

Detection of the total ambient aerosol number concentration and chemical composition TOTALDETECTION

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- **Introduction and motivation**

Atmospheric nanoparticle formation by gas-to-particle conversion has been identified as the dominant source controlling the aerosol number distribution on global scale. Once formed, these nanoparticles are often found to grow to sizes where they can act as cloud condensation nuclei. Thereby the newly formed nanoparticles may contribute to the indirect radiative forcing. However, the mechanisms responsible for these processes remain poorly understood, making their climate impacts difficult to assess.

Part of the difficulties associated with characterizing ambient nanoparticle formation relates to the extremely low concentrations of precursor vapors and particle mass, as well as certain fundamental limits in the detection of nanoparticles by currently available instrumentation. In order to track down potential particle formation mechanisms, a comprehensive approach providing simultaneous measurements of trace gas constituents and particle phase molecular species is needed. Also the evolution of total particle number concentration from the smallest possibly detectable particle/cluster sizes is essential to identify the critical size range where the phase transition is initiated. While the composition provides hints on the actual formation and growth mechanisms the number concentration of newly formed nanoparticles is crucial for estimating the overall climate relevance.

Springtime new particle formation has been observed frequently in the Finnish boreal forest at the SMEAR II field station in Hyytiälä (Finland) and has been connected to the rapid and extensive oxidation of biogenic terpenoid compounds. The high number of particle formation (“event”) days in spring provides the necessary condition to rigorously study particle formation and growth as planned in this project. This proposal was coordinated by Dr. Paul Winkler from the University of Vienna and covered expenses related to travel plus accommodation for a young scientist from the University of Vienna (Tamara Pinterich) and an experienced researcher as well as a postdoc from the US (James N. Smith and Mike Lawler).

- **Scientific objectives**

Kulmala et al. (2013) have shown that clusters in the sub-2 nm size range can be separated into three regimes: A) sizes between 1.1 and 1.3 nm form in the gas-phase and are highly unstable, B) clusters around 1.5 nm grow predominantly by sulfuric acid and are stabilized by ammonia and amines, C) close to 2 nm vapor uptake is enhanced by oxidized organic vapors. This finding implies that a large pool of stable clusters in the order of $10^6 - 10^7$ per cc can be expected during a formation event. Such high concentrations can hardly be counted by regular condensation particle counters. To further enlighten the mechanisms responsible for particle formation in this size range we employed the versatile Size Analyzing Nuclei Counter (vSANC). The chemical composition of the growing particles was explored with the TDCIMS (Smith et al. 2010).

- **Reason for choosing station**

The SMEAR II station is known as one of the world-leading aerosol research stations with an exceptionally long time series of size distribution data and hosted the 2014 spring campaign. The station offers crucial benchmarking data with a suite of long-term mass spectrometers and Particle Size Magnifiers (PSM) (Vanhanen et al., 2011).

- **Method and experimental set-up**

The vSANC (operated by Tamara Pinterich) is an expansion type condensation particle counter (CPC) that is optimized for the detection of nanoparticles down to 1 nm (Pinterich et al., 2013). In contrast to the PSM it is a single stage CPC operated typically with n-propanol or water as working fluid. One of the benefits of this system is that the time resolved monitoring of the scattered light curves allows clear distinction between signals from heterogeneously and homogeneously nucleated droplets (Winkler et al., 2008). Thereby it is possible to operate the vSANC at high vapor saturation ratios at which homogeneous nucleation can be expected. These settings guarantee the activation of any arbitrarily small nanoparticles present in the expansion chamber. The fact, that we do see homogeneous nucleation also serves as an indicator that particle activation is not suppressed by vapor depletion due to high concentrations of simultaneously growing nanoparticles during a formation event. This may have limited the response of PSMs at high particle concentrations in the past as the low vapor pressure of di-ethylen glycol (DEG) could have led to substantial depletion. Accordingly, an important aspect of the campaign was related to the direct comparison of the vSANC to the PSM.

During most of the campaign the vSANC was operated with n-propanol at an inlet flow rate of 10 l/min. Figure 1 shows a flow diagram of the vSANC during ambient air sampling. The comparatively high inlet flow rate was needed to minimize diffusion losses. Measurement of particle number concentration proceeded in a 3-stage cycle consisting of three different expansion ratios. Variation of the pressure drop allowed us to detect particles at different saturation ratios. For the largest pressure drop during each cycle we typically observed significant amounts of particles originating from homogeneous nucleation. At this pressure drop basically all particles that could serve as condensation nuclei should have been activated.

Furthermore, we deployed a version of the Thermal Decomposition Chemical Ionization Mass Spectrometer, or TDCIMS (operated by James N. Smith and Mike Lawler). This instrument samples small particles of a selected mobility diameter onto a wire, and then desorbs them into the ion source of mass spectrometer. In this study, the particle sampling inlet was attached to a ToFwerk APITOF time-of-flight mass spectrometer, which has very good ion transfer characteristics for medium-to-high molecular weight compounds such as biogenic oxidation products. The distribution of collected particle size was measured using a scanning mobility particle sizer.

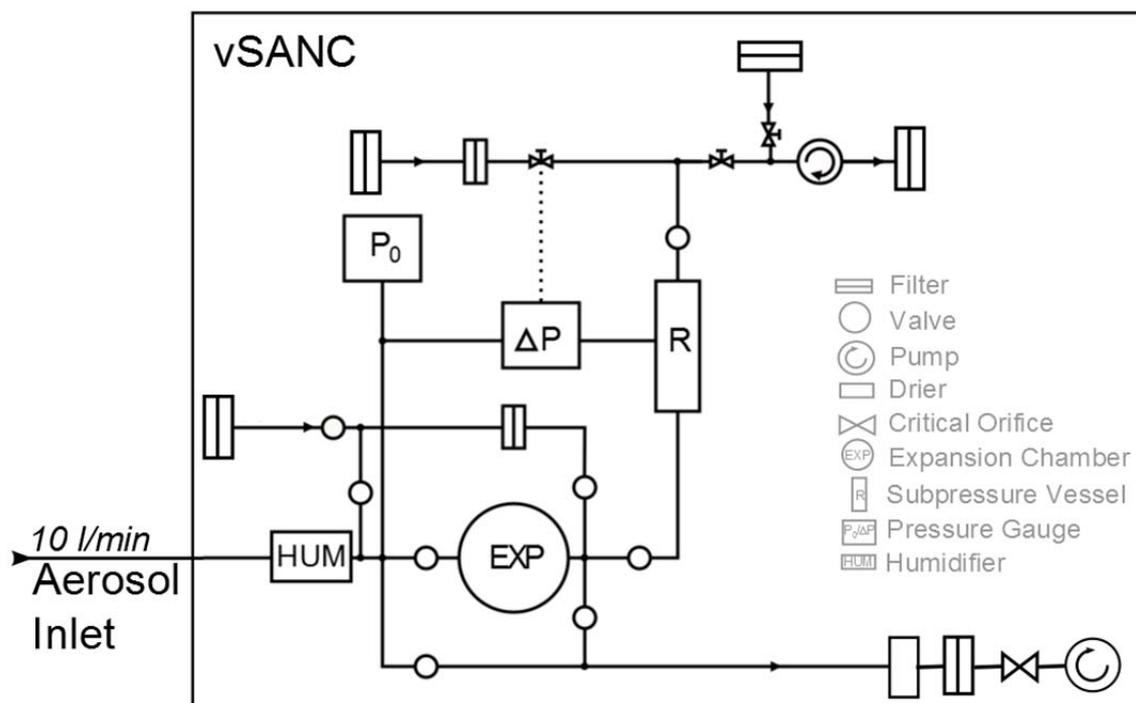


Figure 1: Flow diagram of vSANC. Ambient aerosol was humidified in a saturator (HUM) and passed into the expansion chamber (EXP). After a short period of thermal equilibration the valves regulating the flows through the chamber were closed and expansion was initiated by opening the expansion valve between EXP and the subpressure vessel (R).

- **Preliminary results and conclusions**

The vSANC was operated for most of the campaign from mid-March to End of May. Figure 2 shows the response of the vSANC during a strong event day on April 23rd. The contour plot in the lower part of the figure illustrates the classic picture of a formation event with the sudden appearance of 3 nm particles at about 10 am local time. The colored dots in the top part of Figure 2 refer to concentration measurements of the vSANC at different pressure drops. Red dots refer to concentrations at the highest pressure drop; black ones were measured at the lowest pressure drop. As can be seen for the highest pressure drop, and hence the highest vapor saturation ratio, the automated concentration evaluation software detects roughly 10^6 particles per cc whereas at lower pressure drops ambient particle concentration typically stays below 10^4 per cc. Clearly, the high concentrations refer to homogeneous nucleation. Only during the nucleation event the concentration of seed particles rises sufficiently so that the software can separate the seed particle signal from the signal obtained from homogeneous nucleation. It is remarkable though that despite of an observable increase in number concentration during the event the total number concentration seems to be independent of the applied pressure drop.

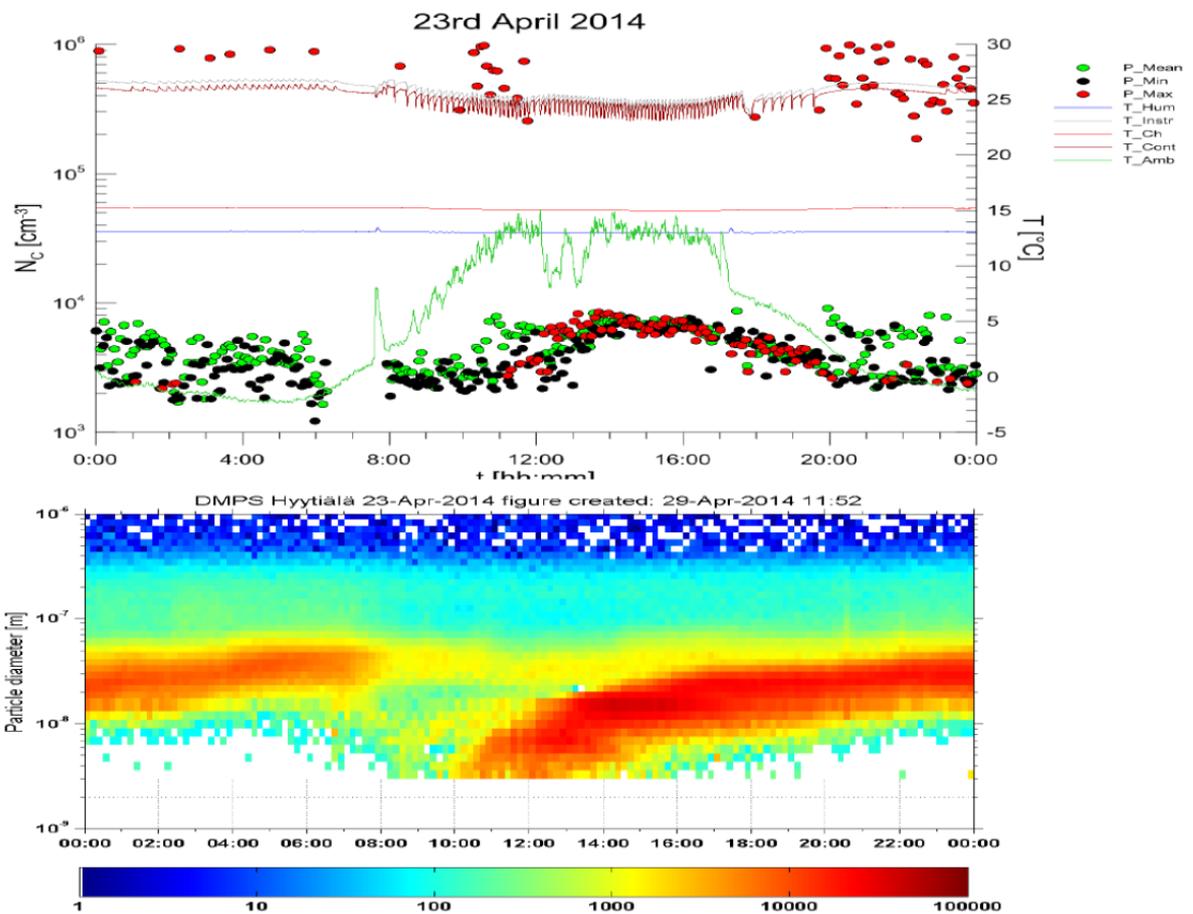


Figure 2: Comparison of vSANC data (top) to size distribution measurements from the DMPS (bottom) during a formation event.

Between April 7th and May 3rd the TDCIMS was present at SMEAR II and measured the composition of nanoparticles. At least two nucleation and growth events were observed by TDCIMS during the period of observations. One was very long, with a growth mode that persisted over two days. These observations will provide new insights into the time-and size-dependent chemistry of newly formed nanoparticles.

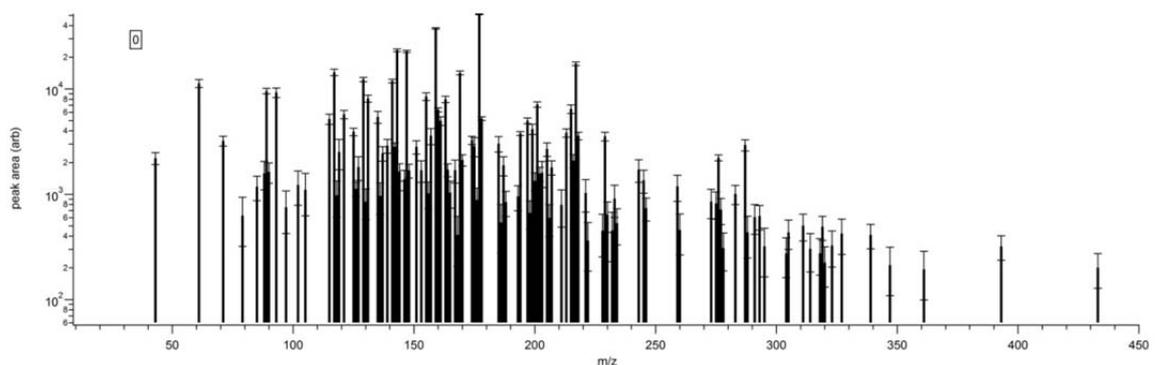


Figure 3. Unit mass resolution background-corrected positive ion spectrum for 20 nm particles during a nucleation event. Most of the signal is concentrated in the range of 110-250 amu. For comparison, monoterpenes have a molecular weight of 136 amu. Many of these peaks are likely to be oxidation products of terpenes.

- **Outcome and future studies**

The data obtained from the vSANC and the TDCIMS provide a profound basis for further analysis. Overall, the concentrations measured with the vSANC agreed fairly well with PSM data. This finding suggests that the PSM signal is not suffering from vapor depletion. On the other hand further research is needed to characterize and optimize the diffusion losses of the vSANC at the inlet. It is remarkable though that the highest saturation ratios applied for particle detection did not reveal substantial increases in particle number concentration except for homogeneously nucleated particles. However, corrections still need to be applied to account for the particle reduction during the expansion. Data evaluation is ongoing and publications can be expected to appear later this year. First official presentations from this project will appear at the end of August during the International Aerosol Conference held in Busan, Korea, where Tamara Pinterich will give an oral presentation about the measurements performed at the SMEAR II station.

- **References**

Kulmala, M., et al. Direct Observations of Atmospheric Aerosol Nucleation (2013), *Science* 339, 943.

Smith, J. et al. (2010) Observations of ammonium salts in atmospheric nanoparticles and possible climatic implications, *PNAS*, 107, 6634–6639.

Vanhanen, J., et al., Particle size magnifier for nano-CN detection, *Aerosol Sci. Technol.* **45**, 533 (2011).

Pinterich, T., et al. (2013), in Nucleation and Atmospheric Aerosols, AIP Conf. Proc. 1527, 161-164.

Winkler, P.M. et al. (2008) Condensation particle counting below 2 nm seed particle diameter and the transition from heterogeneous to homogeneous nucleation, *Atmos. Res.* 90, 125-131.