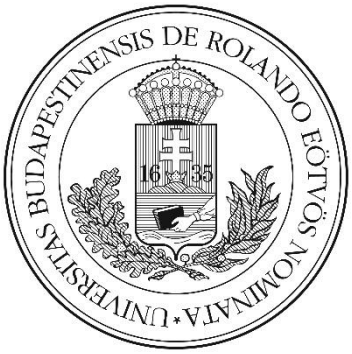
Health and environmental effects of the ultrafine atmospheric aerosol

THESIS

Zoltán Németh

Supervisor: Dr. Imre Salma, professor



Chemistry Doctoral School

Head: Dr. György Inzelt, professor

Analitical Chemistry, Colloid- and Environmental Chemistry, Electrochemistry doctoral program

Head: Dr. Gyula Záray, professor

Eötvös University

Budapest

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1. Introduction

The atmospheric ultrafine aerosol particles in the last two decades have increasingly become the subject of scientific investigations which are in relation with two global challenges. One is the excess risk on the human health that leads respiratory diseases. The particles have effect on the climate of the Earth.

The investigation of aerosol particles was previously performed by offline, and later on by online methods, that is why even smaller particles could be detected with higher time resolution. Therefore we have had less information on ultrafine (d<100 nm) particles than on the coarse (d>2,5 μm) and fine (d<2,5 μm) particles. The ultrafine particles have the largest contribution to the total number of particles. They have small size, big surface area and hence they have significant biological activity. The particles can penetrate into the deepest region of the respiratory tract. Therefore their residence time increase and the insoluble particles enter into the blood circulation by stepping across the cell wall. They can modify the blood coagulation, resulting oxidative stress, and they can be translocated into other organs.

The atmospheric aerosol particles have direct and indirect effects on the climate of the Earth. The particles are able to scatter (mostly sulphate particles) and absorb (e.g. soot particles) the solar radiation. The scattering has cooling, the absorption has warming effects. This is the direct effect of the aerosol. The ultrafine aerosol particles are able to grow in the atmosphere in the presence of supersaturation of water vapor, and so act as cloud condensation nuclei (CCN). The evolving clouds from these seeds scatter the solar radiation back to the space which has a significant influence on the energy balance of the Earth. This is the indirect effect of the aerosol particles.

The ultrafine particles can be primary or secondary particles. The primary sources take in high temperature processes such as vehicle emission, burning, heating. The main formation process of the secondary particles is the atmospheric nucleation. The investigation of the relationship between the two formation processes, the environmental and health effects help us to understand better our atmospheric environment.

2. Objectives

The objective of my work was to determine the aerosol particle number concentration and size distribution in city centre and near-city environtments, and to analyze the atmospheric nucleation in the relation of near-city and city centre environments. The object that I propose myself was the determination of the spatial extension of new particle formation by the investigation of the trajectories of nucleating air masses. My plan was to analyze the incidence and spatial inhomogeneity of nucleation events between the urban and the rural sites. I was supposed to collect aerosol particles and investigate them by electronmicroscope. My objective was to model the aerosol particle deposition in the human respiratory tract according to the measured median particle size distributions in the near-city, city centre, street canyon and tunnel environments by a stochastic lung model during different physical activity. I planned to investigate the hygroscopocity and volatility properties of sub-micron particles.

3. Applied methods

3.1 Experimental methods

The electrostatic precipitator is a vertically installed conductive cylinder, that operates with high voltage. Particles can be collected on the substrate placed on the top of the cylinder. Lacey formwar on copper grid was used (3 mm diameter, 200 mesh) for the collection. Between the earliest and the latest time of the nucleation event, the applied 10 kV was switched on in the negative mode, and so the positively charged particles were caught on the substrate. One substrate was exposed ten times before the analysis by a transmission electronmicroscope.

The Differential Mobility Particle Sizer (DMPS) consists of 3 main parts: a neutralizer, a Differential Mobility Analyzer (DMA), and a Condensation Particle Counter (CPC). The measuring system registers the particle number concentration and size distribution in the diameter range of 6–1000 nm with a time resolution of ~10 min. The measurements were performed in the city centre and in the near-city background for 2 one-year long periods. I determined the total and ultrafine particle concentration, diurnal variation. I investigated the size distributions on nucleation and nonnucleation days. I compared the nucleation frequencies.

The interactions between the aerosol particles and water vapor were studied by a Humidity-Volatility Tandem Differential Mobility Analyzer (HV-TDMA). For this purpose, particles with the diameter of 20, 50, 75, 110 és 145 nm were selected. During the volatility mode, the particles enter into a thermodenuder (290°C) where the volatile compounds evaporate. For the determination of the hygroscopic property, the particles go through a chamber where the RH is set to (90±2)% and they grow in size. Finally the measuring system registers their size distribution and concentration in both modes. I determined the growth factor of the particles. The chemical composition and source of the partices and the dynamics of the sources were concluded.

3.2 Models

The online HYSPLIT code (HYbrid Single-Particle Lagrangian Integrated Trajectory) with embedded meteorological database was used for the modelling study of the air mass trajectories. The advantage of the code is that the Eulerian and Lagrangian approaches are joined together. The trajectory modelling was performed in backward direction with GDAS meteorological database at 200, 500 and 2300 m arriving heights. The vertical motion of the air parcel was set to vertical velocity mode. The starting time of the run was the end of the particle growth (t_e time parameter), and the length of the run was the rounded time between the end of the particle growth and the beginning of the nucleation event (t_e-t_1 hour). I determined the trajectories of the nucleating air masses, arriving sectors and the source areas for nucleation days.

The aerosol particle deposition in the human lung was calculated by a stochastic lung model (**I**nhalation, **D**eposotion and **E**xhalation of **A**erosols in/from the **L**ung, IDEAL). The respiratory tract was divided into extra-thoracic (ET), tracheobronchial (TB) and acinar (AC) regions. The deposition in the extra-thoracic region was calculated by semi-empirical equation. The cylindrical airway in the TB and AC region was assumed to be divided asymmetricaly into two smaller daughter airways. The AC region was ended in hemispherical alveoli. The data of the airway morphology originated from statistical distributions. The route of inhaled particles distribute randomly in the respiratory tract by Monte Carlo method, and they followed the same route during exhalation. Therefore the simulation of large number of particles was needed, where every particle proceeds a new route into the lung. The investigated quantity was the average of the given physical quantity from a given number of simulations. The particle deposition was modelled for a healthy adult Caucasian-type female for sleeping, sitting, light and heavy physical activities. The study was based on the median particle number concentrations and size distributions measured in the near-city background, city centre, street canyon and tunnel environments.

4. Summary of the new scientific results

1. I determined the particle number concentration and size distribution in the diameter range of 6–1000 nm with a time resolution of ~10 min in the city centre and near-city background environments during two 1-year long continuous online (DMPS) measurements. The Aitken- and accumulation modes were alternately dominant. I coupled the relative change of the modes for emission sources and atmospheric processes. The yearly median particle number concentrations were $3{,}4\times10^3$ cm^{-3} and $7{,}9\times10^3$ cm^{-3} in the near-city background and city centre. The contributions of ultrafine particles to the total particle number concentration were 66% and 77%, respectively. The higher ultrafine and total particle concentration in the city centre was caused by vehicle emission.

2. I concluded that the nucleation frequencies were 28% and 20% in the city centre and in the near-city background, and showed significant seasonal variation. The new particle formation had maximum values in spring and autumn according to the biogen emission. The frequencies were in good agreement with the results from remote sites. I registered nucleation event with double onset 8 times in the near-city background. The first and second formation (first onset: J_6=2,1±1,5 cm^{-3} s^{-1}, second onset: J_6=3,7±1,6 cm^{-3} s^{-1}) and growth (first onset: GR= 5,1±1,5 nm h^{-1}, second onset: GR=10,1±1,7 nm h^{-1}) values showed that the first onset was related to regional processes, while the second onset was related to urban origin.

3. I developed a method for the determination of the spatial extent of the nucleation by examining the first channel content in the DMPS spectrum. Based on the introduced nucleation time parameters and backward trajectories, the preveiling directions of the nucleating air mass were northwest-southeast in the city centre and northwest in the near-city background. The identified 32 souce origins were mostly in the Carpathian Basin affected by woody areas. The wind speed and wind direction also showed differences on nucleation and nonnucleation days.

4. I compared the nucleation frequency distributions for two 1-year long (2008–2009 and 2012–2013) campaigns at urban (Budapest) and rural (K-puszta) sites. The frequencies had the same distribution which was verified by the correlation analysis. The formation, growth rate and the start time of the nucleations had differences at the two sites. The investigation of the source and sink terms showed that new particle formation occured exclusively if the condensation sink value was higher than 0,02 s^{-1}. The introduced τ time parameter was 0.34±0.25 in average with

the standard deviation. This implied that the nucleating air mass could not reach the downwind site simply by advection, which showed a bigger spatial extent of the nucleation phenomena. At the same time, the difference between the two sites could be explained by local triggering or quenching effects.

5. I realized the collection of the ultrafine aerosol particles by electrostatic precipitator. I collected freshly nucleated particles from 10 new particle formation and subseqent grwoth events. Sulphate/organic particles, tar balls, nanosphere-soot aggregates were identified on the substrate. We made TEM images about the freshly nucleated particles for first time. These particles occured individually on the grid, and did not show aggregating structure. Their optical median diameter was 27 nm, which was in good agreement with the electrical mobility median diameter parallely measured by the DMPS. The freshly nucleated particles were volatile in the intense electron beam.

6. I determined the aerosol particle deposition in the human lung based on the median particle size distribution from various city environments by a stochastic lung model. The deposition fraction in the respiratory tract was 56% in average, and was quiet uniform irrespectively of physical activity. The deposition fraction changed significantly (26%–9,4%) in the extra-toracic region, while it was nearly constant in the tracheobronchial region. In the acinar region, the physical activity showed remarkable influence on the deposition fraction. The deposition rate was higher in the lung than in the extra-toracic region.

7. I determined the hygroscopic and volatile growth factors of the particles with the diameter of 50, 75, 110 és 145 nm. Two modes appeared in the course of the hygroscopic growth of the particles. The less hygroscopic mode (κ=0,0) appeared in the morning and afternoon due to the vehicle emission. These particles had a more hydrofobic property which was in relation with their soot content. The mode of the more hygroscopic particles (κ=0,2–0,3) increased with the particle diameter, and was in relationship with the regional aerosol particles.

Publications in international journals

Salma, I., Füri, P., **Németh, Z.**, Balásházy, I., Hofmann, W., Farkas, Á.: Lung burden and deposition distribution of inhaled atmospheric urban nanoparticles as the first step in their health risk assessment. Atmos. Environ., 104, 39–49, 2015.

Németh, Z., Salma I.: Source areas and trajectories of nucleating air masses within and near the Carpathian Basin. Atmos. Chem. Phys. 14, 8841–8848, 2014.

Salma, I., Borsós, T., **Németh, Z.**, Weidinger, T., Aalto, P., Kulmala, M.: Comparative study of ultrafine atmospheric aerosol within a city. Atmos. Environ., 92, 154–161, 2014.

Németh, Z., Pósfai, M., Nyirő-Kósa, I., Aalto, P., Kulmala, M., Salma, I.: Images and properties of individual nucleated particles, submitted.

Salma, I., **Németh, Z.**, Kerminen, V.-M., Aalto, P., Nieminen, T., Weidinger, T., Molnár, Á., Bécsi, Zs., Kulmala, M.: Interactions between urban air and regional atmospheric nucleation in the largest basin in Europe, in preparation.

Other publications

Salma, I., Borsós T., **Németh, Z.**: Importance and effects of atmospheric aerosols, Magyar Kémiai Folyóirat 118/2–4, 107–114, 2012.

Németh, Z., Salma, I.: Wandering aerosol particles: where do they come from and where do they tend?, Élet és Tudomány LXX/6., 178–179, 2015.

Conference talks

X. Hungarian Aerosol Conference, oral presentation: Ultrafine aerosol in various environments within a city, 20–21 October 2011, Galyatető, Hungary

1. Hungarian Symposium on Environmental Chemistry, oral presentation: Relationship of atmospheric aerosol with the urban climate and air quality, 11–12 October 2012, Mátraháza, Hungary

2. Hungarian Symposium on Environmental Chemistry, oral presentation: Source areas of nucleating air masses arriving in Budapest, 10–11 October 2013, Dobogókő, Hungary

1st EuCheMS Congress on Green and Sustainable Chemistry, oral presentation: Atmospheric nucleation in various environments within a city, 13–15 October 2013, Budapest, Hungary

Budapest Platform for Aerosol Research and Training opening, oral presentation: Research: atmospheric nucleation and its relevance, 17 October 2013, Budapest, Hungary

3. Hungarian Symposium on Environmental Chemistry, oral presentation: Investigation of the coincidence of nucleation events in the Carpathian Basin, 9–10 October 2014, Lajosmizse, Hungary

FuturICT conference, oral presentation: The role of the Budapest platform for Aerosol Research and Training (BpART) in the research of the atmospheric environment, 27 October 2014, Budapest, Hungary

XII. Hungarian Aerosol Conference, oral presentation: Investigation of individual nucleated particles by electronmicroscopy, 18–20 March 2014, Szeged, Hungary

European Aerosol Conference: Collection and investigation of individual freshly nucleated particles, 6–11 September 2015, Milano, Italy

Posters

Salma, I., Borsós, T., **Németh, Z. Á.**, Aalto, P., Kulmala, M.: Comparative study of ultrafine aerosol particles within a city, European Aerosol Conference, poster, 2–7 September 2012, Granada, Spain

Németh, Z., Salma, I.: Air mass history on 1-year long new particle formation datasets in Budapest, European Aerosol Conference, poster, 1–6 September 2013, Praha, Czech Republic

Németh, Z., Bécsi, Zs., Molnár, Á., Weidinger, T., Aalto, P., Kulmala, M., Salma, I.: Timing and coincidence of atmospheric nucleation events in a region, poster, 6–11 September 2015, Milano, Italy

Salma, I., **Németh, Z.**, Aalto, P., Kulmala, M.: New particle formation events with double onset in a near-city background of Budapest, poster, 6–11 September 2015, Milano, Italy

Kiss, G., Hoffer, A., Kallós, A., **Németh, Z.**, Salma, I.: Chemical analysis of d<30 nm particles collected during new particle formation in urban environment, poster, 6–11 September 2015, Milano, Italy