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Characterisation of local and external contributions of atmospheric particulate matter at a background coastal site

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Abstract

This study applies a methodology for discriminating local and external contributions of atmospheric particulate matter (PM) at a rural background station in the North-western coast of Spain. The main inputs at the nearest scale have come from soil dust, marine aerosol and road traffic. At a larger scale, the highest contributions have come from fossil-fuel combustion sources, giving rise to relatively high ammonium sulphate background levels, mainly in summer. External contributions from long-range transport processes of African dust and nitrate have been detected. Morocco and Western Sahara have been identified as the main potential source regions of African dust, with a higher content of Al and Ti than other crustal components. Geographical areas from central and Eastern Europe have been identified as potential sources of particulate nitrate. The discrimination of the PM contribution from natural and anthropogenic sources at different geographical scales is a necessary information for establishing PM reduction strategies in specific areas.
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1. Introduction

Atmospheric particulate matter (PM) can have both a natural and an anthropogenic origin that influences its composition and size. However, regardless of whether its primary origin is natural or anthropogenic, PM evolves in the atmosphere as a consequence of the multiple physico-chemical processes that can affect this matter from its release point, as a primary aerosol, or via gas-to-particle conversion processes that give rise to a secondary aerosol.

PM measured at a specific site is therefore the result of an ensemble of processes and features that configure the adequate scenario to provide an aerosol with unique and specific characteristics. While a knowledge of local sources is a starting point for characterizing a great number of aerosol properties, other features have to be taken into account as the result of processes that take place at larger (regional to long-distance) scales. These processes can involve input from ageing air masses,

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laden with natural or anthropogenic PM, that can modify the characteristics of the local aerosol and should be especially considered in source apportionment studies or normative accomplishment.

The current European air quality standards (1999/30/CE) approach the origin issue explicitly, by considering specifically the natural contribution on the number of exceedences of the PM10 daily limit value. Accordingly, cases produced by natural phenomena, duly verified and scientifically documented, can be excluded for normative purposes from the total number of exceedences. Because of this, in Southern European countries special attention has been paid to the influence of African dust on surface PM levels (Kubilay et al., 2000; Querol et al., 2004a; Almeida et al., 2005), although other natural contributions such as sea salt spray or dust resuspension, can be also relevant under specific weather conditions. In addition, long-range transport processes of anthropogenic aerosol can have a significant influence on PM concentration levels recorded at a specific site (Güllü et al., 2005; Abdalmogith and Harrison, 2005), but this is not currently well documented at many European geographical areas.

In recent years, an increasing number of numerical and experimental scientific works showing levels and identifying sources of PM10 and PM2.5 in European regions have been published (Querol et al., 2004b; Artíñano et al., 2004; Marcazzan et al., 2003; Putaud et al., 2004; Rodríguez et al., 2004; Almeida et al., 2005). Most are at urban or industrial sites affected by local sources, evidencing a gap of information on rural sites representing different geographical and climatic areas. This fact has also been highlighted by the important discrepancies found between observations and model results relative to levels and composition of PM10 and PM2.5 (Grini et al., 2002). Among other reasons, these differences can be attributed to the scarcity of rural or regional background stations in air quality networks and the lack of comprehensive information on chemical composition on PM10 and PM2.5. It should be mentioned that this type of information is not provided on a routine basis in most of the monitoring sites, including in the regional background air quality network of the UNECE/LRTAP/EMEP (European Monitoring and Evaluation Programme).

This work applies a methodology for discriminating local and external contributions from natural and anthropogenic sources that affect PM concen-tration levels at a representative background site. Firstly, an interpretation of the time series of PM and gaseous pollutant levels jointly with a meteorological analysis allowed identifying high PM concentration periods as well as the main sources involved. Next, receptor-modelling techniques were used to identify the main PM sources affecting this site in general and their contribution to the PM mass. Finally, a statistical analysis of back-trajectories was carried out to locate geographically potential source regions that can contribute to PM levels via transport processes.

2. Methodology

2.1. The study area

The Bemantes monitoring station (latitude $43°20'15''$N, longitude $08°10'50''$W, altitude 170 m ASL) is located 2 Km inland along the main axis of the estuary named Ria de Betanzos, in a rural area in Galicia (Fig. 1). This site is representative of a wet, rainy and well-ventilated Atlantic climate site, rather different from other drier and more arid rural areas in Spain and Southern Europe. Topography of Galicia, the north-westernmost region of Spain, is characterised by a framework of low mountains and small rivers that run into the Atlantic Ocean forming estuaries named Rias that conform a complex coastal relief. Concerning the potential pollution emission sources (Fig. 1), the nearest urban area is A Coruña (250 000 inhabitants) 20 Km to the west in the so-called Ria de A Coruña. This city has medium-size industrial areas with manufacturing activities. It is worth noting that there is a coal-fired power plant (As Pontes, 4×350 Mw h^{-1}) located within a river valley 26 Km northeast straight from Bemantes, the emissions of which are released through a 357 m high stack (Fig. 1). Local landscape comprises mainly agricultural fields (pasture and crops) and disperse rural constructions. There are no dense traffic ways close to the station, as only local and secondary roads cross this area. From an air quality point of view the measurement site can be considered as a rural background station.

2.2. PM measurement and sampling

The experimental study was conducted from January to December 2001. Manual sampling was carried out at a rate of 3 and 2 moving days per
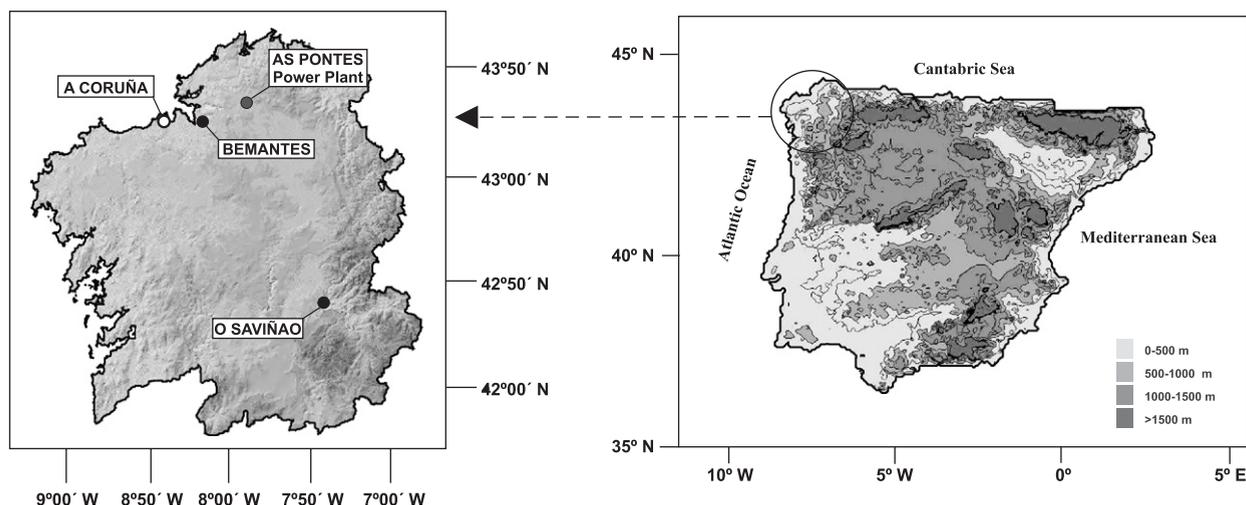
Fig. 1. Location of Bemantes and O Saviñao monitoring sites, As Pontes power plant and A Coruña in the North-western area, Galicia (left), of the Iberian Peninsula (right).

week for PM10 and PM2.5, respectively. Of these, 2 PM10 and 1 PM2.5 were selected for chemical analysis. The 24-h sampling was performed by means of a PM10 EN12341 reference instrument Graseby-Andersen high volume sampler ($68 \, m^3 \, h^{-1}$), and a MCV high volume sampler ($30 \, m^3 \, h^{-1}$) equipped with a PM2.5 inlet and quartz fibre filters (QF20 Schleicher and Schuell). Sampling started at 08:00 am LST and sample collection was performed immediately after finishing the sampling sequence to avoid the loss of semi-volatile compounds. Once PM10 and PM2.5 levels were obtained by standard gravimetric methods, samples were treated and analysed for determining the levels of carbon, anions and major and trace elements, following the procedure of Querol et al. (2004b). The techniques used for chemical analysis included ICP-AES and ICP-MS (Ca, Al, Na, K, Mg, Mn, Sr, Ba, Zn, V, Cr, Ni ,Cu, Ti, P, Fe, Pb, As, Co, Li, Be, Sc, Ga, Ge, Se, Rb, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Sn, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Bi, Th and U), Ion Cromatography (SO_4^{2-}, NO_3^- and Cl^-), Colorimetry-FIA (NH_4^+) and LECO methodology (total C determination based on the thermal oxidation of carbonaceous aerosols and the measure of CO_2 by IR). Levels of SiO_2, CO_3^{2-} and $SO_4^{2-}{}_{marine}$ were indirectly obtained from the content of Al, Ca, Mg and Na on the basis of previous experimental equations ($2Al_2O_3 = SiO_2$; $1.5 \, Ca + 2.5 \, Mg = CO_3^{2-}$; Dulac et al., 1992; Molinaroli et al., 1993) and by stoichiometry from the soluble Na levels ($SO_4^{2-}{}_{marine} = 0.25 \, Na$). The levels of

$C_{non\text{-}mineral}$ ($C_{non\text{-}mineral} = C_{total} – C_{carbonate}$) and $SO_4^{2-}{}_{non\text{-}marine}$ ($SO_4^{2-}{}_{non\text{-}marine} = SO_4^{2-} − SO_4^{2-}{}_{marine}$; Warneck, 1987) were also obtained.

Continuous measurements of PM10, PM2.5 and PM1 at an hourly rate were performed using a GRIMM 1107 laser spectrometer. In 2001, it provided a data capture percentage of around 96%. These data were corrected according to the criteria established by the EC Working Group on Particulate Matter (2002). To this effect automatic PM measurements were compared with the levels obtained simultaneously by means of the EN12341 high volume reference sampler or equivalent gravimetric methods. Additionally, SO_2, NO_2 and NO_x hourly concentration levels were continuously registered by the automatic monitors of the station.

2.3. Meteorological analysis

A daily meteorological analysis was carried out for the study period to identify the different source regions of the air masses influencing the study area. To perform this part of the work, 5-day isentropic back-trajectories at 00:00, 06:00, 12:00 and 18:00 h UTC, and at different heights above the starting point located at ground level were computed on a daily basis by using the HYSPLIT model (Draxler and Rolph, 2003). The 6-hourly FNL archived data (National Climatic Data Center, USA) for the Northern Hemisphere were used as input. The best procedure to illustrate the vertical structure of the atmosphere is to run trajectories at several heights above the point of interest (Draxler and Hess, 1998).

750, 1500, 2500 and 3500 m AGL have been chosen, as representative heights of the mean transport wind at a synoptic scale (Stohl, 1998). It should be noted that in the isentropic framework, air masses are forced to move following isentropic surfaces. Because of the fact that the diabatic effects are neglected, trajectories must be taken at high or medium levels far from the ground influence (Stohl, 1998). Different studies agree that errors of 20% of the distance travelled seem to be typical for trajectories computed from analysed wind fields (Rolph and Draxler, 1990; Stohl, 1998). Daily ECMWF synoptic charts (surface and upper levels) were simultaneously analysed. Special phenomena like African dust outbreaks affecting the Iberian Peninsula were also identified with the aid of daily TOMS-NASA aerosol index maps (http://jwocky.gsfc.nasa.gov), SKIRON (Athens University; http://forecast.uoa.gr) and NAAPS (Naval Research Laboratory-Marine Meteorology Division; http://www.nrlmry.navy.mil/aerosol) models for dust concentration maps and SeaWiFS-NASA satellite imagery (http://seawifs.gsfc.nasa.gov/SEAWIFS.html).

2.4. Data treatment

Time series of PM and gaseous pollutant levels were inter-correlated and interpreted jointly with the meteorological analysis to characterize the episodes of high PM concentration levels. The main sources responsible for the high levels were suggested. Chemical characterization was then used to perform a first approach to the interpretation of PM speciation.

Afterwards, receptor modelling techniques were applied to characterise PM10 and PM2.5 sources in this rural area. To this end, a Varimax rotated factor analysis (FA) was performed to identify the main sources affecting the aerosol composition. Since the data are previously normalized, factors with eigenvalues greater than 1 are retained, as they explain more variance than the original variables. Components obtained indirectly have not been used in this analysis. They do not bring forward information for identifying statistically independent sources (Thurston and Spengler, 1985). Besides, those trace metals that were quantified in less than 80% of the samples, both in PM10 and PM2.5, were also rejected. Finally, a data matrix of 87 PM10 and 45 PM2.5 samples by 23 PM components and gases (SO_2, NO_x, C, Al, Ca, K, Na, Mg, Cl^-, Fe, P, SO_4^{2-}, NO_3^-, NH_4^+, Ti, V, Mn, Ni, Cu, Zn, As, Se, Pb) was

utilized. They meet the requirements relative to the number of variables and samples to obtain accurate results by FA, proposed by Henry et al. (1984). The quantitative contribution of each factor was then derived by multilinear regression analysis (MLRA) using PM concentration values as the dependant variable and absolute factor scores (AFS) as defined by Thurston and Spengler (1985) as independent variables. For the sake of simplicity, the exposition of the procedure is not included, but it is comprehensively described in numerous works (Thurston and Spengler, 1985; Harrison et al., 1997; Salvador et al., 2004). The main limitations of FA are that is unable to produce a fine resolution of sources and that it provides no information on their geographical location (Henry et al., 1984). This is why a statistical analysis of back-trajectories was carried out.

Concentration fields (CF) as defined by Stohl (1996) have been computed. This technique combines air back-trajectory information and concentrations of the components measured at the sampling place. A $2° \text{ longitude} \times 2° \text{ latitude}$ cell grid was superimposed over the region defined by $18°N$–$62°N$ and $27°W$–$21°E$. For each ijth grid cell a weighted concentration C_{ij} was calculated. The procedure is exhaustively illustrated in Stohl (1996). High C_{ij} means that, on average, air parcels passing over the ijth grid cell result in high concentrations of the element C at the receptor site. They should be interpreted as potential rather than exact source regions of the elements. This technique has been applied to locate potential source regions for particulate sulphate (Stohl, 1996), PCB (Hsu et al., 2003) or heavy metals (Han et al., 2004).

3. Results and discussion

3.1. Mean PM levels

Mean annual PM10 and PM2.5 concentrations recorded from gravimetric measurements were $23 \, \mu g$ $PM10 \, m^{-3}$ (123 samples) and $13 \, \mu g \, PM2.5 \, m^{-3}$ (85 samples), respectively. Both are in the range of mean values obtained for rural background stations in Spain, although slightly higher than those obtained at remote EMEP stations (Querol et al., 2004a). Mean concentration values recorded for the same period, at the nearest natural background EMEP station of O Saviñao (Fig. 1) located 87 Km southeast inland, were slightly lower for PM10 ($16 \, \mu g \, PM10 \, m^{-3}$) and PM2.5 ($12 \, \mu g \, PM2.5 \, m^{-3}$).

With regard to gaseous pollutants, mean concentration values (8 μg NO_2 m^{-3}, 9 μg NO_x m^{-3}, 14 μg SO_2 m^{-3}) were much lower than those typically recorded in urban and industrial stations (Artíñano et al., 2004; Baldasano et al., 2003) and similar to other rural stations in Spain and Europe, according to Airbase data (http://air-climate.eionet.eu.int/). This confirms that this is a representative rural background site.

3.2. High PM concentration episodes

The time series and seasonal analysis allowed identifying three types of specific situations accounting for high PM levels, namely power plant plume fumigation episodes, African dust outbreaks and winter pollution episodes. Each one has a specific PM source associated to it.

In relation with the first episode, it has been observed that high PM hourly values were recorded simultaneously with extreme SO_2 hourly values (Fig. 2a), at times higher than 600 μg SO_2 m^{-3}. These peak events have been mainly associated to NE–E wind directions (Fig. 2b) and have been attributed to the impact (fumigations) of the emission plume of the As Pontes power plant at the Bemantes sampling site. They have been more frequently produced in the summer (Fig. 2c), when atmospheric conditions favour the transport of the plume and its abatement by enhanced mixing conditions. During the 23 fumigation episodes identified in 2001, mean daily PM10, PM2.5 and PM1 levels reached 20, 13 and 10 μg m^{-3}, respectively.

In that year, 10 African dust outbreaks, lasting from 2 to 5 days, were identified affecting the North-western Spanish region (Figs. 3a and b). The average daily mean concentration values obtained in these cases were the highest, reaching 47, 30 and 25 μg m^{-3} for PM10, PM2.5 and PM1, respectively.
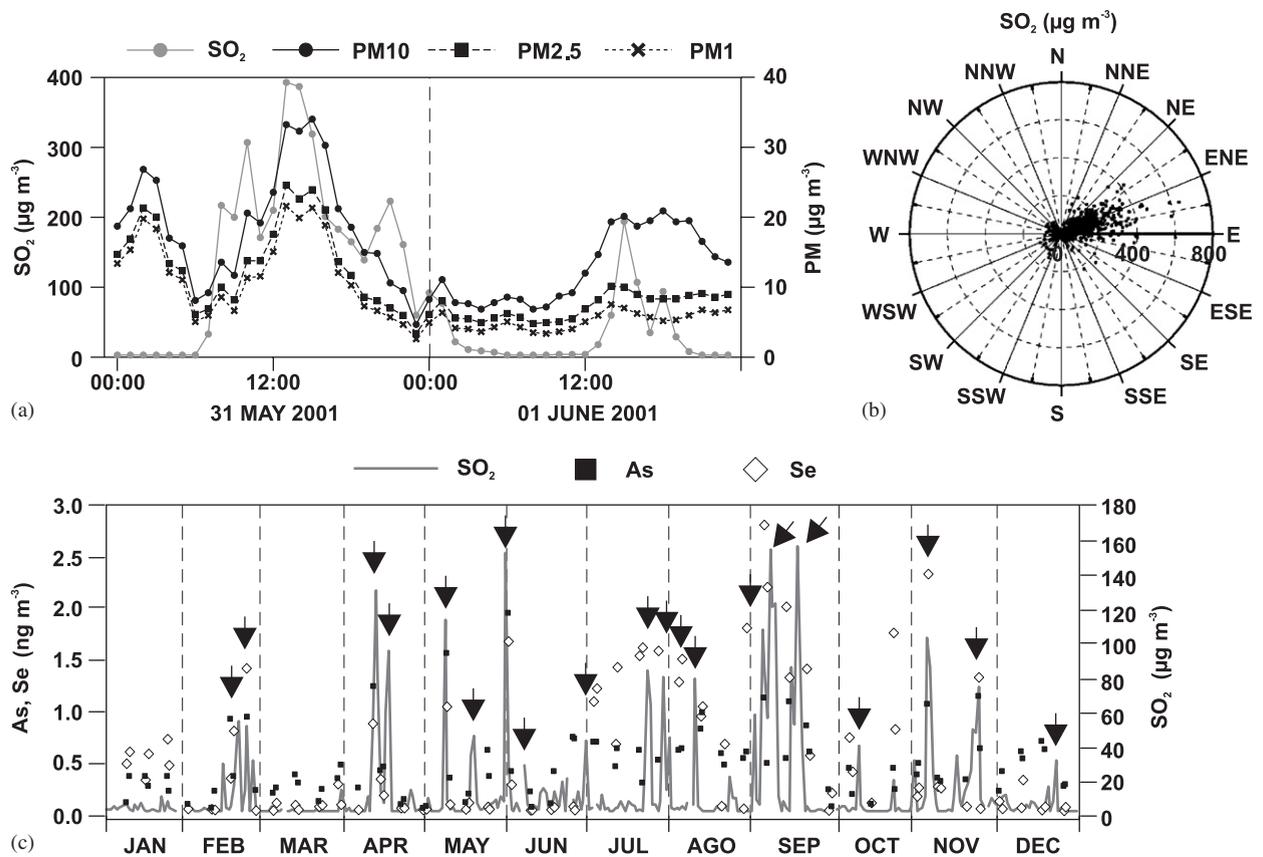
Fig. 2. SO_2, PM10, PM2.5 and PM1 hourly values recorded at Bemantes during an As Pontes SO_2 plume fumigation episode (a) and hourly SO_2 levels recorded at Bemantes plotted according to simultaneous wind direction values recorded at As Pontes meteorological tower (80 m high) (b). Time series of daily mean SO_2 levels and As and Se content in the PM10 samples. SO_2 peak events associated to NE-E wind direction have been marked with arrows (c).
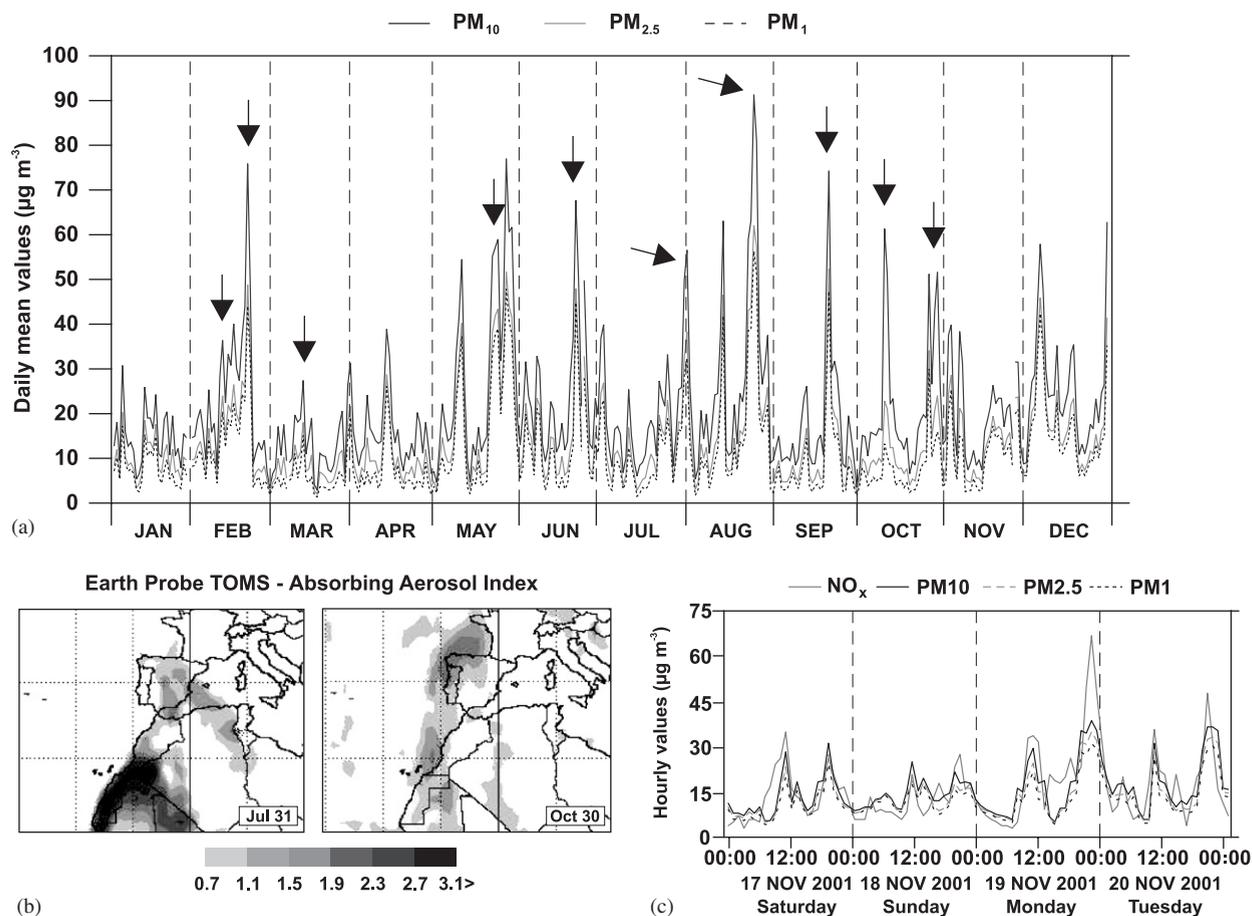
Fig. 3. Time series of daily mean PM10, PM2.5 and PM1 levels recorded at Bemantes with the laser spectrometer during 2001 (a). Documented African dust outbreaks have been marked with arrows. Some examples are illustrated by TOMS aerosol index maps (31 July and 30 October) (b). Hourly values of PM10, PM2.5, PM1 and NO_x levels during a winter pollution episode on 17–20 November (c).

The EU-Directive PM10 daily limit value, $50 \,\mu g$ $PM10 \, m^{-3}$, was exceeded at Bemantes on 22 days in 2001, 13 of which were produced during African dust outbreaks. Thus, long-range transport of mineral dust from North African deserts generated 60% of the daily limit value exceedences. These episodes occurred in the February–March and May–October periods.

The highest incidence of local anthropogenic emissions on PM levels has been observed in the winter months. These are mostly related to the presence of high-pressure systems over the Iberian Peninsula. They give rise to highly stable atmospheric conditions with deep surface thermal inversions and low rainfall rates, which favour the accumulation of pollutants from local sources. These episodes at Bemantes mainly occurred in January, February, November and December, lasting from 1 to 6 days. They were characterised

by a strong correlation of the PM10, PM2.5 and PM1 levels with those from local gaseous emissions, mainly NO_x. Daily cycles could be observed presenting two simultaneous PM and NO_x peaks, morning and evening, linked to traffic in the rush hours. Lower concentration levels were recorded during the weekend (Fig. 3c) pointing at traffic as the main source of these emissions (Artíñano et al., 2004). During the 22 anthropogenic episodes identified, mean daily PM10, PM2.5 and PM1 levels reached 34, 23 and $20 \,\mu g \, m^{-3}$ respectively.

3.3. Chemical characterisation

A number of PM10 (87) and PM2.5 (45) filters were analysed. A summary of the content of major and trace components determined is presented in Tables 1 and 2. On average, the sum of determined compounds accounted for respectively, 82% and

Table 1

Mean, maximum (Max.) and minimum (Min.) concentrations (in $ng\,m^{-3}$) of major components of PM10 and PM2.5 measured at Bemantes from January to December 2001

	PM10			PM2.5		
	Mean	Max.	Min.	Mean	Max.	Min.
N	87			45		
PM	18877	44000	7668	13467	34000	4000
$C_{non-mineral}$	4191	10161	936	3813	8408	1122
$SO_4^{2-}{}_{non-marine}$	2995	16014	209	2944	12086	539
NH_4^+	1329	8440	100	1152	7640	120
Cl^-	1259	11300	190	555	1060	160
Na	1087	5467	97	316	1077	65
SiO_2	965	7373	7	668	3326	32
NO_3^-	862	5890	200	399	2080	140
CO_3^{2-}	582	2051	52	272	632	101
Al_2O_3	322	2458	2	223	1109	11
$SO_4^{2-}{}_{marine}$	272	1367	24	79	269	16
K	175	453	20	118	370	<0.01
Mg	153	649	15	46	140	9
Fe	137	726	10	63	383	11
Ca	134	287	10	106	222	30
Zn	16	113	0.14	17	67	<0.01
P	14	39	2	8	23	<0.01
Cu	8	24	<0.01	9	28	<0.01
Pb	8	54	1	7	49	1
Ti	7	33	0.2	4	20	<0.01
Ba	6	160	0.02	5	23	0.02
V	5	24	0.4	4	15	0.02
Mn	5	20	1	3	10	0.32
Zr	4	56	<0.05	1.9	7.5	<0.05
Ni	3	11	<0.01	4	25	0.71
Mo	3	17	<0.05	2	9	<0.05
Cr	1	9	<0.5	1	5	<0.05
Rb	1	2	0.10	0.5	1.8	0.05
Sr	1	32	<0.05	1	3	<0.05
Sn	1	10	<0.05	1	2	<0.05
Σ Trace metals	73	323	22	64	172	15
Total determined	15387	36998	7262	11858	32303	4652

N is the number of daily valid samples.

Table 2

Mean, maximum (Max.) and minimum (Min.) concentrations (in $ng\,m^{-3}$) of trace components of PM10 and PM2.5 measured at Bemantes from January to December 2001, reaching mean concentration values lower than $1\,ng\,m^{-3}$

	PM10			PM2.5		
	Mean	Max.	Min.	Mean	Max.	Min.
Ce	0.2	1.09	<0.05	0.2	0.64	<0.05
Nd	0.2	0.71	<0.01	0.2	0.89	<0.01
La	0.1	0.64	<0.05	0.1	0.33	<0.05
Sb	0.6	3.5	<0.01	0.4	1.7	<0.01
Se	0.5	2.8	<0.01	0.4	3.5	<0.01
As	0.4	1.2	<0.01	0.3	0.8	<0.01
Ge	0.3	7.0	<0.01	0.1	0.6	<0.05
Ga	0.2	1.5	<0.01	0.1	0.3	<0.01
Hf	0.2	3.3	<0.01	0.2	0.65	<0.01
Cd	0.2	2.5	<0.05	0.2	2.0	<0.05
Th	0.2	2.4	<0.05	0.2	1.5	<0.05
U	0.2	1.3	<0.05	0.2	1.9	<0.05
Bi	0.1	0.4	<0.05	0.1	0.6	<0.05
Co	0.1	0.9	<0.01	0.2	2.1	<0.01
Sc	0.1	0.7	<0.05	0.1	0.79	<0.05
Li	0.1	0.6	<0.05	0.1	0.58	<0.05
Y	0.1	0.4	<0.05	0.1	0.3	<0.05
Ta	0.1	0.6	<0.01	0.05	0.35	<0.01
Tl	0.1	0.6	<0.05	0.1	1.0	<0.05
Pr	0.07	1.04	<0.01	0.03	0.07	<0.01
Er	0.06	0.23	<0.01	0.04	0.22	<0.01
Sm	0.05	0.31	<0.01	0.04	0.14	<0.01
Gd	0.05	0.36	<0.01	0.03	0.19	<0.01
Dy	0.05	0.18	<0.01	0.05	0.26	<0.01
Yb	0.04	0.29	<0.01	0.04	0.40	<0.01
W	0.04	0.37	<0.01	0.04	0.9	<0.01
Cs	0.04	0.17	<0.05	0.03	0.15	<0.05
Be	0.03	0.19	<0.05	0.04	0.37	<0.05
Tb	0.03	0.10	<0.01	0.02	0.09	<0.01
Eu	0.02	0.16	<0.01	0.02	0.08	<0.01
Ho	0.01	0.04	<0.01	0.01	0.02	<0.01
Tm	0.01	0.04	<0.01	0.01	0.05	<0.01
Lu	0.01	0.03	<0.01	0.01	0.05	<0.01
Nb	0.04	0.4	<0.05	0.04	0.20	<0.05

85% of the bulk mass. The undetermined fraction of PM is believed to consist mainly of water condensed on the surface of the aerosols, chemically bound to aerosol or absorbed by the filter (McMurry, 2000). Moreover, a proportion of the undetermined PM fraction may be made up of heteroatoms in organic compounds, which are not adequately accounted for.

Mean mass bulk contribution of PM10 can be summarized as follows: 28% secondary inorganic compounds—SIC (NH_4^+, $SO_4^{2-}{}_{non-marine}$, NO_3^-), 22% $C_{non-mineral}$, 14% marine species ($SO_4^{2-}{}_{marine}$, Cl^- and Na), 13% crustal species (Al and Si oxides, carbonate, Ca, Mg, P, Fe, K), and 0.53% trace metals. SIC and $C_{non-mineral}$ represented 33% and 28% of the mean PM2.5 bulk mass, respectively. Crustal and marine contributions were lower in PM2.5 than in PM10, 11 and 7%, respectively, while the trace metal load was practically the same in both fractions.

It should be stressed the high proportion of $SO_4^{2-}{}_{non-marine}$, NH_4^+ and $C_{non-mineral}$ in the PM10 and PM2.5 mass, which accounts for $8.5\,\mu g$ $PM10\,m^{-3}$ and $7.9\,\mu g$ $PM2.5\,m^{-3}$, respectively. It can be concluded that the PM composition in Bemantes is dominated by chemical components typically associated with anthropogenic source emissions. This agrees with results obtained in other

European rural background sites (Putaud et al., 2004) such as Monagrega, another rural monitoring site located in North-eastern Spain at the Ebro basin, Illmitz (Austria) and Chaumont (Switzerland).

Mineral load in PM10 and PM2.5 has been lower in comparison with other dryer and more arid rural or even urban areas in Spain (Querol et al., 2004b). It should be kept in mind that Bemantes is located in a very humid area with high rainfall. Otherwise, the marine contribution to PM10 levels (2.6 µg PM10 m^{-3}) has been fairly significant at this coastal site, in the range of values observed in other coastal sites in Spain (Querol et al., 2004b) and higher than that found in natural coastal sites in Norway and Finland (Putaud et al., 2004).

The group of all the trace elements analysed in this work reaches a concentration value of 73 and 64 ng m^{-3} in the PM10 and PM2.5 mass contribution, respectively (Table 1). The mean values obtained in the sampling period for the group of metals analysed lie in the range of 0.01–17 ng m^{-3}, with only Mo, Ni, Zr, Mn, V, Ba, Ti, Cu, Pb and Zn exceeding 1 ng m^{-3}.

It should be mentioned that while most of SO_4^{2-} $_{non-marine}$ and NH_4^+, 90% and 80%, respectively, has been contained in the fine mode (PM2.5), NO_3^- has been more evenly distributed between both, fine (44%) and coarse (PM10–PM2.5, 56%) fractions, in simultaneous PM10 and PM2.5 samples. This suggests that SO_4^{2-} $_{non-marine}$ in PM2.5 should be mainly present as $(NH_4)_2SO_4$, and there should be a smaller content of NH_4NO_3 particles. In the coarse fraction, NO_3^- (and to a lesser extent SO_4^{2-} $_{non-marine}$) must be associated with other cations via the reaction of acid gases (HNO_3 and H_2SO_4) with the surface of marine and crustal coarse particles such as NaCl, $MgCl_2$ or $CaCO_3$ (Pakkanen, 1996; Querol et al., 1998).

During the SO_2 fumigation episodes, mean levels of As and Se in PM10 and PM2.5 and of some crustal components and metals (SiO_2, Al_2O_3, Li, Sc, Ti, Cu) in PM10, have been higher than their 80th percentiles. As and Se are good tracers of coal combustion (Thurston and Spengler, 1985; Harrison et al., 1997), and have been well correlated with the SO_2 peaks (Fig. 2c). It is also well known that fly ash emitted from coal-fired power plants, contain small amounts of mineral components in the coarse fraction (Querol et al., 1998; Alastuey et al., 2004; Almeida et al., 2005). Levels of typical crustal components (SiO_2, Al_2O_3, K, Fe, Li, B, Ti, V, Mn)

reached higher concentrations than their 80th percentiles during African dust events in the PM10 and PM2.5 samples. During the winter episodic periods the most abundant components in PM10 and PM2.5 have been $C_{non-mineral}$, NO_3^-, Fe, Zn, Cd, Sb, As and Pb, suggesting that traffic and other combustion processes are the main PM sources for those events (Artíñano et al., 2004; Weckwerth, 2001).

3.4. Identification of PM sources and mass apportionment

FA has revealed six factors for the PM10 and PM2.5 datasets (Table 3). They are interpreted as follows:

Factor 1 in PM10 and PM2.5 have been associated with the crustal contribution since these are characterised by high loadings on typical mineral elements such as Ti, Al, Fe, Mn, P or Ca. This is the result of local and regional dust resuspension by wind and convective processes, and for long-range transport of African mineral dust. The second factor in PM10 and the fifth factor in PM2.5 explain most of the variability of Na, Mg and Cl$^-$. It has been easily recognized as marine aerosol, due to the local influence of sea salt spray. Marine aerosol is mainly contained in the coarse fraction, but in coastal locations it is also currently identified in the fine fraction (Thurston and Spengler, 1985; Pio et al., 1996; Almeida et al., 2005). The third factor in PM10 and PM2.5 have been related with road traffic emissions, as they contain large loadings of typical vehicle exhaust products such as NO_x, Pb, K, Zn, C and NO_3^-. In Spain, leaded fuel was still in use until August 2001. Since then a new fuel including K as a lubricant additive has been used. Additionally, Zn is considered as a good marker for tyre wear emissions (Huang et al., 1994; Weckwerth, 2001). During vehicle motor combustion, high loads of carbonaceous particles are emitted, mainly elemental carbon and gaseous NO_x. The fast atmospheric oxidation of NO_x into NO_3^- explains its association with these factors. Factor 4 in PM10 and PM2.5 has been interpreted as PM emitted by fuel-oil combustion processes, since it has presented high loadings for V, Ni and Cu. According to some authors (Thurston and Spengler, 1985; Harrison et al., 1997), these metals are good fingerprints of fuel-oil combustion. Therefore, it represents the influence of the emissions from distant fuel-oil consuming sources such

Table 3
Factor analysis pattern after varimax rotation for PM10 (a) and PM2.5 (b) elements concentrations

Factor 1		Factor 2		Factor 3		Factor 4		Factor 5		Factor 6	
(a) PM10											
Crustal		Marine aerosol		Road traffic		Fuel-oil combustion		Ammonium sulphate		CFPP plume fumigation	
Al	**0.91**	Mg	**0.96**	Zn	**0.74**	V	**0.87**	NH_4^+	**0.85**	SO_2	**0.73**
Fe	**0.89**	Na	**0.96**	NO_3^-	**0.72**	Ni	**0.74**	SO_4^{2-}	**0.84**	Se	**0.69**
Ti	**0.89**	Cl^-	**0.92**	NO_x	**0.68**	Cu	**0.65**	Mn	0.36	As	0.57
P	**0.79**	Ca	0.49	Pb	**0.63**	As	0.43	K	0.30	Ti	0.27
Mn	**0.72**	Cu	−0.31	C	**0.62**	NO_x	0.39	Ca	0.29	Fe	0.25
Ca	**0.63**	C	−0.36	K	0.56	Mn	0.30				
K	0.53			As	0.36						
SO_4^{2-}	0.43			Ni	0.28						
As	0.38			Fe	0.28						
NH_4^+	0.32			Mn	0.27						
Cu	0.30										
V	0.25										
% Var. = 34		**% Var. = 14**		**% Var. = 10**		**% Var. = 8**		**% Var. = 7**		**% Var. = 5**	
(b) PM2.5											
Crustal		Ammonium sulphate		Road traffic		Fuel-oil combustion		Marine aerosol		CFPP plume fumigation	
Fe	**0.92**	SO_4^{2-}	**0.94**	NO_x	**0.85**	Ni	**0.93**	Na	**0.93**	Se	**0.78**
Al	**0.90**	NH_4^+	**0.94**	C	**0.80**	Zn	**0.78**	Mg	**0.87**	SO_2	**0.67**
Ti	**0.88**	V	**0.65**	Pb	**0.66**	Cu	**0.71**	Cl^-	**0.62**	As	0.40
Mn	0.58	Mn	0.34	K	**0.62**	V	**0.62**			Cu	0.34
P	0.50	P	0.32	NO_3^-	**0.60**	Mn	0.50			Ti	0.31
Ca	0.44	Zn	0.25	As	0.52	K	0.42				
NO_3^-	0.44	Ca	−0.35	Fe	0.26	P	0.30				
Mg	0.40	Cl^-	−0.62								
K	0.29										
% Var. = 27		**% Var. = 16**		**% Var. = 11**		**% Var. = 10**		**% Var. = 8**		**% Var. = 5**	

Only factor loadings with absolute values greater than 0.25 are presented; factor loadings with absolute values greater than 0.6 are in bold.
% Var.: percentage of the variance explained by each factor.

as domestic heating, industrial use, maritime traffic and others. The fifth factor in PM10 and the second factor in PM2.5 have been associated with the formation of ammonium sulphate particles, on the basis of its good correlation with SO_4^{2-} and NH_4^+. This factor probably represents the regional background of ammonium sulphate particles in this region, formed from the local and regional emissions of the different fossil-fuel combustion sources. The sixth factor in PM10 and PM2.5 explain most of the variability of SO_2, Se and As. It has been interpreted as primary PM (fly ash) registered during fumigation episodes of the As Pontes SO_2 plume. Se and As are good fingerprints of coal combustion (Thurston and Spengler, 1985; Harrison et al., 1997). Some metals (Cu, Pb) and mineral components (Ti, Fe) have presented moderate loadings in these factors. Fly ash emitted from coal-fired power plants, may contain different metals and mineral compounds (Querol et al., 1998; Alastuey et al., 2004; Almeida et al., 2005). The relatively low gas-to-particle conversion rate of SO_2 to sulphate (when compared with other species, e.g. nitrate), has generated the formation of separated factors representing on the one hand SO_2 source emissions and on the other hand sulphate particles.

Having identified the main PM sources, their contribution to the daily samples mass was estimated by MLRA. The major PM10 mass contributor at this site has been the crustal source. On average, it has explained 30% of the bulk mass (5.5 μg m^{-3}). Road traffic has accounted for 27% (5.0 μg m^{-3}) while fuel-oil combustion, ammonium sulphate and marine aerosol contributions have been similar, representing 15% (2.9 μg m^{-3}), 14%

$(2.7\,\mu g\,m^{-3})$ and 13% $(2.4\,\mu g\,m^{-3})$ of the PM10 bulk mass, respectively. SO_2 plume fumigation have only accounted for 1% of the PM10 bulk mass $(0.24\,\mu g\,m^{-3})$ on average. As expected in this rural site, anthropogenic contributions (traffic, fuel-oil combustion and ammonium sulphate categories) are very small when compared to other results obtained during recent years with FA and MLRA in urban or industrial sites in Spain (Querol et al., 2004b; Rodríguez et al., 2004; Salvador et al., 2004) and Europe (Marcazzan et al., 2003; Almeida et al., 2005). Concerning marine aerosol, mean contribution to the PM10 mass has resulted higher than that obtained in more inland sites such as Madrid (Salvador et al., 2004) and even in some other coastal sites in Spain such as Huelva or Barcelona (Querol et al., 2004b). However, it has been lower than that obtained at Atlantic coastal sites such as Lisbon (Almeida et al., 2005) or the Canary Islands (Querol et al., 2004b). This suggests a latitudinal effect in marine aerosol production (Grini et al., 2002).

Road traffic have accounted for 35% $(4.7\,\mu g\,m^{-3})$ while fuel-oil combustion and ammonium sulphate categories, have represented 20% (2.7 and $2.6\,\mu g\,m^{-3}$, respectively) of the PM2.5 bulk mass. Estimations of the traffic and industrial contributions to the PM2.5 mass obtained with the same methodology at urban sites, such as Barcelona (Querol et al., 2004b), Milan (Marcazzan et al., 2003) and Lisbon (Almeida et al., 2005) have been much higher. That is a consequence of the rural character of Bemantes and also of the higher number and diversity of PM sources involved in these cities. Otherwise, crustal and marine sources have represented 15% $(1.9\,\mu g\,m^{-3})$ and 2% $(0.3\,\mu g\,m^{-3})$ of the mean PM2.5 mass, respectively. Estimations of the PM2.5 mean mass attributed to crustal particles obtained at Barcelona, Milan and Lisbon have been higher, from 3.4 to $6.5\,\mu g\,m^{-3}$, probably due to the existence of additional sources in these urban sites such as erosion of road pavements, construction and demolition activities, or primary industrial emissions of crustal material. The mean PM2.5 mass attributed to the SO_2 plume fumigation episodes has also been very small on average $(0.1\,\mu g\,m^{-3})$. These episodes are sporadic and generally lasting only some hours (Fig. 2a). Besides, the high efficiency rates (>99%) for the electrostatic precipitators used in power plants, prevent the emission of significant amounts of fly ash.

The seasonal distribution of the PM mass source contribution confirms the influence of the different processes affecting levels and composition. Time series of source contribution for PM10 and PM2.5 samples and mean seasonal source contributions in Bemantes are displayed in Figs. 4a and b, respectively. The PM10 and PM2.5 mass contribution from the crustal, fuel-oil combustion, ammonium sulphate and SO_2 plume fumigation categories has been higher from May to September. Atmospheric conditions produced in this period favoured mineral dust re-suspension, power plant plume fumigation and transport of PM emissions from distant fuel-oil consuming sources. Under high insolation conditions, the mixed layer development is thermally enhanced, which would cause the abatement of the plumes as well as soil dust re-suspension by wind and convective processes (Querol et al., 1998; Alastuey et al., 2004). It should also be considered that in summer there is a higher SO_2 to SO_4^{2-} oxidation rate, $6\%\,h^{-1}$, than in winter, $<1\%\,h^{-1}$ (Querol et al., 1998). In addition, there was a higher frequency of African dust outbreaks produced in this period. Road traffic mean contribution to PM10 and PM2.5 mass has shown a maximum in the winter and a minimum in summer (Figs. 4a and b). This seasonal trend is the consequence of the lower dispersion atmospheric conditions during the winter episodic periods that took place that year, especially in November and December. The marine aerosol contribution to the PM10 total mass was higher during the spring on average (Fig. 4a), when the pass of Atlantic frontal system was more frequent. In PM2.5, substantial differences were not detected in the marine aerosol mass contribution throughout the year (Fig. 4b).

3.5. Back-trajectory statistical analysis

In this work, CF have been obtained and analysed for those components in PM10 and PM2.5, considered the best tracers for each source, in accordance with results obtained in the FA. For each component, CF obtained have been very similar for the PM10 and PM2.5 datasets. Consequently only the results obtained with the PM10 dataset are shown.

Concerning the crustal source, CF were obtained for Ti, Al, Fe and Mn. The greatest potential contribution areas of Ti and Al have been located in North Africa, including Western Sahara and Moroccan Atlas (Fig. 5a and b). These areas have
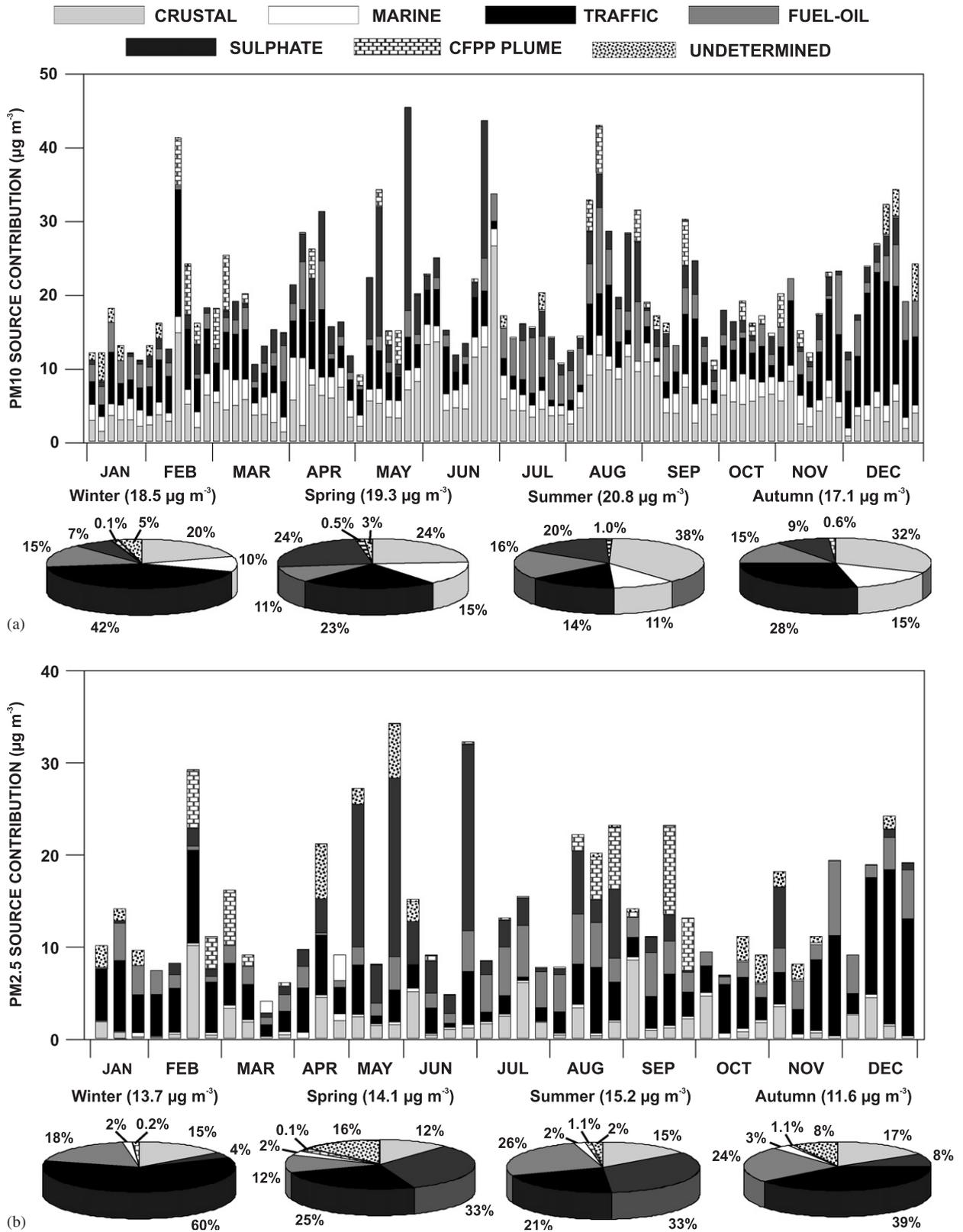
Fig. 4. Time series of the source contribution for PM10 (a) and PM2.5 (b) total mass and mean seasonal total mass in percentage.
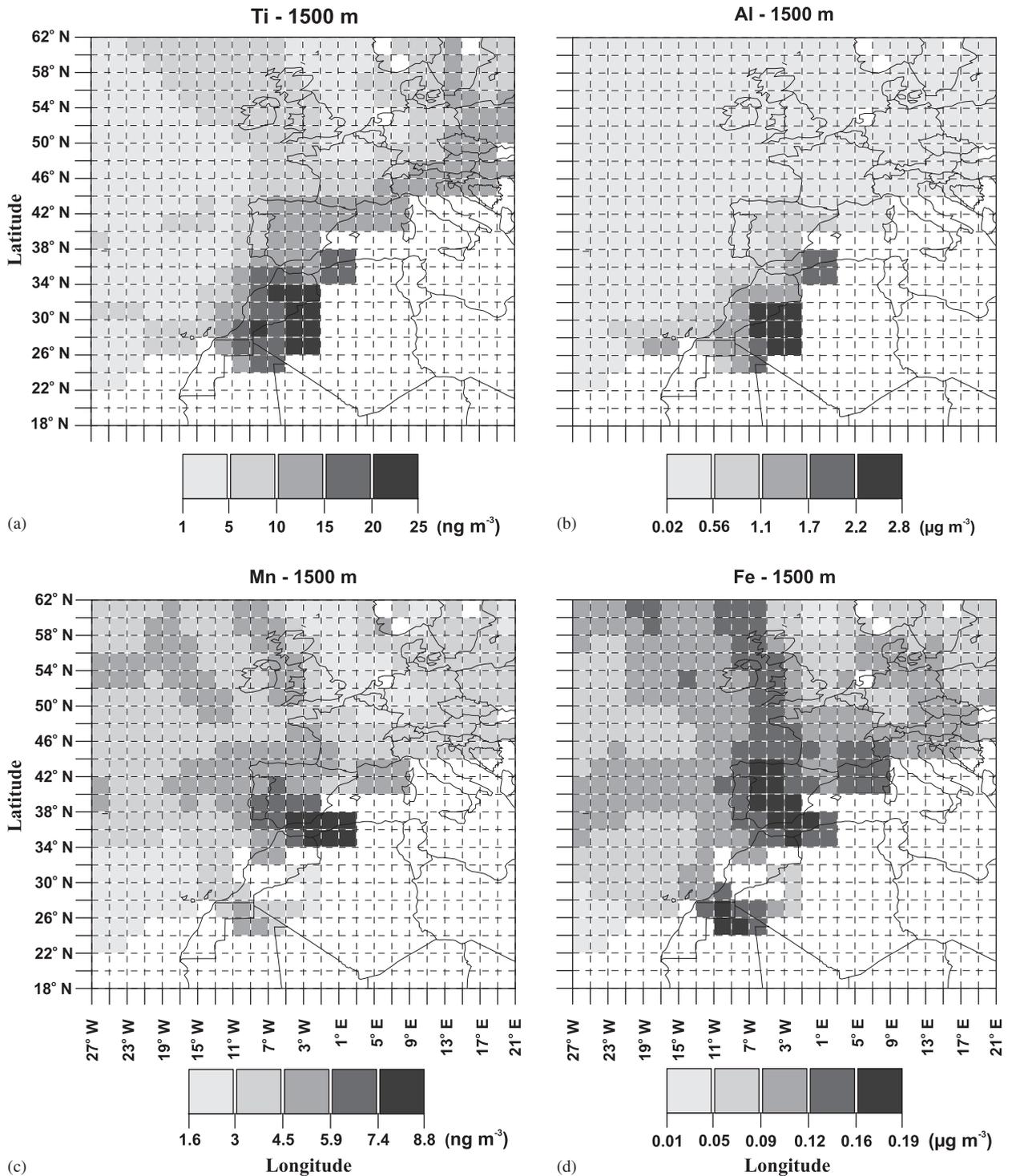
Fig. 5. CF for Ti (a), Al (b), Mn (c) and Fe (d) in PM10 corresponding to back-trajectories starting at 1500 m AGL.

also been identified by other authors (Prospero et al., 2002) as important sources of desert dust in North Africa. Ti and Al are major compounds of

African dust composition and have presented sharp increases in the daily concentration time series during these episodes. It is interesting to observe

that different potential sources have been identified in the CF maps for Mn and Fe (Fig. 5c and d). The highest concentration values have been obtained over and nearby the Iberian Peninsula. Moderate to high concentration values were detected over North Africa. This is interpreted as the contribution from local and regional soil dust to the levels of Mn and Fe registered at Bemantes, which was much higher than the contribution from African dust outbreaks.

Concerning the marine aerosol, CF maps were obtained for Na and Cl^-. They have clearly defined different regions of the Atlantic Ocean as the origin of the air masses that arrive at Bemantes, where their highest concentration values have been obtained (Fig. 6). This confirms the simultaneous sharp increases of Na and Cl^- recorded at the Bemantes site during advections of Atlantic air masses associated to frontal systems. Model estimations of sea salt production present a maximum in winter at mid-latitudes near the Atlantic border of the European continent (Grini et al., 2002). Although marine aerosol has been considered a local source, these results represent the high influence of Atlantic frontal systems in the generation of NaCl particles by the high wind speed and associated surf activity.

In the case of ammonium sulphate, fuel-oil combustion and SO_2 plume fumigation categories, CF maps were analysed for SO_4^{2-} and NH_4^+, V and Se, respectively. All have produced very similar results. The highest concentration values have been obtained over and nearby the Iberian Peninsula (Fig. 7). This can be interpreted as their having been recorded under conditions of regional transport of the air masses. Regional PM episodes are characterised by a lack of significant air mass advection and the prevalence of regional atmospheric circulations under high insolation conditions. This meteorological scenario is typically produced in the summer and favours regional transport from distant sources, fumigation episodes, formation of ammonium sulphate particles by photochemical conversion and turbulence and convective dynamics that cause the re-suspension of soil particles (Millán et al., 1997; Querol et al., 2004a; Alastuey et al., 2004). This is one of the main reasons why, the PM10 and PM2.5 mass contribution from the crustal, fuel-oil combustion, ammonium sulphate and SO_2 plume fumigation categories, have been higher in the summer than in the other seasons (Fig. 4).

The CF obtained for the components mostly associated to road traffic (C and NO_3^-) produced
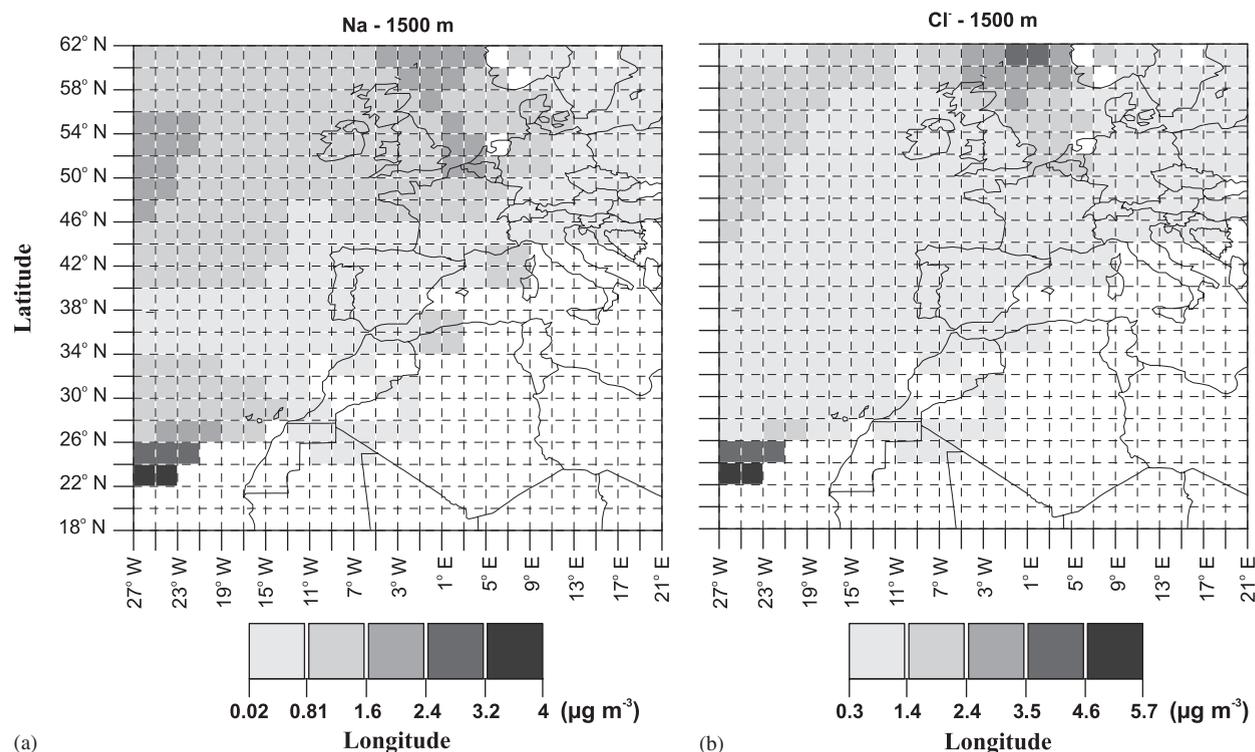
Fig. 6. CF for Na (a) and Cl^- (b) in PM10 corresponding to back-trajectories starting at 1500 m AGL.
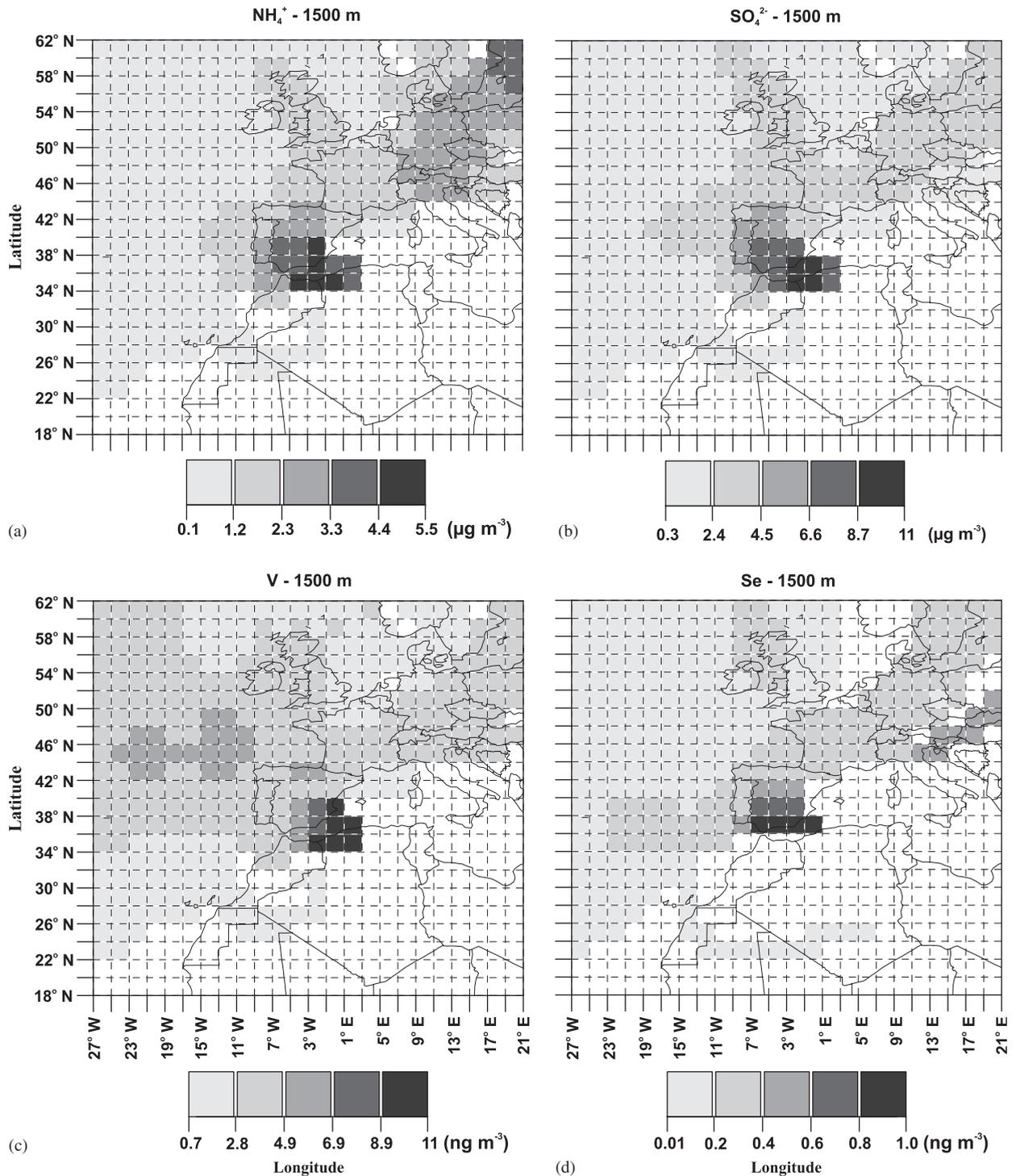
Fig. 7. CF for NH_4^+ (a), SO_4^{2-} (b), V (c) and Se (d) in PM10 corresponding to back-trajectories starting at 1500 m AGL.

different results. The cells with the highest concentration values of C were found over regions of the Atlantic Ocean (Fig. 8a). They are interpreted as transport pathways of air masses produced by

persistent synoptic situations during anthropogenic local episodes, mainly high-pressure systems over the Iberian Peninsula. In these cases of high atmospheric stability, the surface layer is decoupled
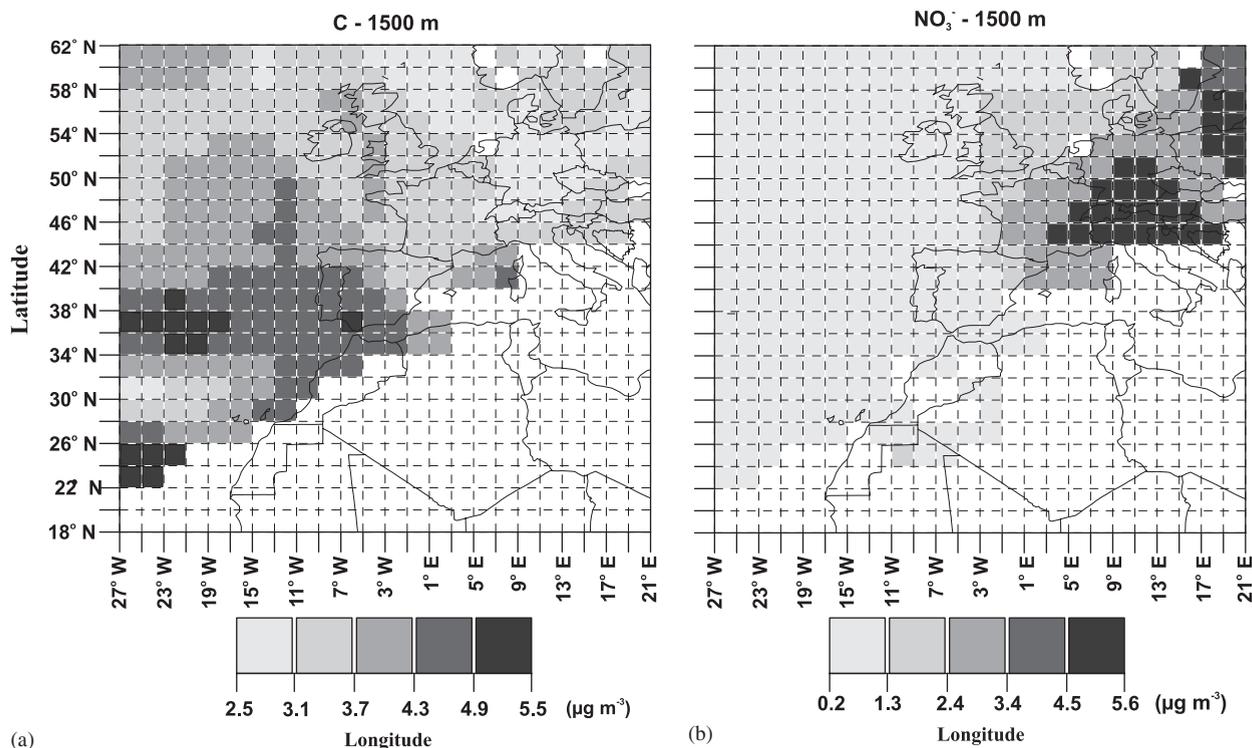
Fig. 8. CF for C (a) and NO_3^- (b) corresponding to back-trajectories starting at 1500 m AGL.

from higher atmospheric layers, so that the trajectories obtained with the air mass trajectory model do not provide a good description. A similar result was obtained with a different back-trajectories analysis performed for C in an urban area (Salvador et al., 2004).

In contrast, the highest concentration values for NO_3^- have been obtained over northern Italy, Germany, Poland, Switzerland, Austria and the Czech Republic (Fig. 8b). All these countries are considered as important source areas of nitrogen oxides emissions in Europe (Lövblad et al., 2004). Moreover, they agree fairly well with maxima in the European nitrate concentration field obtained by Schaap et al. (2002). Significant high concentration values have also been obtained over Eastern Europe. Most of the NO_3^- registered in Bemantes during 2001 must be locally produced, as it has been strongly associated with road traffic (Table 3). However, meteorological analysis has identified some periods in February and December characterized by a European transport pattern of the air masses towards the northwest of Spain. Under this meteorological scenario, the highest NO_3^- concentration values have been recorded. Therefore, a

transport of NO_3^- from highly polluted European urban and industrial regions could contribute to increase concentration values obtained in Bemantes during these periods. This result is consistent with the work of Abdalmogith and Harrison (2005), which used back-trajectory cluster analysis to detect long-range transport episodes of SIC in the UK. These authors have concluded that the highest concentrations of SO_4^{2-} and NO_3^- at a rural and an urban location are recorded when air parcels pass over the European source regions en route to the UK. They also found a greater contribution of NO_3^- than SO_4^{2-} to the PM10 annual mean, and have suggested that continental air may carry higher concentrations of other primary and secondary pollutants.

4. Conclusions

In this study, a methodology has been applied for discriminating PM contributions from sources at different geographical scales, in a rural background site. This methodology combines the characterization of high PM concentration periods with FA and back-trajectory statistical analysis. Each analysis

has been applied separately in different studies. Each has advantages and disadvantages; however, when used in combination they provide information that is not available if only one of them is used. In this study we have tried to relate the information provided by each one. This has allowed to determine that this background site is under the influence of natural and anthropogenic sources from the local scale and from regional and long-distance transport processes. With this methodology we have been able to discriminate the long-range transport PM contribution from the local and regional ones. From the results obtained we would like to emphasize as the main significant finding, the identification of long-range transport processes of anthropogenic PM from Central and Eastern Europe to North-western Spain. As far as we know this is the first time that these processes are identified and characterized in Spain. This knowledge must be taken into account in the design of effective abatement strategies for achieving compliance with the European air quality standards. Currently only a few PM source identification and apportionment studies are being carried out at rural background sites in Europe, but the results obtained strongly confirm the high impact of different anthropogenic sources on PM mass and composition. In consequence, special attention should be placed on regional and long-range transport processes of emissions from anthropogenic sources.

Acknowledgements

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