EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

CERN-SPSC-2011-014
SPSC-SR-082
March 18, 2011

2010 PROGRESS REPORT ON PS215/CLOUD

CLOUD Collaboration

1 OVERVIEW

CLOUD [1] had a very successful first year of operation in 2010. During two 5-week physics runs (31 May - 2 July and 16 October - 22 November) a total of around 330 nucleation events were measured under various conditions of trace gas concentrations, relative humidity, UV intensity, electric field, beam intensity and temperature. The measurements were devoted to investigating and extending the new observations made by CLOUD in the first run at the end of 2009. These concern the critical first step in the conversion of trace atmospheric vapours into cloud condensation nuclei, namely the nucleation of thermodynamically stable aerosol particles.

The measurements obtained by CLOUD at the CERN PS in 2010 represent the most rigorous laboratory evaluation yet accomplished of binary, ternary and ion-induced nucleation of sulphuric acid particles under atmospheric conditions. The results include first measurements of:

- ion-induced vs neutral nucleation,
- molecular composition of the critical clusters,
- binary nucleation of H_2SO_4/H_2O at mid-tropospheric temperatures, and
- ternary nucleation mechanism of $NH_3/H_2SO_4/H_20$ at planetary boundary layer temperatures.

A manuscript on the main findings from the 2010 runs has recently been submitted for publication.

2 CLOUD DETECTOR IN 2010

2.1 CLOUD facility

The CLOUD experimental configuration in the T11 zone during 2010 is shown in Fig.1. The chamber was operated for physics data at temperatures between 292K and 248K, corresponding to temperatures of the planetary boundary layer up to the mid-troposphere, around 6 km altitude. Operation at low temperatures required upgrades of the thermal system—in particular the use of desiccants to dry the circulating thermal air and the installation of an outer vapour barrier to prevent moisture and ice buildup inside the thermal housing and heat exchanger system. Furthermore, in order to minimise effects from the evaporation of molecular clusters when sampling from the chamber at low temperatures, some of the instruments were housed in chilled, thermally-insulated racks (Fig.1).

Numerous other improvements were made to the CLOUD facility during 2010. These included the addition of three more UV light sources, installation of a precision thermo-regulator for the humidifier water temperature, improvements to the water purification circuit which resulted in a factor 5 reduction of organic contaminants, installation of an internal horizontal Pt100 thermometer string to measure the radial thermal uniformity, and addition of a second internal fan to improve the mixing of the chamber atmosphere.

Fig. 1: View of CLOUD in the East Hall T11 zone during the June-July 2010 run. The chamber is surrounded by a thermal housing through which air is circulated via the duct seen to the left. The temperature of the air is controlled to 0.01K stability by a precision thermo-regulator unit seen at the far left. When in operation, the pion beam passes through a counter hodoscope and enters the chamber from the right. The transverse dimensions of the beam at the position of the chamber are around 1.5×1.5 m^2. Instruments surrounding the chamber continuously analyse its contents by extracting small amounts of air through sampling probes.

2.2 Analysing instruments

The contents of the chamber are continuously analysed by instruments connected to sampling probes that project 0.5 m into the chamber. The analysing instruments for the 2010 runs were as follows:

Aerosol particles

- *Condensation Particle Counter battery (CPCb):* an array of 6 CPCs to measure the aerosol particle number concentrations at various threshold diameter cutoffs (2.5–12 nm).
- *Scanning Particle Size Magnifier (PSM):* aerosol particle number concentrations in the 1.3–2.0 nm threshold range.
- *Di-ethylene glycol CPC (DEG-CPC);* aerosol particle number concentrations at 2.0 nm threshold.
- *Radial Differential Mobility Analyser (RDMA):* aerosol size spectrum in the range 2–10 nm.
- *Scanning Mobility Particle Sizer (SMPS):* aerosol size spectrum in the range 10–100 nm.
- *Cloud Condensation Nucleus Counter (CCNC):* cloud condensation nucleus number concentration in the water vapour supersaturation range 0.1–1%.

Mass spectrometers and trace gas analysers

- *Chemical Ionisation Mass Spectrometer (CIMS):* H_2SO_4 concentration at 0.001 ppt sensitivity.
- *LOng Path Absorption Photometer (LOPAP):* NH_3 concentration at 30 ppt sensitivity.
- *Proton Transfer Reaction Mass Spectrometer (PTR-MS):* NH_3 concentration at 30 ppt sensitivity.
- *Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-TOF):* organic vapour concentrations at 10 ppt sensitivity.
- *Atmospheric Pressure Interface Time of Flight Mass Spectrometer (APi-TOF):* positive and negative ion masses and concentrations in the range up to 2000 Th at 0.01 Th resolution.
- O_3 *gas analyser:* ozone concentration at 100 ppt sensitivity.
- SO_2 *gas analyser:* sulphur dioxide concentration at 100 ppt sensitivity.

Ions/charged particles

- *Neutral cluster and Air Ion Spectrometer (NAIS):* positive & negative charged, and also neutral, aerosol size spectra above molecular (0.2 nm) threshold.
- *Gerdien counter:* positive & negative ion concentrations above molecular (0.2 nm) threshold.

Chamber operating conditions

- *Temperature:* a system of about fifty Pt100 thermometers measuring the temperature of the chamber walls, internal gas, thermal system and gas system, to about 0.01K precision.
- *Pressure:* chamber relative air pressure.
- *Dew-point sensor:* relative humidity of the chamber contents to $<0.1\%$ precision.
- *UV intensity:* UV illumination intensity.
- *Environmental conditions:* temperature, absolute pressure and relative humidity in the T11 experimental zone.

3 TYPICAL RUN SEQUENCE

Figure 2 shows a typical sequence of measurements of the nucleation rates, J_n, J_{gcr} and J_{ch}, corresponding to neutral, galactic cosmic ray and charged (pion beam) conditions, respectively. The experimental conditions are first established (gas concentrations, temperature, etc.) and the chamber largely cleared of pre-existing aerosols in order to minimise the losses of freshly-nucleated particles. High voltage is applied to the clearing field electrodes to sweep all ions from the chamber in about 1 s. The run is started by opening the shutter of the UV system at a selected aperture, which rapidly establishes a chosen $[H_2SO_4]$ in the chamber by photolytic oxidation of SO_2 in the presence of O_3 and H_2O.

Particles begin to appear in each counter after a time delay that depends on the particle growth rate and the detection size threshold. The nucleation rates, J ($\mathrm{cm^{-3}s^{-1}}$), are derived from the formation rates measured in the particle counters, dN/dt, (i.e. the gradients of the curves in Fig. 2). When the neutral nucleation rate, J_n, has been measured, the clearing field is turned off, allowing GCRs to generate ion pairs that remain in the chamber. The ions give rise to a distinct increase in the nucleation rate, J_{gcr}, due to ion-induced nucleation at ground-level GCR intensity. In the next step, the chamber is exposed to the T11 beam at a pre-selected intensity and a further sharp increase is observed in the nucleation rate, corresponding to J_{ch}. Finally, the run is ended by closing the UV shutter, turning on the clearing field and starting to clear the chamber of aerosols in preparation for the next run.

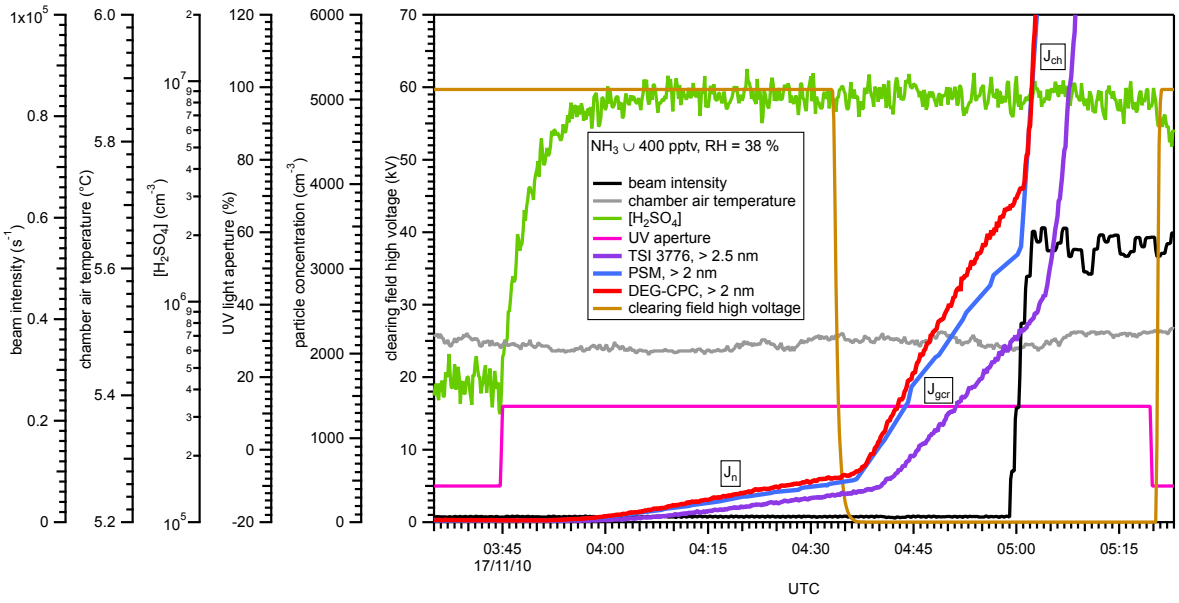

Fig. 2: Example of a typical run sequence to measure a set of neutral, GCR and charged (beam) nucleation rates, J_n, J_{gcr} and J_{ch}, respectively. The production of ions from GCRs and then, at higher rate, from the T11 pion beam causes sharp increases in the particle formation rates, as measured by the TSI 3776, PSM and DEG-CPC aerosol particle counters. (Note that the latter show measurements uncorrected for individual sampling line losses.)

4 CLOUD FACILITY UPGRADES IN 2011

The main improvements planned for the CLOUD facility in 2011 (Fig. 3) are as follows:

Thermal housing: Improvements in the thermal system to allow operation at low temperatures, down to near 183K.

Gas system: Various improvements to the gas system and control software, including new operation for adiabatic chamber expansions of up to -200 mbar.

Chamber cleanliness: Improvements in the purity of the water used for the humidifier, by generating synthetic water from pure hydrogen combustion in pure oxygen. Installation of a quartz tube containing a high-intensity UV source for chemically breaking down and cleaning organic backgrounds in the chamber under high O_3 conditions. Replacement of the ozone generator by a design involving only quartz and stainless steel components in contact with the air flow.

Field cage: Installation of zirconia HV feedthroughs to allow operation up to 50 kV without surface charge buildup. Replacement of the gold-coated Cu-Be springs for electrical contacts with stainless steel springs.

Manhole covers: Construction of the final upper and lower manhole covers with all ports, windows, UV feedthroughs, and fans. Addition of nozzles (hoods) to both fans to improve efficiency at reduced fan speeds.

Sampling probes: Design and installation of custom sampling probes to optimise the performance of individual analysing instruments.

Beam counter: Installation of a new scintillator plate for the first beam counter.

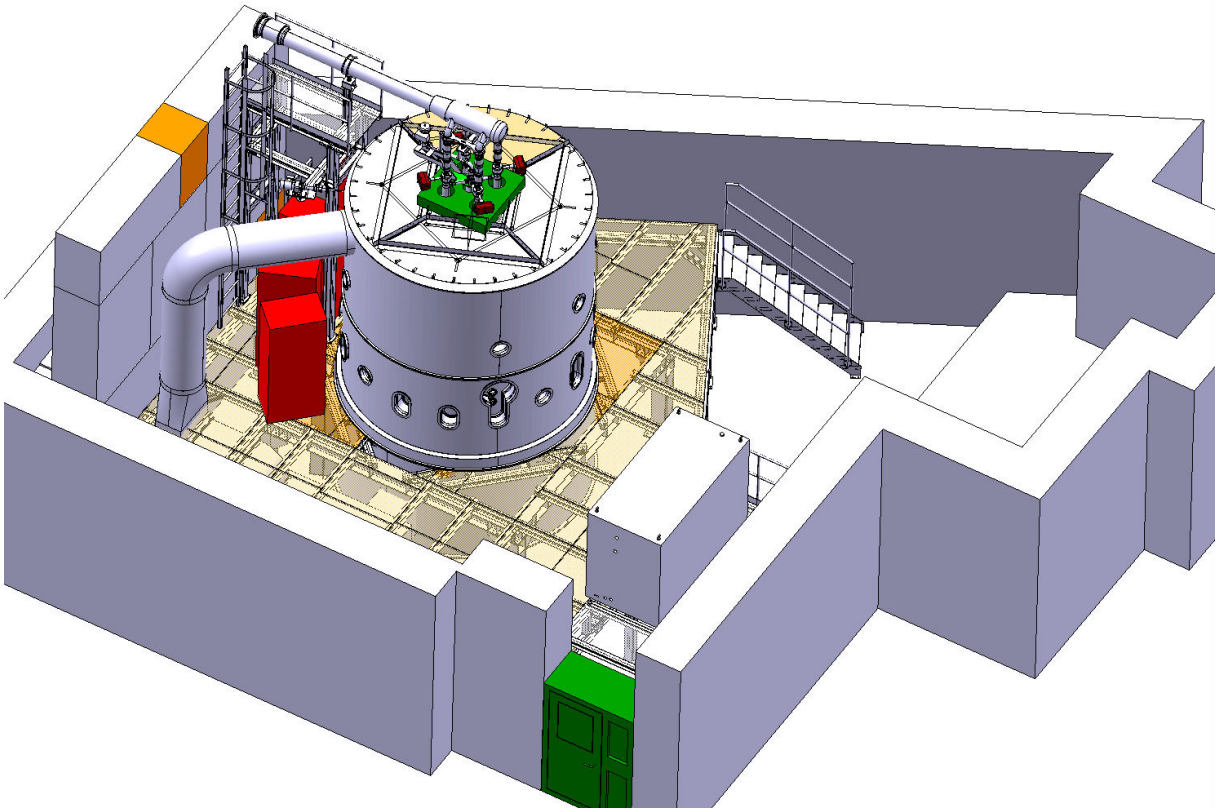

Fig. 3: Graphics showing CLOUD upgrades during 2011 to a) extend the chamber operating temperature range down to near 183K and b) operate the chamber in a classical Wilson expansion chamber mode for generation of liquid and ice clouds. The new 36 kW precision thermo-regulator is located on top of the platform extension near the door of the T11 zone.

5 PUBLICATIONS

The CLOUD results from the November 2009 and June 2010 runs were presented at the International Aerosol Conference, IAC2010, Helsinki, 29 August – 3 September 2010, <http://www.iac2010.fi>. The CLOUD abstracts comprised 7 oral presentations and 6 posters. One of the posters (Kupc, on the CLOUD UV system) won a best poster award at the meeting.

Several invited presentations of CLOUD results were made at other conferences, including the International Accelerator Conference, Kyoto, May 2010 (Kirkby), the American Geophysical Union Annual Meeting, San Francisco, December 2010 (Curtius) and the ASPERA Interdisciplinary Workshop, December 2010 (Baltensperger).

The results of the 2010 and 2011 runs will be presented at the European Aerosol Conference, EAC2011, Manchester, 4–9 September 2011, <http://www.eac2011.com/scientific-programme>. Twelve abstracts have been submitted, and are attached in Appendix A. In addition, CLOUD has been invited to present one of the five keynote plenary talks at the meeting.

Following publication of the recently-submitted CLOUD manuscript, we are planning to submit around 10 additional manuscripts to peer-reviewed journals during 2011.

6 COLLABORATION ASPECTS

During 2010, CLOUD Collaboration meeting were held at PSI, 25–28 January (Data Workshop) and at CERN, 12–16 April (Data Workshop) and 14–15 October.

A one-week CLOUD/CLOUD-ITN workshop was held at the University of Vienna in early 2011 comprising a Data Workshop, 14–16 February, and an Open Workshop, 16-18 February. The Open Workshop included around 25 invited external scientists from Europe and the United States to hear and discuss the CLOUD results.

Several new partners joined the CLOUD collaboration during 2010:

Manchester University, UK: world experts in ice particles and atmospheric electricity, and associated instrumentation.

Aerodyne Research, Inc., Massachusetts, USA: world leader for aerosol mass spectrometers.

Tofwerk AG, Thun, Switzerland: world leader for time-of-flight mass spectrometers.

The current FP7 Marie Curie Network, CLOUD-ITN, was selected as an example of an "ideal MC network" for presentation (Duplissy) at the "Marie Curie Actions for an Innovative Europe" conference, Brussels, 9–10 December, 2010, attended by high-level EU and European research policy-makers <http://mariecurieactions2010.teamwork.fr/en/programme>. A new FP7 Marie Curie network proposal, CLOUD-TRAIN, was submitted in January 2011 (J. Curtius, Coordinator, Goethe-University of Frankfurt) for 13 MC CLOUD Fellows for the period 2012–2014.

7 PHYSICS AIMS AND BEAM REQUEST 2011

During 2011 it is planned to organise the data-taking period around a single 6-week run, as follows:

13 June - 24 July 2011: Ion-induced and neutral nucleation studies of sulphuric acid particles in association with trace organic vapours:

1. Amines (e.g. $(CH_3)_2NH$).
2. Volatile organic compounds (e.g. α-pinene, which is emitted by pine trees).

The purpose of this run is to investigate the roles of organic species and their low-volatility oxidised products in a) nucleation and b) growth of atmospheric aerosols. Three spills per supercycle are requested.

Fall 2011: After the June/July run, CLOUD will have collected what represents the world's foremost laboratory data on atmospheric nucleation and growth. For this reason the physics priority during the second half of 2011 will be data analysis rather than collection of more experimental data. Following a thorough analysis of the CLOUD data during the second half of 2011, we will be better prepared to decide on the optimal scientific goals for the 2012 data taking period.

In parallel, important technical developments will be carried out on the CLOUD facility in the second half of 2011. In particular, we plan to install and commission the rapid adiabatic expansion system for the CLOUD chamber (Fig. 3). We will then make technical runs (without beam) to operate CLOUD in a classical Wilson expansion chamber mode for generation of liquid and ice clouds. In addition we will measure the thermal performance of the chamber down to near 183K with the upgraded thermal housing and new precision thermo-regulator.

Acknowledgements

We would like to thank CERN PH-DT, EN-MME, EN-MEF and TE-VSC for their excellent support of CLOUD and, in addition, to thank the CERN PS machine team and the PS Coordinator for their strong support of CLOUD and for efficient operation of the PS.

References

[1] CLOUD Collaboration: A study of the link between cosmic rays and clouds with a cloud chamber at the CERN PS,
CERN-SPSC-2000-021 <http://cdsweb.cern.ch/record/444592>, 2000;
CERN-SPSC-2000-030 <http://cdsweb.cern.ch/record/462623>, 2000;
CERN-SPSC-2000-041 <http://cdsweb.cern.ch/record/497173>, 2000;
CERN-SPSC-2006-004 <http://cdsweb.cern.ch/record/923140>, 2006.

APPENDIX A
CLOUD ABSTRACTS SUBMITTED TO THE EUROPEAN AEROSOL CONFERENCE, EAC2011, MANCHESTER, 4–9 SEPTEMBER 2011

Nucleation rates and parametrisation in the CLOUD experiment

Almeida-Simões, João[1,2], Curtius, Joachim[1], Kirkby, Jasper[2], and the CLOUD collaboration

[1] Goethe-University of Frankfurt am Main, 60438 Frankfurt am Main, Germany
[2] Physics Department, CERN, CH1211, Geneva, Switzerland

Keywords: CLOUD experiment, cosmic rays, atmospheric nucleation, nucleation rate, parametrisation.

The possible influence of cosmic rays on aerosols and clouds is of considerable interest (Carslaw, 2009). The CLOUD experiment at CERN aims to study under controlled conditions the effects of cosmic rays on nucleation, cloud droplets and ice particles.

The CLOUD experiment involves a 3m stainless steel aerosol chamber exposed to a pion beam from the CERN Proton Synchrotron. A suite of instruments continuously analyse the contents of the chamber via sampling probes. Each instrument has its own data acquisition system which delivers data in real-time to the CLOUD server. The CLOUD chamber is able to reproduce a wide range of well-controlled atmospheric conditions, including temperatures -90°C to 100°C, ion-pair concentrations 1-4000 cm^{-3} and relative humidities, RH, 0-100%. The nucleation and growth of new particles has been studied in the presence of various trace gases, including H_2SO_4 (10^6-10^9 cm^{-3}), NH_3 (35pptv to 1ppbv), amines and organics.

One of the primary goals of CLOUD is a quantitative evaluation of the dependency of the nucleation rate, J, on variables such as [H_2SO_4], [NH_3], [IONS], RH, T, etc. We have developed an accurate, automated method to determine the nucleation rate of critical clusters from the time evolution of the particle number concentration measured by each of the particle counters attached to the CLOUD chamber (CPC, DEG-CPC or PSM). Each particle counter is characterised by certain detection size threshold, d_{50}. To obtain the nucleation rates at the critical size, a correction is required to account for losses before the particles are eventually detected at size d_{50}. The losses occur due to wall-losses, coagulation and chamber air dilution. A Monte-Carlo model (AeroCLOUD) was developed to calculate these corrections numerically (Fig.1). The output of the model has been verified by comparison with experimental measurements made near to the critical size using the Particle Size Magnifier (PSM).

Since 2009, CLOUD has measured the nucleation rate of new particles over a broad range of conditions relevant for the atmosphere. Using measurements from multiple instruments that analyse the CLOUD chamber, we have derived an empirical J parametrisation that combines the measured J values with current theoretical understanding. The parametrisation is tuned using a nonlinear numerical Levenberg-Marquardt algorithm. The parametrisation successfully predicts all nucleation rates measured so far by CLOUD and is designed to be well-behaved when extrapolating outside the experimentally-explored region.

The CLOUD parametrisation is based on the most rigorous laboratory measurements of ion-induced and neutral atmospheric nucleation achieved so far, and so constitutes an important new tool for evaluating the global contributions of nucleation in atmospheric models such as GLOMAP (Dunne, E.M., et al., this conference).

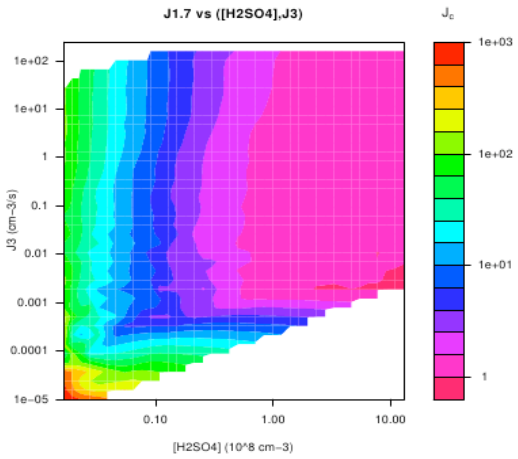

Figure 1. Example AeroCLOUD-calculated corrections for $J_{2.5}$ values (ie. detection with a 2.5nm-threshold CPC). The colour contours relate sulphuric acid concentration (x axis) and $J_{2.5}$ (y axis) with a correction factor that ranges from 1 (plotted in blue-magenta) for high [H_2SO_4] up to 1000 (plotted in orange-red) for low [H_2SO_4] and low $J_{2.5}$ values.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under the grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), and from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence Program (project no. 1118615).

Carslaw, K. (2009). Cosmic rays, clouds and climate. Nature, 460, 332-333.
Dunne, E.M., et al. (2011). The influence of ion-induced nucleation on atmospheric aerosols, this conference.

Ammonia measurements in the gas phase at ppt levels by long-path absorption spectroscopy

Bianchi, F.[1,2], Dommen, J.[1], Baltensperger, U.[1], Mathot, S.[3], and the CLOUD collaboration

[1] Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, Villigen, 5232, Switzerland
[2]University of Milan, Department of Inorganic, Metallorganic, and Analytical Chemistry, Milan, Italy
[3]CERN, Genève, 1211, Switzerland
Keywords: CLOUD experiment, ammonia, nucleation, spectrometer
Presenting author email: federico.bianchi@psi.ch

New particle formation from trace vapours may be responsible for up to one-half of global cloud condensation nuclei, CCN. Sulphuric acid, produced by the photooxidation of sulphur dioxide, is thought to be the primary vapour responsible for the nucleation of new particles in the atmosphere. A mechanism which has been proposed to enhance nucleation rates is ternary nucleation involving ammonia. This process is thought to be effective already at ppt levels of ammonia. In the framework of the EU-ITN project CLOUD (Cosmics Leaving OUtdoor Droplets) this mechanism was investigated in a large simulation chamber at CERN.

We describe here the development of an instrument to measure ammonia at low ppt levels (Figure 1). This is very challenging and hardly reached by any instrument. Furthermore, the inlet of the sampling line plays also a crucial role as ammonia is a rather sticky compound and may adsorb on the walls of the inlet. Therefore, our instrument consists of a specifically designed sampling system to minimize losses of ammonia. Ammonia is stripped from the gas phase into the water phase at the tip of the sampling line. This sample solution is then derivatised by the Berthelot reaction (Patton and Crouch, 1977), which is a reaction between ammonia, hypochlorite and phenol. A blue indophenol is formed which is detected by a long-path absorption spectrometer (Schwab *et al.*, 2007). The latter consists of a liquid core waveguide (LCW) with an effective path length of 5 m. The light source is a red power LED (Luxeon) coupled via a glass fiber to the LCW. Absorbance is measured by a spectrophotometer (Ocean Optics, SD 2000).

The instrument was calibrated with a solution of NH_4^+. We assumed a stripping efficiency of the sampling line of 100% due to the high solubility of ammonia and the very short inlet line of 5 mm without water. The detection limit reached was about 10 nM which corresponds to a gas phase mixing ratio of 40 ppt.

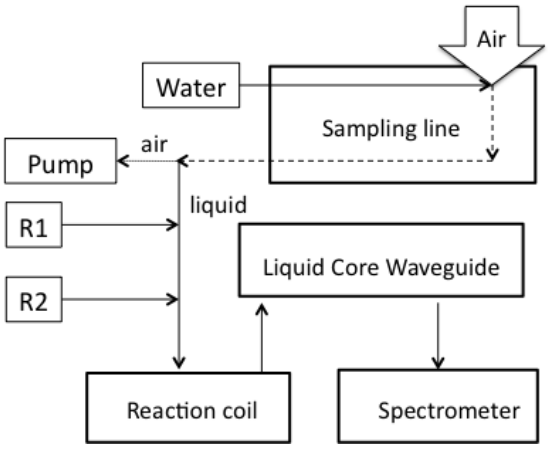

Figure 1. Scheme of the instrument. R1 and R2 denote the reagents phenol and hypochlorite.

We will present the ammonia measurements taken during two CLOUD campaigns. Based on these measurements it was possible to determine the nucleation rate of the system H_2SO_4, /H_2O/NH_3 as a function of different concentrations of ammonia inside the CLOUD chamber.

Acknowledgments: We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the European Commission (Marie Curie Initial Training Network CLOUD-ITN and the Research Infrastructures Programme EUROCHAMP-2), the German Federal Ministry of Education and Research, the Swiss National Science Foundation, and the Academy of Finland Center of Excellence program.

Patton, C.C., Crouch, S.R. (1977) Spectrophotometric and kinetics investigation of the Berthelot reaction for the determination of ammonia. *Anal. Chem.* **49**, 464-469.

Schwab *et al.* (2007) A laboratory intercomparison of real-time gaseous ammonia measurement methods. *Environ. Sci. Technol.* **41**, 8412-8419.

The influence of ion-induced nucleation on atmospheric aerosols based on data from the CERN CLOUD experiment

E.M. Dunne[1], K.S. Carslaw[1], C.L. Reddington[1], J. Almeida[2] and the CLOUD collaboration[2]

[1]School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK
[2]CERN, Geneva, Switzerland
Keywords: aerosol modelling, ion-induced nucleation.
Presenting author email: E.Dunne@leeds.ac.uk

Here we quantify the contribution of ion-induced nucleation to global aerosol based on new results from the CLOUD experiment at CERN. We also quantify the response of aerosols to a change in the nucleation rate in an attempt to explain apparent correlations between aerosol and Forbush decreases. Away from the surface, ion concentrations are controlled by cosmic-ray induced ionization. A range of observations support a connection between cosmic ray intensity and the Earth's climate, on time-scales from days (Pudovkin and Veretenenko, 1995) to centuries (Eichler *et al*, 2010) to millennia (Bond *et al*, 2001).

Because ions stabilise sub-critical nuclei, ion-induced nucleation is a strong candidate for the atmospheric nucleation mechanism, especially in remote regions with low concentrations of precursor vapours. When determining the impact of the phenomena on the climate, a global aerosol microphysics model (such as GLOMAP) is a vital tool due to its inclusion of the various processes which affect particle growth and deposition.

We will present the results of the implementation within a global model of the first parametrization of ion-induced nucleation based on experimental observations rather than theoretical predictions. This parametrization is the result of work in the ternary H_2SO_4-NH_3-H_2O system by the CLOUD collaboration at CERN. We show that nucleation in this "inorganic" system is unable to explain most boundary layer nucleation and observed particle concentrations.

We also quantify the response of aerosol to changes in the nucleation rate that might accompany Forbush decreases. During a period of intense magnetic activity which causes the sun to emit charged matter, the stream of cosmic rays reaching the Earth can be partially blocked. The result is a reduction in atmospheric ion concentrations that lasts for several days. There have been studies showing a strong (Svensmark et al., 2009) and a weak (Laken et al. (2009); Calogovic et al., (2010)) correlation between Forbush decreases and cloud and aerosol properties. The suggested cause of these correlations was a change in the ion-induced nucleation rate.

To test the maximum effect of a Forbush decrease on aerosol, we performed a series of monthly simulations with daily resolution. We reduced the nucleation rate by 15% for a period of ten days in the middle of each month, and analysed the effect on condensation nuclei (CN), cloud condensation nuclei (CCN), aerosol optical depth and the Ångstrom exponent. This allows us to estimate the bounds of a transient change in the nucleation rate on aerosol and cloud properties. In figure 1, we show the mean

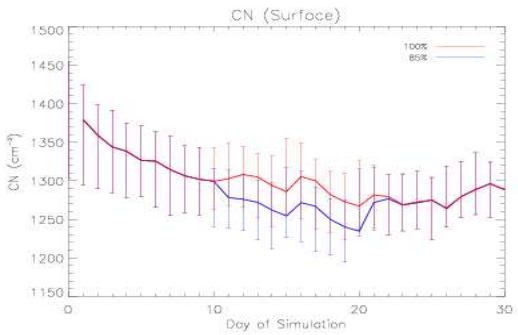

Figure 1: A time-series of globally-averaged perturbed and unperturbed condensation nuclei with radius > 3 nm.

perturbed and unperturbed condensation nuclei over six monthly simulations. We find a negligible change in cloud condensation nuclei concentrations and aerosol optical depth in the atmosphere.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

Bond, G.C., B. Kromer *et al* (2001) *Persistent solar influence on North Atlantic climate during the Holocene*. Science 294:2130–2136

Calogovic, J., C. Albert, F. Arnold *et al* (2010) *Sudden cosmic ray decreases: No change of global cloud cover*. Geophysical Research Letters

Eichler, A., S. Olivier *et al* (2009) *Temperature response in the Altai region lags solar forcing*. Geophysical Research Letters

Laken, B., A. Wolfendale, and D. Kniveton (2009) *Cosmic ray decreases and changes in the liquid water cloud fraction over the oceans*. Geophysical Research Letters

Pudovkin, M.I., Veretenenko, S.V. (1995) *Cloudiness decreases associated with Forbush decreases of galactic cosmic rays.* Journal of Atmospheric and Terrestrial Physics

Svensmark, H., T. Bondo, and J. Svensmark (2009) *Cosmic ray decreases affect atmospheric aerosols and clouds*. Geophysical Research Letters

Binary sulfuric acid–water nucleation, including ion-induced nucleation mechanism

J. Duplissy[1,2], A. Franchin[1], S. Schobesberger[1], K. Lehtipalo[1], D.R. Worsnop[1,3], H. Vehkamäki[1], M. Kulmala[1] and the CLOUD collaboration

[1]Department of Physics, University of Helsinki, FI-00014, Helsinki, Finland
[2]Physics Department, CERN, CH1211, Geneva, Switzerland
[3]Aerodyne Research Inc., Billerica, MA 01821, USA

Keywords: CLOUD experiment, ion-induced nucleation, ions, sulfuric acid, smog chamber.

The possible influence of cosmic rays on aerosols and clouds is of considerable interest (Carslaw, 2009). The CLOUD experiment at CERN aims to study under controlled conditions the effects of cosmic rays on nucleation. CLOUD was installed at CERN in 2009 and three successful campaigns were carried out in 2009 and 2010 to study ion-induced and neutral binary nucleation of H_2SO_4 and H_2O, for tropospheric and stratospheric conditions. Here we present the nucleation data obtain in the CLOUD chamber together with the result of the new model including ion-induced nucleation mechanism.

Methods

Technical input for the CLOUD design was obtained in a pilot experiment in 2006 (Duplissy *et al.*, 2010). The chamber is a 3m-diameter electro-polished stainless-steel cylinder (26.1 m^3). A field cage is installed inside the chamber to allow the removal of ions, when required. The contents of the chamber are irradiated by UV light in the range 250-400 nm. Experimental runs can be performed at stable temperatures between 40°C and -90°C.

The chamber is exposed to a 3.5 GeV/c secondary pion beam from the CERN PS, corresponding to the characteristic energies and ionization densities of cosmic ray muons in the lower troposphere. The beam intensity can be adjusted to cover the natural range from ground level to the stratosphere. Ultra-pure air is obtained from the evaporation of cryogenic liquid N_2 and liquid O_2. The air is humidified with a Nafion humidifier. Ozone is added to the air by UV irradiation. Trace gases such as SO_2 are added from gas cylinders containing pressurised N_2 as the carrier.

The chamber instrumentation includes PTRMS, CIMS, Nano-SMPS, CPC battery, PSM, API-ToF, NAIS, Gerdien, LOPAP, dew point sensor, SO_2 and O_3 analyser, as well as T, P and UV sensors.

Model

The classical nucleation theory including the hydrate interaction model and the ion-induced nucleation will be merged into one model. From this improved model an extension of the parameterisation from Kulmala et al., (1998) and Vehkamäki et al. (2002) will be developed, and compared with the CLOUD data.

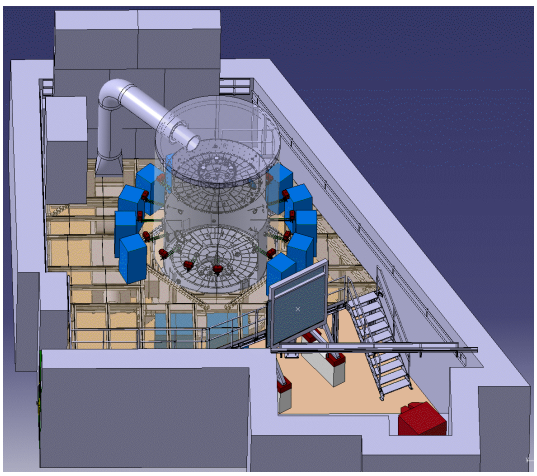

Figure 1. An illustration of CLOUD in the experimental zone at the CERN PS. The de-focused particle beam exits a dipole magnet (bottom right), crosses the hodoscope counter (middle) and then traverses the 3m-diameter CLOUD chamber. The instruments (blue boxes) analyse the contents of the chamber via sampling probes fitted with valves.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

Carslaw, K. (2009). *Cosmic rays, cloud and climate*. Nature, 460, 332-333.

Duplissy, J. *et al.* (2010). *Results from the CERN CLOUD experiment*, Atm. Chem. and Phys., 10, 1635-1647.

Kulmala, M. et al. (1998), *Parametrizations for sulphuric acid/water nucleation rates*, J. Geophys. Res., 103, 8301–8308*et al.* (2010).

Vehkamäki, H *et al.* (2002), *An improved parameterization for sulfuric acid–water nucleation rates for tropospheric and stratospheric conditions*, J. Geophys. Res., 107, 4622

Modelling of ion-induced binary nucleation in the CERN CLOUD experiment

S. Ehrhart[1], L. Ickes[1], J. Kazil[2,3], K. D. Froyd[3], E. R. Lovejoy[3], J. Curtius[1] and the CLOUD collaboration
[1] Institute for Atmospheric and Environmental Sciences, Goethe University, Frankfurt am Main, Hessen, Germany
[2] CIRES, University of Colorado, Boulder, Colorado, USA
[3] NOAA Earth System Research Laboratory, Boulder, Colorado, USA
Keywords: nucleation modelling, ion induced nucleation, CLOUD experiment.
Presenting author email: ehrhart@iau.uni-frankfurt.de

A potential connection between cosmic ray intensity, low cloud cover and climate has been postulated (Marsh and Svensmark, 2000; Carslaw *et al*, 2002; Kirkby, 2007). Ion-induced nucleation could be the mechanism to explain such a connection due to the increased ion-production by galactic cosmic rays. Therefore a better understanding of nucleation mechanisms in general and ion induced nucleation as special case is of crucial importance.

To improve the scientific knowledge about ion-induced nucleation, the CLOUD-project (Cosmics Leaving OUtdoor Droplets) was established at CERN (European Organization for Nuclear Research). The experimental setup consists of an aerosol chamber into which a beam of particles is sent from a Proton Synchrotron to investigate the effects of ions on the aerosol production under controlled laboratory conditions. The chamber itself provides a nearly perfectly clean environment. Concentrations of possible third nucleation agents are almost negligible or are controlled in order to study these.

We modelled the binary sulphuric acid/water nucleation processes in the CLOUD-chamber based on earlier work (Lovejoy *et al*, 2004; Kazil, J., and Lovejoy, E. R., 2007). The models are based on uptake and loss of single sulphuric acid molecules and therefore span a range from a single molecule to particles with a few nanometer size. The special conditions of a chamber experiment makes certain adjustments to the model necessary for instance the main source of losses is the chamber wall. We present results for both steady state conditions and time evolution of nucleation processes. For the time evolution of nucleation we integrate the rate laws numerically using a similar approach to that of Lovejoy *et al*. The steady state solution is calculated with a direct iteration method, which is designed to be suitable to be extended to ternary systems.

The rate constants for charged nucleation are based on laboratory measurements, ab initio results and a smooth parameterisation to bulk phase properties as the particle size increases (Lovejoy te al, 2004). Neutral rate constants are currently based on the liquid drop model with corrections terms. These terms can be optimized with pure binary nucleation experiments. With appropriate parameterisation of neutral nucleation rates we expect to extend the current understanding of transitions from gas to condensed matter.

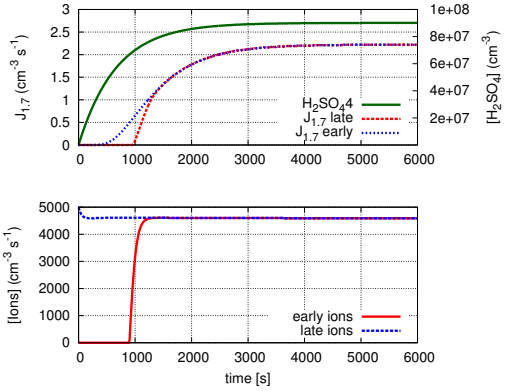

Figure 1: An example model result showing $J_{1.7nm}$ vs time (upper plot) with different starting concentrations of ions (lower plot). The sulphuric acid is shown as function of time (upper plot).

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

Marsh, N. D., and Svensmark, H. (2000) Physical Review Letters, **85**, 5004-5007.

Carslaw, K. S. et al (2002) Science, **298**, 1732-1737.

Kirkby, J. (2007) Surveys in Geophysics, **28**, 333-375.

Lovejoy, E. R., Curtius, J. and Froyd K. D. (2004) J. Geophys. Res. - Atmospheres, **109**, D08204.

Kazil, J., and Lovejoy, E. R. (2007) Atmos. Chem. Phys., **7**, 3447-3459.

Physical characterization of ions in the CLOUD chamber

A. Franchin,[1], S. Schobesberger[1], K. Lehtipalo[1], V. Makhmutov[2], Y. Stozhkov[2], S. Gagné[1], T. Nieminen[1], H. E. Manninen[1], T. Petäjä[1], M. Kulmala[1] and the CLOUD collaboration.

[1]Department of Physics, University of Helsinki, P.O. Box 64, FI-00014, Helsinki, Finland
[2]Lebedev Physical Institute RAS, 119991, Moscow, Russia.
Keywords: atmospheric ions, ion-induced nucleation, sulfuric acid, CLOUD experiment.
Presenting author email: alessandro.franchin@helsinki.fi

Nanoparticle formation in the boundary layer is a frequent phenomenon (Kulmala *et al.*, 2004). Sulfuric acid has been identified as a plausible candidate to participate in the nucleation (Weber et al. 1996). Ion-induced nucleation is one of the possible pathways for new particle formation in the atmosphere, but it is still unclear how important the contribution of ions is with respect to neutral pathways. Ion concentration and their size distribution are key quantities to understand ion-induced nucleation processes and dynamics.

During the CLOUD (Cosmics Leaving OUtdoor Droplets) 2010 fall campaign, several experiments of sulfuric acid-water neutral and ion induced nucleation were performed in an aerosol chamber. In this experiment, Galactic Cosmic Rays (GCR) and the Proton Syncrotron (PS) accelerator at CERN were used as sources to generate ions in the 26.1 m^3 CLOUD aerosol chamber under precisely controlled conditions. Both GCR and the PS pion beam were constantly monitored by a GCR counter and by an hodoscope, respectively.

The ion concentration in the CLOUD chamber was measured with a Neutral cluster and Air Ion Spectrometer, (NAIS, Kulmala *et al.*, 2007). The NAIS is able to measure air ion number size distributions in the mobility equivalent diameter range of 0.8 to 40 nm and correspondingly neutral particle number size distributions from ~2 to 40 nm mobility diameter.

It was also possible to use a PSM (Particle Size Magnifier; Vanhanen e*t al. 2011*), a scanning CPC with a cut off varying from 1 to 2 nm, to retrieve the size distribution of the atmospheric ions created in the chamber and compare it to the NAIS in absence of neutral particles in the chamber (Figure 1).

Based on the measured GCR and beam intensities we were able to calculate the expected ion concentrations in the chamber as a function of beam intensity. The calculated ion concentrations were then compared with the measured values in the NAIS, therefore we retrieved the ion-ion recombination coefficient, performing a dedicated set of experiments at different conditions: at sulfuric acid free ([H_2SO_4]<5e5 cm^{-3}) and at sulfuric acid rich environment ([H_2SO_4]~3e6 cm^{-3}).

The ratio of formation rates of charged and total particles give information about the contribution of ion-induced nucleation. Charged nucleation rates were retrieved from the NAIS ion mode and from two CPCs one of which was equipped with a switchable ion trap both results will be compared.

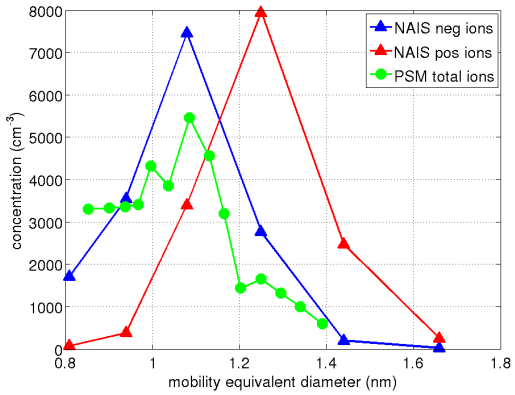

Figure 1. Comparison of number size distribution of ions from NAIS (blue for negative ions red for positive) and from PSM (green).

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation and from the Academy of Finland Centre of Excellence program (project number 1118615).

Kulmala, M. *et al.* (2004). *J. Aerosol Sci.*, 35, 143 – 176.
Kulmala, M. *et al.* (2007). *Science*, 318: 89-92, 2007.
Vanhanen, J. e*t al.* (2011). *Aerosol Sci. Tech.,* 45, 4, 533-42
Weber, R. J., *et al.* (1996). *Chem. Eng. Commun.,* 151, 53–64.

Heterogeneous nucleation of water vapor on nanoparticles and ions, and its temperature dependence

A. Kupc[1], A. Vrtala[1], P.E. Wagner[1], P. M. Winkler[2] and CLOUD Collaboration

[1]Faculty of Physics, University of Vienna, Vienna, A-1090, Austria
[2]Advanced Study Program, National Center for Atmospheric Research, Boulder, Colorado, 80305, USA

Keywords: heterogeneous nucleation, water vapour, aerosols
Presenting author email: agnieszka.kupc@univie.ac.at

Although particle formation processes have been the subject of investigation by many scientists, further research and detailed description of nucleation mechanisms are essential to better understand atmospheric aerosols, their interactions and influence on global climate.

In the present study we focus on the activation of molecular ions, as well as charged and neutral aerosol particles with diameters down to about 1nm in supersaturated water vapor. Seed particles of different composition (e.g. Ag, NaCl, WO_x) are investigated. The aim is to clarify the dependence of the heterogeneous nucleation of water vapor on seed particle size and charging state, with particular focus on nucleation behavior at different nucleation temperatures. Heterogeneous nucleation probabilities are determined using an expansion chamber, the Size Analyzing Nuclei Counter (SANC; Wagner et al., 2003), for measuring droplet number concentration. Besides the SANC, the experimental system consists mainly of aerosol-, and vapor generation units. Particles inducing heterogeneous nucleation in the SANC system at the vapor supersaturations considered, lead to the formation and growth of liquid droplets, which then are optically detected by means of the Constant-Angle Mie Scattering (CAMS, Wagner, 1985) method. Figure 1 presents an example of the growing droplets. Experimental findings on the activation of seed particles by heterogeneous nucleation of water vapour are compared with theoretical calculations (Kelvin and Fletcher theory, Fletcher, 1958), and other results from similar experiments for n-propanol, n-nonane vapour where inorganic insoluble seed aerosol (WO_x, Ag, $(NH_4)_2SO_4$), and soluble NaCl particles were used (Winkler et al. (2008a, b), Schobesberger S. et al., 2010). Currently, a mobile and more versatile version of the SANC is being developed and planned to be integrated in the experiments set up of the CLOUD (Cosmics Leaving Outdoor Droplets) project at CERN. At CLOUD various aspects of the interaction of cosmic rays with aerosols and clouds are investigated, bearing on the possibility of a 'solar indirect' influence on climate. The goal is to contribute to the understanding of mechanisms leading to new particle formation by studying ion induced and binary and ternary nucleation.

Experimental investigations on the activation of nanoparticles and ions by heterogeneous nucleation of water vapour at defined vapour saturation ratios and various temperatures will be presented.

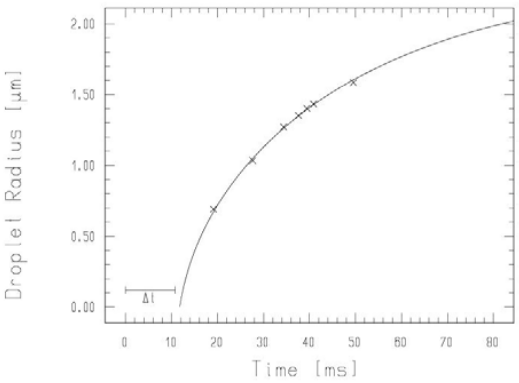

Figure 1. Radii of the growing water droplets measured versus time after expansion for one sample experiment. Oxidised Ag particles at 8nm size are used here. Markers present experimental values, while line presents theoretical calculations.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under the grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), and from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence Program (project no. 1118615).

Fletcher, N. (1958) J. Chem. Phys. 29, 572
Schobesberger S. *et al.,* (2010) *Atmos. Chem. Phys*. 11, 3874-3882
Wagner, P.E. (1985) *Journal of Colloid and Interface Science*, 105: 456-467
Wagner, P.E. *et al.* (2003) Phys. Rev. E 67, 021605
Winkler, P.M., *et al.,* (2008a) *Science* 319, 1374
Winkler, P.M. et al., (2008b) *Atmos. Res.* 90, 187-194

Early stage particle growth rates during the CLOUD experiment

Riccobono, Francesco[1], Weingartner, Ernest[1], Baltensperger, Urs[1], and the CLOUD collaboration

[1]Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Keywords: ion-induced nucleation, growth, CLOUD

Formation of atmospheric aerosol has been observed in a wide range of atmospheric conditions in many different locations and altitudes all over the globe (Kulmala *et al.*, 2004). Nucleation and subsequent condensational growth increase the total number of particles and modify the aerosol size distribution in the atmosphere, affecting the global radiation balance through both direct and indirect effects. Among the various nucleation mechanisms that occur in the atmosphere the ion induced nucleation mechanism is still poorly understood. One of the goals of the CLOUD experiments at CERN is to investigate to what extent the presence of ions in the atmosphere affects the formation of new particles (Kirkby, 2007).

Almost 200 experiments have been performed in the CLOUD aerosol chamber at CERN during the fall 2010 campaign. The CERN Proton Synchrotron provided an adjustable and precisely measurable beam of artificial cosmic rays, spanning the atmospheric ionization range from the upper troposphere to ground level (Kirkby *et al.*, 2011, submitted). Several particle formation events were observed following both neutral and charged pathways with a wide range of nucleation rates and growth rates at sulfuric acid concentrations comprised between 10^6 and 10^9 molecules per cm^3.

The early growth rates of the freshly nucleated particles determine which fraction of these particles can grow to CCN sizes and which fraction is lost by coagulation with larger pre-existing aerosol. In order to study the growth rate in different size ranges as function of the gas and ion concentrations we optimized different instruments. The Scanning Mobility Particle Sizer (SMPS) provides an accurate mean diameter measurement down to ~7 nm, but for particles smaller than this size the SMPS suffers from a poor size resolution due to the extremely low charging probability and to the high particle diffusion losses in the charger and in the DMA column. To retrieve the size information in the 2-10 nm size range we developed the Laminar Diffusion Tube (LDT). This instrument uses the 1.2 meter long sampling line of the CLOUD chamber as a diffusion tube, in which the particles are lost to the walls by diffusion as a function of the sample flowrate and of the particle diameter. Downstream of the LDT the particle concentration is determined with a Condensation Particle Counter (CPC, TSI 3786). By varying the flow rate through the sampling line (by changing the make-up air) the losses are controlled according to laminar diffusion theory.

In a next step, the mean diameter of the particle size distribution of particles with ~2 < *D* < ~10 nm is retrieved by a comparison of the diffusion losses at different make-up flow rates. This calculation does not require any assumption on the shape of the particle size distribution. Another advantage is that it does not depend on the specific detection efficiency curve of the CPC, it only assumes that the diffusion losses in the LDT do not depend on the particle composition.

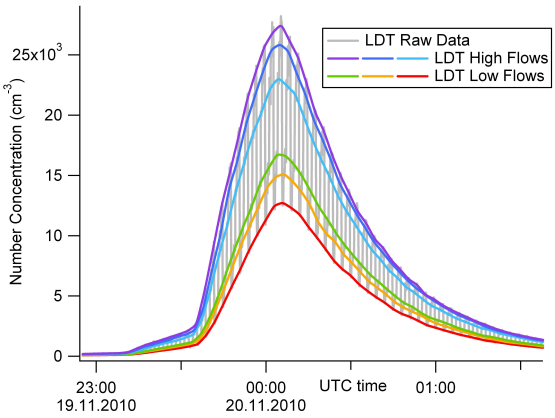

Figure 1. Laminar Diffusion Tube output during CLOUD run 318. The color curves correspond to different make-up flow rates and thereby different effective detection thresholds.

Growth rates enhancement factors obtained with the Laminar Diffusion Tube will be presented for various sets of gases (H2SO4, NH3) and ion concentrations.

Acknowledgments: We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

Kulmala, M. et al. (2004). *J. Aerosol Sci.*, 35, 143-176.

Kirkby, J. (2007). *Surv. Geophys.*, 28, 333-375.

Kirkby, J. et al. (2011), submitted.

Sulphuric acid measurements by CIMS at the CLOUD chamber and cross-check with independent methods to derive [H_2SO_4]

Rondo, Linda[1] , Kürten, Andreas[1], Ehrhart, Sebastian[1], Curtius, Joachim[1] and the CLOUD collaboration
[1]Institute for Atmospheric and Environmental Sciences, University of Frankfurt am Main, Altenhöferallee 1, 60438, Frankfurt am Main, Germany
Keywords: CIMS, sulphuric acid, H_2SO_4 calibration system, CLOUD Experiment

Laboratory studies indicate that sulphuric acid vapor is the most important precursor gas responsible for the nucleation of aerosol particles (Kuang et al., 2008). However, huge discrepancies still exist between different studies trying to determine at what sulphuric acid concentrations the onset of atmospherically relevant nucleation rates occurs.

The CLOUD (Cosmics Leaving Outdoor Droplets) experiment (Duplissy et al., 2009) at the CERN Proton Synchrotron aims to resolve this discrepancy. Additionally, it is designed to investigate the possible link between galactic cosmic rays and aerosol formation.

An instrument based on CIMS (Chemical Ionization Mass Spectrometry) is used for the measurement of gaseous sulphuric acid produced in the CLOUD chamber. The principle of this measurement is based on the reaction between H_2SO_4 and NO_3^- primary ions and the subsequent detection of HSO_4^- ions by a mass spectrometer (Tanner and Eisele, 1993). Mainly due to uncertainties in the reaction rate coefficient and the reaction time in the ion drift region, it is necessary to calibrate the H_2SO_4-CIMS. This is crucial in order to provide the most accurate numbers for the sulfuric acid concentration and to reliably interpret the CLOUD data. Here we present different methods allowing to cross-check the measured concentrations which are based on the calibrated H_2SO_4-CIMS.

The calibration method is based on the production of H_2SO_4 through the reaction of known concentrations of OH and SO_2. OH is formed by the photo-dissociation of water vapor inside a quartz tube, which is illuminated by bandpass-filtered 185 nm light from a mercury lamp (Edwards, 2003). Independently to the calibration, the validity of the measured H_2SO_4 concentrations at CLOUD was cross-checked with two other methods. The first method is based on the measured depletion of SO_2 during the experimental runs when the UV light in the chamber was turned on and the photo chemistry lead to the conversion of SO_2 to H_2SO_4. The concentration of H_2SO_4 is related to the consumption rate of the SO_2 according to the following relation (when a steady-state between the production and the wall loss of H_2SO_4 is reached) : $[H_2SO_4] = d[SO_2] / (dt \cdot k_{wall\ loss})$.
This method, however, allows only a crude estimation of the H_2SO_4 concentrations due to the relatively small changes in $[SO_2]$.

The second method is based on the measurement of the aerosol growth rates which can be used to estimate the H_2SO_4 concentration. The dependence of the particle growth rate on vapour concentrations and its molecular composition is known from theory (Nieminen et al., 2010). Following this theory, the condensational growth rates of aerosol particles smaller than 10 nm are used to determine the concentrations of sulphuric acid.

Such analyses provide very useful indirect information on the concentration of sulphuric acid even in the absence of a direct measurement. It is also an excellent method to cross-check the validity of the measured values with a calibrated H_2SO_4-CIMS. For the experiments during 2009 and 2010, the data evaluation studies showed good agreement between the measured values and the values derived from the independent methods described above (see Fig. 1).

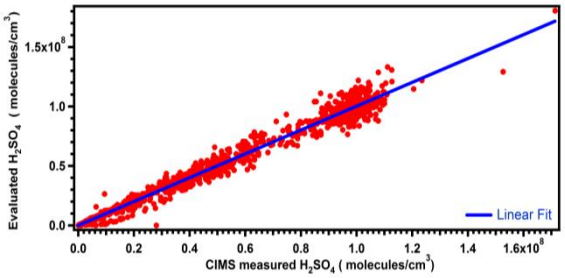

Figure 1. Example of the correlation between the evaluated [H_2SO_4] from the growth rate and the [H_2SO_4] measured by CIMS.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project number 1118615).

Kuang, C., et al., J. Geophys. Res., 113, D10209 (2008).
Duplissy, J., et al., Atmos. Chem. Phys., 10, 1635-1647 (2010).
Edwards, G., et al., Anal. Chemistry, 75, 5317 – 5327 (2003).
Tanner and Eisele, J. Phys. Chem. 104, 830-836, (1993).
Nieminen et al., Atmos. Chem. Phys. Discuss., 10, 9773-9779 (2010).

Measurements of ions and ion clusters in the CLOUD chamber nucleation events by mass spectrometry

S. Schobesberger[1], A. Franchin[1], H. Junninen[1], M. Ehn[1,2], K. Lehtipalo[1], S. Gagné[1], T. Nieminen[1], the CLOUD collaboration, M. Kulmala[1], and D.R. Worsnop[1,3]

[1]Department of Physics, University of Helsinki, Helsinki, FI-00014, Finland
[2]Forschungszentrum Jülich GmbH, Jülich, 52425, Germany
[3]Aerodyne Research, Inc., Billerica, MA 01821-3976, USA
Keywords: nucleation, sulfuric acid, cluster ions, mass spectrometry.
Presenting author email: siegfried.schobesberger@helsinki.fi

Several proposed mechanisms link solar variability with changes in the climate through effects of cosmic rays on weather, aerosols and clouds (Carslaw *et al.*, 2002). However, the details, as well as the significance, of those mechanisms remain unclear.

The CLOUD (Cosmics Leaving OUtdoor Droplets) experiment aims at understanding the possible influence of cosmic rays on aerosol particles and clouds. It provides exceptionally clean and well-defined experimental conditions in an aerosol chamber of 26.1 m^3, together with the possibility of simulating cosmic rays "on demand" by making use of the CERN Proton Synchrotron's particle beam.

It has been well established that nucleation from gaseous precursors form an important source of particles in the atmosphere, and that sulfuric acid (H_2SO_4) plays a crucial role in atmospheric nucleation (e.g. Kulmala *et al.*, 2004, and Riipinen *et al.*, 2007). Hence, the focus was on the investigation of sulfuric acid nucleation under different conditions (e.g. varying beam intensity, concentrations of ammonia (NH_3), relative humidity, etc.).

The APi-TOF (Atmospheric Pressure interface Time-Of-Flight Mass Spectrometer) is a high-resolution mass spectrometer produced by Tofwerk AG, and Aerodyne Research, Inc. It is described in detail by Junninen *et al.* (2010). Sampling occurs from atmospheric pressure through a critical orifice. While passing through differentially pumped chambers, the sampled ions are focused and guided to the mass spectrometer. Note that no ionization of the sampled aerosol was performed, and only naturally charged ions are detected by this setup.

In the course of the experiments, sulfuric acid nucleation events were produced in the chamber. Depending on conditions, nucleation occurred either mainly by negative ions, or mainly by ions of both polarities. During those nucleation events, the ion species registered by the APi-TOF were almost exclusively sulfur-containing compounds or molecular clusters in both polarities. Their composition could be determined based on their exact masses and isotopic patterns, facilitated by the cleanliness of the chamber. Growing clusters of negative and positive polarity could be observed at a time resolution of less than 1 minute, starting at the single ion, up to 3300 Da (corresponding to mobility equivalent diameters of around 2 nm). The identified cluster ions were found to always contain H_2SO_4. Depending on the exact experimental conditions, they also contained NH_3, organic compounds (mainly amines), or both. A part of a typical spectrum during one experiment is shown in Figure 1. The appearance of the larger clusters coincides with the onset of particle formation as detected by other instruments. Clear correlations can be found between features of the steady-state cluster distributions and experimental variables, giving detailed insights into the early steps of new (charged) particle formation driven by sulfuric acid.

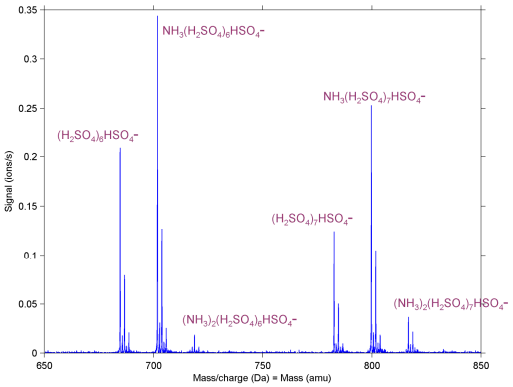

Figure 1. Part of a typical negative ion spectrum, and interpretations for the largest signals in this section.

We thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the PS. This research was funded by the EC's 7th Framework Programme (grant agreement number 215072: Marie Curie Initial Training Network "CLOUD-ITN"), the German Federal Ministry of Education and Research (project number 01LK0902A), the Swiss National Science Foundation, and the Academy of Finland Center of Excellence program (project number 1118615).

Carslaw, K. S., *et al.* (2002). *Science*, 298, 1732
Junninen, H., *et al.* (2010). *Atmos. Meas. Tech.*, 3, 1039–1053.
Kulmala, M., *et al.* (2004). *J. Aerosol Sci.*, 35, 143-176.
Riipinen, I., *et al.* (2007). *Atmos. Chem. Phys.*, 7, 1899–1914.

Hygroscopicity parameter measurements of cloud condensation nuclei from nucleation experiments at the CLOUD chamber

G.T. Tsagkogeorgas[1], H. Wex[1], F. Stratmann[1], and CLOUD collaboration

[1]Department of Physics, Leibniz Institute for Tropospheric Research, Leipzig, 04318, Germany
Keywords: CLOUD experiment, new particle formation, CCN activity.
Presenting author email: george.tsagkogeorgas@tropos.de

The possible effect of cosmic rays on Earth's clouds and climate remains an open question. Atmospheric ions created by cosmic rays may enhance the formation of aerosol particles. A fraction of these may grow into cloud condensation nuclei and may therefore have an effect on climate. The CLOUD 2010 experiments aimed at the investigation of the role of cosmic ray ionization on atmospheric new particle formation and the hygroscopic properties of cloud condensation nuclei.

A variety of laboratory experiments to study the effects of cosmic rays on new particle formation and cloud condensation nuclei activity were carried out under precisely controlled laboratory conditions at the CERN Proton Synchrotron (PS) in 2010. The experiment included several unique aspects such as the CLOUD chamber, a cylindrical electropolished stainless steel research vessel, exposed to a de-focused secondary pion beam from the CERN PS, the capability to create an ion-free environment with an internal electric field cage, precise adjustment of the ultra-violet illumination from a fibre-optic system, and highly stable operation at any temperature between 30°C and -30°C (Duplissy et al., 2010). For atmospheric new particle formation, besides sulphuric acid, which is considered to be the primary vapour responsible, the relative humidity plays a major role. Therefore, the water vapour concentration in the CLOUD chamber was carefully controlled and the gases fed into the chamber were distributed within via two stainless steel fans, operating at selected fan speeds. The contents of the chamber were continuously analysed by trace gas analysers, particle counters, size analysers, mass spectrometers, and a cloud condensation nuclei counter.

We found that the hygroscopicity parameter, κ for a variety of different experimental conditions was substantially below the κ-value found for H_2SO_4 (κ =0.68–0.74 for dry diameters 30–80 nm), Shantz *et al* (2008). κ-values increased with time during the CLOUD Spring campaign 2010 (Figure 1). Mass spectrometer data for organic material concentrations confirm the existence of volatile organic carbon (VOC) vapours inside the chamber of low carbon content (C1-C4). Efforts are underway to reduce these contaminants.

To our knowledge this is the first experimental study to investigate the effect of galactic cosmic ray with the use of a particle beam on new particle formation and cloud condensation nuclei activity. Besides sulphuric acid, trace amounts of organics, even in the cleanest experimental conditions, are responsible for the particle growth (Jimenez, 2009, Wang, 2010).

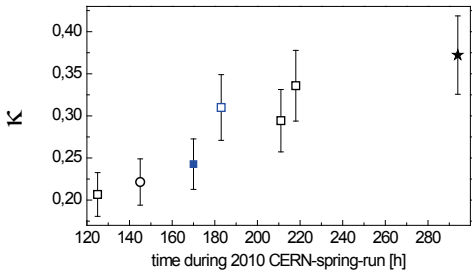

Figure 1. The figure illustrates derived κ-values from CCN activation measurements for different initial experimental conditions of different runs during the CLOUD Spring campaign 2010. Open symbols represent charged pion beam conditions, filled symbols neutral conditions, black symbols low relative humidity and blue symbols higher relative humidity conditions at CLOUD chamber temperature of 20ºC. Star symbol represents CLOUD chamber temperature of 5ºC. Error bars are related to 1σ in dry particle diameter and supersaturation.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation and from the Academy of Finland Center of Excellence program (project number 1118615).

Duplissy, J., et al., (2010) *Results from the CERN pilot cloud experiments.Atmos. Chem. Phys., 10, 1635–1647.*

Jimenez, J.L., et al., (2009) *Evolution of organic aerosols in the atmosphere. Science 326, 1525–1529.*

Wang, L., et al., (2010) *Atmospheric nanoparticles formed from heterogeneous reactions of organics. Nature Geoscience 3, 238–242.*

Shantz, N.C., Leaitch, W.R., Phinney, L., Mozurkewich, M., and Toom-Sauntry, D. (2008) *Atmos. Chem. Phys.,* **8**, 5869-5887.

Performance of an Ultrafine Diethylene Glycol (DEG) based Condensation Particle Counter

Wimmer, Daniela[1], Fabian, Kreissl[1], Metzger, Axel[1], Kürten, Andreas[1], Curtius, Joachim[1], Riccobono, Francesco[2] Lehtipalo, Katrianne[3] and the CLOUD collaboration.

[1]Institute for Atmospheric and Environmental Sciences, Goethe University of Frankfurt, Frankfurt, Germany
[2]Paul Scherrer Insitute, Villigen, Switzerland
[3]Department of Physics, University of Helsinki, Helsinki, Finland

Keywords: nucleation, nano particles, DEG CPC, working fluid, CLOUD experiment

The physical as well as the chemical properties of nano particles are of special interest in various scientific fields, e.g. when atmospheric nucleation events are studied or within the wide field of nano-technology and its applications. Especially for nucleation studies it is crucial to achieve the lowest cut-off diameter possible in order to derive accurate numbers for the nucleation rates (Sipilä et al., 2010). Standard commercial condensation particle counters rely on the activation of aerosol particles using butanol as the condensation fluid and achieve lower cut-off diameters around 2.5 nm. However, using diethyleneglycol (DEG) as the condensation liquid cut-offs well below 2 nm have been realized (Iida et al., 2010). Due to the low vapour pressure of DEG, particles only grow to sizes ~100nm and are therefore too small to be directly detected with the optical systems usually used. This means, whenever using DEG as working liquid a second CPC (the so-called 'booster') is needed to grow the already activate particles further to count them optically.

For the work presented here we modified a standard TSI 3776 ultrafine butanol CPC. The modifications that were necessary are the following. (1) The wick which is used for the butanol version cannot be wetted by DEG therefore it was replaced by a cellulose filter. This filter was wrapped around a perforated stainless steel tube housed in the saturator part of the CPC. (2) Since the TSI software does not allow for controlling the saturator temperature to values larger than 50°C, an additional temperature control was established. It consists of a Pt1000 installed in a bore inside the saturator block and a Watlow PID heat control. (3) The optics part of the CPC was removed and instead an adapter piece was attached to the outlet of the condenser in order to connect it to the second booster CPC. Test measurements were performed to determine the highest saturatuor temperature where no homogeneous nucleation occurs while having the condenser at a fixed temperature of 10°C. This saturator temperature was found to be 52°C.

Detailed calibration measurements were carried out where the DEG CPC was compared to different TSI CPCs and a particle size magnifier (PSM, Vanhanen et al. 2011). The cut-off curves were determined for these CPCs using a high resolution DMA (Herrmann DMA, Hermann et al., 2000) for classifying the particles. Several different methods were used to generate test aerosol particles. These include an electrospray source providing different mobility standards, a Grimm WO_x generator (model nr.: 7.860), a tube furnace for NaCl particles and H_2SO_4 particle generator. Due to its special design the high resolution DMA cannot classify particles bigger than 4nm in mobility diameter. Therefore to provide bigger particles a Grimm nano-DMA (model nr.: 5.710) was used. The CPC concentrations were normalized by the concentrations obtained from two different electrometers (models 5.705 and 3068B). A cut-off curve for the DEG-CPC is shown in Figure 1.

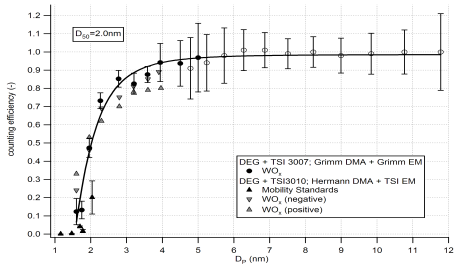

Figure 1 Cut-off curve of the DEG CPC using different types of particles.

During these measurements a TSI 3010 was used as the booster CPC. The cut-off diameter (the size where 50 % of the particles are being detected) of the DEG CPC is 2nm in mobility diameter for this measurement.

The instrument described in this work has also shown to work reliably during a long time period. It was operated during the CLOUD 2010 fall campaign at CERN.

Further tests with the CPC will be performed using a particle generator providing sulphuric acid particles. In addition we would like to test the performance of the CPC in a cool chamber where we can both set and control the temperature well below 0°C, since the temperatures in the CLOUD chamber should be decreased further (down to -90°C)

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD - ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation and from the Academy of Finland Center of Excellence program (project number 1118615).
We would also like to thank TSI Inc., especially Oliver Bischof for providing us important equipment.

Iida, Kenjiro, Stolzenburg, Mark R. and McMurry, Peter H. (2009) *Effect of Working Fluid on Sub-2 nm Particle Detection with a Laminar Flow Ultrafine Condensation Particle Counter*, Aerosol Science and Technology, 43:1, 81 — 96

Herrmann, W., Eichler, T., Bernardo, N., and Fernandez de la Mora, J. (2000). Turbulent Transition Arises at Reynolds Number 35,000 in a Short Vienna Type DMA with a Large Laminarization Inlet. *Annual Conference of the AAAR, St. Louis, Mis souri.*

Vanhanen, J. et al, (2011) *Particle Size Magnifier for Nano-CN Detection*, Aerosol Science and Technology, 45: 4, 533 — 542

Sipilä, M. et al, 2010, *The Role of Sulphuric Acid in Atmospheric Nucleation,* Science