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PII: S1352-2310(14)00162-9
DOI: 10.1016/j.atmosenv.2014.03.001
Reference: AEA 12816

To appear in: Atmospheric Environment

Received Date: 17 December 2013
Revised Date: 25 February 2014
Accepted Date: 1 March 2014

Please cite this article as: Titos, G., Lyamani, H., Pandolfi, M., Alastuey, A., Alados-Arboledas, L., Identification of fine (PM$_1$) and coarse (PM$_{10-1}$) sources of particulate matter in an urban environment, Atmospheric Environment (2014), doi: 10.1016/j.atmosenv.2014.03.001.

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Identification of fine (PM$_{1}$) and coarse (PM$_{10-1}$) sources of particulate matter in an urban environment

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Abstract

PM$_{10}$ and PM$_1$ samples were collected at an urban site in southeastern Spain during 2006-2010. The chemical composition of all samples has been determined and analyzed by Positive Matrix Factorization (PMF) technique for fine and coarse source identification. The PMF results have been analyzed for working and non-working days in order to evaluate the change in PM sources contribution and possible future abatement strategies. A decreasing trend in PM$_{10}$ levels and in its constituents has been observed, being partly associated to a reduction in anthropogenic activities due to the economic crisis. The use of fine and coarse PM in the PMF analysis allowed us for the identification of additional sources that could not be identified using only one size fraction. The mineral dust source was identified in both fractions and comprised 36 and 22% of the total mass in the coarse and fine fractions, respectively. This high contribution of the mineral source to the fine fraction may be ascribed to contamination of the source profile. The regional re-circulation source was traced by secondary sulfate, V and Ni. It was the most important source concerning PM$_1$ mass concentration (41% of the total mass in this fraction). Although V and Ni are commonly associated to fuel oil combustion the seasonality of this source with higher concentrations in summer compared with winter suggest that the most important part of this source can be ascribed to regional pollution episodes. A traffic exhaust source was identified but only in the fine fraction, comprising 29% of the fine mass. The celestite mines source associated with nearby open-pit mines was typified by strontium, sulfate and mineral matter. PM$_{10-1}$ levels were higher in working days, whereas PM$_1$ levels remained fairly constant throughout the whole week. As a conclusion, traffic seems to be the main source to target in Granada.
Keywords: PMF, source apportionment, PM1, PM10, urban aerosols

1. Introduction

Particulate matter (PM) is a pollutant of great concern nowadays due to its negative effects on human health (Pope and Dockery, 2006). Apart of its harmful effects on human heath, PM also affects visibility and alters the Earth’s radiative balance (Forster et al., 2007). For these reasons, European directive 2008/50/EC regulates the levels of PM$_{10}$ (particles with an aerodynamic diameter <10 µm) setting the daily limit in 50 µg/m$^3$ that cannot be exceed more than 35 times per year and the annual limit in 40 µg/m$^3$. In addition to PM$_{10}$, PM$_{2.5}$ (particles with an aerodynamic diameter <2.5 µm) is also regulated in the European directives (annual limit value of 25 µg/m$^3$ mandatory for 2015), however, there is no regulation concerning PM$_1$ (particles with an aerodynamic diameter <1 µm). This fact evidences a gap in the European legislation because it is well known that most anthropogenic pollutants tend to accumulate in the finer fractions and that fine particles present harmful effects on human health (Pope and Dockery, 2006). Thus, a number of papers have shown that, based on size modality of PM and on composition size-dependence, the combination of PM$_{10}$ and PM$_1$ measurements is a good tool for air quality monitoring (e.g. Morawska et al., 2008; Pérez et al., 2008). PM$_{2.5}$ measurements are widely performed and used for source apportionment studies, however, the combination of PM$_1$ with PM$_{10}$ is not so common. In particular, Perrone et al. (2013) highlighted the importance of PM$_1$ measurements because it provides a better estimation of anthropogenic particles than PM$_{2.5}$.
The concentration of PM at a specific location depends on a large number of factors, such as local and regional PM sources as well as the meteorological conditions and geographical situation. Thus, the design of strategies to reduce the concentrations of PM and meet the European targets is a very difficult task. In this sense, several studies were conducted during the past years in order to assess the main sources affecting PM concentration at different environments by applying different methodologies. Receptor models, like Positive Matrix Factorization (PMF, Paatero and Tapper, 1994), are widely used to identify the main sources affecting PM from its chemical composition. Pant et al. (2012) remarked the need of using size fractionated particulate matter in order to have an additional insight on aerosol sources. However, there are only a few published works that use receptor models to identify coarse aerosol sources separately from fine aerosol sources (e. g. Karanasiou et al., 2009; Pandolfi et al., 2011; Minguillón et al., 2012). In addition, most source apportionment studies are focused on sampling campaigns or short measurement periods (e. g. Minguillón et al., 2012). The objective of this study is to assess the results obtained from source apportionment analysis applied on chemical composition of size segregated data (coarse, PM$_{10-1}$, and fine, PM$_1$, fractions) for an extended period of time (from 2006 to 2010). The use of fine and coarse PM in the PMF analysis offers an additional insight into the sources that may affect one of the size fractions and not the other. The exhaustive chemical speciation and the quite long sampling period allow us for the identification of time trends in PM concentration and sources. The study is focused in an urban environment where the identification of sources contributing to PM is of great importance in order to establish abatement strategies and meet the European requisites.

2. Site and Methodology
2.1. Monitoring site

The measurements presented in this study were performed at Granada (37.18°N, 3.58°W, 680 m a.s.l), from 2006 to 2010. Granada is situated in the southeastern part of the Iberian Peninsula and is a medium-sized city surrounded by mountains. Near continental conditions are responsible for large seasonal temperature differences with most rainfall occurring in spring and winter. The sampling site is located in the southern part of the city and it is less than 500 metres away from a highway that surrounds the city.

2.2. Chemical analyses

Simultaneous 24-hour samples (starting at 07:00 GMT) of PM$_1$ and PM$_{10}$ were collected on quartz fiber filters by means of two high-volume samplers (CAV-A/MSb and Digitel DHA-80) with a flow rate of 30 m$^3$ h$^{-1}$. The PM$_1$ and PM$_{10}$ daily samples were collected every eight days from 2006 to 2010, except when failure of the instruments occurred. A total of 197 samples in PM$_{10}$ and 163 in PM$_1$ were collected during the analysed period. The filters were conditioned and treated pre- and post-sampling. The filters were placed in desiccators during 48 hours prior to weighting at stabilized conditions (23°C and 50% RH) using gravimetric techniques.

A complete chemical analysis was performed for all samples following the procedure of Querol et al. (2001). A fraction of each filter was acid digested (HF HNO$_3$:HClO$_4$, 5:2.5:2.5 ml) and the resulting solution was used to determine major and trace elements by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Mass Spectrometry (ICP-MS). Another portion of the filter was water leached with de-ionized water in order to determine the concentration of Cl$^-$, SO$_4^{2-}$ and NO$_3^-$ by ion chromatography.
and NH₄⁺ mass concentration by colorimetry (Flow Injection Analysis). A third portion of the filter was used to determine total carbon (Ct) content (Querol et al., 2013). From 2006 to July 2007 the total carbon mass concentration was determined using a LECO (Querol et al., 2004), whilst since July 2007 the organic carbon (OC) and elemental carbon (EC) mass concentrations were determined separately by means of a thermo-optical transmission method using a Sunset Laboratory OCEC Analyser following the EUSAAR2 thermal protocol (Cavalli et al., 2010). SiO₂ and CO₃²⁻ were indirectly determined on the basis of empirical factors (SiO₂ = 3 x Al₂O₃ and CO₃²⁻ = 1.5xCa; Querol et al., 2004). Marine sulfate (SO₄²⁻m) concentration was calculated taking into account the Na/SO₄²⁻ molar ratio determined for seawater (Drever, 1982). Non marine sulfate (SO₄²⁻nm) was calculated as the difference between total sulfate and marine sulfate. The non-mineral carbon (nmC) was estimated by subtracting the C associated to carbonates from the total carbon content. PM₁₀⁻¹ mass concentrations were calculated as the difference between PM₁₀ and the corresponding PM₁ mass concentrations. PM components were grouped as follows: mineral (Σ Al₂O₃, SiO₂, CO₃, Ca, Fe, Mg, K), secondary inorganic aerosols, SIA, (Σ SO₄²⁻nm, NO₃⁻, NH₄⁺), salt (Σ Na, Cl, SO₄²⁻m), OC, EC and trace elements (Σ Li, P, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Cd, Sn, Sb, Cs, Ba, La, Ce, Lu, Hf, Ta, W, Ti, Pb, Bi, Th and U).

2.3. Source apportionment method

The chemical profiles of the potential sources affecting PM₁₀⁻¹ and PM₁ levels and their contributions were identified by analyzing the PMₓ composition data set with the Positive Matrix Factorization model (PMF2; Paatero, 1997). The PM₁ matrix included 163 cases and 24 variables whilst the PM₁₀⁻¹ matrix consisted of 130 cases and 22 variables. PMF
model is a factor analytical tool that provides the chemical profile and contribution of the identified sources by solving the matrix problem \( X = G \times F + E \) where \( X \) is the matrix of daily chemical speciated data, \( G \) and \( F \) are the unknown matrixes of factor scores (source contribution) and loading (source profile), respectively, and \( E \) is the matrix of residuals (difference between measured and calculated species concentrations) (Paatero and Tapper, 1994; Paatero, 1997). The problem is solved by minimizing the objective function \( Q = E/S \) where \( S \) is the matrix of the uncertainty in each data value. The minimization of \( Q \) is based on the error-weighted least squares method, thus the calculation of the matrix \( S \) is a crucial point so that the model gives the right weight to the input data and consequently the most reliable results. In the present study, the matrix \( S \) for PM\(_1\) and PM\(_{10}\) fractions was calculated following the procedure described by Amato et al. (2009) and Escrig et al. (2009) by propagating the uncertainties of the analytical procedures jointly with the uncertainty related with the subtraction of the blank filters that are different filters from the sampled ones. The applied formula gives higher relative errors for small concentration data near the limit of detection. The uncertainties for the PM\(_{10-1}\) fractions were calculated by propagating the errors calculated for the PM\(_1\) and PM\(_{10}\) fractions with the above described methodology. The number of species used within the PMF model was selected by looking at their signal-to-noise ratio (S/N) which provides a criterion to separate the species which retain a significant signal from the ones dominated by noise. The S/N was calculated as described by Paatero and Hopke, (2003). Only species with S/N values higher than 2 were selected for the present study, thus species with weak signal were not introduced in the model (Paatero and Hopke, 2003). Moreover, the percentage of data above detection limit (%ADL) was used as complementary criterion for species selection. The combination of both criteria resulted in the selection of 24 species in PM\(_1\) and 22 species in PM\(_{10-1}\). Two
species (As and NH$_4^+$) were included in PM$_1$ and removed from PM$_{10-1}$ given that these two elements were found mainly in the finest fraction. In order to avoid bias in the results the data matrix was uncensored, i.e. negative values and data below detection limits were included as such in the analysis without substituting them with below detection limit indicators (Paatero, 1997). Table S1 of the supplementary material reports means, standard deviations, medians, percentage of data above detection limit (%ADL) and signal-to-noise (S/N) for the selected elements. The PMF2 model was run in robust mode (Paatero, 1997) for source identification and apportionment. The optimal number of sources was selected by inspecting the variation of Q from PMF with varying number of sources (from 3 to 6) and by studying the physical meaningfulness of the calculated factors. In the present work, 5 and 4 sources were selected for PM$_{10-1}$ and PM$_1$, respectively. The theoretical value of Q should be approximately equal to the number of degrees of freedom of the system $[n\times m−(p\times(n+m))]$ (Paatero et al., 2002) where n, m and p are the number of samples, species and factors respectively. In PM$_1$ (with p=4) and PM$_{10-1}$ (with p=5) the degrees of freedom were 3356 and 2320, respectively, close to the calculated Q (3626 and 2586 for PM$_1$ and PM$_{10-1}$, respectively). Moreover, in PM$_1$ and PM$_{10-1}$ the solution with 5 and 6 factors, respectively, led to additional factors without a meaningful chemical profile both being loaded with almost all used species. One additional criteria used to evaluate the meaningfulness of the calculated sources was the inspection of the scaled residuals. In both fractions the selected number of factors led to solutions with 90–100% of the scaled residuals located between the optimal range −2 and +2 (Juntto and Paatero, 1994). Once the number of sources was selected the rotational ambiguity was handled by means of the Fpeak parameter by studying the variation in the Q values by varying Fpeak from −0.8 and +0.8. Fpeak rotations were made in order to explore alternative solutions. The issue of local
minimum was assessed by running 20 times the Fpeak=0 solution with different
pseudorandom initializations. After regression of the factor scores from PMF (G matrix) to
PM mass the model was able to simulate on average 100% and 97% of measured PM$_{10-1}$
and PM$_1$ mass, respectively, with coefficients of correlation of 0.97 (PM$_{10-1}$) and 0.75
(PM$_1$) (Figure S1).

3. Results and discussion

3.1. PM concentration: major and trace elements

Mean (± standard deviation) PM levels measured at Granada urban station for the entire
observation period 2006-2010 were 40 ± 30 µg/m$^3$ and 17 ± 9 µg/m$^3$ for PM$_{10}$ and PM$_1$,
respectively. The chemical speciation obtained in this study was very similar to that
reported previously for the year 2006 (Titos et al., 2012). PM$_{10-1}$ was mainly composed by
mineral matter (around 62%) and nmC (12%) whilst PM$_1$ was composed mainly by nmC
(32%) and SIA that contributed around 20%. Figure 1 shows the chemical speciation of
PM$_{10-1}$ and PM$_1$ fractions during winter (November-February) and summer (May-August).
This separation can offer an insight in the possible sources and processes affecting coarse
and fine PM. Also the partitioning between PM$_1$ and PM$_{10-1}$ (expressed through the ratio
PM$_1$/PM$_{10}$) can help to elucidate the origin of the elements analyzed (Figure 2). Mineral
matter was mainly in the coarse mode and its contribution to this fraction was higher in
summer than in winter (Figure 1). Figure 2 also evidences this fact; most of the crustal
elements presented low PM$_1$/PM$_{10}$ ratios denoting that those elements are mainly in the
coarse fraction. The higher contribution of mineral matter to PM$_{10-1}$ in summer can be due
to the drier conditions that favor re-suspension of dust from roads and soils as well as to the
dust intrusions from North Africa that are very frequent in Granada during summer season (Valenzuela et al., 2012). The contribution of nmC to PM_{1} fraction was higher than the contribution to PM_{10-1} and also higher in winter than in summer. This seasonality of carbonaceous material is typical of urban sites and may be due to the increase in anthropogenic emissions (fuel based domestic heating) and lower mixing layer heights during winter season (Granados-Muñoz et al., 2012) that favor accumulation of particles near urban sources. In addition, during winter time, stagnant episodes associated with thermal inversions and low wind speeds are also very frequent producing a large increase in particle matter load near the ground (Lyamani et al., 2012).

[Figure 1]

Non marine sulfate was presented in both PM fractions, with slightly higher contribution in PM_{1} than in PM_{10-1}. This constituent doubled its contribution to PM_{1} during summer due to the higher SO_{2} oxidation rates under high insolation conditions and low regional air mass renovation in summer (Pey et al., 2009). On the contrary, nitrate contribution to PM_{1} decreased considerably during summer due to the thermal instability of the ammonium nitrate in summer (Harrison and Pio, 1983; Querol et al., 2008). Nitrate contribution to PM_{10-1} did not vary significantly between seasons compared with its contribution to PM_{1} and presented a PM_{1}/PM_{10} ratio around 0.56 in winter and 0.15 in summer denoting that in summer nitrate was mainly in the coarse fraction whilst in winter was predominantly in the fine one. Coarse nitrate is formed by interaction between HNO_{3} and coarse marine (sodium chloride) or mineral (calcium carbonate) particles giving rise to the formation of Na and/or Ca nitrates explaining the higher concentrations of coarse nitrate observed in summer (Tobo et al., 2010).
Most trace elements presented relatively low concentrations compared with the typical values observed in other Spanish urban stations (Querol et al., 2008). Elements associated with road traffic such as Cu and Sb (from brake abrasion; Schauer et al., 2006), Ba and Zn (from tyre abrasion; Wahlin et al., 2006) and Ti, Li, and Rb, among others, from road pavement abrasion (Querol et al., 2008; Amato et al., 2011) tended to accumulate in the coarse fraction (50 to 90%). On the other hand, Ni presented a higher PM$_1$/PM$_{10}$ ratio ranging from 0.5 during winter to 0.7 in summer. Other elements associated with industrial processes (As, Pb, Cd and U; Querol et al., 2008) mostly accumulate in the fine fraction. Most elements presented higher PM$_1$/PM$_{10}$ ratios during winter compared with summer, except Bi, Sn, V, Ni and EC. A different seasonality in the PM$_1$/PM$_{10}$ ratio may suggest differences in the sources contributing to these compounds in winter and in summer (see next section). A similar seasonal behavior for the PM$_1$/PM$_{10}$ ratios for Ni, Sn, EC and V was also observed in Switzerland by Minguillón et al. (2012).

Mean PM$_{10}$ annual levels decreased from 50 ± 30 $\mu$g/m$^3$ in 2006 to 40 ± 30 $\mu$g/m$^3$ in 2010. Meteorological conditions and emissions are competitive processes determining the magnitude of PM concentrations in the atmosphere. Thus, the year to year variability observed in PM$_{10}$ levels could be related to inter-annual variations in emissions sources or to changes in the meteorological and synoptic conditions, or to both. In order to detect possible trends in PM$_{10}$ and PM$_1$ component levels, the Mann-Kendall test has been applied to the annual average values. This test reveals a significant decreasing trend (at 0.1 significance level) in PM$_{10}$ and mineral matter concentrations. Saharan dust intrusions over Granada have a large impact on the PM$_{10}$ and PM$_1$ levels and their constituents (Calvo et
al., 2010; Mladenov et al., 2011). Thus, part of the observed year to year variations in PM$_{10}$ and PM$_{1}$ component levels could be due to the inter-annual variation in the frequency and intensity of Saharan dust events. In order to discard the variability caused by African dust events, the samples collected under those conditions have been excluded. A total of 134 PM$_{10}$ samples were collected under African dust free conditions (www.calima.ws). Under these conditions, significant decreasing trends at 0.05 significance level were obtained for PM$_{10}$ mass concentration, mineral matter, nmC and V and at 0.1 significance level for SIA, Cu and Pb. No trends were obtained for trace elements such as Ni, Sn, Sb, Co, Zn or Cr. Lyamani et al. (2011) reported that equivalent black carbon mass concentrations decreased on 2008 due to the decrease in anthropogenic activities in Granada. The current work shows that this decrease has continued until 2010 and that other anthropogenic pollutants have also decreased. On the other hand, annual PM$_{1}$ levels did not experience any significant temporal trend according to the Mann-Kendall test. Recent studies of Barmpadimos et al. (2012) and Cusack et al. (2012) have reported a decreasing trend in PM$_{2.5}$ levels at regional stations across Europe for the periods 1998-2010 and 2002-2010, respectively. In the study of Barmpadimos et al. (2012) the decrease observed in PM$_{2.5}$ was more pronounced than the decrease observed for PM$_{10}$ levels. However, in Granada, the decrease was mainly observed in the PM$_{10}$ fraction. This discrepancy could be ascribed to different sampling sites between studies (regional versus urban) and to different size fractions (PM$_{2.5}$ versus PM$_{1}$). Thus, we believe that the observed decrease in PM$_{10}$ and its constituents may be related, in large part, to a decrease in the anthropogenic activities although part of the observed decrease may be also due to the inter-annual change in the meteorological conditions.
3.2. Apportionment and seasonality of the sources identified by PMF.

Five PM$_{10-1}$ and four PM$_{1}$ sources were identified by PMF analysis. Figure 3 and Figure 4 show the profiles of each source in the coarse and fine fractions, respectively, and the percentages of species apportioned by each source. The sources identified in the coarse fraction were named as mineral dust, regional re-circulation, aged regional, road dust and celestite mines. Fine PM sources were mineral dust, regional re-circulation, traffic exhaust and road dust. Although some sources were identified in both fractions the use of fine and coarse PM in the PMF analysis allows for the identification of additional sources.

- Mineral dust

The mineral source was identified in both fractions and was characterized by crustal elements (Al$_2$O$_3$, Ca, Mg, Fe, Ti, Sr). This source might have contribution of both local (re-suspension from soils and construction activities) and long-range transported dust aerosols. It comprised 36 and 22% of the total mass in the coarse and fine fractions, respectively. It is necessary to highlight the high contribution of this source to the fine fraction since mineral matter commonly accumulates in the coarse fraction (Song et al., 2012). Some authors (Minguillón et al., 2012; Perrone et al., 2013; Cusack et al., 2013) have identified mineral sources by applying PMF. However, none of them reported such high contributions to the fine fraction. This high contribution to the fine fraction may be ascribed to contamination of the source profile although the profile was not cleaner for other Fpeak values. The presence of SO$_4^{2-}$ and C in the mineral PM$_{1}$ profile could be due to: 1) Neutralization of sulfuric acid with available ions such as Ca$^{++}$ and Na$^+$ (also present in the mineral PM$_{1}$ profile) and 2) Contamination by C due to condensations of organic precursors on large
surface mineral particles. Using PMF analysis the contribution of mineral matter doubled
the contribution calculated as Σ Al₂O₃, SiO₂, CO₃, Ca, Fe, Mg, K. Concerning the
seasonality of this source, it showed a higher contribution to PM in summer than in winter
probably connected with the higher frequency of African dust events during spring and
summer and with the dryness of the soil which favor re-suspension processes.

- Road dust

The road dust source was slightly different for each size fraction. In PM₁ it was mainly
categorized by carbonaceous particles and Sb (90% of the total variance of Sb) whereas in
the coarse fraction it was typified by carbonaceous material and road tracers like Fe, Cu,
Sn, Sb and Pb (Amato et al., 2009). This source was predominantly in the coarse fraction,
comprising 8% and 24% of the total fine and coarse PM, respectively. It presented a similar
seasonality in both fractions with higher contribution to the coarse and fine mass in winter
(48% and 11%, respectively) with respect to summer (12% and 7%, respectively) (Figure
5). The interpretation of this source is supported by the polar plots, since higher
concentrations (Figure S3) were obtained for low wind speeds and for southwesterly winds
(in the direction of the highway). A similar contribution of road dust to PM₁₀ was obtained
in a traffic oriented site located in the northern part of the city (Amato et al., 2013).

-Traffic exhaust

This source was only identified in the fine fraction and it was characterized by nitrate,
ammonium and carbonaceous particles, comprising 29% of the fine mass. This source
explained 86% of variance in nitrate that in urban environments is mainly attributed to
vehicle exhaust (Almeida et al., 2006). The presence of some road tracers confirms the
traffic origin of this source. The higher contribution in winter can be connected with higher emissions together with lower mixing layer heights (Granados-Muñoz et al., 2012) that favor accumulation of pollutants near the surface. In addition, fine nitrate concentrations could increase in winter due to the thermal stability of particulate nitrate. In this sense, it is important to have in mind that the formation of secondary products from primary emissions depends on the season and that primary products are not always transformed into the same compounds in the atmosphere. The polar plots (Figure S3) and the seasonality of this source and the road dust source are very similar, confirming a common source.

- Regional re-circulation

This source is traced by secondary sulfate (mainly in the form of ammonium sulfate), V and Ni. It is the most important source concerning PM$_1$ mass concentration, comprising 41% of the total mass in this fraction. Secondary sulfate, V and Ni are commonly associated with fuel-oil combustion and used as tracers for domestic heating and traffic sources (e.g. Calvo et al., 2013). In addition, high concentrations of V, Ni and sulfate, especially during summer season, are commonly reported in Mediterranean environments associated with re-circulation processes (Pey et al., 2013). The seasonality of the regional re-circulation source (Figure 5) with higher contribution in summer (9.5 µg/m$^3$ in PM$_1$ and 2.0 µg/m$^3$ in PM$_{10-1}$) compared to winter (4.0 µg/m$^3$ and 1.1 µg/m$^3$ in PM$_1$ and PM$_{10-1}$, respectively) suggests that an important part of this source may be ascribed to regional pollution and long range transport, especially in summer, although in winter it may be ascribed to domestic heating, being the PMF analysis unable to distinguish between both sources. In this sense, also the variations in the PM$_1$/PM$_{10}$ ratios of V and Ni in summer and winter (Figure 2) evidence differences in the sources contributing to these compounds depending on the season.
- **Aged regional**

This source was typified by nitrate, sulfate, Na, Cl, Se and Ct, and has been interpreted as aged regional, being only identified in the coarse fraction. Its seasonality is characterized by a relatively high contribution during the warm season (14%, 5.5 µg/m³) compared with winter (12%, 2.4 µg/m³). It is thought to be related with the interaction of secondary compounds (sulfates and nitrates) with mineral matter and marine aerosols. Regional recirculation processes together with Saharan dust intrusions (both more frequent in summer season) may favor this interaction. In fact, the presence of coarse nitrate in this source (62% of the variance) is thought to be related with the aforementioned formation of Ca(NO₃)₂ during dust events due to the interaction of mineral dust with anthropogenic pollutants (Tobo et al., 2010).

- **Celestite mines**

The main tracers of this source were sulfate, strontium and crustal elements (mainly Ca and Mg). It was named as celestite mines because it was thought to be related with celestite mines located 20 km south-west of the city. Celestite (SrSO₄) is a mineral consisting of strontium sulfate and is the principal source of the element strontium, commonly used in fireworks and in various metal alloys. This source was only distinguished in the coarse fraction and its mass contribution to this fraction was 20%. This source displayed a seasonal pattern characterized by higher values in summer compared with winter, which could be explained since the mines are open-pit mines, so re-suspension is enhanced during summer. In addition, the fields surrounding the mines would be enriched in Sr, thus agricultural activities in the area will also favor re-suspension of this element. The highest
concentration of this source was obtained for westerly and south-westerly winds, where the mines are located (Figure S3) although relatively high concentrations were also observed for winds from the east sector. This may be due to the contribution of other mineral compounds to this source as can be seen in Figure 3.

![Figure 3](image1)

![Figure 4](image2)

![Figure 5](image3)

### 3.3. Working versus non-working days variability

The average contribution of the different sources for working days (from Monday to Friday), Saturday and Sunday is shown in Figure 6. For the coarse fraction a total of 92 data points are included in the average for Monday-Friday, 20 for Saturday and 18 for Sunday. In a similar manner for the fine fraction 119, 25 and 19 data points are included in the averages for Monday-Friday, Saturday and Sunday, respectively. It is important to take into account the sampling interval of the filters (24 hours starting at 7:00 GMT). In particular, filters collected on Sunday include partially the traffic peak of Monday morning.

PM$_{10-1}$ experienced a large decrease from weekdays (31±23 µg/m$^3$) to Saturdays (20±10 µg/m$^3$), showing also less variability on Saturdays. On Sundays, the average PM$_{10-1}$ mass concentration increase compared to Saturdays, probably due to the traffic peak of Monday mornings. The largest decrease was observed for the mineral dust source that decreased from an average value of 11±7 µg/m$^3$ on Monday-Friday to 5±4 µg/m$^3$ on Saturdays. Celestite mines source also decreased considerably on Saturdays, denoting a reduction in
the working activity of the mines during the weekend. Taking into account the standard deviations, the decrease observed in the contributions of the celestite mines source was more pronounced than in the mineral dust source. Road dust source experienced a slight decrease during the weekend whilst regional re-circulation and aged regional sources did not change significantly from weekdays to weekends. Concerning the fine fraction, PM$_1$ levels did not vary between weekdays and weekends. It is necessary to mention that part of the variability between working and non-working days may be biased by the lower number of samples collected during Saturdays and Sundays.

[Figure 6]

So, reducing anthropogenic activity (like it is supposed to occur on Saturdays) will have a positive impact in PM$_{10}$ levels. However, in the short term the reduction observed occurred mainly in the coarse fraction, whereas the fine fraction remains at the same levels during the weekends.

3.4. Daily exceedances: natural or anthropogenic?

Air quality has been a cause of concern during the past decades throughout the world, especially in developed countries. In particular, PM has become a key pollutant due to its negative effects on human health and many countries have developed abatement strategies in order to control PM levels. Therefore, one of the main aims of source apportionment studies is to identify the causes of exceedance of the thresholds established by the European Directive (2008/50/EC for PM$_{10}$ and PM$_{2.5}$; no regulation concerning PM$_1$). A total of 40 PM$_{10}$ daily exceedances have been recorded during the study period, with most of them occurring during spring and summer seasons (15 and 12, respectively). From the 27 daily
exceedances, 22 occurred during African dust events (www.calima.ws). On average, the ratio fine/coarse mass concentration was 0.5 during the exceedances occurred in spring and summer and the mineral dust source accounted for 24% of the measured PM$_1$ and 48% of PM$_{10-1}$. For days exceeding the PM$_{10}$ daily limit during autumn and winter, road dust and mineral dust sources comprised 42 and 29% of the coarse fraction; and traffic exhaust and regional re-circulation accounted for 55% and 23% of the total PM$_1$, respectively. The fine/coarse ratio was on average 0.9, during those days. Thus, exceedances associated with a natural origin were more frequent during spring and summer and presented a higher impact on the coarse fraction. On the other hand, exceedances related to an anthropogenic origin predominantly affected the fine fraction and occurred more often during the cold seasons. With these results in mind, traffic is the main source to target in Granada throughout the year, but especially in winter. In this sense, Qadir et al. (2013) detected a decrease of 60% in the contribution of traffic source after the implementation of a low emission zone in Munich, evidence that this kind of measurements may help to reduce pollution levels in urban areas.

4. Conclusions

The chemical composition of fine and coarse particulate matter has been studied for the period 2006-2010 at an urban station in southern Iberian Peninsula. A significant decreasing trend in PM$_{10}$ levels has been observed related with a decrease in most of its constituents, specially marked in mineral matter levels and nmC. The concentrations of chemical constituents were found to undergo a clear seasonal behavior. The coarse fraction was mainly composed by mineral matter, which increased considerably during summer due to the drier conditions that favor re-suspension from roads and soils and the more frequency...
of African dust events. Non-mineral carbon was the major contributor to the fine fraction and presented higher levels in winter than in summer mainly due to larger emissions during winter and lower mixing layer heights that favor accumulation of particles near surface.

Concerning the identification of sources, PMF analysis distinguished five sources in PM$_{10-1}$ and four in PM$_1$. The use of fine and coarse PM in the PMF analysis allows the identification of additional sources that could not be identified using only one size fraction. The mineral dust source was identified in both fractions and comprised 36 and 22% of the total mass in the coarse and fine fractions, respectively. This high contribution of the mineral source to the fine fraction may be due to contamination of the source profile. The regional re-circulation source was traced by secondary sulfate, V and Ni. It was the most important source concerning PM$_1$ mass concentration being less important in the coarse fraction. Although V and Ni are commonly associated to fuel oil combustion the seasonality of this source with higher concentrations in summer compared with winter suggest that the most important part of this source can be ascribed to regional pollution episodes. The traffic exhaust source that was characterized by nitrate, ammonium and carbonaceous particles, comprising 29% of the fine mass. Finally, celestite mines source was traced by sulfate, strontium and crustal elements (mainly Ca and Mg) and it was only identified in the coarse fraction.

A reduction in PM$_{10-1}$ levels from working versus non-working days has been observed, especially in mineral dust, celestite mines and road dust sources. On the other hand, PM$_1$ levels remain fairly constant throughout the week. PM$_{10}$ exceedances (2008/50/EC) associated with a natural origin were more frequent during spring and summer and presented a higher impact on the coarse fraction, whereas exceedances related to
anthropogenic origin predominantly affected the fine fraction and occurred more often
during the cold seasons. Concluding, traffic seems to be the main source to target in
Granada throughout the year, but especially in winter. Since no significant temporal trend
or changes between working and non-working days have been observed in the fine fraction,
it is clear that further investigation is needed concerning PM$_1$ fraction and its sources in
order to establish future abatement strategies.

**Acknowledgments**

This work was supported by the Andalusia Regional Government through projects P12-
RNM-2409 and P10-RNM-6299, by the Spanish Ministry of Science and Technology
through projects CGL2010-18782, CSD2007-00067, CGL2011-13580-E/CLI and
CGL2011-15008-E; and by EU through ACTRIS project (EU INFRA-2010-1.1.16-
262254). Information on African dust available on CALIMA is obtained in the framework
of a contract between CSIC and the Spanish Ministry of Agriculture, Food and
Environment (MAGRAMA). We would like to thanks also Openair project. G. Titos was
funded by Spanish Ministry of Economy and Competitiveness – Secretariat of Science,
Innovation and Development.
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Figures captions

**Figure 1:** Chemical composition of PM$_{10-1}$ (lower panel) and PM$_{1}$ (upper panel) in winter and in summer expressed in µg/m$^3$ and percentage (%).

**Figure 2:** PM$_{1}$/PM$_{10}$ ratios of the major and some trace elements.

**Figure 3:** Source profiles found for the coarse fraction (PM$_{10-1}$) and percentage of ambient species concentration apportioned by each source.

**Figure 4:** Source profiles found for the fine fraction (PM$_{1}$) and percentage of ambient species concentration apportioned by each source.

**Figure 5:** Contribution of sources to PM$_{10-1}$ (upper panel) and PM$_{1}$ (lower pannel) in winter (left) and summer (right) expressed in µg/m$^3$ and corresponding percentage.

**Figure 6:** Average concentrations of each source for Monday to Friday, Saturday and Sunday, for the coarse fraction (upper panel) and for the fine fraction (lower panel). The error bars represent the standard deviations (SD). The average ± SD measured PM mass concentration for each period is also shown in a box.
Figure 1

Winter

Summer

PM$_1$

PM$_{10-1}$

nmC  nmSO42-  NO3-  NH4+  mineral  salt  trace elements  indet
Figure 3

![Graphs showing different sources of mineral dust and their contributions.](image-url)
Figure 4

![Graphs showing source profiles and percentages of species for different sources: Mineral dust, Regional re-circulation, Traffic exhaust, and Road dust.](image-url)
Figure 5

Winter

PM$_{10-1}$

Summer

PM$_1$

- Mineral dust
- Regional re-circulation
- Aged regional
- Road dust
- Celestite mines
- Traffic exhaust
- Road dust
Figure 6

**PM$_{10-1}$**
- Mineral dust
- Regional re-circulation
- Aged regional
- Road dust
- Celestite mines

**PM$_1$**
- Mineral dust
- Regional re-circulation
- Traffic exhaust
- Road dust

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<td><strong>PM$_{10-1}$</strong></td>
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<tr>
<td>Concentration (µg/m$^3$)</td>
<td>31±23</td>
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<td>23±22</td>
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<td>Concentration (µg/m$^3$)</td>
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<td>15±7</td>
<td>17±9</td>
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Figure 1 (black and white)
Figure 2 (black and white)
Figure 3 (black and white)
Figure 4 (black and white)
Figure 5 (black and white)
Figure 6 (black and white)
**PM$_{10-1}$**

- **Mineral dust**
- **Regional re-circulation**
- **Aged regional**
- **Road dust**
- **Celestite mines**

**Concentration (µg/m$^3$)**

- **Monday-Friday**
  - 31±23 µg/m$^3$
  - 20±10 µg/m$^3$
  - 23±22 µg/m$^3$

- **Saturday**

- **Sunday**


**PM$_1$**

- **Mineral dust**
- **Regional re-circulation**
- **Traffic exhaust**
- **Road dust**

**Concentration (µg/m$^3$)**

- **Monday-Friday**
  - 16±7 µg/m$^3$

- **Saturday**
  - 15±7 µg/m$^3$

- **Sunday**
  - 17±9 µg/m$^3$
Highlights

1. Chemical composition of fine and coarse PM has been studied.
2. Decreasing trend was observed in the coarse fraction but not in the fine fraction.
3. PMF technique was used for the identification of fine and coarse sources.
4. To abate exceedances, traffic is the main source to target, especially in winter.
Supplementary material

Table S1: Mean, standard deviation (SD), percentage of data above detection limit (%ADL) and signal-to-noise (S/N) for the elements in the PM$_{10-1}$ and PM$_1$ fractions included in the PMF analyses.

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<tr>
<th></th>
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**Figure S1**: Scatter plots of PM experimental versus PM simulated concentrations by PMF technique (in $\mu$g/m$^3$).
**Figure S2:** Contribution of sources to PM$_{10-1}$ (upper panel) and PM$_1$ (lower panel) expressed in $\mu$g/m$^3$ and corresponding percentage for the study period 2006-2010.
**Figure S3:** Location map (top) of the monitoring site and polar plots (bottom) of the PM source concentration in µg/m³ obtained with PMF according to wind direction.