CLOSING SCIENTIFIC REPORT

on the NKFIH grant entitled

Climate and health significance of atmospheric aerosol - water vapour interactions in urban environment

Identifier: K116788

Period from 01–01–2016 to 31–12–2020

Major fields of achievements are briefly listed below together with the indications of the related, full international publications that acknowledge the financial support from the grant and that involve its participants. Additional results and conclusions or more detailed explanations of the issues outlined here can be found either in these or in further publications available on the website of the Budapest platform for Aerosol Research and Training (BpART) Laboratory (https://salma.elte.hu/BpART).

1. We *identified and elaborated a completely new chemical mechanism for atmospheric nucleation* from vapours which is driven by iodic oxoacids (iodic acid and iodous acid). The study was based on experiments in the CLOUD environmental reaction chamber operated in CERN, Switzerland and was backed by ambient atmospheric measurements all over the word including those realised in Budapest. The nucleation rates of iodic acid particles are extremely rapid, even exceeding the rates of sulfuric acid-ammonia under similar conditions. Freshly formed particles are composed almost entirely of iodic acid, which drives rapid growth at the kinetic limit. The process is a very efficient source of cloud condensation nuclei (CCN) since a single vapour species is responsible for both nucleation and growth. The resultant increase of CCN could intensify longwave radiative forcing from clouds and could provide a positive feedback that accelerates the loss of sea ice pack in the Arctic.

   Further info: He et al., Role of iodine oxoacids in atmospheric aerosol nucleation, *Science* 371, 589–595, 2021 and https://ttk.elte.hu/content/science-cikk-a-legkori-nukleacio-uj-kemiai-mechanizmusarol.t.4183.

2. We *revealed and proved* that new aerosol particle formation (NPF) and consecutive particle growth processes in Budapest and its regional background *occur in a consistent and spatially coherent way as a result of a joint atmospheric phenomenon taking place over the Carpathian Basin*. The NPF events at the urban site are usually delayed by >1 hour relative to the rural site or even inhibited above a critical condensational sink level. The urban processes require higher formation rates and growth rates to be realised, by mean factors of 2 and 1.6, respectively, than the regional events. Regional- and urban-type NPF events sometimes occur jointly with multiple onsets, while they often exhibit dynamic and timing properties which are different for these two event types.

   Further info: Salma et al., Regional effect on urban atmospheric nucleation, *Atmos. Chem. Phys.* 16, 8715–8728, 2016; Salma and Németh, Dynamic and timing properties of new aerosol particle formation and consecutive growth events, *Atmos. Chem. Phys.* 19, 5835–5852, 2019.

3. We *reported the existence and discussed the consequences of arch-type NPF events, which were surprising since the freshly nucleated particles were assumed to contain low-volatility constituents*. There are some nucleation occurrences in which the particle growth is followed by continuous decrease in the nucleation-mode number median diameter. The shrinkage rate (from –4.8 to –2.3 nm h^{-1}) was similar to the growth rate in absolute values, while the concentrations $N_{6–25}$, $N_{6–100}$ and N decreased by 30–50% during this phase. Most of these events could be explained by changes in the coagulation sink and meteorological properties, although some of them could not be fully explained by them. The latter cases were linked to variability in growth rates above different territories involved.

   Further info: Salma et al., Measurement, growth types and shrinkage of newly formed aerosol particles at an urban research platform, *Atmos. Chem. Phys.* 16, 7837–7851, 2016.

4. We *developed and proposed a new calculation procedure for gas-phase H_2SO_4, which includes the H_2SO_4 dimer formation* and SO_2 oxidation by Criegee biradical. It was based on international field measurement and evaluation exercise in diverse environments. The variation in the environmental conditions and the difference in concentrations of air pollutants could affect the coefficients derived. They do not, however, showed substantial differences among the different locations. The proxy could therefore be used at locations with no prior H_2SO_4 measurements, provided that the environmental conditions are approximately similar to those in one of the four sites described. The new proxy is a more flexible and an important improvement over the previous proxies. Following our recommendations, a proxy for a specific location can be derived.

   Further info: Dada et al., Sources and sinks driving sulfuric acid concentrations in contrasting environments: implications on proxy calculations, *Atmos. Chem. Phys.* 20, 11747–11766, 2020.

5. We *established a reactive molecular dynamics modelling method* for systems of H_2SO_4-H_2O-NH_3, H_2SO_4-H_2O-$(CH_3)_2NH$ and HIO_3-HIO_2-H_2O to predict the very beginning onset process of vapour nucleation at molecular level. The concentrations which could express the ambient conditions were set to those typically present in Budapest, while some others were scaled over typical overall ranges. We found that molecular clusters in the 1st system are formed by H_2SO_4 dimers surrounded by NH_3 molecules, while H_2SO_4 molecules and amines are located in an exchanging manner in the 2nd system. Considering a completely new mechanism of NPF just discovered (see item 1 of this report), we decided to amend the modelling by the 3rd option as well and to publish the results and conclusions together. This caused some time delay in our publication plans, which will hopefully be balanced by the novelty of these objectives and approach.

   Further info: Lbadaoui-Darvas et al., Reactive molecular dynamics simulations of atmospheric nucleation from different vapour systems, in preparation, 2021.

6. We *determined and interpreted the time trend and diurnal patters of particle number concentrations* in the diameter ranges from 6 to 1000 nm ($N_{6–1000}$), from 6 to 100 nm ($N_{6–100}$), from 25 to 100 nm ($N_{25–100}$) and from 100 to 1000 nm ($N_{100–1000}$), concentrations of SO_2, CO, NO, NO_x, O_3, PM_{10} mass, of air temperature, relative humidity, wind speed, atmospheric pressure, global solar radiation, condensation sink, gas-phase H_2SO_4 proxy,

classes of NPF events and meteorological macro-circulation patterns by an advanced dynamic linear model and a generalized linear mixed model for a time interval of 2008–2018. Most particle number concentrations showed decreasing decennial statistical trends. The estimated annual mean decline of $N_{6–1000}$ was (4–5)% during the 10-year measurement interval. This was interpreted as a consequence of the decreased anthropogenic emissions at least partly from road traffic alongside to household heating and industry. Similar trends were not observed for the air pollutant gases.

Further info: Mikkonen et al., Decennial time trends and diurnal patterns of particle number concentrations in a Central European city between 2008 and 2018, *Atmos. Chem. Phys.* 20, 12247–12263, 2020.

7. We *introduced and applied the nucleation strength factor (NSF) to quality NPF events as a single source of ultrafine (UF) particles* separately for a nucleation day (NSF_{NUC}) and for a general day (NSF_{GEN}). The former characteristics represents the concentration increment of UF particles specifically on nucleation days with respect to regional background concentration due solely to nucleation process. The latter factor expresses the contribution of nucleation to particle numbers on general days thus, it represents a longer time interval such as season or year. We revealed that nucleation source became the major source of particles in the near-city background around noon and early afternoon. New particle formation increased the daily mean concentrations on nucleation days by mean factors of 2.3 and 1.58 in the near-city background and city centre, respectively. On annual time scale, 37% of the UF particles were generated by NPF in the near-city background, while it produced 13% of these particles in the city centre. These results are to be utilised for assessing the health risk of inhabitants from UF particle exposure.

   Further info: Quantification of an atmospheric nucleation and growth process as a single source of aerosol particles in a city, *Atmos. Chem. Phys.* 17, 15007–15017, 2017.

8. We *propose and applied a novel, coupled radiocarbon-levoglucosan marker method for source apportionment of the total carbon (TC=OC+EC) into contributions of EC and OC from fossil fuel (FF) combustion, EC and OC from biomass burning (BB) and OC from biogenic sources* on samples collected in regional background environment of the Carpathian Basin, a suburban area and central part of its largest city, Budapest in each season for 1-year-long time interval. Carbonaceous aerosol species made up 36% of the $PM_{2.5}$ mass with a modest seasonal variation. Fossil fuel combustion showed rather constant daily or seasonal mean contributions, while the BB and biogenic sources changed radically over the seasons at all locations. In autumn, the three major sources contributed equally to the TC in all environments. In winter, it was the BB that was the major source with a share of 70% at all sites. The contributions from biogenic sources in winter were the smallest. In spring, FF combustion and biogenic sources were the largest two contributors at all locations. In summer, biogenic sources became the major source. Biomass burning in winter and autumn offers the largest and considerable potentials for improving the air quality in cities as well as in rural areas of the Carpathian Basin.

   Further info: Salma et al., Source apportionment of carbonaceous chemical species to fossil fuel combustion, biomass burning and biogenic emissions by a coupled radiocarbon-levoglucosan marker method, *Atmos. Chem. Phys.* 17, 13767–13781, 2017; Salma et al., Fossil fuel combustion, biomass burning and biogenic

sources of fine carbonaceous aerosol in the Carpathian Basin, *Atmos. Chem. Phys.* 20, 13767–13781, 2020; Blumberger et al., Mass size distribution of major monosaccharide anhydrides and mass contribution of biomass burning, *Atmos. Res.* 220, 1–9, 2019.

9. We *derived and utilised hygroscopic growth factors (GFs) and volatility GFs* for monodisperse particles with median dry diameters of 20, 50, 75, 110 and 145 nm *under subsaturated conditions* of RH=90±2% or in a thermal denuder with a temperature of 270±10 °C. The hygroscopic GF values were related to hygroscopicity parameter (κ). The urban aerosol population in Budapest was found to be externally mixed, with a strong bimodality with respect to hygroscopic and volatile properties. The overall hygroscopicity was found to be low, when compared to previous studies at urban environments. Traffic had a significant influence on both hygroscopicity and volatility properties and contributed to a constantly present nearly hygrophobic (NH) mode. The NH mode was associated with less volatility (LV) mode, and both followed the typical diurnal pattern of road traffic and its workday/weekend cycles. The other mode, less hygroscopic (LH), was composed of some slightly hygroscopic components, and typically exhibited a volatility GF around 0.6.

   Further info: Enroth et al., Wintertime hygroscopicity and volatility of ambient urban aerosol particles, *Atmos. Chem. Phys.* 18, 4533–4548, 2018.

10. We *determined, characterised, and interpreted the water uptake properties of ambient aerosol particles in Budapest under supersaturated conditions* of 0.1, 0.2, 0.3, 0.5 and 1.0% over 1 full measurement year in 2019–2020. For our specific purposes, we also created a dedicated computer program (AeroSolUtions) for the joint validation and evaluation of the huge data sets obtained by CCNc, DMPS and CPC systems over the years. Some specific time intervals that were associated with intense NPF events or vehicle road traffic emissions were selected, and the cloud formation properties over these intervals were studied separately and intercompared between each other. We also showed seasonal dependency in the modelled variables particularly in the hygroscopicity parameter and determined their overall possible consequences on the urban climate in the Budapest area.

    Further info: Salma et al., Water uptake properties of urban aerosol particles under supersaturated conditions and their consequences on cloud formation, submitted, 2021.

11. We *contributed to internationally coordinated studies to gain deeper insights on the spatial distributions of NPF events* and their dynamic properties on larger-scales, e.g. in three capital cities of Prague, Vienna and Budapest in central Europe and in a word-wide perspective consisting of 36 research locations by supplying our critically evaluated results and calculations. In addition, we played a leading role in the former study. As an outcome of this activity, we were able to place the studied phenomena into a larger frame.

    Further info: Németh et al., Comparison of atmospheric new particle formation and growth events in three Central European cities, *Atmos. Environ.* 178, 191–197, 2018; Nieminen et al., Global analysis of continental boundary layer new particle formation based on long-term measurements, *Atmos. Chem. Phys.* 18, 14737–14756, 2018.

In total, we published 15 full international and 4 full Hungarian articles directly associated to the grant and with the acknowledgement of its financial support. Of them, 1 was in *Science* (IF=41.85), 12 in *Atmos. Chem. Phys.* (5.41), 1 in *Atmos. Res.* (4.68) and 1 in *Atmos. Environ*. (4.04). Three more related international papers were or are to be submitted. The articles in Hungarian appeared in *Magyar Kémiai Folyóirat*, *Magyar Kémikusok Lapja* and *Természet Világa*. We presented 4 lectures and 6 posters at *European Aerosol Conference* (EAC) series or at *International Conference on Nucleation and Atmospheric Aerosol* between 2016 and 2019. (We finally decided to skip the online EAC in 2020 with approved 1 oral and 2 poster presentations.) The PI also served as invited lecturer of the *Summer School: Basic Aerosol Science* organised by the University of Vienna (Austria) for 1 week in 2017 and 2019 each.

Infrastructure and background

The achievements listed above were mainly based on the online measurements performed at the *BpART Lab*, Eötvös University in Budapest. The methods deployed included a wide variety of up-to-date measuring systems, e.g. DMPS, CPC, CCNc, VH-TDMA, CI-APi-TOF MS, PSM and AIS, which are explained and described in the related publications. Some measurements were maintained continuously over the full course of the project for 5 years (in total, 9 full years!), while some others were operated for 1 year or several months. The aerosol data were complemented by meteorological properties (*T*, RH, WS, WD, GRad) also measured online by the BpART Lab over the whole interval. We also collected aerosol samples by HiVol filter-based devices and MOUDI inertial impactors at the BpART Lab (city centre of Budapest), Marczell György Main Observatory of the Hungarian Meteorological Service (suburban area of Budapest) and K-puszta station (its regional background) for 1 year. These filters were analysed by OC/EC analyser, GC-MS, AMS and ICP-OES. Some other dedicated measurements are still in progress and are expected to yield additional valuable result and conclusions for further publications as continuation within the frame of a new NKFIH research grant, which was approved.

Some dedicated experiments and measurements were realised in international or national scientific teamwork with the University of Helsinki (Finland, according to the Letter of Intent submitted with the original proposal), EPFL Swiss Federal Institute of Technology in Lausanne (Switzerland), University of Vienna (Austria), University of Ghent (Belgium), Institute for Nuclear Research (Debrecen), Hungarian Meteorological Service (Budapest), University of Pannonia (Veszprém) and Budapest University of Technology and Economics (Budapest). Their details are described, discussed, and acknowledged in the corresponding publications.

We closely involved 2 Ph.D. and 6 university students into the research work. Of the latter group, all students prepared students' scientific work (TDK), and participated in national competitions (OTDK or OFDK), where 2 students won the 2nd prize, 2 students won the 3rd prize, while 2 competitions are in progress in 2021. Two post-graduate students from Spain and India stayed in the BpART Lab for 6 months each. We organised 5 connected international symposia (*Advances in Aerosol Science* series, see the webpage at https://salma.elte.hu) in Budapest with leading scientists in the field as invited lecturers.

The PI obtained the *Academy Award* for outstanding scientific achievements of the Hungarian Academy of Sciences in 2016 and the *Award for Excellence in Scientific Publishing* of the Faculty of Science in 2019.

We would also like to note as feedback for the NKFIH that the scientific referent in charge of the grant, *Dr. Krisztina Bádonyi* showed constructive and valuable administrative support over the years, which also contributed to the fulfilment of the goals and aims of the research project in the attained extent.

12 February 2021

Imre Salma
principal investigator