

Direct observation of atmospheric new-particle formation using air ion spectrometers

H. E. Manninen¹, T. Nieminen², A. Hirsikko², A. Franchin², S. Schobesberger², T. Yli-Juuti², S. Gagné², A. Mirme³, S. Mirme³, U. Hörrak³, H. Tammet³, M. Sipilä², T. Petäjä², E. Asmi⁴, V.-M. Kerminen⁴, and M. Kulmala²

1. Department of Physics, P. O. Box 64, FI-00014 University of Helsinki, Finland,
2. Department of Physics, P. O. Box 64, FI-00014 University of Helsinki, Finland
3. Institute of Physics, University of Tartu, Ülikooli 18, 50090 Tartu, Estonia
4. Finnish Meteorological Institute, Research and Development, P.O. Box 503, FI-00101 Helsinki, Finland

ABSTRACT: Aerosol particles play an important role in the Earth's atmosphere and in the climate system: They scatter and absorb solar radiation, facilitate chemical processes, and serve as seeds for cloud formation. Secondary new-particle formation (NPF) is a globally important source of these particles. Currently, the mechanisms of particle formation and the vapors participating in this process are, however, not truly understood. In order to fully explain atmospheric NPF and subsequent growth, we need to measure directly the very initial steps of the formation processes. Air ion spectrometers measure the mobility distributions of charged aerosol particles in the mobility diameter range of 0.8–42 nm. Neutral cluster and air ion spectrometers measure additionally the mobility distribution of neutral particles larger than 2 nm in diameter by charging the aerosol sample with unipolar corona chargers. According to earlier studies, the atmospheric nucleation and cluster activation take place at the mobility diameter range of 1.5–2 nm. Therefore, the ion spectrometers allow direct measurements at exactly the size where atmospheric nucleation takes place. The results indicate that the ion-induced nucleation contributes ~1-30% to the new-particle formation events in most atmospheric conditions.

1. INTRODUCTION

Aerosol particles exist everywhere in the atmosphere, they are diverse and complex, and they are in a constant movement and interaction with their surroundings. The particle number size distribution changes constantly as particles are formed by nucleation, grown by condensation, become smaller by evaporation, and are lost by deposition. All this makes aerosol particles extremely difficult to measure. The very small size of these particles causes several difficulties in sampling and analysis. In its last report, the Intergovernmental Panel on Climate Change (IPCC) listed atmospheric aerosol particles as the most poorly understood part of the climate system. Aerosol particles affect Earth's radiation budget and climate in several ways. The result is a cooling effect. The interactions of aerosol particles with sunlight result in the direct effect on climate. Also, several types of indirect effects result from the interactions of particles with clouds and exert a cooling influence.

Atmospheric aerosol particles are formed by nucleation and grown by condensation as vapours condense on them. This phenomenon, called secondary particle formation, is observed to take place frequently in various environments in the boundary layer as well as in the free troposphere (Kulmala et al., 2004; Hirsikko et al., 2011). Several formation mechanisms for atmospheric aerosol particles have been suggested. The relevance of ion-induced nucleation in NPF is still under discussion (Manninen et al., 2010; Hirsikko et al., 2011). In order to understand the particle formation and growth processes, we investigated the magnitudes of the particle formation and growth rates at the size where the real atmospheric nucleation and activation occur. In a case of parallel ion and neutral cluster measurements, we could also estimate the relative contribution of ion-induced and neutral nucleation to the total particle formation.

2. METHODS

From a physical point of view, two very different cluster types in the sub-3 nm size range can be distinguished: charged (ion clusters) and neutral species. The existence of atmospheric ion clusters as small as 0.5-1 nm in diameter has been known for decades (Israël, 1970), and measurements with ion spectrometers, such as the Air Ion Spectrometer (AIS, Mirme et al., 2007) and Balanced Scanning Mobility Analyzer (BSMA, Tammet, 2006), have demonstrated that such clusters are present practically all the time (Hirsikko et al., 2011). The production rates of ion clusters are, however, generally too low to explain the observed aerosol formation rates.

* Correspondence to: H. E. Manninen, Department of Physics, P. O. Box 64, FI-00014 University of Helsinki, Finland. E-mail:

The recently developed Neutral cluster and Air Ion Spectrometer (NAIS, Kulmala et al. 2007) can be reliably used to measure ions and neutral species near the sizes where atmospheric particle formation begins. The main purposes of the NAIS are to: 1) charge particles efficiently in sub-3 nm size range, 2) detect the fraction concentration of charged particles down to 10 cm⁻³ in air, 3) measure with a high enough time resolution that enables the detection of rapid changes in size spectra during particle formation bursts, and 4) cover the whole size range from cluster molecules up to 42 nm, which approaches the climatically relevant sizes where the particles act as cloud condensation nuclei. The instrument classifies the particles according to their electrical mobility, which is dependent on the particle size and charge. The main working principle of the NAIS is described in more detail in Manninen et al. (2009).

The ion spectrometers were calibrated and intercompared, and found to be in good agreement with the reference instruments both in the laboratory and in the field (Asmi et al., 2009; Gagné et al., 2011). It was concluded that NAIS can be reliably used to measure small atmospheric ions and particles directly at the sizes where NPF begins. Ehn et al. (2011) reported a good agreement between the ion mobility spectrometers and atmospheric pressure interface time-of-flight mass spectrometer (APi-TOF) at small ion sizes. Together with previous validation of the instruments at sizes above 5 nm, it can be stated that the ion spectrometers can measure the whole size range that is important for NPF. A similar comparison was performed for the BSMA data. To get good agreement some corrections had to be made for the ion spectrometer transfer functions and mobility channels. Nevertheless, the mass and mobility spectra complement each other, with the APi-TOF giving superior chemical information on the small ions, whereas the mobility spectrometers are better suited for quantitative concentration measurements.

3. OBSERVATION OF ATMOSPHERIC PARTICLE FORMATION

NPF occurs when nucleated particles grow to a size that can be detected with instruments lower detection limit. Typical particle size distributions together with NAIS derived ion distributions from Hyytiälä during NPF events are presented in Fig. 1. The figure shows particle and ion number size distributions in the size ranges of 2-1000 nm and 0.8-40 nm, respectively, during 12 consecutive days. Size is on the y-axis and time on the x-axis. Particle concentration is on the z-axis. The more red the colour is the more particles there exists in the given size class and time. Particles transported to the site further away have typically size around 100 nm or more. Particles produced locally by e.g. traffic, industry and other primary sources have size between 10 and 100 nm. Particles produced regionally by gas to particle formation have a diameter less than 10 nm as they are freshly formed. With time more material condenses on them and their size increases.

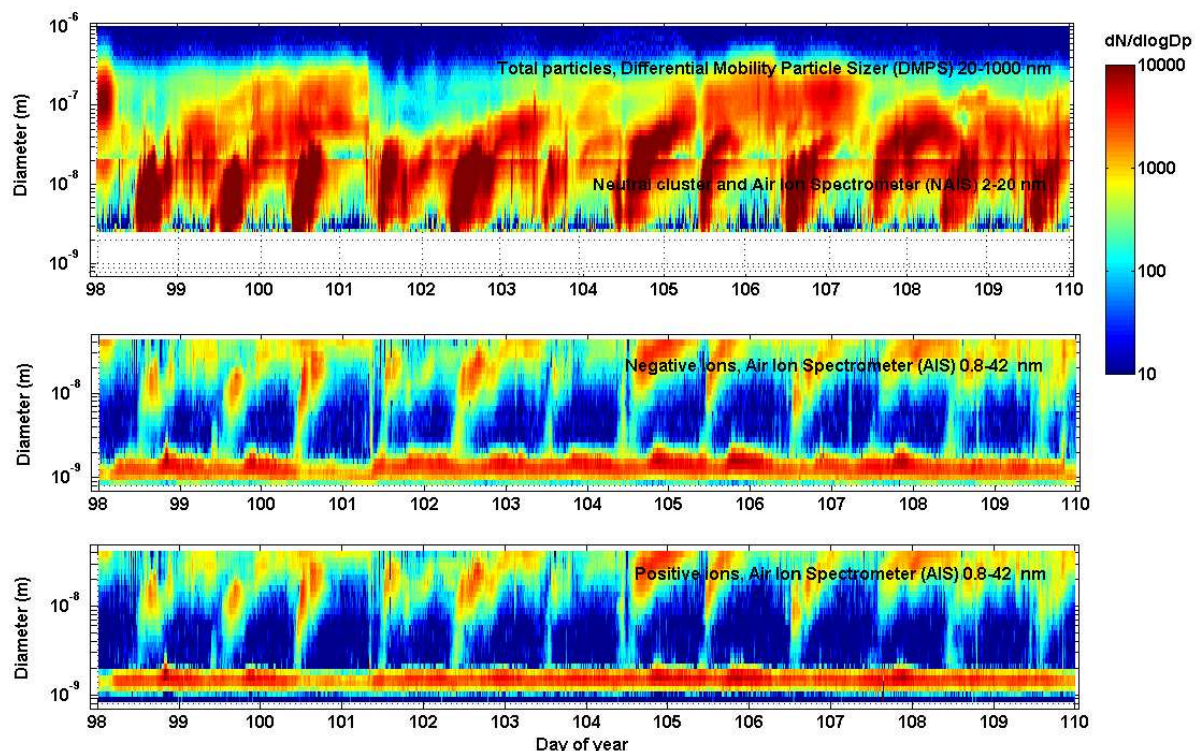


Figure 1. Particle size distribution measured with the NAIS in the size range 0.8–20 nm and with the DMPS in the size range 20–1000 nm (top). Negative (middle) and positive (bottom) ion distributions were also measured with the NAIS (0.8–42 nm) on 12 consecutive particle formation event days 8–19 April 2007 in Hyytiälä, Finland.

On all the 12 days the distinct shape of the formation and growth, called a ‘banana’ event, were observed. In Fig. 1, the formation of sub-3 nm particles began before noon and the growth of the particles continued for several hours; in other words, clusters activated in the morning and started growing by condensation. In Hyytiälä, NPF events are observed typically on sunny days when the pre-existing particle background concentrations were low. This indicates that direct solar radiation enhances the photochemistry needed to form both nucleating and condensing vapors. Particle formation (30% of all days) usually takes place during daytime as the NPF starts before noon and the growth of the particles continues all afternoon to CCN sizes. On an annual scale, particle formation is most frequent in the springtime (March-May) and during the autumn (September).

4. ATMOSPHERIC NUCLEATION MECHANISMS AND ROLE OF IONS IN PARTICLE FORMATION

The ion spectrometer measurements performed within the EUCAARI project (European Integrated project on Aerosol Cloud Climate and Air Quality interactions) present, so far, the most comprehensive effort to experimentally characterize nucleation and growth of atmospheric molecular clusters and nanoparticles at ground-based observation sites on a continental scale (Manninen et al., 2010). The particle formation events seem to take place on a regional scale. The overall horizontal extent of NPF events seem to be between 100 and 1000 km. The observed site-to-site variations are evidence of differences in the particle formation limiting factors, which include sources of nucleating and condensing vapors, scavenging by pre-existing particles and meteorological effects. Atmospheric ions participate in the initial steps of NPF, although their contribution was minor in the boundary layer. The highest atmospheric particle formation rates (ranging from 0.9 to 32 $\text{cm}^{-3} \text{s}^{-1}$) were observed at the most polluted sites where the role of ions was the least pronounced (Manninen et al., 2010).

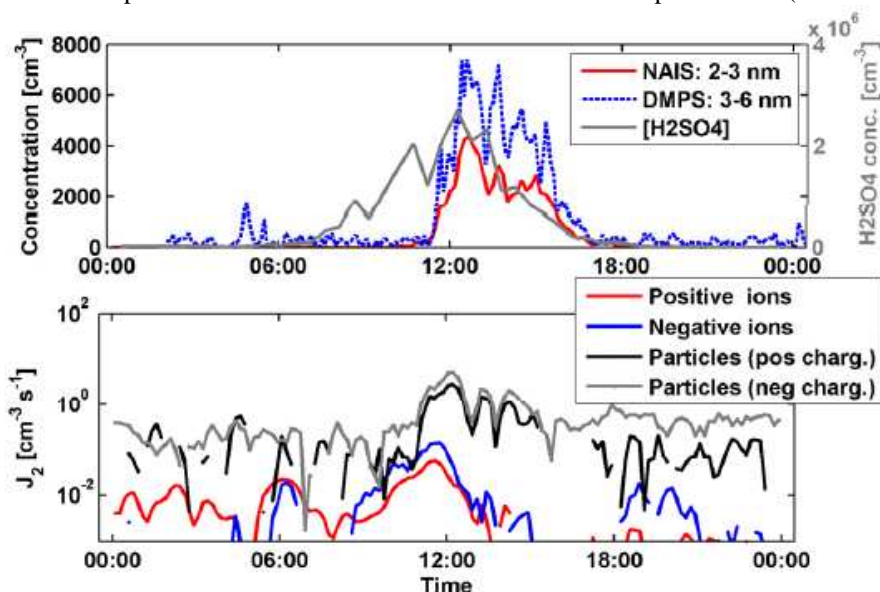


Figure 2. Upper panel: Concentrations of 2-3 nm particles measured with the NAIS, 3-6 nm particles with the DMPS, and sulphuric acid. Lower panel: Ion and particle formation rates during the NPF event on 5 May 2007.

In Fig. 2 the concentration of 2-3 nm particles measured with the NAIS started increasing at almost the same time as the 3-6 nm particle concentration measured with the DMPS (upper panel). The growth rates were 1.7 and 4.5 nm h^{-1} , respectively, for 1.3–3 and 3–7 nm charged particles and 5.2 nm h^{-1} for total particles in 3-7 nm size range. The ion concentration in the 1.7-6.5 nm size range (see Hörrak et al. in these proceedings) started to increase already around 9 a.m., whereas the total concentration of 2-6 nm particles started to increase at 11 a.m. The upper panel in Fig. 2 also shows the gas phase sulfuric acid concentrations during the event. The different activation properties of charged and neutral particle are visible in Fig. 2 (lower panel): the ion-induced formation rates increased somewhat before a corresponding increase in the total J_2 is seen. The fraction of ion-induced nucleation becomes less important in the middle of the event: ion-induced nucleation is more important at the beginning of the event.

Sulphuric acid is considered to be one of the key components in these particle formation events. The growth of freshly-nucleated atmospheric aerosol particles cannot usually be explained without a significant contribution by vapors other than sulphuric acid. An example of utilizing calculated nucleation parameters in atmospheric NPF studies is presented in Paasonen et al. (2010). They investigated the relative contribution and spatial variability of sulphuric acid and organic vapors in atmospheric NPF at Hyytiälä (Finland),

Hohenpeissenberg and Melpitz (Germany), and San Pietro Capofiume (Italy). At three out of four measurement sites the nucleation rate was closely connected to sulphuric acid concentration, whereas in Hohenpeissenberg low-volatility organic vapors were observed to be dominant. Under atmospheric conditions, both sulphuric acid and low-volatility organic vapours, in addition to ammonia and possibly amines, are likely participants in nucleation.

5. CONCLUSIONS

As a significant new result, we found out that the total particle formation rate varied much more between the different sites than the formation rate of charged particles. The results infer that the ion-induced nucleation has a minor contribution to particle formation in the boundary layer in most of the environments. These results give tools to better quantify the aerosol source provided by secondary NPF in various environments. The nucleation mechanism initiating aerosol formation is likely to vary with location and atmospheric conditions. The detailed formation and growth mechanisms of these freshly formed particles are still unclear in many respects. At most sites, the particle growth rate increased with the increasing particle size indicating that different condensing vapors are participating in the growth of different-sized particles. The results suggest that, in addition to sulfuric acid, organic vapors contribute to the initial steps of NPF and to the subsequent growth, not just later steps of the particle growth.

The observed global occurrence of atmospheric aerosol formation provides a good reason to include this phenomenon in large-scale atmospheric models, such as regional air quality models and global climate models. The instrumental developments described here have made it possible to observe small neutral particles about a nanometer smaller than previously measured. This offers a possibility to test existing nucleation theories against real atmospheric data. By conducting continuous measurements in different environments and altitudes, it should be possible to develop simple yet sufficiently accurate nucleation parameterizations for large-scale modeling using the data presented here (already done by Paasonen et al., 2010; Nieminen et al., 2011; see Nieminen et al. in these proceedings).

ACKNOWLEDGMENTS

This work has been supported by European Commission 6th Framework program projects: EUCAARI, contract no 036833-2 (EUCAARI) and EUSAAR, contract no 026140 (EUSAAR). The support by the Academy of Finland Centre of Excellence program (project nos. 211483, 211484 and 1118615) is also gratefully acknowledged.

REFERENCES

- Asmi, E., Sipilä, M., Manninen, H. E., et al.: Results of the first air ion spectrometer calibration and intercomparison workshop, *Atmos. Chem. Phys.*, 9, 141-154, 2009.
- Ehn, M., Junninen, H., Schobesberger, et al.: Comparing mobility and mass measurements of atmospheric small ions, *Aerosol Sci. Technol.*, 45:522–532, 2011.
- Gagné, S., Lehtipalo, K., Manninen, H. E., et al.: Intercomparison of air ion spectrometers: an evaluation of results in varying conditions, *Atmos. Meas. Tech.*, 4, 805-822, doi:10.5194/amt-4-805-2011, 2011.
- Hirsikko, A., Nieminen, T., Gagné, S., et al.: Atmospheric ions and nucleation: a review of observations, *Atmos. Chem. Phys.*, 11, 767–798, 2011.
- Israël, H.: *Atmospheric Electricity*, Vol. I. Israel Program for Scientific Translations, Jerusalem, 317 p, 1970.
- Kulmala, M., Vehkamäki, H., Petäjä, T., et al.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, *J. Aerosol Sci.*, 35, 143-176, 2004
- Kulmala, M., Riipinen, I., Sipilä, M., et al.: Towards direct measurement of atmospheric nucleation. *Science*, 318, 89-92, 2007.
- Manninen, H.E., Petäjä, T., Asmi, E., et al.: Long-term field measurements of charged and neutral clusters using Neutral cluster and Air Ion Spectrometer (NAIS). *Boreal Env. Res.* 14, 591–605, 2009.
- Manninen, H.E. et al., EUCAARI ion spectrometer measurements at 12 European sites – analysis of new particle formation events, *Atmos. Chem. Phys.*, 10, 7907–7927, 2010.
- Mirme, A., Tamm, E., Mordas, G., et al.: A wide-range multi-channel Air Ion Spectrometer, *Boreal Environ. Res.*, 12, 247–264, 2007.
- Nieminen, T., Paasonen, P., Manninen, H. E., Sellegri, K., Kerminen, V.-M., and Kulmala, M.: Parameterization of ion-induced nucleation rates based on ambient observations, *Atmos. Chem. Phys.*, 11, 3393-3402, 2011.
- Paasonen, P., Nieminen, T., Asmi, E., et al.: On the role of sulphuric acid and lowvolatility organic vapours in new particle formation at four European measurement sites, *Atmos. Chem. Phys.*, 10, 11223-1124, 2010.
- Tammet, H., Continuous scanning of the mobility and size distribution of charged clusters and nanometer particles in atmospheric air and the Balanced Scanning Mobility Analyzer BSMA, *Atmos. Res.*, 82, 523–535, 2006.