Long Time Measurement of Aerosol Hydroscopicity at Košetice Backround Station

Ondráček, Jakub
2011

LONG TIME MEASUREMENT OF AEROSOL HYGROSCOPICITY AT KOŠETICE BACKGROUND STATION

Jakub ONDRÁČEK, Petr VODIČKA

Institute of Chemical Process Fundamentals of the AS CR, Rozvojová 2, 165 02 Prague 6 - Suchdol, Czech Republic, email: ondracek@icpf.cas.cz

Keywords: HTDMA, atmospheric aerosol, growth factor, background station

INTRODUCTION

The ability of submicron aerosol particles to absorb water can, to a large extent, influence their physical and chemical properties. On the other hand, these particles serve as condensation nuclei for cloud formation and thus also the resulting cloud properties depend on the chemical composition as well as on the size distribution of aerosol particles. Furthermore, the deposition pattern of aerosol particles in the human respiratory tract may significantly change with changing size of aerosol particles, and therefore depends also on hygroscopic properties of aerosol particles. Moreover, the hygroscopicity of aerosol particles affects the amount of light scattered by the aerosol particles and changes their chemical reactivity. Thus the hygroscopic properties of atmospheric aerosols are of major importance affecting the life cycle of the aerosol and the direct and indirect effects of aerosols on climate (Swietlicki et al., 2008).

The hygroscopic growth of aerosol particles can be studied in a great detail using the HTDMA systems (Hygroscopic Tandem Differential Mobility Analyser), a system used for a long time (Sekigawa, 1983). Generally, these on-line spectrometers are suitable mainly for long time measurements at background sites or at sites with slow and/or small changes in chemical composition and size distribution of the atmospheric aerosol (Fors et al., 2011).

This work describes the design of the LACP HTDMA and some of the results obtained during long time measurement at Košetice background station (Czech Republic), where it was deployed within the frame of two EU projects (EUSAAR and EUCAARI). The measurement campaign lasted from May 2008 until September 2009 with smaller or larger gaps in the data coverage.

EXPERIMENTAL SETUP

Generally, the HTDMA system measures the growth factor of aerosol particles or in other words the ratio between the diameter of particle under certain humidity and the „dry" diameter of the same particle, so called growth factor. In order to perform such a measurement, the HTDMA first lowers the RH of sampled ambient aerosol down to about <20%. The particles having low RH then pass through the first DMA, where the selected monodisperse fraction of the aerosol sample is cut. This narrow fraction of aerosol then undergoes humidification (usually at 90% RH) and continues to the second DMA (connected to CPC), where the resulting particle size distribution of humidified sample is measured.

The HTDMA system described here was built in the Laboratory of Aerosol Chemistry and Physics (LACP), ICPF, AS CR (Ondráček et al., 2008). This system is the first and the only one HTDMA system in the Czech Republic.

The LACP HTDMA is based on two Vienna type DMAs built in the workshop of ICPF (see Fig. 1). The temperature in both compartments of the two DMAs was kept constant by using PID controlled Peltier elements. CPC 3772 (Condensation Particle Counter, TSI) was used to count the number of aerosol particles coming from second DMA and thus giving the information about resulting particle number size distribution.

The most important component of HTDMA system is the part, which allows the particles to reach the desired humidity. The RH conditioning system as well as the drying system in the LACP HTDMA is based on the set of Nafion driers and humidifiers. The aerosol sample reaches the desired humidity using the Nafion humidity exchanger. The conditioning (purge) clean air of the Nafion humidity exchanger comes up from the automatic valve system controlled with PID controller. The valve system controls and combines the amount of the dried and the humidified clean air coming from the lines equipped with Nafion dryer and Nafion humidifier, respectively.

The whole HTDMA system was controlled by a LabVIEW program developed in LACP (based on SMPS code from Lund's University).

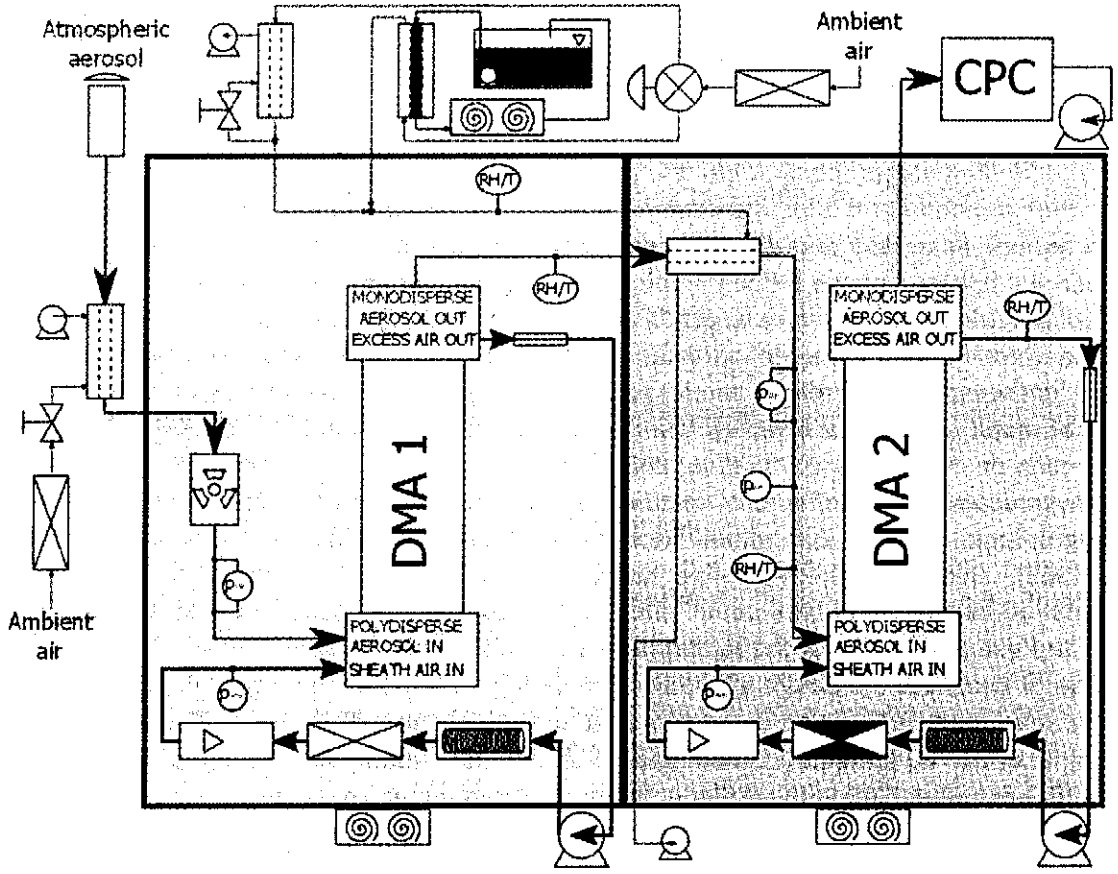

Fig. 1: LACP HTDMA setup.

RESULTS AND DISCUSSION

The LACP HTDMA was deployed at Košetice background station from beginning of May 2008 till the end of September 2009 within the frame of EUSAAR project. The instrument was in operation during the whole period with some gaps measuring 7 different dry particle size diameters between 22 nm and 225 nm. One scan for each particle size takes 10 minutes (up and down scan) and 20 seconds (changing the particle size), thus the time resolution for the whole size range is 1 hour, 12 minutes and 20 seconds. The resulting data from the LACP HTDMA system were analyzed using the HTDMA inversion toolkit provided by M. Gysel (Gysel et al., 2009).

During the long time measurement campaign of HTDMA at Košetice background station several hardware and software problems occurred causing the gaps in the data coverage (see Fig. 2). Nevertheless, the data coverage during the whole period was high enough to allow the evaluation of the hygroscopic properties of background aerosol particles in the Czech Republic. The issues with the HTDMA system included damages of several electrical components as well as broken pumps, etc. The LACP HTDMA system did not follow the EUSAAR recommended sizes of aerosol particles selected in the first DMA (25, 35, 50, 75, 110, 165, 265 nm). The deviation was caused by incorrect effective

lengths of both DMAs implemented in the measurement code, resulting in the sizes of dry particles as follows: 22, 31, 44, 66, 96, 142, 225 nm. Nevertheless, the sizing was recalculated to account for these wrong settings, so the resulting data has just shifted the size of selected monodisperse fraction and did not change the resulting hygroscopic properties of aerosol particles. Another challenging task arrised during the long time operation of the HTDMA system. The low RH (<20%) of sampled aerosol was not met in majority of the cases due to issues accompanying the inlet drying system. However, for most of the measured data it does not change the resulting growth factors dramatically.

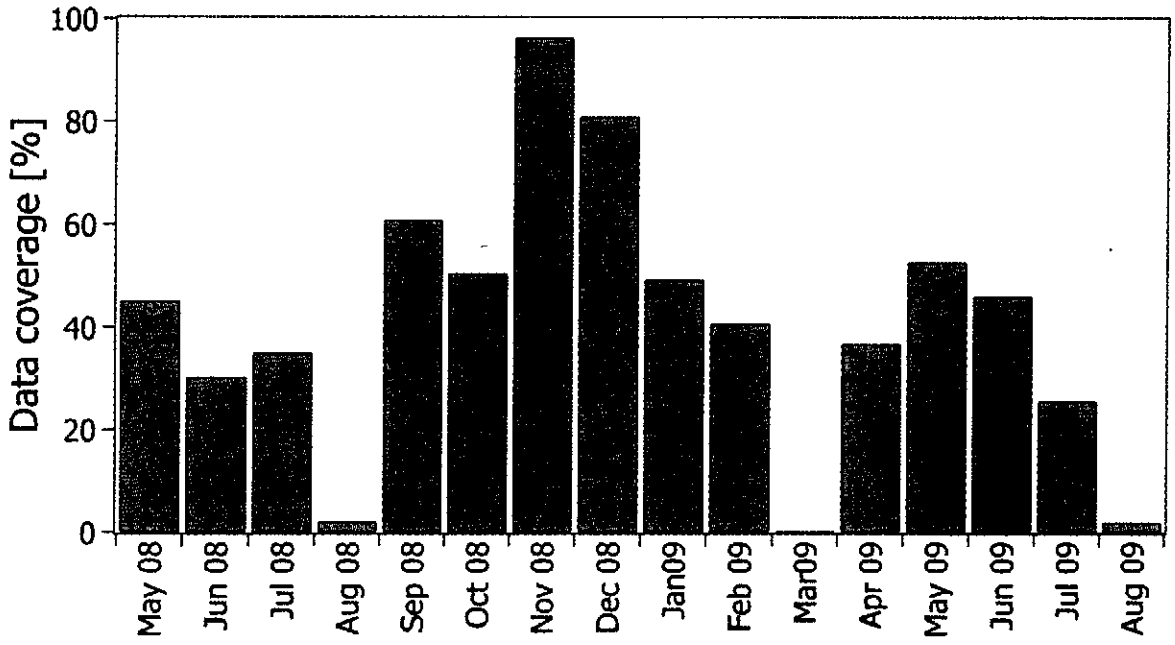

Fig. 2: Data coverage for measured period.

The resulting data are presented as a growth factor calculated for individual dry sizes of sampled ambient atmospheric aerosol particles. Fig. 3 shows the probability density function of the growth factor of the individual dry sizes averaged for the whole measurement period. It can be seen that the amount of water uptaken by particles is increasing with increasing size of the dry aerosol particles. Such behavior corresponds most probably to the higher content of inorganic salts in larger particles. Moreover, the particles in the size range above 100 nm represent usually aged aerosol having more oxidized surface, which leads to higher hygroscopicity of these particles. The smaller particles have the average growth factors close to 1, which means that they don't absorb so much water vapors.

The averaged diurnal variation of growth factor does not exhibit any significant trend (see Fig. 4). The growth factor depends again only on the particle size, having increasing trend with increasing size of the particles.

The monthly averaged growth facors for individual dry particle sizes (see Fig. 5) show the gap in the data during the early spring of 2009, caused by the malfunctioning HTDMA system. The seasonal variation for all the particle sizes display increasing hygroscopicity of aerosol particles during the spring season. Even though the increase is discontinued because of the malfunctioning HTDMA, the content of inorganic salts (mainly sulphates and nitrates) was increased during the spring season, resulting in higher hygroscopicity of aerosol particles. The chemical composition of aerosol particles was based on the chemical analysis of PM2.5 samples taken on filters, parallel to HTDMA system, during the same sampling period (Schwarz, 2011).

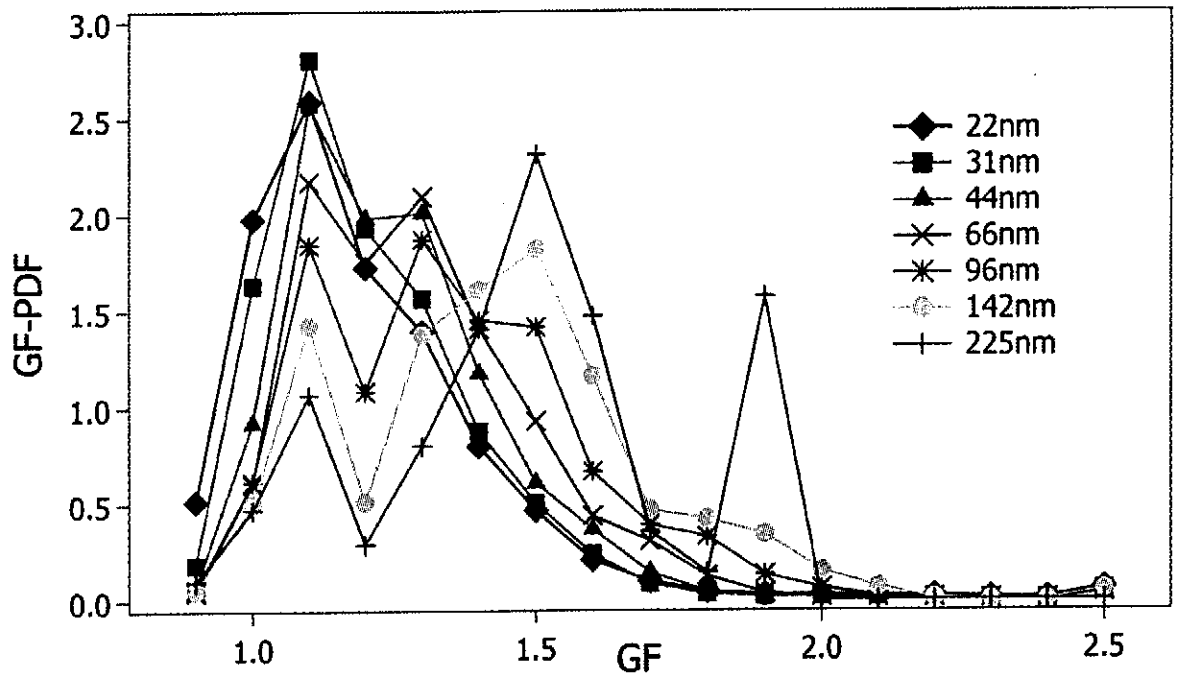

Fig. 3: Average GF-PDF for the complete data set, for each dry size.

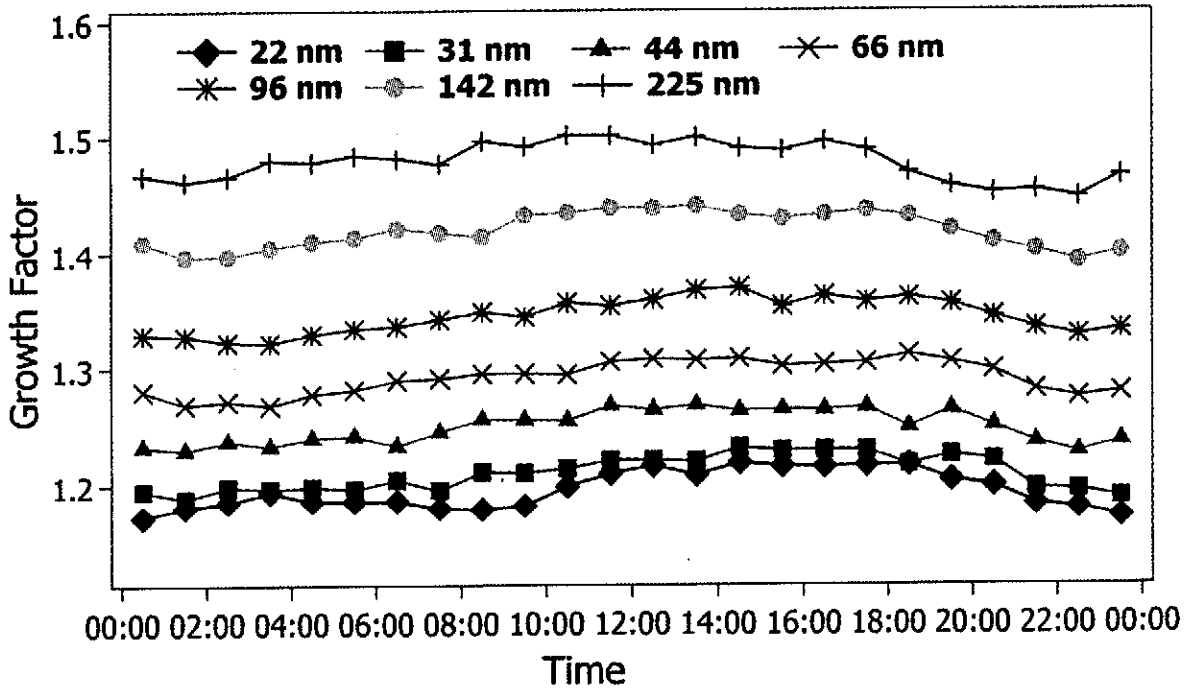

Fig. 4: Diurnal variation of average GF for the complete data set and each dry size (1 hour resolution).

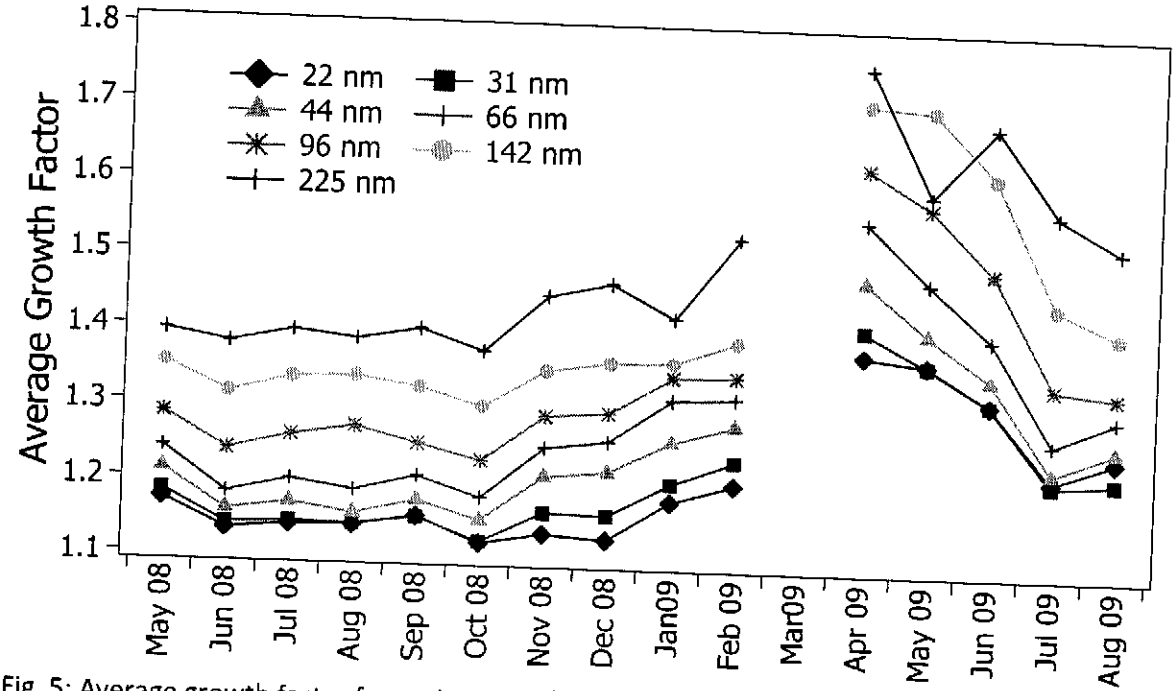

Fig. 5: Average growth factor for each month, for each dry size.

CONCLUSIONS

This work shows the results of the first measurement campaign dealing with measurements of atmospheric aerosol hygroscopicity using the HTDMA system in the Czech Republic. The instrument presented within this work represents the first generation of LACP HTDMA, thus some issues and unexpected failures occured during the measurement period. The second generation of LACP HTDMA is now being built.

The dry sizes measured by the LACP HTDMA don't correspond to values recommended by the EUSAAR project. This deviation was caused by incorrect length of both DMAs applied in the measurement and control LabVIEW code. Nevertheless, all the sizes were recalculated to reflect the real measured values. The EUSAAR recommendation regarding the maximum acceptable RH in DMA1 (20%) was unfortunately not met in our case in majority of the measurement period. The data were evaluated with RH limitations set to <30% for DMA1 and in the range of 88-92% for DMA2.

Generally, the results show the increasing water uptake with increasing size of aerosol particles. This is most probably caused by increasing content of hydrophilic inorganic salts in larger particles. Furthermore, the particles in accumulation mode are more aged and thus their surface is more oxidized. The higher level of oxidation leads to higher hygroscopicity of aerosol particles. Seasonal variation of growth factors show the increasing hygroscopicity of aerosol particles during the spring season. Chemical analysis of PM2.5 samples showed the increased relative content of inorganic salts in PM2.5 (mainly nitrates and sulphates) during spring season, which results in higher hygroscopicity of aerosol particles.

ACKNOWLEDGEMENTS

Authors would like to gratefully acknowledge the financial support of the EU FP6 project EUSAAR (FP6-026140), project EUCAARI (FP6-036833-2) and the Grant Agency of the Czech Republic under grant P209/11/1342.

Moreover, the authors would like to express their thanks to M. Gysel, E. Fors and other colleagues from HTDMA community for their help and support.

REFERENCES

Fors, E., Swietlicki, E., Svenningsson, B., Kristensson, A., Frank, G.P. and Sporre, M., Hygroscopic properties of the ambient aerosol in Southern Sweden - A two year study. *Atmos. Chem. Phys. Discuss.*, 11, 6601-665, (2011).

Gysel, M., McFiggans, G.B. and Coe, H., Inversion of tandem differential mobility analyser (TDMA) measurements. *J. Aerosol Sciences*, 40, 2 134-151, (2009).

Ondráček, J., Dohányosová, P., Ždímal, V., Schwarz, J., Krejčí, P., Smolík, J., Nový typ HTDMA systému pro dlouhodobá měření hygroskopických vlastností atmosferických aerosolových částic. *Sborník konference České Aerosolové Společnosti*, 28-27, (2008).

Schwarz, J., The ionic composition of PM2.5 at a rural background site in Central Europe on daily basis, *European Aerosol Conference – EAC2011 Manchester*. Poster 4P307, (2011).

Sekigawa, K., Estimation of the Volume Fraction of Water Soluble Material in Submicron Aerosols in the Atmosphere. *Journal of the Meteorological Society of Japan*, 61, 359-366, (1983).

Swietlicki, E., Hansson, H.-C., Hämeri, K., Svenningsson, B., Massling, A., McFiggans, G., McMurry, P.H., Petäjä, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E., Baltensperger, U., Rissler, J., Wiedensohler, A., Kulmala, M., Hygroscopic properties of submicron atmospheric aerosol particles measured with H-TDMA instruments in various environments - a review. *Tellus, Series B: Chem. and Phys. Meteorology*, 60, Issue 3, 432 – 469, (2008).