Hygroscopic Properties of Atmospheric Aerosol Measured with an HTDMA in an Urban Background Site in Madrid

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Abstract. The observation of high aerosol hygroscopic growth in Madrid is mainly limited to specific atmospheric conditions, such as local stagnation episodes, which take place in winter time. One of these episodes was identified in December 2014 and the hygroscopic growth factor (GF) measurements obtained in such episode were analysed in order to know the influence of the meteorological conditions on aerosol hygroscopic properties.
The prevailing high atmospheric stability triggered an increase of the particle total concentration during the study period, with several peaks that exceeded 4.0 10^4 particles cm^{-3}, as well as an increase in the inorganic fraction of the aerosol, the NO_3^- concentration, which in this case corresponded to 25% of the total PM_1 non-refractory composition.
The aerosol hygroscopic growth distribution was bimodal during the episode, with an average GF around 1.2 for the five dry particle sizes measured and an average GF spread ≥ 0.15. In addition, it is important to note that when a reduction in the concentrations of NO_3^- is observed, it coincides with a decrease of the GF and its spread. These data suggest, on the one hand, a high degree of external mixing state of the aerosol during the episode and, on the other hand, a notable association between the GF and the inorganic fraction of the aerosol.

1. Introduction

Hygroscopicity is one of the most uncertain properties of the atmospheric aerosol [1, 2], principally because it involves two aspects: the aerosol composition and size, and the humidity/temperature ambient conditions. The growth that atmospheric aerosols may experience due to their hygroscopicity is relevant in some processes in which they participate, as the direct and indirect aerosol effects on radiative forcing and climate, in the atmosphere, or the potential damage to the health inside the human body.

The hygroscopic behaviour of atmospheric aerosols based on measurements of the particle size through a Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) has been investigated at different European locations, especially in Northern Europe, e.g. [3], [4] or [5]. However, such investigations are scarce in Southern Europe [6, 7], with rather different climatic conditions.

In the city of Madrid, the primary sources of pollutants determining the aerosol composition, and consequently its hygroscopicity, are emissions from traffic and domestic activities, predominantly of carbonaceous nature. As it will be seen in this study, the meteorological conditions of this geographical area will also play an important role on the aerosol hygroscopic properties.

This work analyzes the aerosol growth during a pollution episode in the 2014 winter season. To this aim, the aerosol GF measurements have been complemented with data on aerosol size distribution, aerosol composition and meteorological conditions.

2. Sampling site and measurements

This study has been conducted during winter 2014 in an urban background area located at CIEMAT facilities (40º 27′ 23.2″ N, 03° 43′ 32.3″ E and 650-700 m asl), in Madrid.

During this season local stagnation episodes are usual. The meteorological scenario corresponds to an anticyclone situation over the Iberian Peninsula, leading to a high atmospheric stability and consequently to the presence of intense thermal inversions, which are constant throughout this type of episodes [8, 9, 10].

A wide variety of instruments have been measuring the different properties of atmospheric aerosols at the CIEMAT station complemented with meteorological parameters:

1) The hygroscopic growth factor of atmospheric aerosol has been obtained with an HTDMA. The measurements have been acquired at RH of 90% for five dry particle sizes (50, 80, 110, 190 and 265 nm) covering the submicrometer fraction of the atmospheric aerosol. The temporal resolution of the measurements was 3 min. More detailed information on this equipment can be found in [11] and [12].

The measurements have been corrected by the $TDMA_{inv}$ program [13] and the GF has been recalculated at 90% RH from $TDMA_{inv}$ for RH variations of ±2% about target value (90% RH). After correcting the RH, data coverage of 90 % for the study period was reached. The number of lost scans was higher when the dry particle size selected was increased.

The GF values collected in this work corresponded to GF_{avg} provided by the $TDMA_{inv}$. This parameter was defined as the growth factor that would be observed if the absorbed water were equally distributed among all particles in a sample [3]. In addition, the spread of growth factor was used to evaluate the aerosol mixing state; a GF spread ≤ 0.10 indicates an internal mixture, or a quasi-internal mixture, while a GF spread ≥ 0.15 can be considered externally mixed, or quasi-internally mixed [3, 4].

2) The aerosol size distribution between 14 and 660 nm has been provided by a Scanning Mobility Particle Sizer (TSI-SMPS: DMA3081 with CPC 3775), with temporal resolution of 4.5 min. The particle concentrations for each of the three modes, nucleation ($N_{<30\ nm}$), Aitken ($N_{30\text{-}100\ nm}$) and accumulation ($N_{>100\ nm}$), were obtained from the aerosol size distributions.

3) The PM_1 non-refractory composition (organics, NO_3^-, SO_4^{2-}, NH^{4+} and Cl^-) has been obtained by an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research, Inc.). The ACSM resolution was around 30 min for each species.

4) A meteorological tower registered data on precipitation, pressure, temperature at two levels (obtained with a difference of 50 m), relative humidity (RH) and wind speed and direction at the measurement site every 10 minutes.

Additional information on PM_{10}, $PM_{2.5}$, NO_2 and O_3 was provided by the suburban station of Casa de Campo (3º 44' 50.44" W, 40º 25' 09.68" N, 645 m asl) located at 4.5 km South from the measuring place. This station belongs to the Air Quality Monitoring Network of the Madrid municipality and is representative of the environmental characteristics of the study area.

Furthermore, the pressure field maps at surface level provided by UK Meteorological Service (http://www.metoffice.gov.uk/) have been used to interpret the atmospheric meteorological situation at synoptic scale.

3. Results and discussion

3.1. Identification of the episode

A local stagnation episode was identified from 14 to 28 December 2014. The synoptic maps showed a high pressure system over the Iberian Peninsula, which remained during the whole episode inhibiting the dispersion of pollutants (Figure 1).

The average temperature for the episode was 7.1±1.0ºC, with the presence of intense thermal inversions during night time. In addition, precipitation was not observed and the average RH was 74±9%.

The average wind speed was 2.7±1.5 m/s and the wind direction in the area followed the typical pattern with a NE-SW steering axle, characteristic of the measurement area [14].

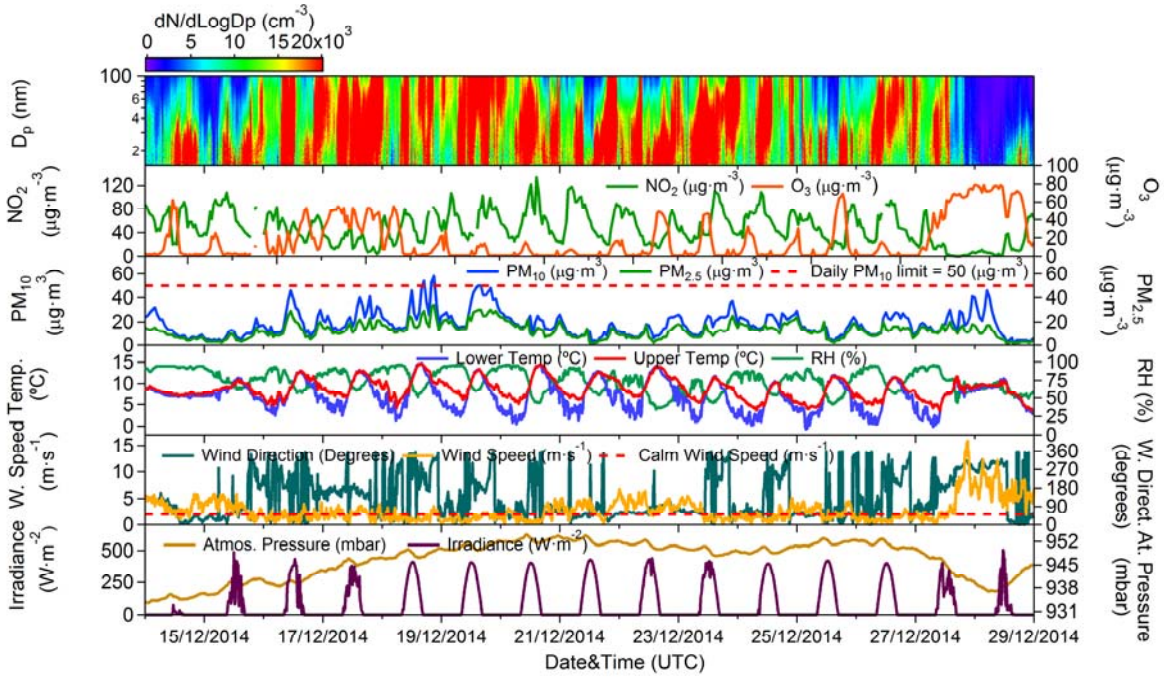

Figure 1. Evolution of the aerosol size distribution and meteorological conditions (temperature, relative humidity, wind speed, wind direction, and irradiance) obtained in the Ciemat station as well as NO_2, O_3, PM_{10}, and $PM_{2.5}$ concentrations provided by the air quality station Casa de Campo during the local stagnation episode.

The evolution of the aerosol size distribution indicated a high particle concentration throughout the period, which as evidenced by the high concentrations of NO_2, possibly originated from traffic sources. Nevertheless, the daily PM_{10}limit value (24 hours) established by Spanish legislation (*Royal Decree* **102/2011** of January 28: 50 $\mu g \cdot m^{-3}$), based on the *European Directive* **2003/17/CE**, was not exceeded. However, PM_{10} concentrations higher than 50 $\mu g \cdot m^{-3}$ were observed for some time intervals during the study period. Also high $PM_{2.5}$ concentrations higher than 25 $\mu g \cdot m^{-3}$ were also recorded.

3.2. Aerosol growth factor during the local stagnation episode

The characteristics of the meteorological scenario indicated in the previous section not only triggered an increase in the pollutant concentration but also their chemical aging. This facilitated an increase in the inorganic fraction of atmospheric aerosol.

The total particle concentration was high throughout the period, with an average value of $16\times10^3\pm1\times10^3$ particles$\cdot$cm^{-3} and peaks that exceeded 40×10^3 particles$\cdot$cm^{-3} (Figure 2). The PM_1 non-refractory composition during the local stagnation episode was mainly organic, 62% of the total composition, followed by NO_3^- (25%).

During the episode, the aerosol growth factor distribution was bimodal for all measurements, with an average GF centred on 1.2 for the five dry particle sizes. In addition, on average for the study period, the GF spread for the particle sizes measured was ≥ 0.15, which suggested a high degree of external mixing of the aerosol. It has to be emphasized that the GF spread was high for larger particles i.e. for a dry size of 50 nm it was 0.15±0.02 while for a dry size of 265 nm was 0.19±0.07.

In relation to the GF daily variation, the GF maximum corresponded to a maximum concentration of NO_3^- as shown in figure 2. Furthermore, the situation observed on 21 and 22 December 2014 should be noted. Wind speed was greater than 3 $m \cdot s^{-1}$ and NO_3^- concentration did not rise above 0.3 $\mu g \cdot m^{-3}$ on both days. This involved a significant reduction of the GF in the five particle sizes measured, which did not reach 1.2 (average value during the study period). This scenario was also observed in the GF spread, which indicated a reduction of the mixing state of aerosol in all the measured particle sizes.

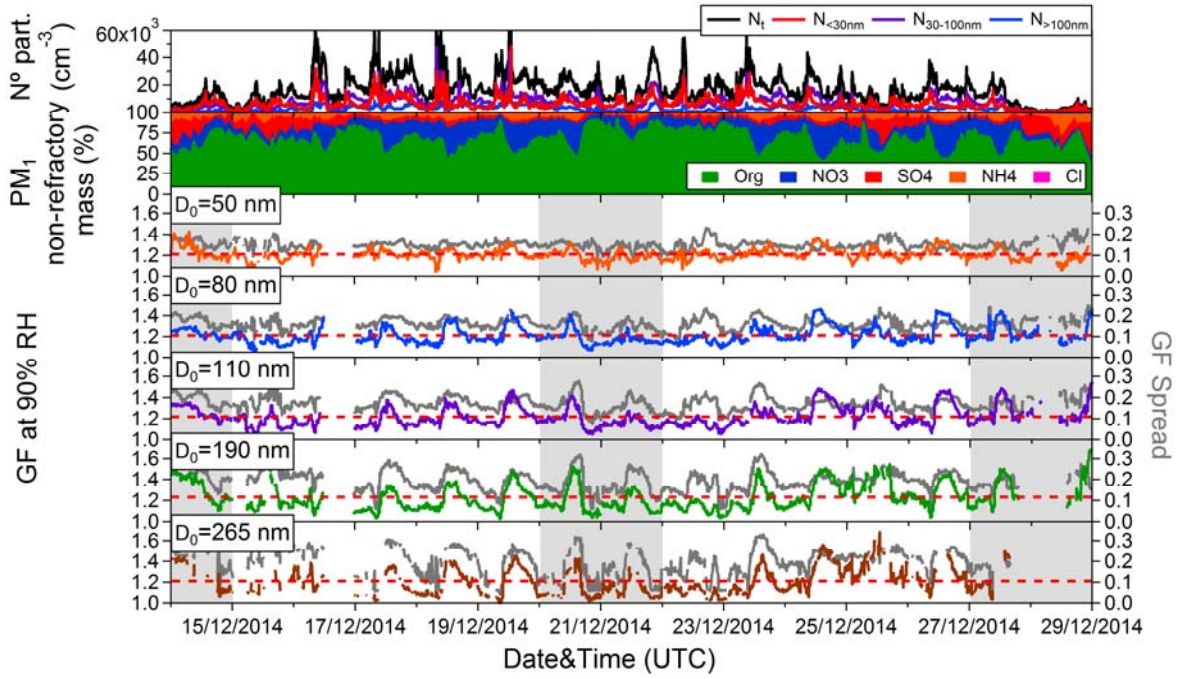

Figure 2. Temporal evolution of GF and its spread for dry particle sizes (D_0) of 50, 80, 110, 190, 265 nm at RH=90% as well as the evolution of the PM_1 non-refractory composition and modal particle concentrations during the local stagnation episode. The red line on each plot represents the average GF for each measured particle size. For a better interpretation of pollutant data, the weekend period has been indicated by a shaded area.

4. Conclusions

The aerosol hygroscopicity has been studied during a winter episode under local stagnation conditions in Madrid.

The strong atmospheric stability during the episode influenced the chemical composition of the atmospheric aerosol and consequently its hygroscopicity.

A high concentration of particles was observed, exceeding 40×10^3 particles$\cdot cm^{-3}$ during several time intervals. Also, the formation of ammonium nitrate was high in such events, reaching 25% of the PM_1 non-refractory composition.

The aerosol growth distribution measurements were bimodal for the entire episode, with an average GF of 1.2 for the five dry particle sizes measured and a GF spread $\geq$ 0.15. In those days, when the formation of NO_3^- was reduced, the GF and its spread also decreased. This situation suggested that the increase of the inorganic fraction of the aerosol during the episode led to a high degree of aerosol external mixing in all measured particle sizes.

These preliminary results will be part of a deeper study which will compare the aerosol hygroscopic growth in Madrid under different meteorological scenarios.

Acknowledgments
This work has been supported by the Spanish Ministry of Science and Innovation funding the MICROSOL (CGL2011-27020) and PROACLIM (CGL2014-52877R) projects and Ramón Areces Foundation, the AEROCLIMA project (CIVP16A1811) and Autonomous Community of Madrid, the TECNAIRE project (P2013/MAE-2972). The authors are grateful to Martin Gysel for the development of $TDMA_{fit}$ algorithm to invert HTDMA data ($TDMA_{inv}$) and allowing free use within the scientific community.
E. Alonso-Blanco acknowledges the FPI grant to carry out the doctoral thesis/PhD at the Research Center for Energy, Environment and Technology and of Economy and M. Becerril the FPI predoctoral research grant BES-2012-056545 at the Spanish Ministry of Economy and Competitiveness (MINECO).

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