Estudio de la contaminación por partículas atmosféricas en Madrid (II): procesos de transformación y transporte

Study of atmospheric pollution by particulated matter in Madrid (II): transformation and transport processes

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RESUMEN
En la segunda parte de este trabajo dedicado al estudio de la contaminación por partículas atmosféricas en Madrid se aborda la caracterización experimental de los procesos de transporte y transformación del aerosol mediante la utilización de técnicas de medida en continuo de algunas de sus propiedades físico-químicas. En esta parte el interés se ha centrado en estudiar la evolución temporal de alguno de sus componentes mayoritarios (aerosol orgánico y nitrato) así como su distribución por tamaños, y en intentar establecer los vínculos entre ambos procesos al analizarlos en paralelo y en tiempo real. En muchas ocasiones los cambios registrados no se producen por la transformación de las partículas y gases existentes en el aire urbano sino como consecuencia de la llegada de masas de aire con otro tipo de aerosoles. Estos fenómenos de transporte y en especial los procesos de larga distancia se han podido estudiar mediante el uso de técnicas de teledetección activa como el Lidar, cuya aportación de cara al futuro también es comentada.
Palabras clave: Aerosoles; transformación físico-química; distribución por tamaños; perfiles verticales; Lidar.

ABSTRACT
The second part of this work dedicated to the atmospheric pollution by particles in Madrid has been devoted to the experimental characterization of aerosol transport and transformation processes by using continuous measuring techniques of some of its physico-chemical characteristics. In this part the interest has been focussed on studying the temporal evolution of certain major components of aerosol (carbonaceous and nitrate content) as well as its number size distribution, trying to establish the relation between both processes when they are analysed in parallel and in real time. Many of the registered changes do not take place due to the transformation of particles and gaseous precursors in urban air but as a result of air masses advection with different aerosol content. The use of active remote sensing techniques like Lidar has allowed studying the spatial

and temporal evolution of the transport processes, especially those cases related to long-range phenomena. The future implications of this experimental strategy are also discussed.
Key words: Aerosol; physico-chemical transformation; number size distribution; aerosol vertical profile; Lidar.

SUMMARY: 1. Introduction. 2. Composition and transformation processes in Madrid urban aerosol. 3. Aerosol Long-Range Transport. 4. Summary and Conclusions. 5. Acknowledgements. 6. References

1. INTRODUCTION:

Atmospheric particulate matter (PM) or atmospheric aerosol is produced by different formation mechanisms: primary (directly emitted) or secondary (formed from the oxidation compounds of gaseous precursors by nucleation or by condensation or reaction on existing particles). Epidemiological and toxicological studies have demonstrated that specific exposure to urban particulate matter is associated with several adverse health effects (de Kok et al., 2006; Peters et al., 1997). In a typical urban non-industrial environment as Madrid represents, traffic emissions and natural apportionment are the main sources contributing to urban aerosol, as it has been pointed out in the first part of this work (Artíñano et al., 2009) while meteorological, climatic and geographical conditions are the main modulating factors on the concentration and composition of PM in this region. Local and regional anthropogenic gaseous and particle emissions interact with each other producing PM ambient concentrations, while long-range transported aerosol reaching the central Iberian Peninsula in occasional episodes also play a relevant role on surface PM levels.

PM from combustion sources have a grain size lower than 2.5 μm ($PM_{2.5}$) and most of the total number corresponds to particles smaller than 0.5 μm, while particles generated by mechanical processes, such as mineral dust and sea spray are typically greater than 2.5 μm.

Major species of $PM_{2.5}$ aerosol are carbonaceous compounds, secondary inorganic species as nitrate and sulphate and crustal compounds. Changes in traffic emission pattern, as the increase of diesel passenger vehicles occurred during the last decade, have produced a dramatic increase of ultrafine particle levels (< 0.1 μm) in urban air.

In the recent past, the Atmospheric Pollution Group of CIEMAT has carried out characterization studies on $PM_{2.5}$ temporal evolution in Madrid, paying special attention to composition, particle number size distributions and the incidence of long-range transport of desert dust on ambient PM concentration.

2. COMPOSITION AND TRANSFORMATION PROCESSES IN MADRID URBAN AEROSOL

The main results concerning the studies on the evolution of the most important chemical components of urban aerosol in the $PM_{2.5}$ fraction (nitrate and elemental and organic carbon) are summarized in the following subsections. A review of the more recent conclusions about the particle size growth in Madrid urban air is also given.

2.1 $PM_{2.5}$ elemental and organic carbon measurements

Inorganic carbon (IC) from carbonate crustal material is mostly present in the coarse aerosol whereas organic aerosol (OA) is mainly associated to the smallest particle sizes (Malm et al., 2004).The total content of carbonaceous material in $PM_{2.5}$, expressed as total carbon mass can be divided into elemental carbon (EC) and organic carbon (OC). EC has a graphitic or aromatic/cyclic structure and is directly emitted from incomplete combustion. OC is a mixture of more volatile hydrocarbons and oxygenates compounds and originates from a wide range of biogenic and anthropogenic sources. Organic aerosol can be classified in two fractions, primary organic aerosol (POA) with a prevailing anthropogenic origin, and secondary organic aerosol (SOA), which formation can be related to both anthropogenic and biogenic gaseous precursors. In spite of global models predict that urban sources of OA are small compared with biomass burning emissions and biogenic SOA formation (Kanakidou et al., 2005) the actual influence of urban emissions may be larger (de Gouw et al., 2005) due to the rapid growth of SOA in urban air within a few hours of photochemical activity.

Using a semi-continuous thermal analyzer (Rupprecht & Patashnick model ACPM5400), OC and EC concentrations have been measured in CIEMAT, a Madrid urban background site, with an hourly temporal resolution during long-term periods from 2003 to 2008. OC and EC averages (and standard deviation) for this period were 3.7 (±2.0) $\mu g\ m^{-3}$ and 1.3 (±1.6 $\mu g\ m^{-3}$).

The EC/TC mean ratio was 0.26, revealing the predominance of the organic fraction in the carbonaceous aerosol in Madrid. A seasonal change of the ratio OC/EC can be observed, from lower winter values to higher values in spring summer, and more due to the decrease of EC average, since OC monthly averages showed less seasonal variation. This would indicate the presence of a different OC source and/or the enhancing of processes leading to OC formation during spring-summer months.

Two empirical approaches have been used to estimate SOA concentrations from measured EC and OC concentrations, the EC tracer and the minimum OC/EC ratio models (Turpin et al., 1995; Castro et al., 1999). Both models assume a pure primary character for EC and differ from the treatment of OC concentration. The estimation of the primary OC associated to EC emission (the primary OC/EC ratio) is needed in both approaches and has been calculated, ranging from 0.6 to 0.8 during summer to around 1.0 in winter months using the EC tracer model (Plaza et al., 2006).

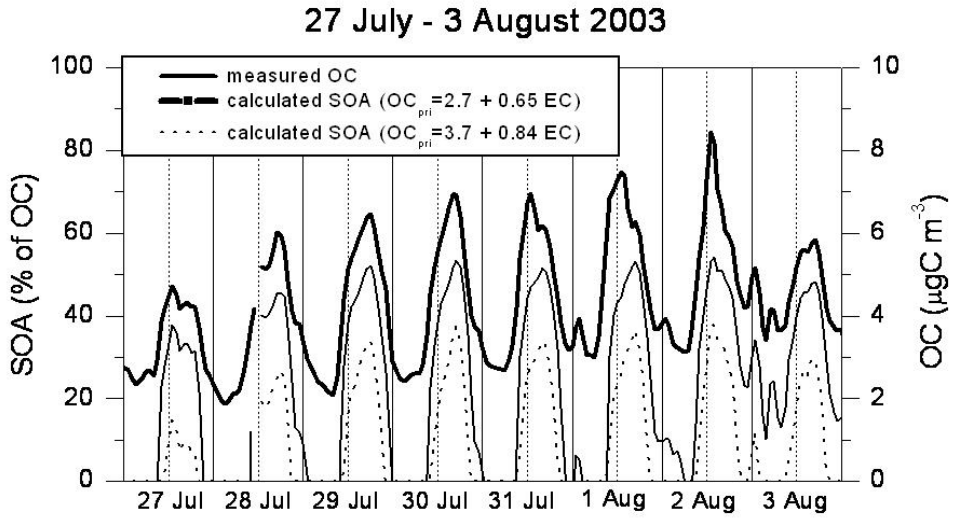

Figure 1. Measured OC and SOA estimation from the EC tracer model during a summer episode

Figure 1 shows an example period of the measured OC concentration and its estimated SOA fraction by the EC tracer model using two linear regressions. Although this model gives lower values of SOA than the minimum OC/EC ratio model, hourly values of 50% were estimated at midday and afternoon hours. During winter episodes, SOA formation also takes place in a lower but significant proportion, due to the greater concentration of gaseous precursors caused by stagnant conditions.

2.2 $PM_{2.5}$ particulate nitrate

Particulate nitrate is a secondary aerosol component, the final step of gaseous NO_x atmospheric oxidation being considered gaseous nitric acid its direct precursor. The main daytime reaction for the atmospheric nitric acid generation is limited by the concentration of photochemical OH radical: $NO_2 + OH \rightarrow HNO_3$, while some nocturnal pathways involving the nitrate radical can be considered in rural areas. There are two possible pathways for the transfer of this nitric acid to the aerosol phase. The first possibility is through neutralization by a base, mainly the ambient ammonia: HNO_3 (g) + NH_3 (g) ↔ NH_4NO_3 (s). This ammonia comes in urban areas from the emissions of vehicles equipped with catalytic converters (Perrino et al., 2002). This equilibrium is influenced by temperature and humidity, and by the presence of other inorganic compounds, especially sulphate, because the ammonia preferentially reacts with it and only the remaining NH_3 can react with the nitric acid. Considering the recent efforts undertaken to reduce sulphur from traffic fuels and the evidence that oxidative diesel particulate filters emits more

NO_2 than non-catalysed vehicles, nitrate is increasing in urban areas and its contribution to fine aerosol during winter and to coarse aerosol in summer is becoming quite significant. The second pathway is absorption of the nitric acid by water droplets producing acid aerosols. Nitric acid is one of the most water-soluble atmospheric gases and after dissolution it dissociates to nitrate increasing its solubility and the droplet acidity.

A comprehensive study about formation of fine particulate nitrate was conducted along a year (March 2004-March 2005) by measuring every 10 minutes this species using the Rupprecht & Patashnick model 8400N, as well as its gaseous precursors NO and NO_2 and meteorological parameters (F.J. Gómez-Moreno et al., 2007). Due to the semi-volatile nature of ammonium nitrate, nitrate concentrations were lower in summer and higher in winter (0.32 μg m^{-3} minimum monthly average in August and the maximum during December (3.0 μg m^{-3}). A typical pattern during days with low dispersive conditions was characterized by a steep rise of particulate nitrate in the morning, reaching maximum values between 9 and 14 UTC, followed by a decrease during the evening (Figure 2). Analysis of particulate nitrate and related gaseous species indicated the photochemical origin of the morning maxima, delayed with respect to primary NO and closely associated with secondary NO_2 maximum values.

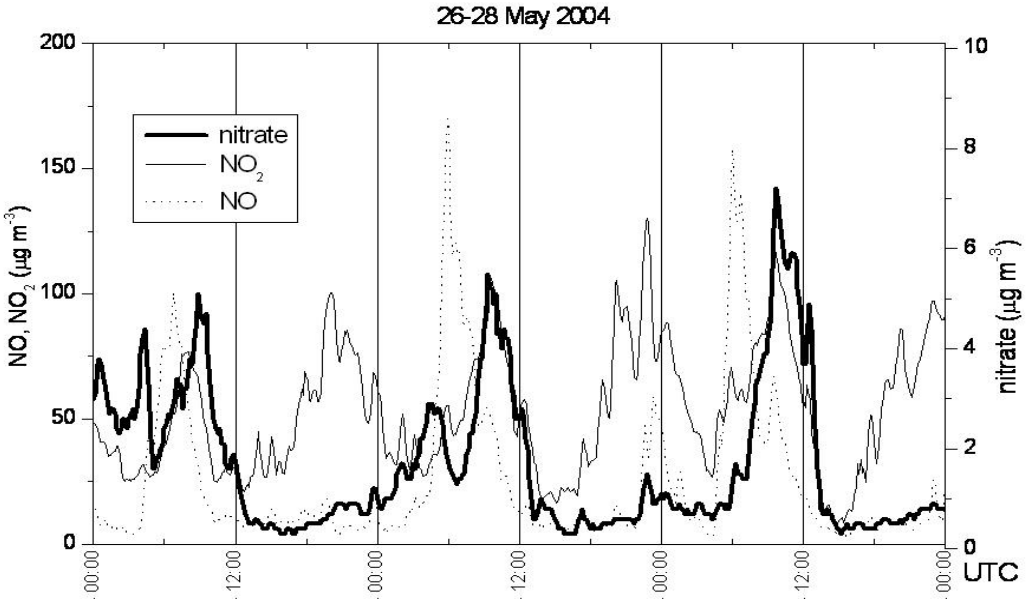

Figure 2. Representative polluted days showing NO, NO_2 and nitrate daily evolutions

2.3 Particle size growth in polluted urban airmasses

In the CIEMAT urban background site, particle number size distribution is being measured since 2006 using the differential electrical mobility technique and a condensed particle counter. This system, known as Scanning Mobility Particle Sizer (SMPS), allows obtaining a distribution every 12 min. of an aerosol size range from 15 to 600 nm of particle diameter. One of the most interesting results derived from SMPS measurements is the characterization of particle growth taking place from the traffic early-morning rush hour to a few hours later. In the Figure 3 the particle size distributions from 4:00 to 12:00 UTC of the episodic day 9th February 2006 are depicted, and in Figure 4 OC, EC and nitrate $PM_{2.5}$ concentrations for the same day are shown. Particle number distributions were fitted to log-normal functions showing two main population modes in the background nocturnal atmosphere (4:00 UTC). In the 6:00 and 8:00 UTC distributions the prevailing mode has a mean diameter of 30-40 nm, typical of diesel vehicle emission that is simultaneous to a sharp increase of EC. In the 9:00 and 11:00 UTC distributions the two population modes are similar number of particles, while in the 12:00 UTC distribution the second mode with a mean diameter greater than 100 nm is clearly prevailing, just when OC, nitrate (and also EC) experienced a huge increase denoting the presence of secondary aerosol that can be associated to the growth of emitted particles by condensation of semi-volatile compounds.

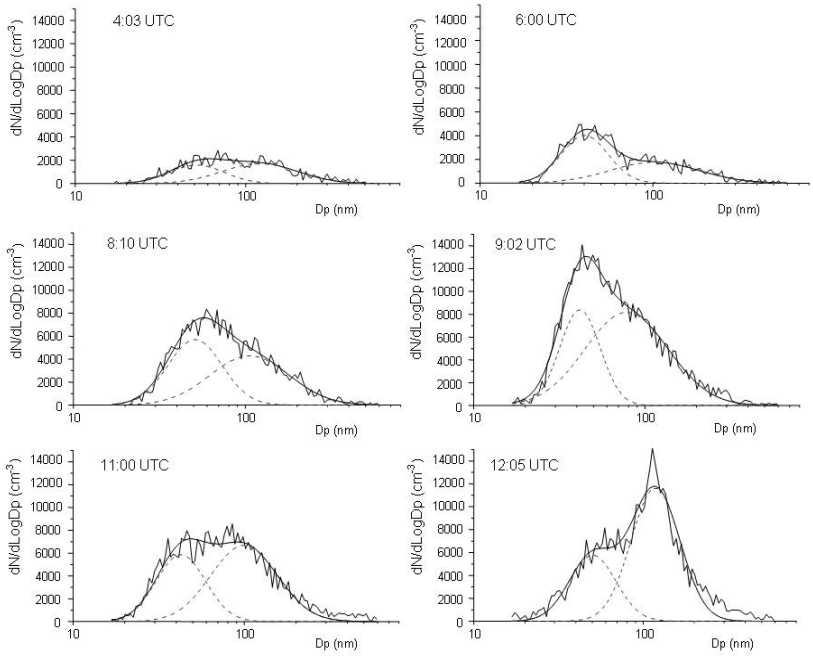

Figure 3. Evolution of particle number size distribution in an episodic winter day, 9th February 2006.

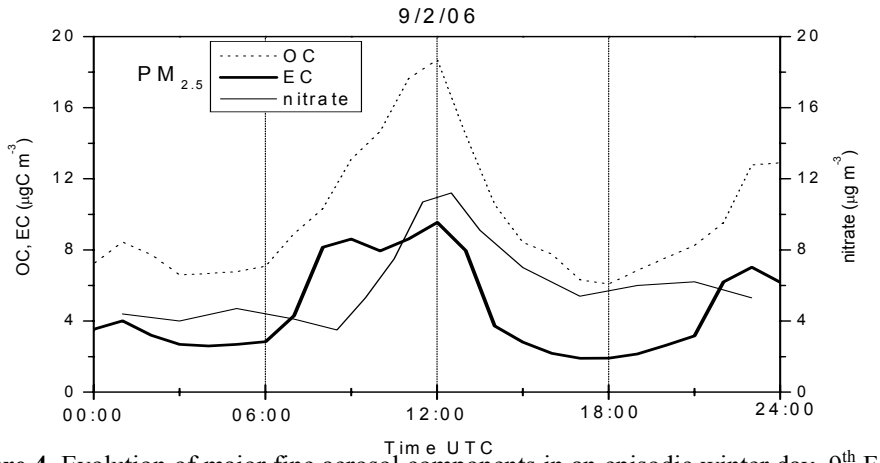

Figure 4. Evolution of major fine aerosol components in an episodic winter day, 9th February 2006.

3. AEROSOL LONG–RANGE TRANSPORT

As it has been documented (Querol et al. 2004), dust outbreak episodes, originated in North-African regions, especially Sahara and Sahel deserts, affect ambient PM concentrations in the Iberian Peninsula. In the particular case of Madrid, this mineral dust advected from those areas has a direct incidence on PM levels on 8% of days along a year (Salvador et al. 2008).

Due to the large spatial extent of these processes, their effects go from air quality influence up to a great variety of atmospheric consequences at global scale, including climate change. To investigate this kind of issues other experimental strategy different from the point sampling procedures used in the previous sections is required.

An experimental approach based on aerosol remote sensing to study the long-range transport of natural particles will be discussed in the following subsections. Moreover, some examples of desert dust transport detected over Madrid region with Lidar (Light Detection and Ranging) technique will be presented.

3.1 Remote sensing as measurement strategy

The high variability of atmospheric aerosol distribution over time and space and their inherent complexity as atmospheric constituent, strongly condition the experimental strategy that must be followed to investigate aerosol transport, especially the long-range processes. Describing the aerosol presence at different scales (global, continental, regional, etc.) and its environmental impacts require also extensive measurement programs capable of providing and updating aerosol 3D distributions and very ambitious data assimilation and calculus tools.

To face up to this challenge, remote sensing techniques represent the best option: they can provide several aerosol parameters (concentration, optical properties, microphysical data, etc.) and, depending on the passive or active character of those techniques, they provide respectively integrated or range resolved results on the troposphere and the stratosphere. There are currently different ground based networks using different and complementary systems and these deployments are the ideal complement of the satellite remote sensors that represent the last border in this kind of research.

Briefly summarizing, the main current tools that provide data for studying the global aerosol system are the following:

- Sun photometers Networks: Aerosol Robotic Network (AERONET) & associated (PHOTONS, RIMA, etc.). (Holben et al. 1998; Dubovik et al., 2000)
- Lidar Networks: European Aerosol Research Lidar Network (EARLINET), Micro-Pulse Lidar Network (MPLNET), CIS-LiNet, etc., are networks based on the use of Lidar ground-based instruments. The use of this laser technology provides vertical profiles of aerosol distribution and microphysical properties. (Schneider et al., 2001; Pappalardo et al., 2006)
- Satellite instruments capable of providing aerosol useful data (TOMS, AVHRR, ATSR, etc.) or designed for aerosol remote sensing (passive sensors like MODIS and MISR on Terra and Aqua satellites respectively; active sensors like CALIOP (Cloud-Aerosol Lidar with Orthogonal Polarization) on CALIPSO mission and GLAS (Geoscience Laser Altimeter System) Lidar on ICESat platform.

The atmospheric aerosol vertical distribution is the key information to investigate long-range transport phenomena and at present probably one of the most important observational gaps. Among all those instrumental systems and facilities, Lidar techniques represent the best option to close it. Lidar networks are crucial to study aerosol on large spatial scales and to investigate long-term evolution of different processes.

At present EARLINET, the European Aerosol Research Lidar Network established in 2000, consists of 28 Lidar stations spread over 14 European countries. EARLINET is developing a very complete database of different aerosol products, being aerosol extinction and backscatter profiles the most significant. This kind of information contributes strongly to the quantification of long-range transport and energy budget, and prediction of future trends on European and global scale. Other important benefits consist in providing support to improve model treatments on a wide range of scales and to help for a better exploitation of present and future satellite data.

3.2 Aerosol Long-range transport over Madrid. An example of CIEMAT-Lidar results

At present, EARLINET counts with 3 Spanish stations being CIEMAT one of them (CIEMAT-Madrid EARLINET #21 station) (Rocadenbosch et al., 2008). The

experimental strategy of EARLINET includes a program of scheduled measurements and other of intensive measurements for special events like long-range transport episodes of African dust. Based on dust forecast models like SKIRON (http://forecast.uoa.gr/dustindx.php) and DREAM (http://www.bsc.es) is possible to anticipate these situations and to perform that non-scheduled special measurements. To illustrate this kind of results in some aerosol profiles obtained in Madrid with the CIEMAT- Lidar system are presented in Figure 5.

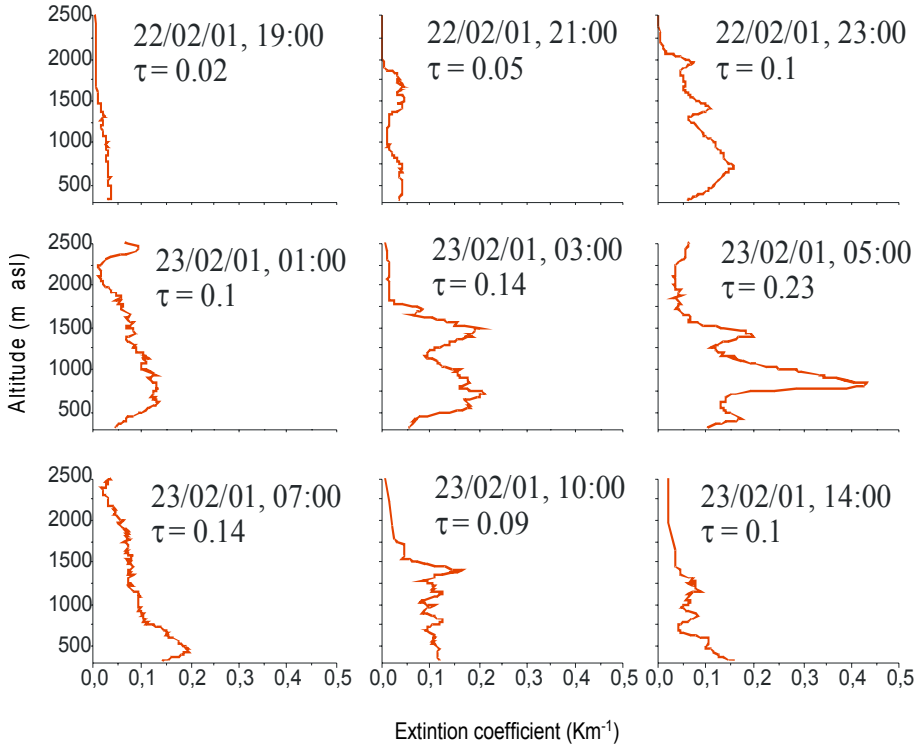

Figure 5. Extinction coefficient profiles obtained with the Lidar at CIEMAT site.

In this sequence the time evolution of extinction coefficient profiles obtained during 22th and 23th February 2001 is shown. This parameter calculated by applying Lidar signal inversion algorithms is related with the vertical atmospheric aerosol distribution. The changes in extinction coefficient are due to the arrival of Saharan dust over Madrid at the end of day 22. In this case of nocturnal long-range transport of desert particles, the process took place on atmospheric layers located 400-500 m above surface with scarce impact on ambient PM. The backward trajectories calculated by HYSPLIT model (http://www.arl.noaa.gov/ready/) confirm the African origin of the dust (Figure 6). During the first hours of day 23 the transported air masses arrived Madrid area but the lower layers were practically unaffected.

This nocturnal long-range transport could only be studied by using active remote sensing techniques like Lidar due to the absence of solar light that prevented the use of passive techniques.

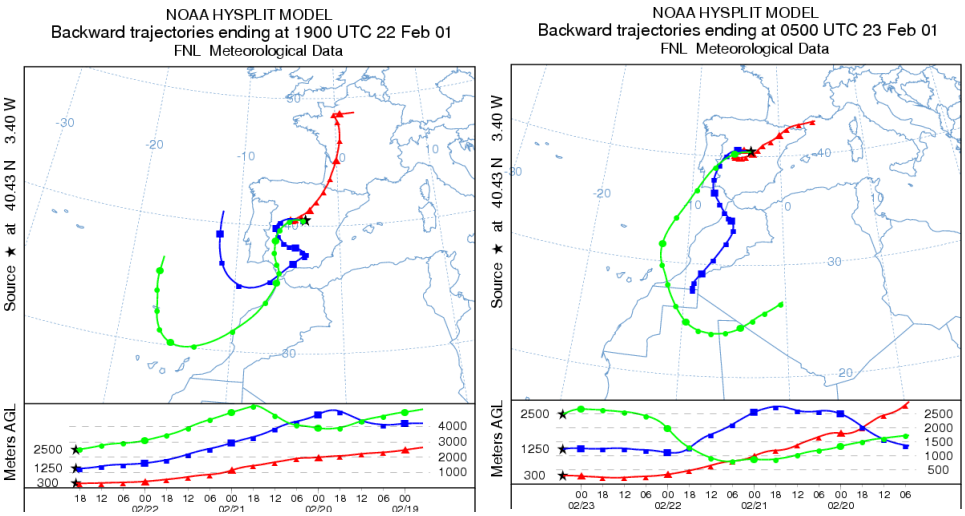

Figure 6 . Backward trajectories ending over Madrid (CIEMAT location) produced with HYSPLIT model.

3.3 Present and future role of ground-based Lidar systems.

Finally, ground-based Lidars play another key role on some satellite mission support, in particular in those devoted to characterize aerosol distribution at global scale. Since June 2006 all the EARLINET´s stations are developing a relevant work in the CALIPSO satellite validation scheme and in the full exploitation of the satellite data. In coordination with NASA (responsible for CALIPSO operation) EARLINET started in a correlative measurements schedule for CALIPSO validation purposes. This strategy has been defined on the basis of the analysis of the high resolution ground-track of the satellite, and those ground-based stations that are near enough of the track in each CALIPSO orbit must measure simultaneously to the satellite. CALIPSO provides aerosol vertical profiles pointing to NADIR and the stations measure vertical profiles from ground to zenith.

Two examples of this kind of exercises are presented in Figure 7. The plots show the results of comparing measurements taken from the EARLINET #21 station (CIEMAT-Madrid) in coincidence with the passing of CALIPSO. In spite of the spatial differences between the location of CIEMAT Lidar station and CALIPSO ground-track, the Total Backscatter Coefficient at 532 nm profiles obtained from both instruments can be compared directly. In general the agreement is quite good but there are evidences about the existence of noticeable discrepancies in several circumstances. The reasons for it are at present under study. These examples point

out the importance of a collaborative relation among the ground based networks and the satellite missions conceived and designed for aerosol investigation to consolidate and go deeper into knowledge about the aerosol role in a great variety of atmospheric phenomena.

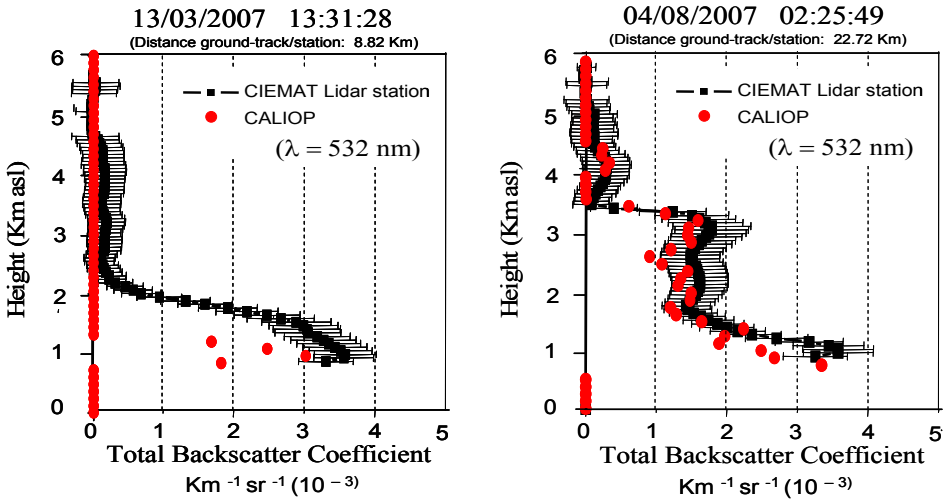

Figure 7. Different profiles of the Total Backscatter Coefficient obtained with the Lidar over the Ciemat site and observations from the CALIOP instrument.

4. SUMMARY AND CONCLUSIONS

In this second part of the study about atmospheric pollution by particles in Madrid some processes affecting the urban aerosol evolution have been presented. The techniques involved in the experimental characterization are usually continuous or semi-continuous systems and their short response times are key factors to obtain representative data of the occurrence of these phenomena.

Among the different results produced with this instrumentation, some obtained with specific EC/OC and nitrate analysers have illustrated the formation of these major aerosol components and their correlation with boundary ambient conditions. To document the size aerosol evolution associated to secondary formation of particles, some SMPS results have been presented. Finally, the general role of remote sensing techniques on 3D aerosol distribution has been discussed. In the particular case of ground based Lidar measurements, its role in the study of dust long-range transport processes and their incidence over this urban area have been illustrated with a well documented case from CIEMAT Lidar station. All these results offer a nice picture about the current status of CIEMAT research in this field, taking Madrid as an excellent scenario for urban air pollution studies.

5. ACKNOWLEDGEMENTS

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En algún momento de nuestras carreras profesionales Elvira jugó un papel decisivo pero desgraciadamente esa deuda ya no podemos saldarla. Sirva este pequeño trabajo elaborado desde el cariño y el reconocimiento que Elvira nos inspira como humilde homenaje nuestro. Las grandes personas como Elvira siembran sabiduría y bondad a lo largo de su vida y siempre recogen el ciento por uno, aunque a veces no puedan hacerlo en este mundo.

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