Composition analysis of ice particle residuals combining aerosol mass spectrometry and counterflow virtual impactor technique, INUIT-RP2-TROPOS

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- Introduction and motivation

Ice formation in super-cooled clouds is an essential prerequisite for the initiation of any kind of precipitation at mid-latitudes. After their nucleation, the ice particles can grow at the expense of the super-cooled water drops in these emerging mixed-phase clouds. At the altitude level of such mixed-phase clouds, temperatures are mostly warmer than -38°C and therefore ice particles can only be formed by heterogeneous ice nucleation. Several pathways of heterogeneous ice formation are known, like deposition, condensation, immersion or contact freezing but their atmospheric relevance is not clear up to know. The same is true for the different types of atmospheric aerosol particles that serve as ice nuclei (IN). It is essential to investigate the chemical and microphysical properties (composition, morphology, size) that determine the surface properties that in turn enable an aerosol particle to act as an IN at a given temperature and super-saturation for each of the heterogeneous freezing mechanisms.
Laboratory experiments yielded instructive results in recent years, however it is not clear whether realistic atmospheric scenarios were reproduced and whether the investigated aerosol particles are atmospheric relevant. For example pure mineral dust and biological particles were found to be good IN especially at rather high temperatures, but it is not clear whether they are generally present at the altitudes where mixed-phase clouds form. In 2011, a new DFG funded research unit (INUIT = Ice Nuclei Research Unit) was established with the objective to acquire further and better understanding on atmospheric relevant heterogeneous ice formation processes and the respective ice nuclei.

- Scientific objectives

This research activity is part of the research unit INUIT (research project 2) of the German research foundation DFG. It should contribute to a better understanding of the heterogeneous nucleation of ice particles in middle and lower tropospheric super-cooled clouds. A question closely related to the different heterogeneous ice nucleation mechanisms is the nature of the IN with respect to their chemical composition and microphysical properties. Especially the anthropogenic influence on tropospheric ice formation is hardly known as well as the atmospheric relevance between mineral dust and biogenic aerosol particles, both known as efficient IN from lab studies. In order to tackle these questions, INUIT co-organized a joint field campaign in real atmospheric mixed-phase clouds at the high alpine research station Jungfraujoch, called CLACE 2013. By in-situ sampling in mixed-phase clouds at this site the role of lead in ice nucleation was found to be important (Cziczo et al. 2009; Kamphus et al. 2009). The significance of black carbon, that was observed to be enhanced in ice residuals, to serve as IN at the Jungfraujoch (Mertes et al. 2007; Cozic et al. 2008) is still controversially discussed. In addition, the importance of primary biological particles acting as ice nuclei found to be very high (Pratt et al. 2009) could be not yet confirmed at this site.
The possibility to measure in real atmospheric mixed-phased clouds also allows the separate characterization of ice particle residuals (IPR) and IN identified by an IN counter. For the IPR there exists no direct proof that they actively contribute to ice formation although they are found in real atmospheric ice

particles, whereas the particles forming ice in an IN-counter are well-defined but limited by the artificial thermodynamic conditions and heterogeneous nucleation mechanisms that can be simulated in the counter.
Thus, the objectives are the physico-chemical characterization of (a) IPR within natural mixed-phase clouds (objective 1) and of (b) IN of ice particles formed in an ice nucleus counter (objective 2) at the high alpine research station Jungfraujoch in the Swiss Alps. The determination of the IPR and IN aerosol properties requires the coupling of the counterflow virtual impaction (CVI) techniques with single particle mass spectrometry. Whereas the latter is applied by the cooperation partner MPI Mainz measuring the chemical composition and mixing state, the CVI technique is developed by TROPOS.

- Reason for choosing station

Although process understanding obtained in model simulations and laboratory experiments are indispensible to improve our knowledge about heterogeneous ice nucleation, its atmospheric relevance needs to be investigated in field experiments. Even if ice nuclei characterization by IN counter measurements can be conducted more or less everywhere, the collection of IPR requires a site where atmospheric mixed-phase clouds occur. The High Alpine Research Station Jungfraujoch (3500 m asl) as the highest European research station offers the highest probability to encounter those clouds in winter within a relevant temperature range between -5 and -30°C. Moreover, new findings could be meaningful compared to former ones (Mertes et al. 2007; Cozic et al. 2008; Cziczo et al. 2009; Kamphus et al. 2009; Ebert et al. 2011) observed at the same site. The infrastructure of the High Alpine Research Station Jungfraujoch is excellent for the most part, and this research activity reverts to the experiences gathered in the previous projects CLACE3 to CLACE6. Especially, one of the TROPOS CVI systems, the so-called Ice-CVI, is particularly designed for the Jungfraujoch research station.

- Method and experimental set-up

In order to investigate the scientific objectives described above, two different CVI systems have been operated at JFJ:
For objective 1, the physico-chemical characterization of IPR, the unique Ice-CVI inlet system (Mertes et al. 2007) was setup on the Sphinx platform, which consists of a virtual impactor (VI), a drop pre-impactor (PI) and a standard CVI, respectively. Under mixed-phased cloud conditions this sampler extracts small, freshly produced ice particles from all other solid/liquid components of the cloud by consecutively pre-segregating large ice aggregates, super-cooled drops and interstitial particles. In the PI supercooled drops freeze on the cool impaction plates whereas the small ice particles bounce off and remain in the sampling flow. Inside the Ice-CVI the ice water of the sampled ice particles is evaporated releasing the IPR for analysis. Restricting the collection to ice particle sizes between 5 and 20 µm by means of the combination of VI and standard CVI the IPR can be attributed to the original ice nuclei, because in this size range ice particles grow only by water vapor deposition. The IPR are analyzed within this proposal for number concentration, size distribution and black carbon mass by a condensation particle counter (CPC), a optical particle sizer (OPS), a ultra-high- sensitivity aerosol spectrometer (UHSAS), and a particle soot absorption photometer (PSAP).
For objective 2, the physico-chemical characterization of IN, a pumped CVI was coupled between the ice nucleus counter FINCH (U Frankfurt) and the single particle mass spectrometer ALABAMA (MPI Mainz). FINCH was connected to the total aerosol inlet, heterogeneously forming ice particles on atmospheric aerosol under controlled conditions. The task of the pumped CVI (IN-CVI) was to collect and separate the ice particles from non-activated particles and drops and transfer the atmospheric IN to the ALABAMA after

evaporating the ice water. Moreover, the IN number concentration and size distribution was determined by CPC, APS and UHSAS.

- Preliminary results and conclusions

Up to know 24 different cloud events during the CLACE 2013 campaign were identified. Exemplarily, the number concentration time series for cloud event #12 (event indicated by the red horizontal line) measured by the CPC, OPS and UHSAS are shown in Fig.1. The small concentration of ice particles residues is significantly higher than the background counts before and after the event. Depending on the occurrence of heterogeneously nucleated ice particles the IPR number concentration measured by the CPC (measured size range 0.01 – 30 µm) varies between 50 and 400 L^{-1}. The OPS (0.3 – 10 µm) and UHSAS (0.06 – 1 µm) see the same time course of the IPR concentration but on lower density levels due to their limited size sensitivity. Although it is expected that larger aerosol particles are the more efficient IN, the IPR number concentration is dominated by sub-micrometer particles.

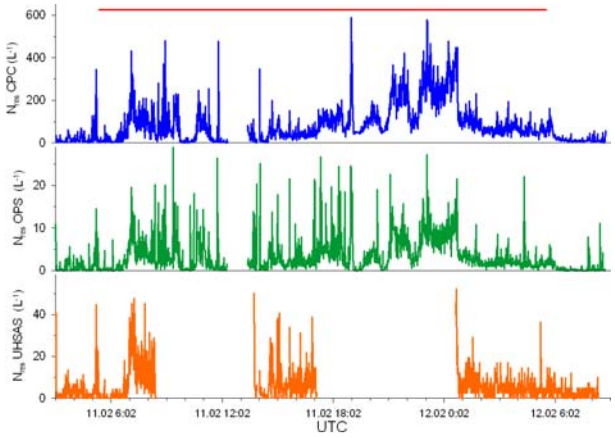

Fig.1: IPR number concentration measured during cloud event 12

In Fig.2 the IPR size distributions for three different cloud events derived from the UHSAS and OPS measurements are illustrated. The distributions from both instruments show a good agreement in the overlap region between 0.3 and 1 µm. Overall, the IPR number size distributions are very broad in comparison to background particles which indicates that larger particles are enriched in the ice particles and thus are preferred to act as ice nuclei. The maxima vary but are in the size range from 0.2 to 0.3 µm.

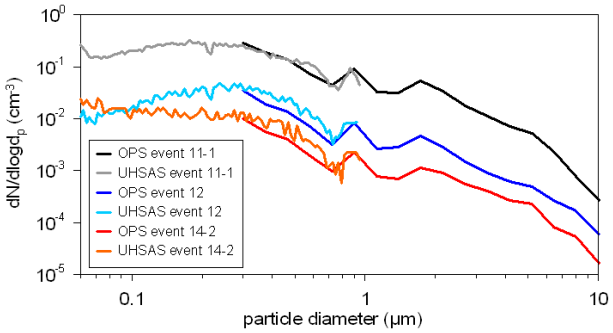

Fig.2: IPR number size distributions derived for three different cloud events

For the validation of the particle measurements behind the IN-CVI, the temperature and super-saturation data sets of the IN-counter were analyzed in order to determine time periods of constant conditions. During the up to now evaluated periods the IN concentrations are in the range of 1 L^{-1} and thus substantially lower than the IPR concentrations.

- Outcome and future studies

The measurements of TROPOS during CLACE 2013 yield the following results so far:

- During the encountered cloud events IPR concentrations were found to be between 50 and more than 1000 L^{-1}.
- The IPR number density and is substantially larger than the derived IN number density.

- IPR number size distributions are very broad indicating that larger particles are preferred to act as ice nuclei
- The main IPR size modes are found to have their peaks between 0.2 and 0.3 µm.

The next step in the analysis is to determine the contribution of ice particle shattering, but also natural ice multiplication processes on the IPR results by means of the size resolved aerosol and ice-particle measurements (latter carried out by collaborating groups). IPR number and size needs furthermore to be related to the microphysical and chemical properties of the ambient background aerosol in order to validate the assumption that the IPR have been dominantly served as atmospheric IN. In this context, the IPR results will be compared to the IN-counter based ice nuclei measurements in more detail.
Although the actual CLACE 2013 campaign has substantially increased the IPR and IN microphysical data set, there is a strong need to continue the mixed-phase cloud field measurements in order to further characterize IPR and IN. Only then it is possible to average over the year to year variability of air mass origins and prevailing meteorological conditions during the single field experiments.

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