

Identification and characterisation of sources of PM₁₀ in Madrid (Spain) by statistical methods

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Abstract

A source apportionment study was performed to characterise PM₁₀ sources in the urban area of Madrid. Receptor modelling techniques were applied to obtain the different source contributions, identifying four main sources that contribute to most of the analysed PM₁₀ mass, namely: road traffic, crustal/mineral, secondary and marine aerosol. PM₁₀ mean concentration and chemical profile were obtained for each source category by multilinear regression analysis. Road traffic was found to be the major contributor to the PM₁₀ mass (48%), together with crustal (26%) and secondary particles (18%). A minor contribution has been associated to marine aerosol (3%), while 5% of the PM₁₀ mass has been attributed to non-identified sources. An analysis of the geographical origin was performed for remote sources. Residence time probability values were calculated based on air mass back trajectories information. Different elements have been selected as tracers of the sources. Desertic regions from North Africa have been identified as the most significant source area for crustal particles, with a high content of Al and Ti. Atlantic ocean regions have been identified as weak to intermediate source areas of Na, supporting the marine source identified by the factor analysis. Then the influence of remote natural sources on the PM₁₀ levels in central Spain has been detected by the use of single components as tracers, even at urban sites highly affected by traffic.

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1. Introduction

The entry into force of the EU-Directive 1999/30/CE on air quality revealed the gap on existing information concerning particulate matter and indirectly their sources. This was particularly critical for PM₁₀ (airborne particulate matter with aerodynamic diameter < 10 µm), the particle fraction for which an annual limit value (20 µg m⁻³) and a 24 h limit value (50 µg m⁻³) not to be exceeded more than 7 ds/yr, have been established. These limits will be in force by 2010. Exceedances of

the daily limit value due to natural events, should be informed and justified to the Commission.

In Spain the information provided by local and regional air quality monitoring networks mainly refers to TSP or PM₁₀ ambient concentration levels. This, together with the variety of natural and anthropogenic sources and atmospheric processes affecting specific areas, makes it highly difficult to gain a deeper insight on PM₁₀ sources and thereby establish abatement strategies. Furthermore, diffuse sources and long range transport processes can also play a role in the source apportionment.

Recent studies on PM₁₀ levels assessment in different Spanish areas have shown high particulate matter concentrations recorded in several urban and industrial

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areas (Artiñano et al., 2001, 2003a, b; Querol et al., 2001a, b, 2002). Even at rural background stations, concentration levels exceeded or were very close to the annual limit value (Querol et al., 2003) pointing at natural contribution as an important particulate matter source in this country. Long-range transport processes have also been pointed out as a significant source of natural particles, and the influence of Saharan dust outbreaks on PM₁₀ levels has been specifically addressed in several of these works (Querol et al., 1998, 2002; Rodríguez et al., 2001). Artiñano et al. (2001, 2003a) show evidences and describe some of these events affecting the Madrid area. Chemical characterisation of particulate matter constitutes a key tool for understanding the sources and some of the atmospheric processes involved.

Mathematical techniques based on receptor modelling allow identification of aerosol sources and assessment of their relative mass contribution. These use as input the ambient airborne particle concentrations obtained at the sampling site and apportion them among possible sources considered. Receptor modelling techniques have been reviewed by Henry et al. (1984), Thurston and Lioy (1987) and Gordon (1988) and have been extensively used in particulate matter source apportionment studies (Henry and Hidy, 1979; Alpert and Hopke, 1981; Pio et al., 1989; Glover et al., 1991; Chow et al., 1992). The most commonly used ones are the chemical mass balance (CMB) and multivariate models such as factor analysis. Since the CMB technique assumes a previous knowledge of the sources and their composition, not totally available for the Madrid site, factor analysis has been used in this case. This technique provides the main factors or sources that can be identified, but provides no information on their local or external origin and even less on their geographical location. This requires information on the origin of the air mass arriving at the sampling site, related to the meteorological and atmospheric dynamics conditions, from local to larger scales.

Air mass back-trajectories are computed by meteorological models and analysed jointly with pollutant concentrations. The simplest and most frequently used analysis involves mapping single trajectories for days of interest, considering that they establish a direct link between a source and a receptor. In addition to the uncertainties associated to trajectory models, it must be assumed that a trajectory is just an estimation of the general pathway of an infinitesimally small air parcel (Kahl, 1993). In view of this, statistical methods that employ large trajectory ensembles are more suitable (Stohl, 1998). Some statistical techniques have been developed for identifying pollutant source regions combining air back trajectories information and concentrations of any element measured at the sampling place. One of these, known as residence time analysis

(Ashbaugh et al., 1985), proposes using different functions to determine the geographic origin and transport pathways of air masses that arrive at a site under any given pollution scenario. This technique has been applied successfully for years to locate sulphur source areas affecting National Parks in the USA (Ashbaugh et al., 1985; Malm et al., 1990), acid rain sources, (Zeng and Hopke, 1989; Hernández et al., 1996), gaseous pollutants (Rúa et al., 1998) and particulate matter components (Gao et al., 1994; Gebhart et al., 2001). This work uses the conditional probability function (CPF) (Ashbaugh et al., 1985) which involves determining the probability of air masses arriving at the receptor from different locations under specific conditions.

In this case, the set of data used was obtained in a comprehensive experimental study (Artiñano et al., 2003a) carried out at an urban site in Madrid. Firstly, a factor analysis was performed to identify the main particle sources affecting this site. Then the main compounds associated with each source were determined by multilinear regression. Finally, geographical areas or origin regions were identified for remote or external particle sources using specific compounds as tracers.

2. Methodology

2.1. Experimental

The experimental part of the particulate matter study was performed from June 1999 to May 2000. PM₁₀ measurements were carried out by means of a MCV high-volume sampler (flow rate 30 m³ h⁻¹) with a DIGITEL cut-off inlet. Sampling was performed twice per week on working days collecting a total of 67 PM₁₀ daily samples. The sampler was located at a representative urban monitoring station (Escuelas Aguirre) belonging to the municipal network, located at a heavy traffic street intersection in downtown Madrid (Fig. 1). The distance to the kerbside was approximately 5 m.

Daily PM₁₀ ambient air concentrations were determined by gravimetry from filters collected throughout the sampling period. Quartz fibre filters were used for subsequent chemical analysis of carbon, anions and major and trace elements. A detailed explanation of the experimental details and the analytical procedures can be found in Artiñano et al. (2003a) and Querol et al. (2001a, b).

2.2. Statistical methods for data treatment

A varimax rotated factor analysis (FA) was performed to identify the main sources affecting the aerosol composition at the sampling site. In this statistical

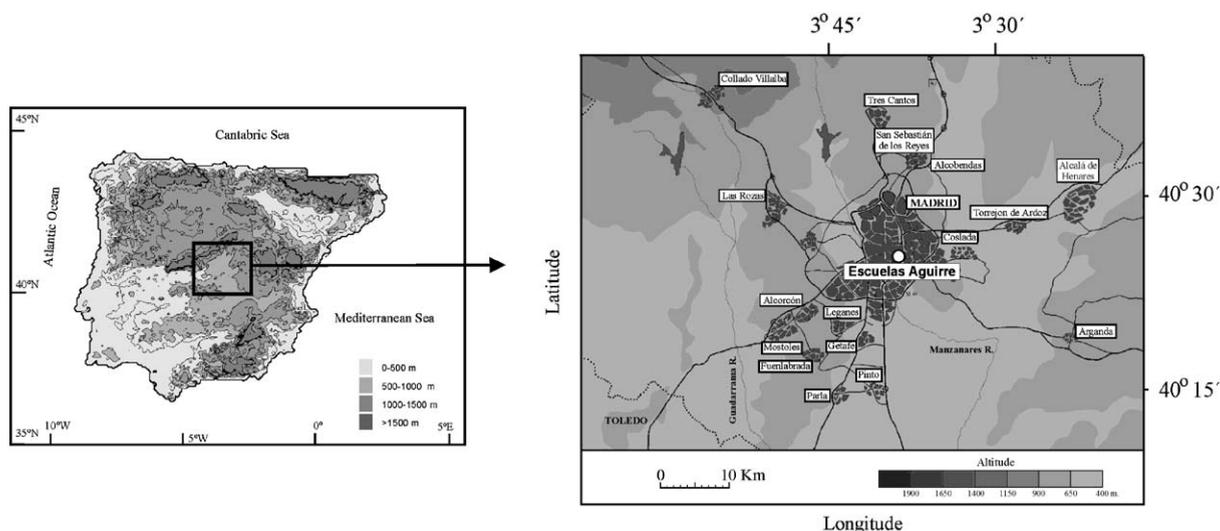


Fig. 1. Location of the Iberian Peninsula (left) and the Madrid metropolitan area (right) represented by the city of Madrid and satellite towns. The location of Escuelas Aguirre monitoring site is shown in the city centre. Main roads are also depicted in this figure.

method a set of multiple intercorrelated variables (the chemical elements analysed) is replaced by a smaller number of independent variables (factors) by orthogonal transformations (rotations). This is achieved by diagonalising the correlation matrix of the variables, i.e. by computing their eigenvalues and eigenvectors (Henry and Hidy, 1979). Each factor is a linear combination of the original variables that explain a maximum of the total variability of the data set, and is uncorrelated with the rest. The coefficients of the linear combinations (loadings) represent the degree of correlation between the variables and the factor. Thus, the chemical elements with higher loadings in each factor are interpreted as fingerprints of the emission source that it represents. Since interpreting the FA results is not straightforward, the factors are usually rotated again following a maximisation criterion that tends to drive their loadings towards either zero or one. The most frequently used one is the varimax rotation (Thurston and Spengler, 1985a).

After running a FA a number of factors equal to the number of variables is obtained. However, not all of them have a physical meaning and just the first few factors typically explain almost all the variability of the original data. The decision of which eigenvectors to retain is not straightforward. If the data have been previously normalised (with mean zero and standard deviation equal to one), the most commonly used criterion is to retain those factors with eigenvalues greater than one, since they explain more variance than the original variables. The normalisation procedure is recommended to equalize the opportunity of both large and small magnitude variables to influence the analysis.

The main limitations of multivariate techniques are that they can only recognise a limited number of individual sources (about eight) and that the data set must contain a high enough number of samples, preferably no less than 50 (Henry et al., 1984; Thurston and Spengler, 1985b). Obtaining reliable results with this procedure also requires analysis of a set of elements including known source tracers for each major sources. In this case 67 PM_{10} samples were available, for which 22 components were chemically determined.

After the identification of the main PM_{10} sources, the respective quantitative contributions were derived. In this work the methodology described by Thurston and Spengler (1985b) was used. Multilinear regression analysis (MLRA) was applied, using PM_{10} as the dependent variable and absolute factor scores (AFS) as independent variables. The scores are the result of inserting the daily values of each element in the factor equations. Since the element values are previously normalised, the resulting scores are also normalised so that they refer to the mean value. Thurston and Spengler (1985b) proposed obtaining the score for an artificial sample with concentrations equal to zero for all the variables, and then obtaining new scores, the AFS, by subtracting this zero-score from the original ones. In this way the AFS are now referred to a true zero, being proportional to the daily sources impact. Estimations of the daily source contributions are obtained as the product of the daily AFS and the multilinear regression coefficients. The interception constant represents the amount of PM_{10} mass not explained by the sources identified. Having done this, the source profiles for each element can be derived by regressing their daily

concentration values on the estimated daily source contributions. This procedure is comprehensively described in the works of Thurston and Spengler (1985b) and Harrison et al. (1996).

Finally, conditional probability functions (CPF) have been used to identify external contributions produced by long-range transport processes. They allow establishment of a connection between the PM₁₀ sources and the most probable origin of the air mass sampled using back-trajectories information.

Air mass back-trajectories have been calculated with the HYSPLIT_4 model (Draxler and Hess, 1998a, b). Every sampling day, a 4-day back-trajectory was computed at 00:00, 06:00, 12:00 and 18:00 h UTC, and at different heights above the starting point located at ground level, (750, 1500, 2500 and 3500 m AGL). Meteorological data fields supplied by the National Climatic Data Center (NCDC, USA), have been used as input. The model output is a set of latitude–longitude coordinates of the air parcel estimated position for every hour.

A 2° longitude × 2° latitude cells grid has been superimposed over the region defined by 18°N–62°N and 27°W–21°E. The CPF for the *ij*th grid cell is defined as the ratio between m_{ij} and n_{ij} , where n_{ij} is the number of trajectory segment endpoints falling into the *ij*th grid cell, for all the trajectories computed during the whole study period, and m_{ij} the number of endpoints corresponding to all the trajectories that arrived at the sampling place, when pollutant concentrations higher than a pre-specified value were recorded. This function 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 a specific geographical cell. Areas with high CPF can be considered as source regions of the pollutant under study. It must be pointed out that the same air mass that crossed a source region could travel through another adjacent region which can not be considered a source region. This is why marine areas may have high CPF values associated (Rúa et al., 1998) as they can be identified as preferred air mass pathways. However, it must be assumed that the CPF values obtained at any area could be accidentally high, implying that there is no association between the surface concentrations and the pathways of arriving air. Due to this it is necessary to check the statistical significance of every grid cell CPF value. To determine this Vasconcelos et al. (1996) proposed two statistical tests, one using a bootstrapping technique and the other one based on the binomial distribution. Since the binomial test is the most commonly used one, due to its greater computational simplicity compared to the other technique this was the one used in this study.

As the sampling site was located at an urban environment affected by traffic emissions, the influence

of external PM₁₀ contributions will only be noticeable in extreme cases. This is why the CPF has been computed at each grid cell only for the sampling days with critical values of the element considered, i.e. higher than the 90th percentile (Gebhart et al., 2001). The analysis has been performed for those elements that presented the highest contribution for each source category.

3. Results and discussion

The mean concentration values and standard deviations of major and selected trace components in the PM₁₀ samples for the study period, are summarized in Table 1. The sum of the experimentally determined species, accounted for a mean of 83% of the bulk PM₁₀ mass concentration for the study period. The lowest and extreme mass concentration values of PM₁₀ were 20 and 113 μg m⁻³ respectively during the measurement period.

3.1. FA and multilinear regression results

Multivariate analysis of the PM₁₀ data for Madrid, has revealed four factors with eigenvalues > 1 (Table 2). These four sources have accounted for 87% of the PM₁₀ variance in Madrid. The communalities, which represent

Table 1

Arithmetic mean concentration and standard deviation of major and trace components of PM₁₀ obtained at Escuelas Aguirre, from June 1999–May 2000

		Mean	Standard deviation
PM ₁₀	μg m ⁻³	47.68	20.77
C	μg m ⁻³	15.67	8.42
NH ₄ ⁺	μg m ⁻³	1.15	0.63
SO ₄ ²⁻	μg m ⁻³	4.46	1.88
NO ₃ ⁻	μg m ⁻³	2.09	1.63
Al	μg m ⁻³	0.97	0.7
Ca	μg m ⁻³	1.92	0.94
Na	μg m ⁻³	0.31	0.15
K	μg m ⁻³	0.39	0.23
Fe	μg m ⁻³	1.93	0.88
Mg	μg m ⁻³	0.25	0.15
Cl	μg m ⁻³	0.38	0.29
Pb	ng m ⁻³	118	66
Cu	ng m ⁻³	112	56
Zn	ng m ⁻³	93	53
Ba	ng m ⁻³	82	37
Ti	ng m ⁻³	56	39
P	ng m ⁻³	56	22
Mn	ng m ⁻³	22	11
Cr	ng m ⁻³	9	15
Sr	ng m ⁻³	8	5
Ni	ng m ⁻³	4	5
V	ng m ⁻³	4	3

Table 2
Factor analysis pattern after varimax rotation for PM₁₀ elements concentrations

	Factor 1	Factor 2	Factor 3	Factor 4	Communalities
C	0.17	0.90	−0.01	0.02	0.85
Al	0.98	0.07	−0.02	−0.01	0.96
Ca	0.84	0.47	0.09	0.09	0.95
K	0.93	0.24	0.04	0.03	0.92
Mg	0.95	0.23	0.05	0.14	0.97
Mn	0.66	0.67	0.16	0.00	0.91
Sr	0.70	0.26	0.35	0.13	0.69
Ba	0.40	0.84	0.23	0.07	0.93
Zn	0.17	0.81	0.34	0.11	0.82
V	0.52	0.19	0.57	0.24	0.69
Cu	0.26	0.89	0.24	0.03	0.92
Ti	0.94	0.21	−0.02	0.03	0.93
P	0.58	0.66	0.10	−0.15	0.80
Fe	0.55	0.79	0.16	0.05	0.95
Pb	0.19	0.91	0.23	0.04	0.92
NH ₄ ⁺	−0.10	0.14	0.89	−0.19	0.87
SO ₄ ^{2−}	0.21	0.29	0.86	−0.01	0.87
NO ₃ [−]	−0.12	0.63	0.60	0.05	0.77
Cl	−0.36	0.47	−0.24	0.63	0.80
Na	0.47	−0.10	0.01	0.79	0.86
Eigenvalues	6.89	6.53	2.76	1.21	
Total variance explained	34.4%	32.6%	13.8%	6.1%	86.9%
Source	Crustal	Traffic	Secondary	Marine	

Factor loading values greater than 0.60 are in bold.

the amount of variance of each element explained by the factorial model, are also given in this table.

The lowest communalities were obtained for Sr and V. These trace metals and others such as Cr and Ni are present in very low concentrations, close to the analytical detection limit in most cases (Table 1), pointing at the lack of significant sources of these elements near the sampling site. Cr and Ni have not been included in the final model as they always have contributed as unique factors in the FA, with eigenvalues < 1.

The first factor obtained contains large loadings of crustal elements such as Al, Mg, Ti, K, Ca and Sr, pointing at soil dust as the main source involved. This can be the result of local and regional dust resuspension by wind and convective processes, and for long-range transport of mineral dust. These elements are major compounds of African (Saharan or Sahel) dust, whose mineral composition includes clay minerals apart from quartz, calcite and dolomite (Coude-Gaussen et al., 1987; Avila et al., 1997). It is noticeable that elements such as of Fe and Mn which are usually good fingerprints of African mineral dust, only presented moderate loadings in crustal factor. Also noteworthy is

the relative high loading of V in this factor. V(III) is one of the classical substitutes of Al(III) in the clay structure. Thus, this implies that most of V in PM₁₀ in this area arises from natural sources.

The second factor has been related with road traffic, since it explains most of the variance of total C and Pb. It is also correlated with Cu, Zn, and NO₃[−]. Cu and Zn can be associated with tyre wearing (Harrison et al., 1996). In addition, Zn has been suggested as a good marker for unleaded fuel powered motor vehicle emissions (Huang et al., 1994). The positive NO₃[−] loading is related to the atmospheric oxidation of the NO_x emitted by motor vehicles. Cl presents a relatively high loading and is explained as being an additive to petrol in form of ethylene dihalide ‘scavenger’ (C₂H₄Cl₂). The moderate to high loadings of typical crustal elements such as Fe, Mn and Ca, indicate a contribution of soil dust resuspended by local traffic flow included in this factor. The Ca contribution arises mainly from the pavement abrasion. Besides, Fe and Mn can be also produced by brake-drum abrasion (Harrison et al., 1996). Brake linings can be enriched in Ba, explaining their high loading in this factor (Hopke et al., 1980).

The next factor represents the formation of secondary inorganic aerosols due to their high loadings for SO_4^{2-} , NO_3^- and NH_4^+ . A moderate loading value has been found for V, which is considered a tracer element of fuel–oil combustion. It suggests that an additional source of secondary particles could be the SO_2 emissions produced by combustion sources other than traffic, such as heating devices in the fall–winter season. This could also account for further NO_3^- emissions. Hence, this factor probably represents the regional background of secondary inorganic pollutants in Central Spain, together with the local contribution of combustion sources.

The last significant factor can be interpreted as marine aerosol, based upon its good correlation with Cl and Na. Although Madrid is not under the direct influence of sea salt spray, it has been found that Cl^- and Na^+ ions are major compounds of wet deposition collected in the central area of the Iberian Peninsula especially associated with the passage of Atlantic frontal systems (Hernández et al., 1996). Thus, although present in low levels, this natural source should be considered.

After the main sources affecting PM_{10} at the sampling site were identified their contribution to the daily levels were assessed. The AFS have been computed for each sample and factor following the procedure previously described. The PM_{10} mass concentrations for the samples were then regressed on the AFS. The results of the analysis of the variance have shown that this relationship could be considered statistically significant at a 99% confidence level, while the adjusted coefficient of multiple determination R_a^2 , indicated that the model explains 95% of the PM_{10} variability. All the regression coefficients were statistically significant at the 95% confidence level and even at the 99%, except the marine coefficient. They were then used to convert the daily AFS to estimates of the PM_{10} source mass contributions.

On average, road traffic has been the major mass contributor accounting for 48% of the PM_{10} mass. Otherwise, crustal and secondary particles explained 26% and 18% of the bulk mass respectively, while sea-salt has just represented only 3%. The contribution of the non-explained sources has been estimated to be roughly 5%. Fig. 2 shows a good fitting between predicted and experimental PM_{10} values. A residuals analysis has been performed contrasting homocedasticity (error variance equal over all observations), normality and linear independence. It did not detect any serious correlation in the residuals nor observations significantly deviated from the model predictions.

Fig. 3 shows the time series of PM_{10} source contributions expressed as percentages. Crustal PM_{10} mass contribution has been higher in summer and during sporadic Saharan dust outbreaks, marked with

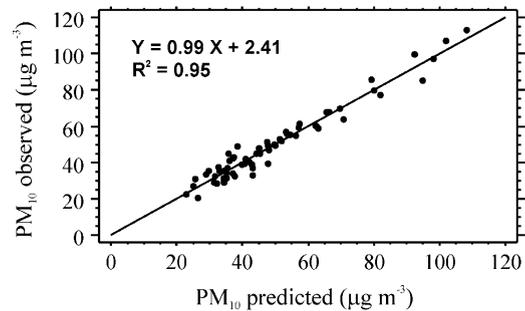


Fig. 2. Comparison of observed daily PM_{10} concentrations and predicted with the model.

black arrows in Fig. 3. These specific episodes have been documented by Artúñano et al. (2003a). The traffic related PM_{10} contribution shows a marked seasonal trend typical of urban environments, with a maximum during autumn and winter and a minimum in July and August. The highest values for this source category have been recorded during typical autumn–winter pollution episodes, linked to stagnant meteorological conditions, as described by Artúñano et al. (2003a, b). Secondary aerosols contribution during summer and autumn has been higher on average than during winter and spring, possibly due to the enhanced atmospheric photochemical activity which drives the formation of secondary particles, especially $(\text{NH}_4)_2\text{SO}_4$ (Harrison and Jones, 1995). Finally, although there is not a clear seasonal trend for sea-salt, the marine aerosol contribution seems to be higher during the winter–spring term, when the Atlantic frontal systems have been more frequent (white arrows in Fig. 3). In contrast during summer months, when these frontal systems scarcely occur, the Cl concentration values have been the lowest obtained through the sampling period. The negative loading of Cl in the crustal and secondary factors (Table 2) can now be explained because during this season, crustal and secondary PM_{10} sources have reached their highest values.

The source profiles were then obtained by regressing the daily mass concentrations of each element on the daily sources contributions. Table 3 shows the MLRA results for each PM_{10} component, expressed as the mass percentage attributed to each source. Only statistically significant mass contributions (at the 99% confidence level), have been depicted. A residual analysis was carried out again in each case, to verify the validity of the models. When a negative value was obtained for the interception constant (which represent the mass contribution of non identified sources), the multilinear regression was forced to pass through the origin since it has no physical meaning (Harrison et al., 1996; Pio et al., 1998).

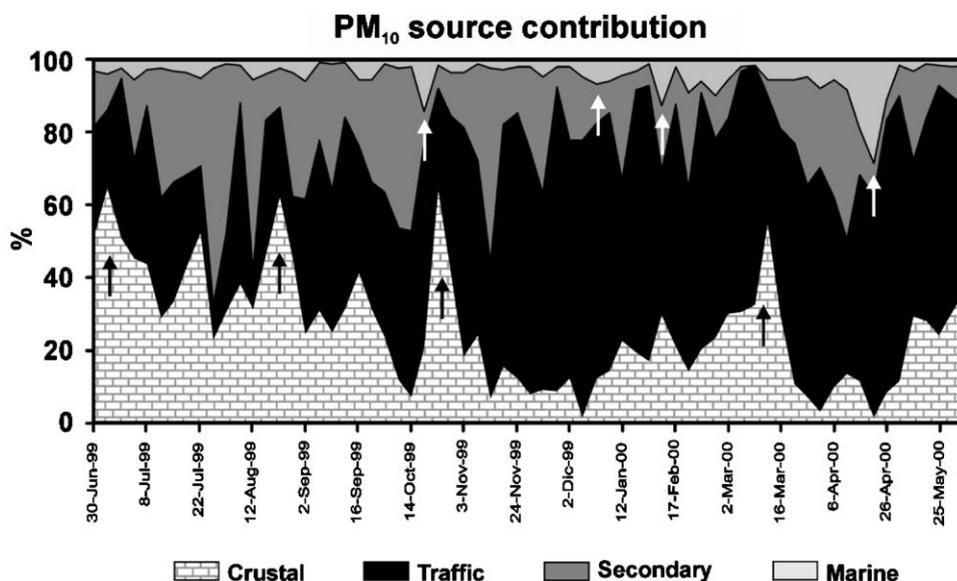


Fig. 3. Time series of recorded PM_{10} daily source contributions, expressed as percentages, at Escuelas Aguirre from June 1999 to May 2000. Black arrows highlight the identified Saharan dust events in the crustal source category. White arrows indicate the main peaks in the Marine source category produced during the passage of Atlantic frontal systems.

Table 3
Multilinear regression analysis results

PM_{10}	Crustal	Traffic	Secondary	Marine
PM_{10}	26	48	18	3
C	11	82		
Al	84	10		
Ca	48	37	6	6
K	68	22		
Mg	68	22		10
Mn	38	53	10	
Sr	56	26	20	
Ba	22	60	12	
Zn	10	68	22	
V	38	18	38	
Cu	15	71	14	
Ti	72	27		
P	32	50	12	
Fe	29	59	9	
Pb	7	82	15	
NH_4^+		27	75	
SO_4^{2-}	13	32	56	
NO_3^-		72	34	
Cl				49
Na	32		8	55

Values are presented as mass contribution (%) of PM_{10} and components attributed to each source. Only statistically significant contributions at 99% confidence level are shown.

The element with highest contribution to the crustal source has been Al (84%), while Ti, Mg and K have presented roughly 70% of their mass associated to this

source. About 50% of the Sr and Ca mass obtained in Escuelas Aguirre, has also been related to this category. From 22% to 40% of levels of Mn, Ba, V, P, Fe and Na in PM_{10} have also a crustal origin. About 10% of the C mass is associated with this source, probably derived as carbonate associated to Ca and Mg. The traffic category explains more than 80% of the C and Pb mass, about 70% of NO_3^- , Cu and Zn and 37% to 60% of Fe, Ca, Mn, Ba and Cl. It is the result of sampling in an urban area directly affected by intense traffic emissions, i.e. a kerbside site, being in accordance with other results carried out in similar environments (Pio et al., 1998; Querol et al., 2001b). In the case of secondary inorganic aerosols, most of NH_4^+ and half of the SO_4^{2-} is related to this source category. Ionic balance studies point to SO_4^{2-} being associated with NH_4^+ as the predominant cation forming mainly $(NH_4)_2SO_4$ and/or NH_4HSO_4 (Harrison and Jones, 1995). Also around 35% of V and NO_3^- , is related to this category. In the case of NO_3^- , it is produced in a higher proportion by the vehicular than the secondary sources, 72% vs. 34%. This could be attributed to the instability of the ammonium nitrate phases. It is well known that ammonium nitrate is a semi-volatile specie which may re-dissociate into the gas phase precursors if the concentration product necessary for the NH_4NO_3 particle formation is not achieved. Previous studies have shown that the formation of NH_4NO_3 is thermodynamically favoured at low temperatures, whereas in warmer environments gaseous HNO_3 is more favourable (Warneck, 1987; Adams et al., 1999; Rodriguez et al., 2002). Hence, in Madrid site significant

amounts of fine NH_4NO_3 can only be produced during winter, while in the warm season nitrate formation is attributed to the reaction of gaseous HNO_3 with coarse-mode mineral species such as calcium carbonate, to form $\text{Ca}(\text{NO}_3)_2$ (Pakkanen, 1996). As expected, the marine aerosol category explains the significant mass contributions of Na and Cl, around 50% and the lower amounts of Mg and Ca.

Similar PM_{10} sources have also been identified at other urban sites in Spain, although their relative contributions varied. The crustal source appeared to be also significant in Huelva (Querol et al., 2002) and Barcelona (Querol et al., 2001b) although the traffic contribution at these cities was much lower than at the Madrid site. On the opposite, the higher marine contribution reflects their coastal location.

3.2. CPF analysis

The CPF analysis has been performed for those elements that presented the highest source contribution for crustal, traffic, secondary and marine categories, i.e. Al, C, NH_4^+ and Na (Table 3). To assess quantitatively the CPF values, the criteria proposed by Zeng and Hopke (1989) and used in other studies (Hernández et al., 1996; Rúa et al., 1998), have been followed. These criteria interpret in a qualitative way the possibility of each grid cell as being a source of the specific elements, according to the CPF values ranges. Thus CPF values in the 0.0–0.2 range means very weak, 0.2–0.4 weak, 0.4–0.6 intermediate and higher than 0.6 means very strong source of the specific compounds. Only CPF values statistically significant at the 95% confidence level, have been considered in this analysis.

The CPF results showed that the areas with the greatest potential contribution for Al, are located in North Africa including the Sahara desert (Fig. 4a). Moderate to high CPF values have also been found in Atlantic areas near the north western African coast. This can be explained by the transport pattern of dust plumes originated in the Sahel region, moving northward over the Atlantic ocean before reaching the central part of the peninsula (Reiff et al., 1986; Rodríguez et al., 2001). In order to support these conclusions, the aerosol index imagery derived from the Earth Probe total ozone mapping spectrometer (TOMS), have been analysed. Positive values of the aerosol index are associated with UV absorbing aerosols (desert dust and smoke) present in the atmosphere (Herman et al., 1997). In Fig. 4b a set of selected TOMS daily aerosol index maps, obtained during the sampling period has been depicted. As deduced from the comparison of Figs. 4a and b, the highest aerosol index areas, i.e. those with high mineral aerosol concentrations, coincide with those derived from the conditional probability values, confirming the results obtained.

Saharan dust transport takes place at high altitudes, from 1.5 to 5–7 km above sea level (Chiapello et al., 1997). This can be the reason why CPF values for trajectories corresponding to heights 1500, 2500 and 3500 m, are more representative of the Sahara desert as a source area of Al (Fig. 4a). Al has been used as a good tracer of African dust in other previous works (Gatz and Prospero, 1996; Kubilay and Saydam, 1995; Kubilay et al., 2000). Al, Mg, Fe and Ti have been found as the best tracers of Saharan dust outbreaks at a rural site in eastern Spain (Rodríguez et al., 2002). At the Madrid site very similar CPF values to those identified for Al have been obtained for Ti, so this component could be also considered a Saharan dust tracer. This is not the case for Fe and Mg, given that in this study these elements are mainly associated with traffic emissions and local sources of dust respectively. It is important to note that even at an urban place highly influenced by local emissions, it has been possible to identify valid tracers of Saharan dust outbreaks.

The CPF maps obtained for C do not clearly identified any source area. Nevertheless, those cells with significant CPF values were found in the north western Atlantic areas, being interpreted as the most probable air masses pathways during local episodes of high C concentration values (Fig. 5a). These pathways are produced by strong high-pressure systems placed over or nearby the Iberian Peninsula during episodic situations, which inhibit the ventilation of air masses at the surface. At higher levels they give rise to north western flows over the Iberian Peninsula, which are represented by weak to moderate CPF values in the cells placed over north western Atlantic areas. This confirms the local origin of the C sources at the surface layer, which is decoupled from higher atmospheric layers under these anticyclonic conditions.

In the case of NH_4^+ , it seems that local or regional sources are also the main contributors during high value episodes, since source regions have not been clearly determined. Relative high or intermediate CPF values have been obtained for 750 and 1500 m trajectories, over France (Fig. 5b). This could indicate a possible transport of secondary aerosols from Continental Europe but taking into account that these secondary particles are generated from gaseous precursors through time consuming atmospheric processes, the CPF method in this case may not provide so straightforward results to interpret.

Finally, CPF values obtained for extreme values of Na, considering this component as a possible tracer of marine aerosol, define the Atlantic ocean as a source region of this element for back-trajectories obtained at different heights (Fig. 5c). CPF values range from 0.0 to 0.6 in most cells. It supports the marine origin of an important amount of the Na sampled in the central area of the Iberian Peninsula, in accordance with the results obtained with the FA/MLRA method.

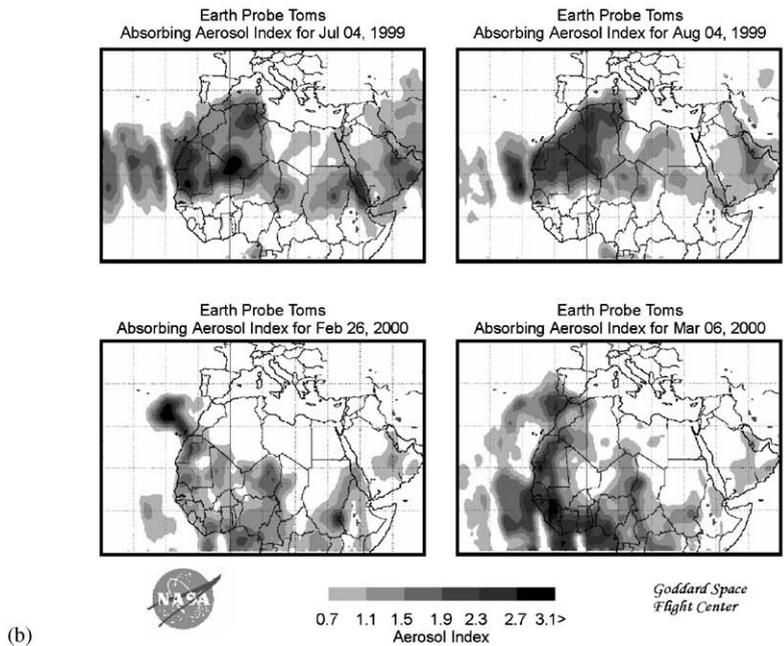
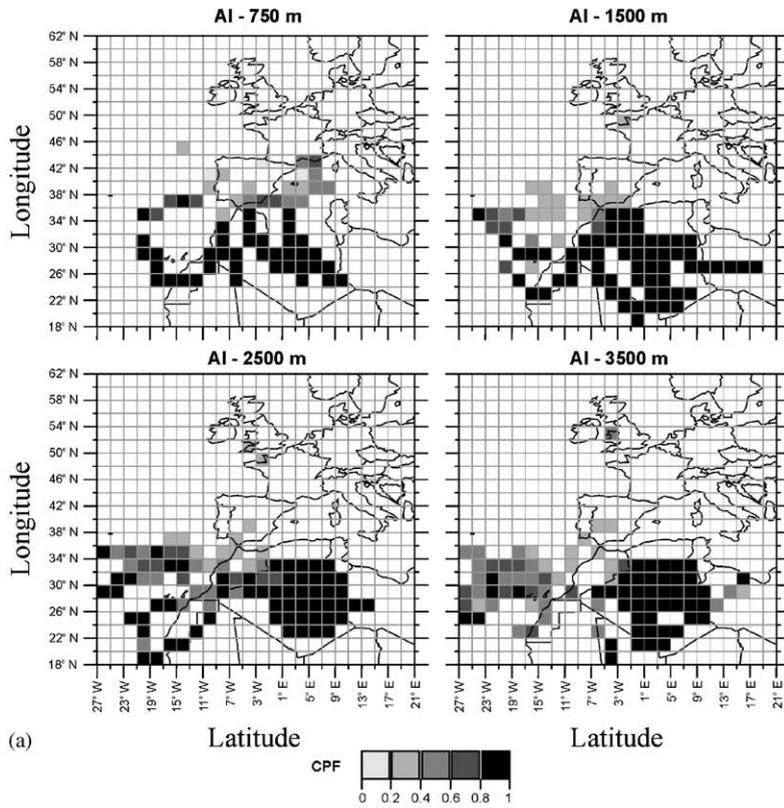


Fig. 4. CPF values for extreme values of AI in Madrid, corresponding to back-trajectories starting at 750, 1500, 2500 and 3500 m AGL. Only significant CPF values at the 95% confidence level are displayed (a). Aerosol Index maps selected for representative days of the PM₁₀ sampling period, showing Saharan and Sahel dust plumes in accordance with CPF values obtained (b).

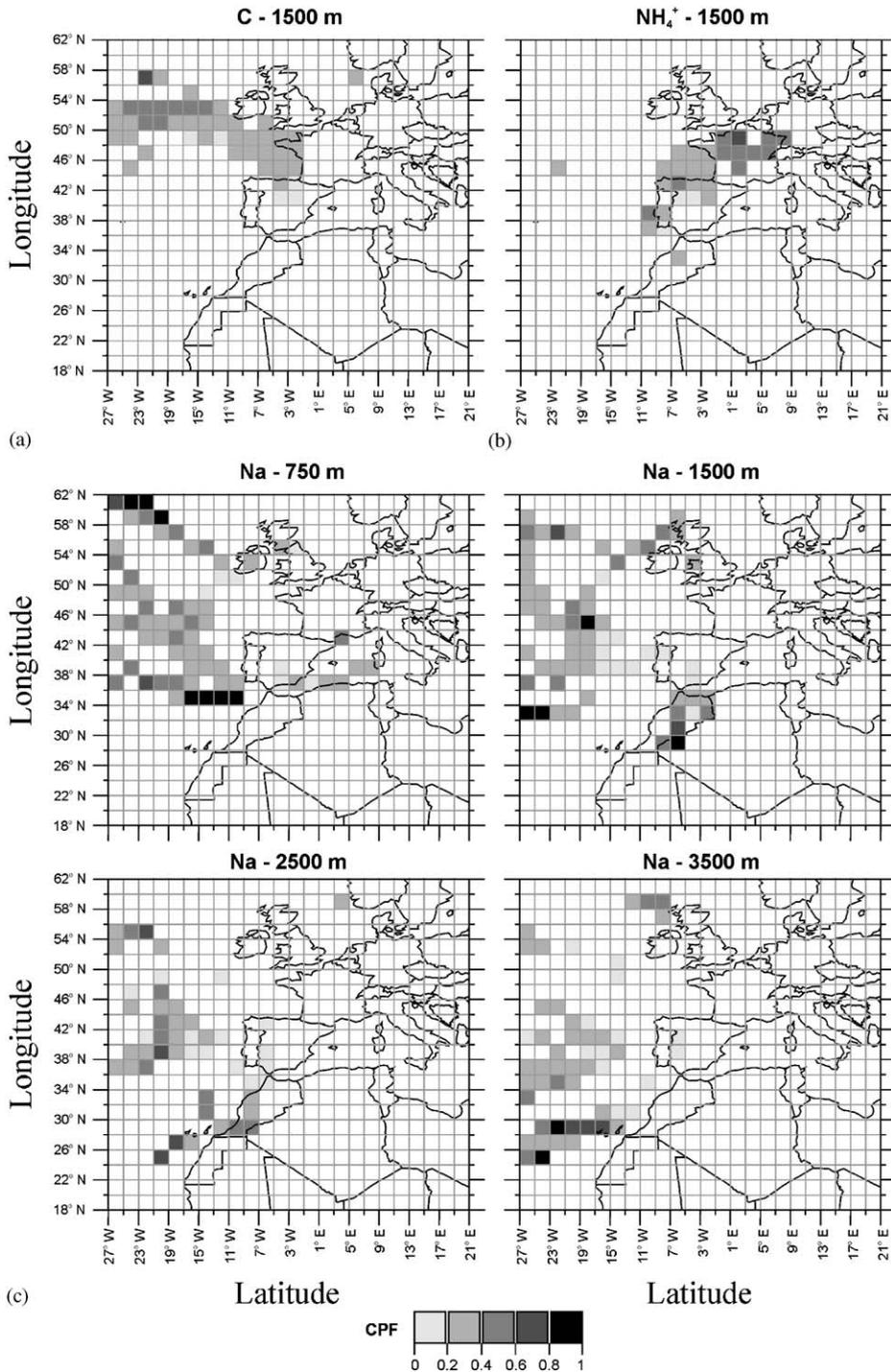


Fig. 5. CPF values for extreme values of C (a) and NH_4^+ , (b) in Madrid, corresponding to back-trajectories starting at 1500 m AGL. CPF values for extreme values of Na in Madrid, corresponding to back-trajectories starting at 750, 1500, 2500 and 3500 m AGL (c). Only significant CPF values at the 95% confidence level are displayed.

4. Conclusions

In this work some statistical techniques have been successfully used to identify and characterise PM₁₀ sources. The application of factor analysis, a multivariate technique, has allowed us to qualitatively identify crustal, vehicular, secondary and marine aerosol as the main PM₁₀ sources, at an urban site in Madrid (Spain). The contribution of these four sources to PM₁₀ mass concentration was obtained by multilinear regression analysis. Road traffic has explained almost one-half of the PM₁₀ mass. Crustal and secondary contributions have been similar and also relevant. As expected, the marine particles contribution has been almost negligible. The multilinear regression analysis has also provided the percentage of each element in the sources composition, i.e. the elemental source profiles, which has been discussed in each case.

To identify external sources and their geographical origin, conditional probability functions have been computed including information on air mass trajectories. Only those days with extreme values of some PM₁₀ components were considered in the analysis. Results point at the Sahara desert as a major source of crustal elements for days when this element reaches its highest values in Madrid. Atlantic ocean areas near the north–western African coast have also been identified as the path followed by dust plumes originated in the Sahel region. Al and Ti have been found as good tracers of the Saharan dust transport processes affecting the Madrid metropolitan area. On the other hand, the Atlantic ocean has been identified as an intermediate source of Na. It points at an important influence of remote natural PM₁₀ sources in Central Spain, detectable even at urban areas. No well-defined remote source regions have been derived for NH₄⁺ and C, pointing at local and regional sources as the main contributors of PM₁₀, related to traffic and secondary source categories.

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