

—— Theses of Ph.D. Dissertation ——

TIBOR BORSÓS

**Formation and properties of
ultrafine atmospheric aerosol
in urban environments**

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Introduction

Ultrafine aerosol particles (electrical mobility diameter, $D_p < 100$ nm) have received considerable scientific interest in the last two decades due to their climate and health effects. Aerosol particles can be emitted directly into the atmosphere (as primary particles) or can be formed in the air via atmospheric chemical processes (as secondary aerosol). One of the most important formation processes of secondary particles is atmospheric nucleation, where condensed phase, i.e. particles are formed from gaseous components. The studies on nucleation and ultrafine aerosol have been conducted mostly in background and clean environments, and mainly focused on climate effects and formation process. Health effects and urban environments have gained scientific interest recently.

Aims of the study

The major objectives of my doctoral research work were to study the atmospheric nucleation, to determine the seasonal and spatial variation of aerosol particle number concentrations and size distributions in various urban environments. To achieve the objectives, measurements were performed in four environments of Budapest: city centre (Lágymányos campus of the Eötvös University), traffic microenvironment (Castle District Tunnel), street canyon (Rákóczi street campus of the Eötvös University) and near-city background (KFKI site). In addition, a short indoor campaign (in the Ortvyay Rudolf lecture hall of the Faculty of Science, Eötvös University, 1 week) was also performed. Measurement results of the longest campaign were compared to the data sets obtained for Prague and Vienna. Seasonal variation of size distributions was utilised to study the atmospheric nucleation. Basic properties such as particle formation rates (J_6) and growth rates were determined. The most important sinks, coagulation and condensation were also studied. Concentrations and number size distributions in the different environments were compared for different periods: days with and without nucleation, as well as for workdays and weekends. Meteorological conditions favouring nucleation were assessed by comparing the former periods, while the anthropogenic sources can be estimated by the latter ones. Detailed information on the seasonal variation of certain parameters can be obtained by comparing the diurnal variation of concentrations, size distributions and meteorological parameters, thus the properties of sources and sinks can be determined. Modal parameters (concentration, median diameters, geometric standard

deviations) were determined by fitting lognormal functions. Variation of these parameters were also investigated.

Methods

The main instrument of the measurements was a flow-switching type differential mobility particle sizer (DMPS). In this system, the aerosol particles are separated due to their (size dependent) electrical mobility, and concentrations are determined with a condensation particle counter (CPC), with pulse counting. This system measures number size distributions in the diameter range of 6–1000 nm, in 30 channels. A measurement cycle takes ca. 10 min, so approximately 138–139 spectra can be obtained a day. The aerosol measurements were supplemented with meteorological parameters (global radiation, temperature, relative humidity, wind speed, wind direction) as well as with pollutant gas concentrations (SO₂, O₃, NO_x, as well as PM₁₀ mass) obtained from the Hungarian Air Quality Network (OLM). Backward trajectories were calculated using the HYSPLIT model to compare days with nucleation and days with no nucleation.

New scientific results

1. Atmospheric aerosol number concentrations were determined for different environments in Budapest. Daily medians of ultrafine (N_{6-100}) particle number concentrations were 2.6×10^3 , 3.1×10^3 , 9.3×10^3 , 19×10^3 , $124 \times 10^3 \text{ cm}^{-3}$ for the indoor measurements, near-city background, city centre, street canyon and traffic microenvironment, respectively. Daily medians of particles with diameter 6–1000 nm (N_{6-1000}) were found to be 3.7×10^3 , 4.3×10^3 , 11.8×10^3 , 23×10^3 , $140 \times 10^3 \text{ cm}^{-3}$ for the same environments. Concentration difference in the daily medians between the near-city background and street canyon was more than five fold. The ultrafine contribution defined as the ratio of these two fractions (N_{6-100}/N_{6-1000}) slightly increased depending on the anthropogenic impact. It was $(76 \pm 9)\%$ in the near-city background, $(79 \pm 6)\%$ in the city centre, $(86 \pm 3)\%$ in the street canyon, and $(86 \pm 2)\%$ in the traffic microenvironment. The ultrafine contribution during the indoor measurements was significantly less than that for the outdoor sites, only $(69 \pm 7)\%$, owing to active air filtering.

2. Diurnal variation of concentrations showed similar tendencies at all urban sites, and was mainly determined by activities related to anthropogenic sources (principally to vehicular traffic). Concentration decreased from approximately 10 pm to 4–5 am, then it starts increasing due mainly to the direct emission of vehicles, and reaches a maximum between 7–8 am. After this, concentration starts to decrease in the city centre, while it remained elevated in the street canyon till approximately 9 pm. After morning rush hours, concentrations decrease in the city centre. A new peak is formed between 9–10 pm due to the combination of afternoon rush hours and the height change of the boundary mixing layer. Residences have a significant role in direct emissions, which is more emphasised during the heating period. Concentration changes in the near-city background markedly differed from the sites mentioned previously, as anthropogenic impact is insignificant. Only one peak is formed, which peaked between 12 pm and 1 pm, then the concentration decreased continuously till 7 am. The peak formed around noon was related to new particle formation, while the afternoon concentration decrease is mainly due to the coagulation of particles.

3. Monthly mean size distributions varied slightly throughout the year in the city centre. The distribution consisted of a single, very broad peak. No seasonal tendency was observed in the change of the median diameter of the peak. Similar, broad distributions were observed for the other urban sites, median diameters in the street canyon were practically the same as in the city centre. Median diameter in the near-city background was shifted towards larger particle sizes. This can be explained by the fact that the limited extent of the anthropogenic source particles can grow larger than in the city centre or in the street canyon. Mean distributions for days with nucleation were shifted towards smaller diameters, and concentrations were larger than those for days with no nucleation. This difference was most significant in the near-city background. Difference was smaller between the distributions determined for workdays and weekends. Distributions for the weekends were practically identical with the curves for the workdays. Only concentrations were smaller which were related to the less intense vehicular traffic.

4. Frequency of new particle formation for the different sites was determined by the inspection of the diurnal variation of size distributions. Atmospheric nucleation was observed for the first time in Budapest. New particle formation occurred on 27% of days on a yearly basis, least frequently in winter (7.3%) and most frequently in spring (44%). The frequency was similar in summer and autumn (28% and 29%, respectively). Frequency showed local maxima in two months, April and September with 59% and 43%, respectively. These maxima can probably be explained by increased biogenic emission. New particle formation frequencies in the near-city background were larger compared to the city centre (35% vs. 29% in June, and 36% vs. 26% in July), while it was less frequent in the street canyon (24% vs. 59% in April, and 23% vs. 27% in May). Differences can be related to the source and sink strengths, as well as to differences in meteorological parameters. Based on these results, it seems that new particle formation is sometimes restricted to certain parts of the city.
5. Particle formation rate (J_6) varied between 1.65 and 12.5 $\text{cm}^{-3} \text{s}^{-1}$, with a mean and SD of $(4.2 \pm 2.5) \text{cm}^{-3} \text{s}^{-1}$. Formation rate did not have seasonal tendencies. Despite the difference of almost an order of magnitude between the individual values and that summer values seem to be larger, difference on a monthly scale is insignificant. Particle growth rates varied between 2.0 and 13.3 nm h^{-1} , with a mean \pm SD of $(7.7 \pm 2.4) \text{nm h}^{-1}$. Values in winter were below the mean while they were usually above the average in summer. However, due to the limited number of days suitable for evaluation, no evident seasonal trends can be established. This is probably due to the urban environment and to the continuous anthropogenic emission.
6. Diurnal variation of particle concentrations shows seasonal variation as well. Curves are very similar to those described in thesis 2, but can be classified into two groups. Larger similarities are observed between colder (autumn, winter) and warmer (spring, summer) seasons regarding both N_{6-100} and $N_{100-1000}$ concentrations as well. Differences are larger for the ultrafine particles. Mean $N_{100-1000}$ concentrations in warmer seasons are smaller than in colder seasons, during the whole day. This can be explained by the fact that the boundary mixing layer is thicker in warmer seasons, resulting in more significant dilution.

7. By comparing one-year data sets of Budapest, Prague and Vienna, it was concluded that the largest aerosol concentrations were observed in Budapest. Daily median particle concentrations were $7.3 \times 10^3 \text{ cm}^{-3}$ in Prague and $8.0 \times 10^3 \text{ cm}^{-3}$ in Vienna. The ultrafine contribution was smallest in Vienna, with $(74 \pm 9)\%$ mean \pm SD value, while in Prague it was larger than in Budapest, with $(84 \pm 10)\%$. Shape of the diurnal variation of particle concentrations was similar at the three sites, difference was only in the concentration values. Properties of new particle formation were compared for the Budapest and Prague sites. Changes in monthly frequencies were similar in the two cities. There were two maxima in Prague as well, in April and in August (57% and 56%), while those were April and September in Budapest. Frequency of new particle formation was 23% in Prague on a yearly scale. It was least common in winter with 3.9%, its maximum was in summer, with 41%, followed by spring with 34%, and finally by autumn with 10%. New particle formation frequency was smaller in Prague for the months of spring compared to Budapest, while it was larger for the summer months.
8. Frequency of atmospheric nucleation depended on meteorological parameters, thereby it showed seasonal variation. Due to photochemical reactions, the strongest dependence was on global radiation. Larger global radiation favouring the phenomenon also resulted in larger temperatures and smaller relative humidities. Additionally, O_3 concentration was significantly larger on days with nucleation, 42% on average. Beginning of nucleation practically did not depend on SO_2 concentrations which is the precursor gas of sulphuric acid because it was probably always available in sufficient quantity. H_2SO_4 proxy related to the assumption of sulphuric acid concentration, containing global radiation and condensation sink as well ($[\text{H}_2\text{SO}_4] \propto [\text{SO}_2] \cdot \text{Rad}/\text{CS}$, where $[\text{H}_2\text{SO}_4]$ and $[\text{SO}_2]$ are concentrations of sulphuric acid and sulphurdioxide, *Rad* is global radiation and *CS* is condensation sink), was significantly, two times on average larger for days with nucleation. In the colder months, the difference was larger between the proxies obtained for days with and without nucleation (181% and 109% for winter and autumn, respectively), while in the warmer seasons, differences were much smaller (48% in spring and only 32% in summer). Wind speed was larger on days with nucleation.

Publications on which the thesis is based

- Salma, I., Dosztály, K., Borsós, T., Söveges, B., Weidinger, T., Kristóf, G., Péter, N., Kertész, Zs., 2013. Physical properties, chemical composition, sources, spatial distribution and sinks of indoor aerosol particles in a university lecture hall. *Atmos. Environ.* 64, 219–228, IF: 3,465.
- Borsós, T., Řimnáčová, D., Ždímal, V., Smolík, J., Wagner, Z., Weidinger, T., Burkart, J., Steiner, G., Reischl, G., Hitzenberger, R., Schwarz, J., Salma, I., 2012. Comparison of particulate number concentrations in three Central European capital cities. *Sci. Tot. Environ.* 433, 418–426, IF: 3,286.
- Salma, I., Borsós, T., Aalto, P.P., Kulmala, M., 2011. Time-resolved number concentration and size distribution of aerosol particles in an urban road tunnel. *Boreal Env. Res.* 16, 262–272, IF: 1,803.
- Salma, I., Borsós, T., Weidinger, T., Aalto, P., Hussein, T., Dal Maso, M., Kulmala, M., 2011. Production, growth and properties of ultrafine atmospheric aerosol particles in an urban environment. *Atmos. Chem. Phys.* 11, 1339–1353, IF: 5,520.

Additional publications

- Dosztály, K., Borsós, T., Gyöngyösi, Z., Péter, N., Weidinger, T., Kristóf, G., Salma, I., 2013. Chalk powder in the air – Sources, properties and sinks of aerosol in a university lecture hall. *Természet Világa* 144/6, 277–279.
- Salma, I., Borsós, T., Németh, Z., 2012. Importance and impacts of atmospheric aerosol. *Magyar Kémiai Folyóirat* 118/2–4, 107–114.
- Borsós, T., Salma, I., 2011. In the middle of the Castle District Tunnel. *Természet Világa* 142/6, 257–260.
- Borsós, T., Salma, I., 2010. Banana curve in Budapest. *Élet és Tudomány* 65/21, 643.
- Borsós, T., Salma, I., 2009. Nanoparticles in the air: blessing or curse? *Élet és Tudomány* 64/51–52, 1654–1656.

Oral presentations

- Borsós, T., Salma, I., Study of ultrafine aerosol particles in different urban microenvironments. Turbulence, transfer, transport, and transformation: interactions among environmental systems Conference, 24–25 May 2012, Budapest.
- Borsós, T., Salma, I., Aalto, P., Kulmala, M., New particle formation in Budapest. X. Magyar Aeroszol Konferencia, 20–21 October 2011, Galyatető.
- Borsós, T., Salma, I., Weidinger, T., Aalto, P., Kulmala, M., Ultrafine particles in various urban microenvironments in Budapest. European Aerosol Conference, 4–9 September 2011, Manchester.
- Salma, I., Borsós, T., Weidinger, T., Aalto, P., Dal Maso, M., Kulmala, M., Relationship between new particle formation and pollutant gases in an urban environment. European Aerosol Conference, 4–9 September 2011, Manchester.
- Řimnáčová, D., Borsós, T., Ždímal, V., Salma, I., Schwarz, J., Smolík, J., Comparison of ultrafine atmospheric aerosols in Prague and Budapest. Conference of the Czech Aerosol Society, 12–13 November 2009, Čejkovice.
- Borsós, T., Salma, I., Aalto, P., Kulmala, M., New particle formation and growth in Budapest. IX. Magyar Aeroszol Konferencia, 27–28 April 2009, Balatonfüred.

Posters

- Salma, I., Borsós, T., Németh, Z., Aalto, P., Kulmala, M., Comparative study of ultrafine aerosol within a city. European Aerosol Conference, 2–7 September 2012, Granada.
- Borsós, T., Salma, I., Weidinger, T., Aalto, P.P., Hussein, T., Kulmala, M., Ultrafine aerosol in Budapest: results of a 1-year campaign. International Aerosol Conference, 29 August–3 September, Helsinki.
- Borsós, T., Salma, I., Weidinger, T., Aalto, P.P., Hussein, T., Kulmala, M., Ultrafine aerosol and the first observed nucleation burst in Budapest. European Aerosol Conference, 6–11 September 2009, Karlsruhe.
- Borsós, T., Salma, I., Weidinger, T., Aalto, P.P., Hussein, T., Kulmala, M., New particle formation and growth of aerosol particles in an urban environment. 18th International Conference on Nucleation and Atmospheric Aerosols, 10–14 August 2009, Prague.