangoiti et al., 2006). Although Salvador et al. (2007) have identified long-range transport processes of NO_3^- from central and eastern Europe to north-western Spain, these episodes are very complex to identify and quantify because they are closely linked to simultaneous local and regional anthropogenic pollution episodes. It should be stressed that Borge et al. (2007) identify long-range transport influences from continental Europe on urban PM10 registered at Birmingham, but not at Madrid. The present paper considers a longer period, 7 years, and interprets a more comprehensive data set of PM levels and chemical composition at different grain sizes from representative monitoring sites including rural and urban background sites. Hence, we have been able to identify this external influence on PM2.5 and SIC concentration levels at the Madrid air basin.

4. Conclusions

In this work different statistical techniques have been applied to a set of 7 years of back-trajectories to describe the main flow patterns over central Spain. The results have also been used to interpret PM levels and composition registered at a rural background station in this area, and to identify geographical areas for remote PM sources.

Air mass back-trajectories have been grouped into 8 clusters, each one representing a characteristic meteorological scenario. Results have shown a marked longitudinal component in the transport patterns of the air mass towards central Spain. A clear seasonal pattern has been observed with marked fast westerly and north-easterly flows during the winter, to low baric gradient situations in summertime. Frequent moderate Atlantic flows have been observed during transition periods in spring and autumn.

Significant differences in concentrations of receptor PM (TSP, PM10, PM2.5, SO_4^{2-}, NO_3^- and NH_4^+) have been observed between the trajectory patterns at the background monitoring station under study. The CA and RTA results have shown the high influence of long-range transport processes from different north-African desert regions in the TSP and PM10 levels recorded in the center of the Iberian Peninsula. In addition, they have provided associations of high PM2.5 and SIC concentrations with trajectories arising within the European mainland and the western and central Mediterranean basin. The analysis of data registered at urban and sub-urban sites in the Madrid air basin during sampling campaigns, confirms that PM10 and PM2.5 mean concentrations rise above their mean values during North-African and European episodes as a consequence of the transport of mineral particles and SIC respectively.

These results imply that the effectiveness of abatement strategies for achieving compliance with the European air quality standards in the center of the Iberian Peninsula might be compromised by long-range transport processes. These episodes caused 23%, 27%, 44% and 95% of the total number of exceedances of the PM10 daily limit value at the urban, suburban, regional and rural background monitoring sites respectively. Most of them have been attributed to African dust outbreaks. The main meteorological scenarios that give rise to them have been described in this paper. This information can be used as a complementary tool for their prediction, analysis and interpretation.

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