

Estudio de la contaminación por partículas atmosféricas en Madrid (I): contribución de fuentes

Study of atmospheric pollution by particulated matter in Madrid (I): source apportionment

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Received: 24 June 2009

Accepted: 18 September 2009

RESUMEN

Este estudio se presenta dividido en dos trabajos incluidos en este mismo número, en los que se aborda la caracterización de distintas propiedades y aspectos relacionados con el aerosol atmosférico. Ambos tienen en común un mismo ámbito geográfico que es el área de Madrid. En el primero de ellos que se presenta a continuación, se aborda el tema de la identificación de las principales fuentes que generan este tipo de contaminación, sobre la base de los modelos de receptor que utilizan la composición química y el perfil típico de cada fuente. Para ello se ha caracterizado la composición química de dos fracciones de tamaño denominadas PM10 y PM2.5 de gran interés en temas de calidad del aire, y en tres diferentes entornos, identificando mediante un análisis factorial seguido de una regresión multilínea, las principales fuentes en ambas fracciones y su contribución a la masa del aerosol. Las fuentes mayoritarias del aerosol atmosférico que se respira en Madrid son el tráfico, la materia crustal o mineral, el aerosol marino, un fondo remanente de aerosol secundario, originado a partir de gases precursores y, en algún caso particular, alguna fuente procedente de actividades industriales además de la quema de biomasa producida en incendios forestales que han tenido lugar durante el estudio. La segunda parte del mismo (Pujadas et al., 2009) está enfocada a la caracterización de los procesos de transporte y transformación del aerosol mediante la utilización de técnicas de monitorización en continuo de algunas de sus propiedades físico-químicas.

Palabras clave: Aerosoles; PM10; PM2.5; contribución de fuentes; análisis factorial.

ABSTRACT

This study is divided into two works included in this issue. They tackle the characterization of different properties and aspects related to the atmospheric aerosol. Both share the same geographical domain, which is the Madrid area. The first one addresses the identification of the main sources of this type of pollution, based on receptor models that use the chemical composition and the typical profile of each source. For that, the chemical composition of the two size fractions PM10 and PM2.5, of great interest from the air quality point of view, has been characterized at three different sites. The main sources and their contribution to aerosol mass have

been identified by applying a factor analysis followed by a multilinear regression analysis. The main sources of the atmospheric aerosol inhaled in Madrid are: traffic, crustal material, marine aerosol, a secondary inorganic background and in any particular case, some industrial source besides the biomass burning from forest wild fires. The second part of this study (Pujadas et al., 2009) is focused on the characterization of aerosol transport and transformation processes through the utilization of continuous monitoring techniques of some of its physical-chemical properties.

Key words: Aerosol; PM10; PM2.5; source apportionment; factor analysis.

SUMMARY: 1. Introduction. 2. Methodology and data sets. 3. Results. 4. Summary and conclusions. 5. Acknowledgements. 6. References

1. INTRODUCTION

Atmospheric pollution has been a known phenomenon from the antiquity. However, it became a matter of concern as result of the dramatic consequences on population of several severe pollution episodes that took place in US and Europe (Lippman, 1989, Whittacker et al., 2004) in the middle of the last century. These episodes were rapidly known by the immediate effect on human health that were associated to those pollutants more known or documented at that times, particulate matter and sulphur dioxide. However a new concept was then introduced, the so called smog, a mixture in fact of gaseous components and particulate matter whose exact composition and components were still unknown. The major use of fossil fuels in the last century, mainly high sulphur content coals, concentrated the attention to their primary emissions: gases like SO₂ and black smoke, as any kind of primary particulate matter derived from the incomplete combustion of fuels used in industry and home consuming.

As a consequence of the increasing deterioration of the air quality in industrial and urban areas, the European legislation developed on the seventies regulating the standards for a number of gaseous pollutants and for total suspended particles (TSP). This regulation resulted in a clear improve of the air quality during the following decades, both in the industrial and the urban areas, as was reflected by the observed decreasing trend in most of the monitoring networks, including the city of Madrid (Serrano et al 1989).

Knowledge of atmospheric particles characteristics has evolved enormously in the last fifteen years in relation with air quality problems, also in other fields, enhanced by the improvement of the measurement techniques that have made possible the study of a great variety of different properties related to atmospheric aerosol.

Taking into account the definition of this atmospheric pollutant as “any liquid (except pure water) or solid particle suspended in the atmosphere”, we can realize that we are not only dealing with an isolated component, as this is in fact a mixture of components out of them only a few have been chemically identified and whose individual effects on human health are still unknown.

In addition to this particular problem, this atmospheric component plays a key role in the some global scale issues, like climate change. Aerosols have become an

important element to approach observations to results from global models, even when it has been recognized their high uncertainty degree, one of the greatest ones amongst all the considered radiative forcing elements (IPCC 2007). This is in part due to the direct and indirect effects that aerosols have in the radiative balance, making even more difficult their quantification. To increase the knowledge on vertical distribution of aerosols and their optical properties, also linked to other ones like shape, chemical composition, or hygroscopicity, among others, are therefore fundamental to tackle that challenge.

At smaller scales, atmospheric aerosols represent a subject of interest looking at regional impacts on climate change as the heterogeneity in their spatial distribution can give rise to different types of impacts due the diverse nature, properties and atmospheric concentrations.

Looking at the sources, atmospheric aerosols can be anthropogenic or natural. But considering their emission process they can be primary or secondary, i.e. directly emitted by the source or formed by chemical reactions in the atmosphere from gaseous precursors. Being in the atmosphere as a complete heterogeneous mixture in continuous evolution, some properties of the aerosols such as size distribution and chemical composition can provide us invaluable information on their source or about their formation and transformation processes. In both cases that information can be one of the main steps to tackle a management and control strategy for abatement their ambient levels.

In the field of air quality, one of the key properties related with health effects is the aerosol size, directly related to their capacity of penetration in the human respiratory system. Results from epidemiological studies in the last decades (Pope et al., 1992) contributed to demonstrated that the PM_{10} (particle matter with aerodynamic diameter $< 10 \mu m$) was a parameter most appropriated for air quality purposes regulation than the exiting one TSP, not taking into account the aerosol size. This lead to a new battery of European Directives that made PM_{10} and the smaller size range $PM_{2.5}$, be the parameters of control for particulated matter pollution. More recent studies (Dockery and Stone, 2007) are pointing at more acute effects associated to finer particles, promoting therefore a research line of measurements and studies on the aerosol properties at the sub-micrometric range.

Chemical composition is also a property subject to certain controversy that has piled up a lot of research effort. Despite this is not routine information in air quality networks, only obtained through research projects, knowing the major components and several trace elements of the particle mass can provide invaluable information on the emission sources as well as some transformation processes that the aerosol has experienced once in the atmosphere. Results shown in this work are an example of the important insights on the characteristics of the aerosol in Madrid provided by the characterization of some of these relevant properties. Following, the main emissions sources, anthropogenic or natural, such as natural dust or marine aerosol, have been identified and quantified their contribution. These results demonstrate the utility of some statistical tools that can be used to manage atmospheric pollution and improve the air quality in certain areas.

2. METHODOLOGY AND DATA SETS

Mathematical techniques based on receptor modelling allow identifying aerosol sources and assessing their relative mass contribution. These use as input the ambient concentrations of as much as possible major and trace chemical compounds of airborne particles obtained at the sampling site and apportion them among possible sources considering their chemical profile.

Receptor models techniques and their applications have been extensively used in particulate matter source apportionment studies (Henry and Hidy, 1979; Serrano et al., 1989; Querol et al., 2004). One of the most commonly used multivariate models, the varimax rotated Factor Analysis (FA), has been performed in Madrid to identify the main sources affecting the aerosol composition at different characteristic sampling sites. In this statistical 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 diagonalizing 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 they represent. 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 is the varimax rotation. After running a FA a number of factors equal to the number of variables are 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 shall be retained is not straightforward. If the data have been previously normalized (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 normalization procedure is recommended to equalize the opportunity of both large and small magnitude variables to influence the analysis. After the identification of the main particulate matter sources, the respective quantitative contributions can be derived. In this case a Multilinear Regression Analysis (MLRA) was applied using the methodology described by Thurston and Spengler (1985).

Different data sets were obtained during experimental studies carried out in the Madrid air basin. The sampling campaigns were carried out to characterize mean PM_{10} and $PM_{2.5}$ concentration levels and their chemical composition at three representative sites of the Madrid air basin (Fig. 1). High volume devices were deployed with PM_{10} and $PM_{2.5}$ specific inlets to sample ambient air on quartz fibre filters. The first study was conducted from June 1999 to June 2000 at an urban traffic site (Escuelas Aguirre-EA) in the Madrid city downtown. The second study was conducted throughout the year 2001 at an urban park located in Alcobendas (ALC), a

smaller town 13 km away from Madrid city. The third one was carried out from May 2004 to April 2005 at the outskirts of Chapinería (CHA), a small village 25 km southwest from Madrid City. The second place can be considered as suburban, whereas the CHA site located in a rural area can be representative of the airshed background. A number of PM₁₀ and PM_{2.5} filters were collected and analysed systematically throughout a complete year at EA (67 and 38), ALC (84 and 34) and CHA (98 and 96) sites, respectively. Particulate matter (PM) concentrations were obtained by gravimetry. Sampling and analytical used procedures can be found elsewhere (Querol et al., 2004).

3. RESULTS

Annual mean levels of PM₁₀ and PM_{2.5} mass fractions at the three sites are shown in Fig. 1, decreasing from the most polluted site EA, to the rural one. Major compounds levels are also shown pointing at the carbonaceous aerosol (sum of organic matter OM and elemental carbon EC) as the main component of the aerosol at both fractions. Crustal elements that constitute the mineral dust is also an important contributor, mostly in the coarse size, and at the traffic site, this in part due to soil resuspension produced by traffic but also to meteorology and other process like African dust transports taking place during the experimental phase at that site. An important contributor that can be ascribable to different sources is the secondary inorganic compound group (SIC) that group the secondary aerosol formed from precursors emitted in the area and can be found mostly in the fine fraction.

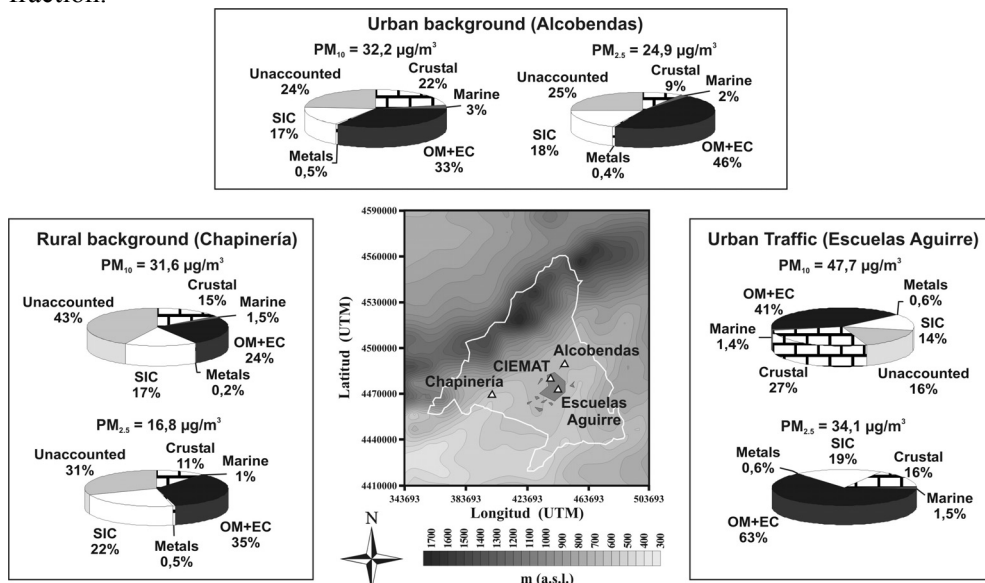


Figure 1. Location of the experimental sites and results of chemical composition of PM₁₀ and PM_{2.5} at Chapinería, Alcobendas and Escuelas Aguirre.

Other compounds like salts and trace elements were found in the chemical analysis of the mass at both fractions and used to identify some specific sources.

One of the limitations of multivariate techniques are that the data set must contain a number of samples higher than 50 to obtain accurate identification of the sources (Thurston and Spengler, 1985). For this reason only the results obtained with the PM₁₀ datasets at the three sites are shown. Multivariate analysis revealed four factors or sources with eigenvalues > 1 at the urban site and five factors at the suburban and rural sites. These sources have accounted for the 87%, 83% and 85% of the PM₁₀ variance in EA, ALC and CHA, respectively. The first factor obtained contained 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 of long range transport of African dust. Moderate loadings of *Fe* and *Mn* have also been found. The second factor was related with road traffic, since it explains most of the variance of total *C* and *Pb*. It is also correlated with *Cu*, *Zn*, and NO_3^- . *Cu* and *Zn* can be associated with tyre wearing. In addition, *Zn* has been suggested as a good marker for unleaded fuel powered motor vehicle emissions. The positive NO_3^- loading found was related to the atmospheric oxidation of the NO_x emitted by motor vehicles. The moderate to high loadings of typical crustal elements such as *Fe*, *Mn*, and *Ca*, indicated a contribution of soil dust resuspended by local traffic flow included in this factor. The next factor represented the formation of secondary inorganic aerosols due to their high loadings for SO_4^{2-} , NO_3^- and NH_4^+ . Hence, this factor probably represents the regional background of secondary inorganic pollutants in the Madrid airbasin, together with the local contribution of combustion sources. The fourth factor could be interpreted as marine aerosol, based upon its good correlation with *Cl* and *Na*. Although present in low levels, this natural source should be considered. The last significant factor at the suburban site was related with industrial emissions, as it contained large loadings of metals such as, *Cr* or *Ni*. On the contrary at the rural site the fifth factor was recognized as biomass burning, due to the local and regional influence of wildfires and biomass burning during agricultural activities. This factor was characterised by high loadings on typical elements associated to biomass burning such as *K* and *C*.

At the next step, the contribution of the main sources affecting PM₁₀ at the three sampling sites was estimated following the procedure previously described. On average, road traffic was the major mass contributor accounting for 48% of the PM₁₀ mass at the urban traffic site and 34% at the suburban and rural sites. Otherwise, crustal contribution represented 26%, 31% and 32% of the mass at the urban, suburban and rural sites, respectively. The relative contribution of the secondary particles was higher at the suburban site, accounting for 22% of the bulk mass, than at the urban, 18%, and the rural sites, 15%. Sea-salt contribution was similar at the three sites, representing only 3% to 5% of the total PM₁₀ mass. Industrial and biomass burning contributions explained 6 and 7% of the bulk mass at ALC and CHA, respectively. The contribution of the non-explained sources was estimated to range from 1% at the suburban site to 5% at the urban site.

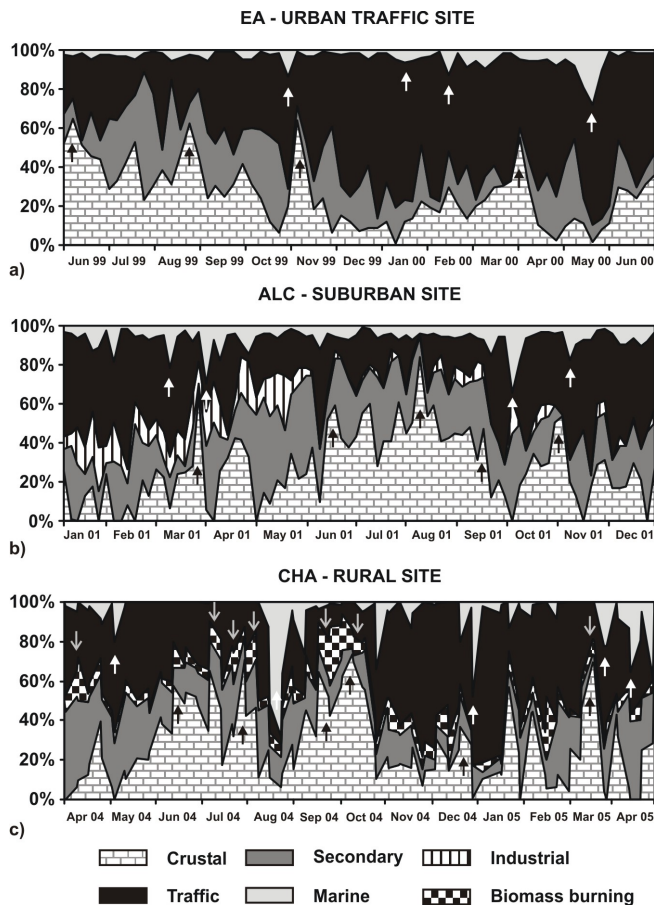


Figure 2. Time series of recorded PM₁₀ daily source contributions expressed as percentages at ESC a), ALC b) and CHA c). Black arrows highlight the identified African dust outbreaks in the crustal source category. White arrows indicate the main peaks in the marine source category produced during the passage of Atlantic frontal systems. Grey arrows show the identified wildfires produced in the Madrid area in the biomass burning category.

Figure 2 shows the time series of daily values for these source categories. Crustal PM₁₀ mass contribution is higher in summer and during sporadic Saharan dust outbreaks marked with arrows in this figure. The traffic and industry related PM₁₀ contributions showed a marked seasonal trend typical of urban and suburban environments, with a maximum during autumn and winter and a minimum in July and August. The highest values for this source category were recorded during typical autumn-winter pollution episodes, linked to stagnant meteorological conditions. Time series of secondary aerosol category presented higher average concentration values during the spring and summer, possibly due to the enhanced atmospheric

photochemical activity which drives the formation of secondary particles, especially $(\text{NH}_4)_2\text{SO}_4$. The marine aerosol contribution seems to be higher during the winter-spring term, when the Atlantic frontal systems are more frequent. Finally, although there was not a clear seasonal trend for biomass burning, their contributions were sporadic but significant during the spring-summer term.

4. SUMMARY AND CONCLUSIONS

This work gives some examples of the research and results obtained by the Characterization of Atmospheric Pollution Group of CIEMAT on the aerosol issue. This group has been working on this subject from the last ten years, by using different experimental and statistical techniques. The large experience acquired for more than twenty years in the atmospheric pollution field, and more specifically in the Madrid area, has allowed obtaining an interesting perspective of some of the processes that take place in the atmosphere under the very specific climatic and dynamics conditions in our country and in this area. Atmospheric aerosol is perhaps one of the most complex pollutants, directly or indirectly involved in many processes that are in the first research line nowadays. The interdisciplinary approach for its study, presented in two separate and complementary works in this number, is perhaps the most appropriated one to understand some properties that can be relevant in many aspects, like the emission sources, the formation and evolution processes in the atmosphere that affect its chemical composition and size, among other properties, or its distribution in the atmosphere.

In this work it is shown how the chemical composition of the two fractions PM_{10} and $\text{PM}_{2.5}$ obtained through daily integrated measurements along one year can provide the main sources at different sites and its contribution to the mass of the atmospheric aerosol. Traffic, mineral material, sea spray, biomass burning and industry, have been identified influencing in a different manner the aerosol concentrations. Receptor models such as FA and MLRA have been demonstrated as useful tools for source apportionment analysis.

5. ACKNOWLEDGEMENTS

This research has been funded by the Spanish Ministry of Science and Innovation (projects AMB98-1044, CGL 2003-08603-C04-02 and CGL2007-64117/CLI) and the Ministry of Environment, Rural and Marine Affairs study coordinated by the IJA-CSIC.

Desde estas líneas los autores queremos expresar nuestro más profundo reconocimiento a Elvira Zurita, a quien tuvimos la gran oportunidad de conocer como profesora, tutora, compañera y amiga. Este trabajo no es sino una pequeña muestra de la aplicación de sus enseñanzas y sabiduría en el terreno científico. Para aquellas que lo fueron en el terreno humano no habría habido sitio suficiente...

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