

Name of research institute or organization:

**Department of Physics, University of Helsinki**

Title of project:

Study on atmospheric nucleation and the precursor gases in free troposphere

Project leader and team:

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Project description:

During the project, state-of-the-art atmospheric aerosol measuring techniques were deployed at the Jungfraujoch high alpine research station. The aerosol size range discovered by the deployed instrumentation covered the whole nucleation relevant range: starting at the molecular level with the detection of sulphuric acid and other gaseous components to particles up to 40nm in diameter.

Sulphuric acid is found to be a critical molecule that participates in new particle formation, it was measured with atmospheric pressure interface time of flight APiTOF (Junninen et al, 2010) equipped chemical ionization, CI unit (Jokinen et al 2012). The smallest particles in the size range of 1-2nm in diameter were measured with a particle size magnifier, PSM (Vanhanen et al 2011). Neutral clusters and an air ion spectrometer, NAIS was utilized to measure concentrations of particles in the mobility diameter 2-40 nm and 0.5-40 nm for neutral and charged particles, respectively. Air ion chemical composition was determined with the APiTOF.

Due to the high altitude location the ambient pressure at Jungfraujoch station is about 0.6 atm compared to 1 atm at the sea level, where the instruments were originally calibrated. In order to obtain reliable results, an additional calibration was performed at the site. Sulphuric acid was calibrated utilizing the method described in Kürten et al 2012. This is the first field  $H_2SO_4$  calibration performed in free tropospheric conditions. Figure 1 shows the results of the calibration performed.

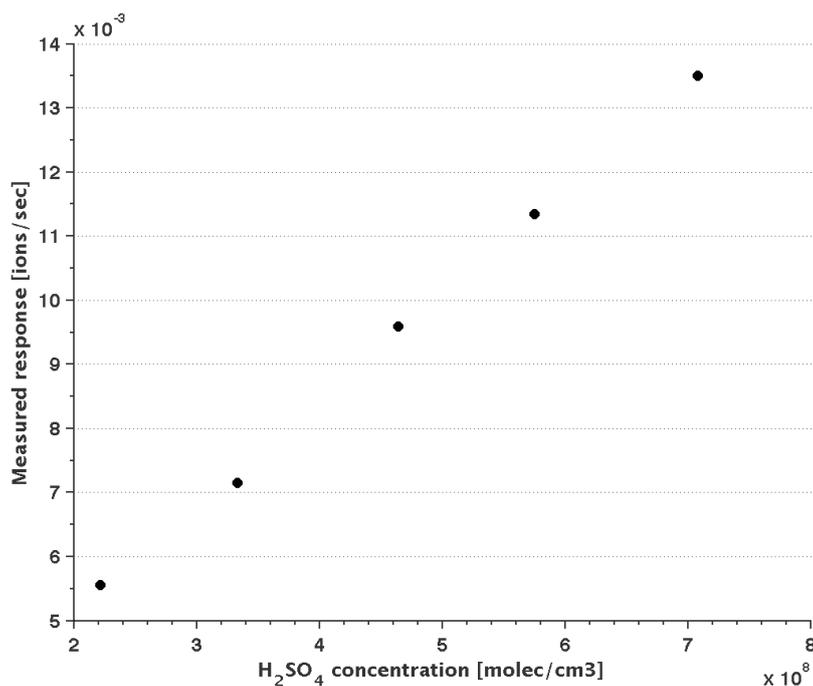


Figure 1. Instrument response to known  $H_2SO_4$  concentration.

Measured sulphuric acid at the Jungfraujoch station showed a clear diurnal variation with highest concentrations during the day. Daytime concentrations varied from  $7 \cdot 10^4$  to  $6 \cdot 10^6$  molec/cm<sup>3</sup> and nighttime concentrations varied from  $1 \cdot 10^4$  to  $5 \cdot 10^4$  molec/cm<sup>3</sup> (Figure 2). A clear connection between particle concentration and sulphuric acid concentration was not observed, which means that the particle concentration was controlled by other factors than the new particle formation.

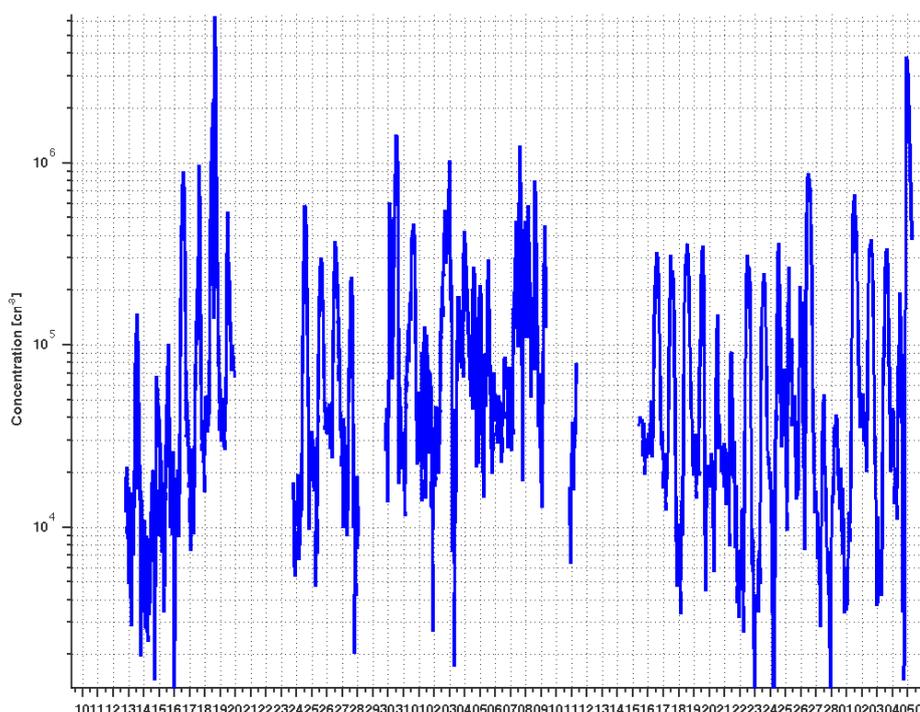


Figure 2. Concentration of sulphuric acid during the whole campaign measured with CI-API TOF. X-axis are days in February and March 2013.

Measurements of air ion concentration and composition did partly fail during the first half of the campaign due to the unexpected sink of ions around the Sphinx building. Off-site measurements showed that the problem indeed was a vicinity of the Sphinx building and that the ion instruments were performing well. The instruments were moved to a new location at the apartment complex of the High Alpine Research Station and ion measurements were conducted there for the rest of the campaign. However, even at the new location the concentrations showed very fast fluctuation which is not observed at other locations. Figure 3 illustrates this behavior. Ion formation through galactic cosmic radiation is a fairly stable process and the only reason for fast ion concentration fluctuation are the sink processes, like preexisting aerosols, cloud droplets, snow and ice crystals. The sampling location was at a mountain slope and re-suspended snow and ice crystals occur even at sunny days, causing the fluctuations in air ion concentrations.

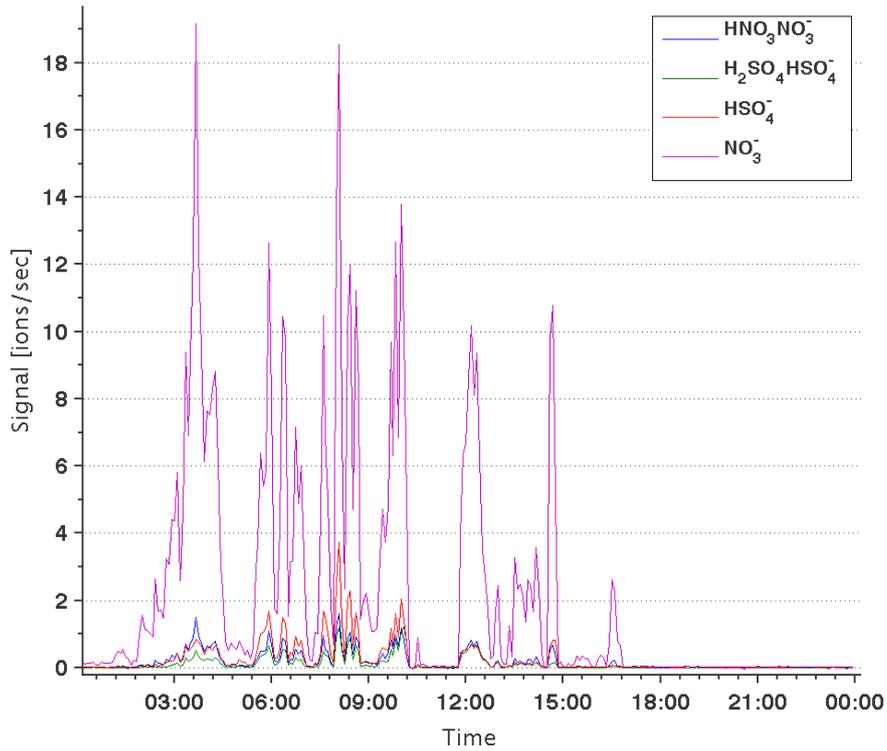


Figure 3. Concentration of air ions on 9th of February 2013 measured with APiTOF. Concentrations show very fast fluctuation which indicates a presence of a fast sink process.

High fluctuation is only visible in smallest ions, the ions measured with APiTOF, Figure 3 and the lowest channels of NAIS, Figure 4. For larger ions the fluctuations were not observed.

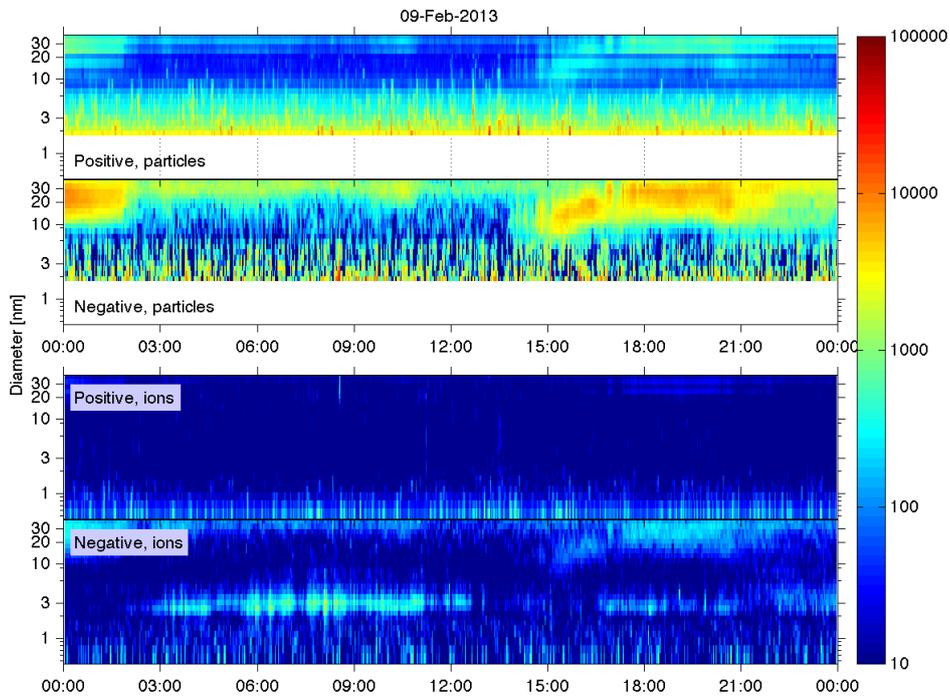


Figure 4. Neutral clusters and air ion spectrometer measurements on 9th of February. Top 2 panels are measurements of neutral particle size distribution which are charged by corona, the lower two panels are naturally charged air ion size distributions.

References:

- Jokinen, T., M. Sipilä, H. Junninen, M. Ehn, G. Lönn, J. Hakala, T. Petäjä, R. L. Mauldin, M. Kulmala and D. R. Worsnop (2012) "Atmospheric sulphuric acid and neutral cluster measurements using CI-API-TOF." *Atmospheric Chemistry and Physics* 12 (9) 4117-4125
- Junninen, H., M. Ehn, T. Petäjä, L. Luosujärvi, T. Kotiaho, R. Kostianen, U. Rohner, M. Gonin, K. Fuhrer, M. Kulmala and D. R. Worsnop (2010) "A high-resolution mass spectrometer to measure atmospheric ion composition." *Atmospheric Measurement Techniques* 3 (4) 1039-1053
- Vanhanen, J., J. Mikkilä, K. Lehtipalo, M. Sipilä, H. E. Manninen, E. Siivola, T. Petäjä and M. Kulmala (2011) "Particle Size Magnifier for Nano-CN Detection." *Aerosol Science and Technology* 45 (4) 533-542
- Kürten A, Rondo L, Ehrhart S, Curtius J. (2012) "Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid." *Journal of Physical Chemistry A* 116 (24) 6375-86

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Mass spectrometry, APiTOF, nucleation, air ions

Collaborating partners/networks:

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