Doctoral Thesis

Laboratory and field measurements of immersion freezing utilizing a newly developed cloud chamber

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Laboratory and field measurements of immersion freezing utilizing a newly developed cloud chamber

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presented by

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Abstract

The occurrence and properties of clouds in the atmosphere significantly influence the Earth’s energy budget and climate. Aside from direct effects on cloud radiative properties, ice formation is a crucial mechanism leading to precipitation. Therefore, a comprehensive understanding about the constraints effecting atmospheric ice formation is required to predict weather and climate correctly. Mechanisms that lead to the formation of ice crystals are not yet fully understood. In the atmosphere, ice crystals can form homogeneously or heterogeneously. For the latter, an ice nucleating particle (INP) provides a surface upon which ice forms. Different modes of heterogeneous ice nucleation exist, which can be investigated in the laboratory or by deploying instrumentation in the field to measure ambient INP concentrations. In mixed-phase clouds, where ice crystals and supercooled cloud droplets co-exist, freezing mechanisms involving the liquid phase such as immersion freezing are particularly relevant.

During this study, the newly developed Portable Immersion Mode Cooling chAmber (PIMCA), which is a vertical extension of the Portable Ice Nucleation Chamber (PINC), is introduced. The PIMCA-PINC setup is currently the only available portable instrument measuring immersion mode INPs in-situ. It is deployable in the field, and can be used for inter-comparison studies in other laboratories, allowing for the measurement of the ice nucleating properties of a population of single aerosol particles. Computational fluid dynamics simulations and freezing experiments were used to validate the performance of the chamber.

The first field study investigating ambient in-situ immersion freezing took place in spring 2014 during the Zurich AMBient Immersion freezing Study (ZAMBIS). Ice nucleation was observed and has been able to be quantified with PIMCA-PINC mainly close to homogeneous freezing temperatures. Two additional drop freezing methods using bulk sampling allowed for immersion freezing measurements over a wide temperature range between 233 K and 269 K. Due to differences in the sampled aerosol particles sizes, utilizing these three independent ice nucleation techniques allowed interpretation of the particle size effects of ambient INPs. Parallel measurements of bioaerosols and meteorological conditions were used to investigate which factors influence the ambient INP concentration. Spring was chosen as it is the pollen season of birch, allowing estimation of the atmospheric relevance of pollen. During the peak of the pollen season, an increase in INP concentration was observed.

The portability of the new PIMCA-PINC setup made a direct inter-comparison with other state of the art ice nucleation devices for measurements of immersion freezing possible.
PIMCA-PINC was compared to LACIS (Leipzig Aerosol Cloud Interaction Simulator) in parallel, both instruments measuring single-immersed aerosol particles and yielded excellent agreement. Additionally, two continuous flow diffusion chambers (CFDCs) PINC and SPIN (the Spectrometer for Ice Nuclei) were used for measurements in water sub- and supersaturated conditions (deposition nucleation/condensation freezing). Differences in PINC and SPIN could be explained by taking residence time effects and ice crystal growth rates into account. A comparison of all four instruments was conducted in order to better understand which ice nucleation mechanisms are measured and how results differ. A discrepancy between the immersion freezing devices and the CFDCs was observed and was dependent on both temperature and aerosol type investigated. Apart from the possibility of differences in ice nucleation mechanisms, instrument specific parameters such as detection methods and the residence time in the chambers are observed to be important.
Zusammenfassung


Im Rahmen dieser Arbeit wurde eine neue und portabel einsetzbare Immersionsgefrierkammer (PIMCA) entwickelt, die eine vertikale Erweiterung der portablen Eisnukleationskammer (PINC) ist. PIMCA-PINC ist das einzige portable Instrument für in-situ Messungen in der Immersionsgefriermode. Es ist sowohl im Feld als auch für Vergleichsstudien mit anderen Laborinstrumenten einsetzbar und erlaubt die Messung von Eisnukleationseigenschaften einer Population von einzelnen Partikeln. Die Kammer wurde mit CFD-Simulationen und Gefrierexperimenten validiert.

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Chapter 1

Introduction

The Earth’s energy budget is strongly coupled to the presence of clouds (Boucher et al., 2013), which influence the hydrological cycle by transporting water and are necessary for precipitation formation in the atmosphere (Chahine, 1992). In addition to cloud droplets, ice crystals contained in cirrus and mixed-phase clouds (MPCs) influence the radiative budget by reflecting incoming solar radiation back to space and by absorption of outgoing (terrestrial) radiation from the Earth’s surface. These effects can lead to a cooling or warming of the atmosphere depending on the properties of cloud particles and aerosol particles upon which they form.

1.1 Impact of aerosol particles and clouds on climate

Aerosol particles can affect the climate system in different ways by changing the radiative forcing ($RF$), which is obtained as the net change in the net radiative flux at the top of the atmosphere due to an external perturbation of the climate system. $RF$ due to aerosol particles is distinguished in $RF$ due to aerosol-radiation interactions and $RF$ due to aerosol-cloud interactions. The impact of aerosol particles on climate is not completely understood and estimated to be $-0.9 \text{ W m}^{-2}$ ($-1.9$ to $-0.1 \text{ W m}^{-2}$) (Boucher et al., 2013).

The aerosol direct effect occurs when particles directly reflect and scatter incoming solar radiation and due to their strong scattering properties induce a negative forcing (cooling). In addition, aerosol particles can absorb solar radiation leading to a warming of the surface and the atmosphere by re-emitting longwave radiation. Additionally, aerosol particles can change the cloud properties by acting as cloud condensation nuclei (CCN) or ice nucleating particles (INPs). In a first approximation, clouds containing cloud droplets reflect solar radiation depending on their optical thickness (cloud albedo effect, Twomey effect; Twomey, 1974). For example, an increased number of CCN results in a higher number density of smaller cloud droplets assuming the same liquid water content in the cloud. This leads to a higher optical thickness and a higher cloud albedo, thus results in a stronger cooling of the
atmosphere. On the other hand, absorption and emission of longwave radiation by aerosol particles and clouds inducing a warming of the atmosphere is known as the greenhouse effect. Changes in the number and properties of aerosol particles and composition of the atmosphere can lead to a change in the lifetime of a cloud and thus cloud coverage.

In addition to aerosol induced effects, the clouds have an impact on the radiative budget depending on their properties. The total net effect due to clouds is a cooling and is estimated to be $-20 \text{ W m}^{-2}$ (Boucher et al., 2013).

A major fraction of clouds in the atmosphere are composed of ice particles. Ice is found in two different cloud types, cirrus and mixed-phase clouds. Cirrus clouds occur at high altitudes and at cold temperatures and are only composed of ice crystals. Ice crystals mainly grow from water vapor deposition at temperatures below 235 K. Due to the cold temperatures and small ice crystal growth rates in this regime, ice crystals are typically small (smaller than 100 µm) and number concentrations of ice crystals are much lower than cloud droplets in warm clouds. Ice crystal concentrations are observed to be on the order of $10^{-3} - 10 \text{ cm}^{-3}$ (Krämer et al., 2009). Due to the size and number concentrations of ice crystals, cirrus clouds are optically thin and have a warming effect. They absorb longwave radiation and re-emit it back to the surface, whereas the reflection of shortwave radiation is much smaller due to their low optical thickness. Meanwhile, MPCs consist of both supercooled cloud droplets and ice crystals. They are optically thicker, and therefore have a higher net cooling effect compared to cirrus clouds. Their cloud radiative properties are highly influenced by the microphysical properties such as number and size distribution of the hydrometeors and therefore also by ice formation processes.

Due to the clouds large impact on the climate, ice formation and subsequent cloud formation have to be well parameterized in models. To reduce the uncertainties accompanied by different cloud and ice formation mechanisms, a better understanding of these processes must be gained.

### 1.2 Atmospheric ice formation

The formation of ice crystals (ice nucleation) can significantly change the cloud physical properties and additionally is one of the key processes that initiates precipitation, thus affecting cloud cover and lifetime (DeMott et al., 2010; Lohmann and Feichter, 2005).

Other than the effect on the radiative properties of the atmosphere and the climate as described in Section 1.1, ice formation is particularly relevant for precipitation formation from MPCs. Precipitation can be formed by droplet growth by diffusion and collision-coalescence; but these processes alone are not efficient processes in MPCs. On a global average in 50% of the precipitation events exceeding 1 mm d$^{-1}$, the formation and growth of ice crystals is involved somewhere in the cloud (Field and Heymsfield, 2015). As much as 80% of land-falling precipitation is initiated through the ice phase (Miilmenstüdt et al., 2015). In tropical
regions, the ice phase is decisive for 69% of the total precipitation (Lau and Wu, 2003). For mid-latitudes, precipitation from warm clouds without the ice phase being involved is even smaller. Warm clouds only account for 10% of the total global precipitation, which is also due to the smaller cloud droplet sizes over the continents in contrast to marine clouds (Mühlmenstädt et al., 2015). The microphysical processes occurring in clouds are challenging and provide the largest uncertainty in the climate system (Boucher et al., 2013).

MPCs are typically found at mid-levels in the troposphere where temperatures are between 273 K and 235 K as required for the co-existence of supercooled cloud droplets and ice crystals. Due to the vapor pressure over ice being smaller than the vapor pressure over water, growth by diffusion is favorable for ice crystals at the expense of cloud droplets (Murphy and Koop, 2005). Therefore in MPCs ice crystals can rapidly grow to large sizes while cloud droplets in the environment shrink due to the depletion of water vapor, leading to glaciation of the cloud. This process is known as the Wegener-Bergeron-Findeisen-Process (Bergeron, 1935; Findiesen et al., 1938; Wegener, 1911). It is most pronounced at 261 K, where the difference between the vapor pressure over ice and water is greatest. Secondary ice formation processes can additionally lead to an increase in the number of ice crystals (ice multiplication) by mechanical fracturing, shattering or rime splintering of existing ice crystals. Secondary ice formation by rime splintering is called the Hallett-Mossop process and takes place at warmer temperatures (265 − 270 K, Hallett and Mossop, 1974).

Ice nucleation in the atmosphere can occur through two main pathways. Homogeneous nucleation is a phase transition where water freezes without the aid of a foreign substance and occurs below 235 K, while heterogeneous nucleation takes place when an INP is required to initiate freezing and occurs already at warmer temperatures (Pruppacher and Klett, 1997).

### 1.2.1 Homogeneous ice nucleation

A brief summary of homogeneous ice nucleation based on the concept and equations of Volmer and Weber (1926), Pruppacher and Klett (1997) and references therein is given here: A nucleation process is specified by a phase transition from a parent phase (e.g. liquid phase) to a new phase (e.g. solid ice phase). The formation of the new phase starts with a cluster (ice embryo) of molecules, which reach a critical size beyond which it can grow to macroscopic size until the phase transition has completely taken place. For the formation of ice, the Gibbs free energy \( \Delta G_n \) for the formation of a cluster containing \( n \) molecules has to be overcome in order to initiate the phase change and reach a lower thermodynamic energy state. It can be derived by integrating the first law of thermodynamics for the thermodynamic potential \( G \):

\[
\Delta G_n = 4\pi r^2_n \sigma_{i,w}(T) + (\mu_i(T) - \mu_w(T)) \cdot n,
\]

where \( r_n \) is the radius of the cluster, \( \sigma_{i,w}(T) \) is the interfacial tension, and \( \mu_i(T) - \mu_w(T) \) is the chemical potential difference.
where the chemical potentials of the ice and the water phase are $\mu_i$ and $\mu_w$, $r_n$ is the radius of the cluster and $\sigma_{i,w}$ the surface tension between the ice and the water phase. The first term in Equation 1.1 is the surface term. It expresses the energy which is necessary to form the interface of the ice embryo. The second term (volume term) in Equation 1.1 shows the decrease in the chemical potential for the ice embryo in comparison to the parent phase. It can be expressed by the saturation vapor pressures over ice ($e_{\text{sat},i}$) and supercooled liquid water ($e_{\text{sat},w}$) as

$$\mu_i(T) - \mu_w(T) = -kT \ln \left( \frac{e_{\text{sat},w}(T)}{e_{\text{sat},i}(T)} \right),$$

with the Boltzmann constant $k$. Thus, the difference between the chemical potentials is dependent on the temperature, $T$. The ratio between the saturation vapor pressures over water and ice denotes the saturation ratio over ice

$$S_i = \frac{e_{\text{sat},w}(T)}{e_{\text{sat},i}(T)}.$$  

(1.3)

In a spherical ice embryo, the number of the water molecules, can be expressed through the radius of the ice embryo:

$$n = \frac{4\pi}{3} r_n^3 \nu_{\text{ice}}(T)$$

(1.4)

where $\nu_{\text{ice}}$ is the volume of a water molecule in ice. Thus, the Gibbs free energy can be written as:

$$\Delta G_n = 4\pi r_n^2 \sigma_{i,w}(T) - \frac{4\pi r_n^3 kT}{3} \ln S_i.$$  

(1.5)

For cases of small ice embryos, the dominating term is the surface term, thus, increasing $\Delta G_n$ until the energy barrier $\Delta G^*$ is reached. The energy barrier is given as (Ickes et al., 2015):

$$\Delta G^* = \frac{16\pi}{3} \frac{\nu_{\text{ice}}^2 \sigma_{i,w}^3}{(kT \ln S_i)^2}.$$  

(1.6)

The energy barrier shown in Figure 1.1a is the maximum in $\Delta G$ and the point at which the critical radius of the ice embryo, $r_c$, is reached. After this point, the embryo is in an energetically favorable state and spontaneous growth follows due to the decrease in energy and molecules of water are added. For the formation of an ice crystal, this energy barrier $\Delta G^*$ has to be overcome in the nucleation process. The energy barrier for the formation of an ice embryo depends on ambient conditions such as temperature and supersaturation (Eq. 1.6). Thus, the energy barrier decreases for higher supersaturations.

The homogeneous nucleation rate, $J_{\text{hom}}$, for the formation of a critical ice embryo is given by:

$$J_{\text{hom}} = K \exp\left(-\frac{\Delta G^*}{kT}\right)$$

(1.7)

where $K$ is the kinetic prefactor (Pruppacher and Klett, 1997).

In the atmosphere, homogeneous ice nucleation from the vapor phase (homogeneous de-
1.2. Atmospheric ice formation

Figure 1.1: a) Energy barrier $\Delta G^*$ for homogeneous and heterogeneous nucleation at $T = 253 K$ as a function of ice embryo radius. b) Different contact angles ($\theta$) of the INP are illustrated (Figure taken from Lohmann et al., 2016).

Position nucleation does not occur due to the high energy barrier and because ambient supersaturations do not exceed a few percent above saturation because of the presence of an aerosol particle. However, the surface tension between ice and water is much smaller and therefore homogeneous nucleation of ice in water or solution droplets is atmospherically more relevant. The rate for nucleation depends on the temperature, the nucleation time and water saturation. Experimentally, the nucleation rate ($J_{\text{hom}}$) can be described as

$$J_{\text{hom}} = \frac{-\ln(1-P)}{\nu_{\text{drop}} \cdot t_{\text{nuc}}}$$

(1.8)

with the probability $P$ of a droplet with volume $\nu_{\text{drop}}$ to freeze in the nucleation time ($t_{\text{nuc}}$).

For experimental studies, the residence time ($t_{\text{res}}$) is typically used analogously to $t_{\text{nuc}}$. Homogeneous nucleation in the atmosphere occurs at cold temperatures ($T < 235 K$) and therefore occurs in cirrus clouds or in conditions with deep convection such as in anvil cirrus clouds.

1.2.2 Heterogeneous ice nucleation

Heterogeneous ice nucleation due to the presence of an INP is initiated at warmer temperatures and lower supersaturations with respect to ice than those required for homogeneous nucleation. The INP reduces the energy barrier $\Delta G^*$, which leads to an increase in the nucleation rate $J_{\text{het}} > J_{\text{hom}}$. The energy barrier for heterogeneous freezing $\Delta G_{\text{het}}^*$ can be obtained
Figure 1.2: Homogeneous and heterogeneous ice nucleation modes. Trajectories in the atmosphere are illustrated for supersaturation with respect to ice ($S_i$) as a function of temperature ($T$). (Figure taken from Hoose and Möhler, 2012).

\[ \Delta G^*_{\text{het}} = f(\theta) \Delta G^* \]  

with the compatibility parameter $f$ reducing the energy barrier in the presence of an INP. The compatibility factor depends on the contact angle ($\theta$), which is the angle between the surface of the INP and the ice embryo as shown in Figure 1.1b. A small contact angle is referred to as a rather hydrophilic surface, which corresponds to a positive property of the INP surface for the ice embryo to form on. The (small) contact angle significantly reduces the energy barrier by reducing the number of water molecules required to form the critical ice embryo. In Figure 1.1a the relationship between the radius of the ice embryo and the energy barrier that has to be overcome is shown for different contact angles.

1.2.2.1 Heterogeneous ice nucleation pathways

Different pathways are possible for heterogeneous ice nucleation. They occur at different conditions with respect to cloud type, phase of the hydrometeors and temperature. Four heterogeneous ice nucleation pathways have been identified as atmospherically relevant (Curry and Webster, 1999; Pruppacher and Klett, 1997; Rogers and Yau, 1989), which were first described by Vali (1985). A summary of the known heterogeneous ice nucleation modes in the atmosphere is illustrated in Figure 1.2 with their formation trajectories with respect to temperature and saturation ratio. They are described in more detail below.

Immersion freezing is ice nucleation from the liquid phase. A CCN first activates into a cloud droplet prior to being exposed to ice nucleation conditions. The cloud droplets contain
1.2. Atmospheric ice formation

a solid and insoluble inclusion which can act as an INP. Typically, immersion freezing occurs in the atmosphere at water saturation. It is relevant in the atmosphere when cloud droplets already exist such as in MPCs. In contrast, immersion freezing of solution droplets could occur at subsaturated conditions with respect to water if the temperatures are low enough to overcome the freezing point depression.

Condensation freezing is the process where an intermediate liquid layer is formed on the INP. Cloud-free air can be exposed to saturated conditions with respect to water e.g. by ascending and reaching the condensation level at a supercooled temperature. When water saturation is approached, water vapor condenses on the INP providing an intermediate liquid phase on the surface of the particle prior to freezing (Pruppacher and Klett, 1997). This process is favored in particular when the INP contains soluble material, which can deliquesce prior to water saturation, forming a liquid layer on the surface of the particle. Due to the short intermediate liquid phase, condensation freezing only occurs in a small range of supersaturation conditions in the atmosphere.

Contact freezing is the process when a supercooled droplet and an INP collide, which induces freezing of the cloud droplet upon collision. Due to the pre-existence of cloud droplets, the process occurs at water saturation and is limited by the collision rate of the INP and the cloud droplet. The collision rate depends on the temperature gradient, Brownian motion, interception and impaction. A particular case, where contact freezing occurs below water saturation is evaporation freezing. It occurs when the cloud droplet shrinks and freezing takes place when the INP comes in contact with the surface of the droplet from the inside. It is also known as contact nucleation inside out (Durant and Shaw, 2005).

Deposition nucleation describes a process occurring at conditions below water saturation but supersaturated conditions with respect to ice. Water vapor deposits directly on the surface of an INP and nucleates to an ice crystal. This mechanism is often thought to be cirrus cloud relevant, when the water vapor for example deposits on mineral dust particles (Cziczo et al., 2013). In contrast to earlier findings by Roberts and Hallett (1968) and Schaller and Fukuta (1979), more recent studies have shown that deposition nucleation can occur at $S_i$ below 1.2 and warmer than 255 K (Kanji and Abbatt, 2006; Möhler et al., 2006; Welti et al., 2009). The distinction of deposition nucleation from other heterogeneous nucleation mechanisms such as immersion freezing or condensation freezing is not fully understood. Most recently, Marcolli (2014) suggested that deposition nucleation does not exist. Instead, the mechanism occurring is condensation freezing in pores, where the curved liquid phase can already be in equilibrium with the vapor phase before water saturation is reached due to the inverse Kelvin effect.

In MPCs, immersion freezing is found to dominate over deposition nucleation and condensation freezing. This was observed with LIDAR measurements in clouds at $T$ warmer than 253 K by Ansmann et al. (2008).
1.2.2.2 Approaches to describe heterogeneous ice formation

Independent of the heterogeneous ice nucleation pathway, two hypotheses exist to describe the ice nucleation process first, deterministic (singular) and second, stochastic, which will be summarized in the following.

**The singular hypothesis:**
The singular hypothesis is a deterministic approach, where each INP has distinct properties (temperature and supersaturation) at which it activates. Freezing is associated with active sites e.g. cracks, steps, faults or few molecules of contaminants on the surface of the INP. In this case, freezing occurs instantaneously and independent of time if the particles carries an active site and its characteristic conditions (temperature or supersaturation with respect to ice) are fulfilled. The number of active sites per particle increases with the surface area of the aerosol particle and is assumed to be uniform with particle size.

**The stochastic hypothesis:**
The frozen fraction of a population of cloud droplets depends not only on the available surface onto which the ice embryo can form, but is also a time dependent approach, where the probability of freezing increases with time. All embryos have equal probability to reach the critical size. The INP reduces the energy barrier and the freezing process can be described by the heterogeneous nucleation rate, $J_{het}$.

The Classical Nucleation Theory describes heterogeneous freezing as a stochastic process. Experimental studies investigating the time dependence of immersion freezing show a stochastic component of the ice nucleation process (Murray et al., 2011; Niedermeier et al., 2011; Pinti et al., 2012; Welti et al., 2012). However, differences found in the freezing temperatures of individual INPs for the same particle type and size cannot be explained by the stochastic process alone. It has to be assumed that INPs can be of different efficiencies such as differences in the active sites or contact angles, which is a deterministic contribution.

1.2.3 Characteristics of atmospheric INPs

Only few aerosol particles in the atmosphere are able to act as INPs, which are typically on the order of 1 in $10^6$ aerosol particles (Pruppacher and Klett, 1997). Besides the ice nucleation conditions also chemical and physical properties define the ice nucleation ability of aerosol particles.

1.2.3.1 Sources of atmospheric INPs

INPs are directly emitted into the atmosphere and appear in a wide variety of sizes and chemical compositions. In the ambient air, different techniques are used to investigate the chemical properties of ambient INPs in ice residual (IR) analyses (e.g., Kamphus et al., 2010; Worringen et al., 2015). The main groups of atmospherically relevant INPs are summarized
1.2. Atmospheric ice formation

by Hoose and Möhler (2012) together with a brief overview of potential sources. The sources of INPs include mineral dust, soot, biological particles, glassy aerosols, crystalline salts, soil dusts, biomass burning aerosol and other sources such as volcanic ash.

The most common and most studied type of INPs is mineral dust. It is of particular relevance due to its large abundance in the atmosphere resulting from large source regions (e.g. the Saharan desert) and large emission rates (Hoose and Möhler, 2012; Murray et al., 2012). Mineral dust includes both desert aerosol and soil dust from farmlands. Good INPs induce ice nucleation at much warmer temperatures than homogeneous freezing. Mineral dust particles were found to be efficient INPs even after long range transport in the atmosphere (DeMott et al., 2003b; Klein et al., 2010b; Sassen et al., 2003). Depending on the mineralogy of the dust, its IN ability changes significantly. K-feldspar was found to be the most active component tested in immersion freezing and deposition nucleation (Atkinson et al., 2013; Augustin-Bauditz et al., 2014; Yakobi-Hancock et al., 2013; Zimmermann et al., 2008; Zolles et al., 2015). The larger the surface area, the higher the probability of the particle to contain active sites. The size for a particle containing at least one active site is found to be 100 nm in diameter in the case of Arizona test dust (ATD) (Marcolli et al., 2007). The IN ability of mineral dust was found to increase with increasing particle size (Welti et al., 2009) and milling (Hiranuma et al., 2014; Zolles et al., 2015). Ice nucleation initiated by volcanic ash is not well understood as its freezing behavior was found to be contradictory (e.g., Bingemer et al., 2012; Hoyle et al., 2011).

Sources of soot particles include fossil fuel burning and biomass burning (e.g. wood stoves, agricultural fires and heating). The IN ability of soot particles in the deposition mode is contradictory as some studies found IN properties above homogeneous freezing and others not (Chou et al., 2011; Crawford et al., 2011; DeMott et al., 1999; Kanji and Abbatt, 2006; Kanji et al., 2011; Koehler et al., 2009). However, soot can varies in composition and often contains organic carbon depending on the combustion technique (Möhler et al., 2005), which may change the IN ability.

Primary biological aerosol particles (PBAP) are naturally emitted aerosol particles, that consist of pollen, fungal spores, bacteria and biomass such as plant fragments. Some species of bacteria were found to nucleate ice at very warm subzero temperatures (e.g. Snomax®, Wex et al., 2015). However, the atmospheric relevance of PBAP mainly depends on the atmospheric concentration and emission rates which are typically orders of magnitudes smaller compared with those of mineral dust (Despres et al., 2012). In ambient measurements, an increase in the INP concentration after precipitation was found to be associated with an increase of bioaerosol particles (Huffman et al., 2013; Prenni et al., 2013). It was found that the ice nucleation ability can be associated with ice nucleating macro-molecules (INMs) separated from the biological carrier such as pollen grains (Augustin et al., 2013; Pummer et al., 2012). Other sources for atmospheric INPs are metal oxides from smelting and aircraft emissions, organics, glassy aerosols and secondary organic aerosol and crystalline salts (e.g. ammonium sulphate, Abbatt et al. (2006) or oxalic acid, Zobrist et al. (2006)).

In the atmosphere, aerosol particles can be exposed to conditions that may change their IN
properties. This includes processes such as aging in acidic environments that can irreversibly suppress ice nucleation (e.g., Sullivan et al., 2010) or mixing with biological material that can increase the IN ability of the particles (e.g., Augustin-Bauditz et al., 2016).

### 1.2.3.2 Requirements of INPs

The prerequisites of INPs are not completely understood. Pruppacher and Klett (1997) identified five properties of the INP that promote heterogeneous ice nucleation: 1) Insolubility to provide a solid surface to nucleate ice upon, 2) size, 3) free hydrogen bonds on the surface of the INP, 4) a crystallographic structure which is similar to that of ice crystals and 5) heterogeneities such as steps, cracks, or cavities on the surface. Insolubility is common for most of the typical INPs such as mineral dust, bioparticles or soot. However, aerosol particles which are crystalline at specific conditions also act as INPs such as crystalline ammonium sulphate in the deposition mode or glassy aerosols in the immersion mode (Abbatt et al., 2006; Murray et al., 2010). The size of the particle needs to be comparable or larger than an ice germ to provide a surface for ice to nucleate upon. In the atmosphere, typical IRs were found to be smaller than 300 nm for a study in MPCs in the Swiss alps (Mertes et al., 2007). Laboratory studies found size effects for particle sizes larger than 200 nm (e.g., Archuleta et al., 2005; Connolly et al., 2009; Kanji and Abbatt, 2009; Welti et al., 2009). The INPs associated with pollen grains, were found to induce freezing being of much smaller size than those of pollen grains themselves and are known as ice active macro-molecules (INMs) (Augustin et al., 2013; Pummer et al., 2012).

### 1.3 Ice nucleation measurement techniques

INPs can be measured with various techniques and experimental principles. Online instruments are able to detect INP concentrations in-situ such as continuous flow diffusion chambers (CFDCs). Other sample techniques are based on offline techniques such as sampling aerosol particles on filters or suspensions prior to exposing them to ice nucleation conditions. Expansion chambers have large sample volumes in which clouds can be formed under controlled conditions and the ice nucleation properties can be investigated by analysis of the hydrometeors and unactivated aerosol during cloud formation. An overview of most common techniques is given in Table 1.1 and a brief description is given in the following.

#### Continuous flow diffusion chambers

In the past, various instruments to determine the INP concentration depending on temperature and relative humidity have been developed. These devices are based on different setups, but all use a similar experimental principle. The most common INP counter, a CFDC, was
### Table 1.1: An overview of common ice nucleation techniques and their characteristics.

Instrument specific ice nucleation modes are listed as homogeneous ice nucleation (hom), deposition nucleation (dep), condensation freezing (cond), immersion freezing (imm) for cloud droplet activation prior to exposure to ice nucleation conditions and contact freezing (contact).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Freezing modes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuous flow diffusion ch.</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CSU-CFDC (cylindrical)</td>
<td>hom, dep/cond</td>
<td>e.g. Rogers et al. (2001b)</td>
</tr>
<tr>
<td>ZINC (parallel plate)</td>
<td>hom, dep/cond</td>
<td>Stetzer et al. (2008)</td>
</tr>
<tr>
<td>PINC (parallel plate)</td>
<td>hom, dep/cond</td>
<td>Chou et al. (2011)</td>
</tr>
<tr>
<td>IMCA-ZINC</td>
<td>hom, imm</td>
<td>Lüönd et al. (2010)</td>
</tr>
<tr>
<td>PIMCA-PINC</td>
<td>hom, imm</td>
<td>Kohn et al. (2016)</td>
</tr>
<tr>
<td>SPIN (parallel plate)</td>
<td>hom, dep/cond</td>
<td>Garimella et al. (2016)</td>
</tr>
<tr>
<td>UT-CFDC (horiz. parallel plate)</td>
<td>hom, dep/cond</td>
<td>Kanji and Abbatt (2009)</td>
</tr>
<tr>
<td>PNNL-CIC (parallel plate)</td>
<td>hom, dep/cond</td>
<td>Friedman et al. (2011)</td>
</tr>
<tr>
<td>CLINCH</td>
<td>contact</td>
<td>Ladino et al. (2011)</td>
</tr>
<tr>
<td><strong>Expansion chamber</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AIDA</td>
<td>hom, dep/cond/imm</td>
<td>e.g. Möhler et al. (2006)</td>
</tr>
<tr>
<td>MICC</td>
<td>hom, dep/cond/imm</td>
<td>Connolly et al. (2012)</td>
</tr>
<tr>
<td><strong>Flow tube</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LACIS</td>
<td>hom, imm</td>
<td>Hartmann et al. (2011)</td>
</tr>
<tr>
<td>FINCH</td>
<td></td>
<td>Bundke et al. (2008)</td>
</tr>
<tr>
<td><strong>Wind tunnel</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mainz-WT</td>
<td></td>
<td>e.g. Szakáll et al. (2009)</td>
</tr>
<tr>
<td><strong>Static isoth. diffusion ch.</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FRIDGE</td>
<td>dep/cond</td>
<td>e.g. Klein et al. (2010a)</td>
</tr>
<tr>
<td></td>
<td>imm</td>
<td>Schrod et al. (2016)</td>
</tr>
<tr>
<td><strong>Other methods</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drop freezing (impingers)</td>
<td>imm</td>
<td>Hader et al. (2014)</td>
</tr>
<tr>
<td>Drop freezing (PM$_{10}$ filter)</td>
<td>imm</td>
<td>Conen et al. (2012)</td>
</tr>
<tr>
<td>Drop freezing (coldstage)</td>
<td>imm</td>
<td>e.g. Wright and Petters (2013)</td>
</tr>
<tr>
<td>DSC</td>
<td>imm</td>
<td>Zobrist et al. (2006)</td>
</tr>
<tr>
<td>Leeds-NIPI</td>
<td>imm</td>
<td>Whale et al. (2015)</td>
</tr>
<tr>
<td>Cryo-microscopy</td>
<td>imm</td>
<td>Pummer et al. (2012)</td>
</tr>
<tr>
<td>BINARY</td>
<td>imm</td>
<td>Budke and Koop (2015)</td>
</tr>
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</table>

designed to nucleate ice crystals at prescribed relative humidities and temperatures relevant for atmospheric ice nucleation. Briefly, a CFDC consists of two (cylindrical or parallel-plate) ice-coated walls. A temperature gradient is applied between the two ice-coated walls. This establishes an ice supersaturation profile between the two plates with its maximum close to the center of the chamber. The sample aerosol fed into the chamber is layered between a particle-free sheath flow which allows for a narrow sample lamina reducing the uncertainty in relative humidity ($RH$) and temperature. The aerosol is exposed to steady state conditions in $RH$ and $T$ for a few seconds during the experiment, which allows ice to nucleate. Above
water saturation, cloud droplets can activate and grow to similar sizes as the ice particles. In order to remove erroneous counting of the cloud droplets as ice, an evaporation section follows the ice growth section of the chamber. The evaporation section is held at ice saturation by setting both walls to the same temperature, ensuring that the cloud droplets evaporate while the ice crystals maintain their size. Ice crystals are counted at the bottom of the chamber with an optical particle counter (OPC) and are distinguished from unactivated aerosol particles by an experiment specific size threshold. The number of ice crystals per volume of air (INP concentration) is derived from the sample air flowing through the chamber. In laboratory experiments, often the activated fraction (AF) being the ratio of ice crystals to the total number of aerosol particles entering the chamber is derived.

This technique was first described by Rogers (1988) with the Colorado State University-CFDC (CSU-CFDC, cylindrical chamber walls). A parallel-plate design was later introduced as the Zurich Ice Nucleation Chamber (ZINC, Stetzer et al., 2008) and in a portable version with the Portable Ice Nucleation Chamber (PINC, Chou et al., 2011). The same parallel-plate design is used in different instruments including the University of Toronto-CFDC (UT-CFDC). A horizontal design was introduced by Kanji and Abbatt (2009) (the University of Toronto-CFDC, UT-CFDC). CFDC instruments allow for ice nucleation measurements in the homogeneous regime and in the heterogeneous regime at ice supersaturated conditions and below and a few percent above water saturation. The highest possible supersaturation condition is limited by the droplet breakthrough. The droplet breakthrough is the instrument specific supersaturation threshold, after which cloud droplets cannot sufficiently be evaporated in the evaporation section prior to ice detection. In this case, cloud droplets may falsely be counted as ice crystals. An additional possible limitation is the unknown dynamical influence for measurements above water saturation. Large temperature gradients between the closely spaced chamber walls can change the dynamic conditions in the chamber, e.g. by establishing a reverse flow on the warm chamber wall due to buoyancy, which can lead to particle losses. In experiments by DeMott et al. (2015) a wider sample lamina than expected has been observed, which increases the uncertainty in RH and T significantly.

An extension to ZINC, the Immersion Mode Cooling chamber (IMCA, Löönd et al., 2010) allows for cloud droplet activation prior to exposing the supercooled cloud droplet to ice nucleation conditions in ZINC. A portable setup, the Portable Immersion Mode Cooling chamber (PIMCA) as an extension to PINC is introduced by Kohn et al. (2016) and is the focus of Chapter 2 of this thesis. In IMCA-ZINC (PIMCA-PINC), cloud droplets and ice crystals are distinguished via depolarization with the Ice Optical DEtector (IODE, Nicolet et al., 2010) and the frozen fraction (FF) of cloud droplets is obtained. In contrast to AF, the FF is the ratio between ice crystals and the number of total particles i.e., the sum of detected cloud droplets and ice crystals.

In addition to the traditional CFDC instruments, the CLINCH chamber (Ladino et al. 2011) allows for measurements in the contact freezing mode. Cloud droplets are exposed to a
population of aerosol particles which collide and induce freezing of the cloud droplets on collision.

Flow tube

The Leipzig Aerosol and Cloud Interaction Simulator (LACIS, Hartmann et al., 2011; Stratmann et al., 2004) is a laminar flow tube for ice nucleation experiments in which the freezing conditions of single-immersed aerosol particles can be investigated. Activation of cloud droplets prior to further supercooling allows for measurements in the immersion freezing mode. LACIS consists of a 7 m tube, with sections that can be independently temperature-controlled. Humidified sheath air and the aerosol sample are fed into the tube at the top. The sheath air provides the vapor source to obtain supersaturation conditions during the cooling of the aerosol traveling through the tube. Subsequent supercooling leads to prescribed sub-zero temperatures at the bottom of LACIS where particles are detected and distinguished as cloud droplets and ice crystals by measurements with the Thermo-stabilized Optical Particle Spectrometer (TOPS-Ice, Clauss et al., 2013).

Bundke et al. (2008) introduced a technique with a similar principle, which is an in-situ chamber using mixing of the sample aerosol with a warm, humid and a cold, dry air mass to achieve supersaturation called the Fast Ice Nucleus CHamber. FINCH permits sample volumes of up to 10 liters per minute and detection of INPs is realized by separating crystals with a virtual impactor and by phase discrimination (DeMott et al., 2011).

Wind tunnel

A vertical wind tunnel provides measurements of droplets levitated in a vertical air stream. The air stream is $T$ and $RH$ controlled. The droplets containing sample material at freezing conditions are observed by optically detecting the freezing of cloud droplets. When freezing occurs, the abrupt reduction in the terminal velocity can be observed (Pitter and Pruppacher, 1973). A more detailed description can be found elsewhere (e.g. the Mainz wind tunnel, Diehl et al., 2011; Szakáll et al., 2009).

Static isothermal diffusion chamber

Filter techniques have been used for many decades to collect aerosol particles for investigations of their IN properties (e.g., Bigg, 1967). A more recent laboratory-based instrument which investigates the IN ability of individual aerosol particles on a solid substrate is the static isothermal diffusion chamber (FRIDGE, Bundke et al., 2008; Klein et al., 2010a). Aerosol particles are collected on hydrophobic silicon wafers by electrostatic precipitation with a small, portable electrostatic sampling unit in which an electrostatic field is deployed. Filters are
subsequently analyzed in the laboratory. For this purpose, the filter is cooled in a low pressure chamber. An external water vapor source with set ice supersaturation conditions provides the water vapor for the growth of ice crystals, which are optically detected with a camera. The INP concentrations are obtained with the volume of air sampled per filter. Measurements can be conducted in the deposition nucleation and condensation freezing modes. Most recently, an improvement and adaptation was introduced allowing for measurements in the immersion freezing by suspending aerosol in a liquid solution (see Schrod et al., 2016, for more details).

**Expansion chambers**

Expansion chambers are used to mimic atmospheric processes of cloud and ice formation in the laboratory. The process in an expansion chamber mimics the lifting of an air parcel and the subsequent cloud formation in the atmosphere. The AIDA cloud chamber (e.g., Mangold et al., 2005; Möhler et al., 2006) is an adiabatic expansion chamber, in which aerosol particles are exposed to supersaturation and ice nucleation temperatures by decreasing the pressure in the chamber. The size and number concentrations of ice crystals, cloud droplets and unactivated aerosol particles are detected with standard aerosol measurement techniques. Experiments can be performed for relative humidities up to water saturation. Homogeneous nucleation, deposition nucleation as well as condensation and immersion freezing experiments can be conducted. A similar instrument is the Manchester Ice Cloud Chamber (MICC, Connolly et al., 2012). It is a large fall tube with a diameter of 1 m and also operates on the principle of adiabatic expansion.

**Other IN detection methods**

In addition to the techniques described above, multiple filter techniques and bulk sampling methods are used for the quantification of INPs in the lab and for ambient sampling. A liquid impinger, also known as the swirling aerosol collector, is a technique to collect ambient aerosols with particle sizes larger than 0.5µm aerodynamic diameter by liquid impaction into a suspension, while the sampled air volume is controlled and quantified (Hader et al., 2014). A recent study by Conen et al. (2012) introduced a method to obtain INPs from PM$_{10}$ filters, which are widely used to monitor air quality. Small cut-outs of the filters are used for ice nucleation measurements after suspension in a known volume of pure water. The air sampled per filter is obtained from the flow rate of the high volume sampler. Both sampling methods allow for analysis in the laboratory via a drop freezing array. The sample is distributed into small aliquots and exposed to ice nucleation temperatures in a cooling bath to obtain the freezing spectra. This is either done by dividing the sample suspension from impinger sampling into aliquots or by distributing the filter cut-outs (∼2 mm in diameter) and suspending each cut-out in an aliquot of pure water.

The differential scanning calorimeter (DSC) can also be used to obtain the ice nucleation
1.4. Motivation and objectives

Despite the numerous studies on ice nucleation, the atmospheric importance of the heterogeneous ice nucleation modes is still not well understood. Based on radar and LIDAR measurements, Westbrook and Illingworth (2011) found that 95% of ice particles formed at temperatures above 253 K originated from a supercooled droplet. In stratiform clouds at temperatures above 253 K, Ansmann et al. (2008) observed the liquid phase to be a necessary prerequisite for ice formation and the development of MPCs. Murray et al. (2012) summarized based on previous field experiments and modeling studies that liquid water droplets are a prerequisite for ice formation. Therefore, a better understanding of INPs that act in the immersion mode is needed due to their large role in atmospheric ice formation.

Ice nucleation techniques for ambient measurements in the immersion mode are related to bulk measurements and droplet freezing arrays. Despite the simple method and performance of these techniques, a major disadvantage is that INP concentrations are only related to the most active INP in the sample volume tested, whereas potential INPs which are less efficient are not accounted for. Additionally, filter measurements often have low temporal resolutions due to longer aerosol sampling times required for a sufficiently large number of aerosol particles to be sampled. In contrast to that, methods with single-immersed aerosol particles such as IMCA-ZINC and LACIS allow for the investigation of the IN properties of individual particles. Immersion freezing on individual aerosol particles can be performed at much colder temperatures because all potential INPs are investigated rather than the best INP in a sample volume containing multiple potential INPs. Both of these instruments are real-time instruments, but are only suitable for the laboratory. A portable setup of this kind to measure ambient INPs on single-immersed aerosol particles is so far not available.

Ambient measurements are needed to gain a better knowledge about INPs. Parameterizations for regional scale and climate modeling are often empirical and based on measurements in the laboratory or data from ambient measurements (DeMott et al., 2010, 2015; Lohmann and Diehl, 2006; Murray et al., 2011; Niemand et al., 2012; Phillips et al., 2008; Tobo et al., 2013). However, a good predictability of INP concentrations, which is necessary to simulate ice crystal number concentrations in clouds correctly, remains difficult due to scattering in
the data and shows the need of a higher temporal and spatial density of INP measurements in the atmosphere. The development of more flexible instrumentation is needed to understand immersion freezing in the atmosphere. Furthermore, the development of such a method allows for measurements extending the temperature regime commonly used for ambient samples of immersion freezing techniques of bulk samples. Real-time measurements provide a higher temporal resolution for ambient INP sampling. This allows for investigating which environmental conditions trigger the INP concentrations when combined with measurements of meteorological conditions and aerosol properties such as number and size distribution leading to a better understanding of conditions at which ice formations occurs.

Mineral dust particles have been known to act as good INPs and are of interest in ice nucleation research due to their high atmospheric abundance for a long time. Bioaerosol particles such as pollen, bacteria and fungi were found to induce ice nucleation at relatively warm subzero temperatures and therefore induce ice formation much earlier in the atmosphere. However, the uncertainties in the understanding and quantification of the ice nucleation efficiency of biological particles remains large (DeMott and Prenni, 2010; Möhler et al., 2007). Also, the relative importance of biological INPs is likely to vary on regional and seasonal scales analogous to that of the observed bioaerosol (Burrows et al., 2009; DeMott and Prenni, 2010). The relationship of biological INP sources, their distribution, which factors contribute to their IN ability and their atmospheric relevance remain uncertain and request further investigation.

Which heterogeneous ice nucleation mechanisms occur in the atmosphere under which conditions remain unclear. A number of different ice nucleation techniques make the direct comparison of measurements and the interpretation of data difficult. To better understand and potentially reduce the uncertainty between numerous IN measurements techniques, inter-comparison campaigns are conducted to compare different IN measurement techniques under comparable conditions in the laboratory (e.g., Hiranuma et al., 2015; Wex et al., 2014). Parallel measurements are in particular needed, because experimental designs differ. While sample specific differences can be ruled out by distributing the same sample to different laboratories and instruments, factors influenced by particle treatment and particle generation or differences by the instruments itself can not be excluded. For these tests, parallel measurements are necessary requiring portable instrumentation.

1.5 Outline of the present thesis

Within this work, a new instrument capable of ice nucleation measurements in the immersion mode on single-immersed aerosol particles is introduced. The portable setup has two advantages: It allows for ambient measurements and inter-comparison with other non-portable ice nucleation techniques addressing the current needs of ice nucleation research summarized in Section 1.4. This thesis is structured as follows:
In Chapter 2, a new instrument based on the laboratory version IMCA-ZINC is introduced. The new Portable Immersion Mode Cooling chAmber (PIMCA) coupled to PINC is the first instrument allowing for ice nucleation experiments on single-immersed aerosol in a portable setup, which can also be deployed in the field. The specifications of the new setup are described. The geometry of the chamber is adapted from the laboratory instrument and computational fluid dynamics simulations are used to predict residence time and cloud droplet size during ice nucleation conditions. Validation experiments for comparison with theory and literature are shown. Results from the first deployment in the field during the Zurich AMBi-ent Immersion freezing Study (ZAMBIS) are presented.

Chapter 3 gives further insight into the ZAMBIS field campaign with two additional ice nucleation techniques for immersion freezing measurements. The combination of the three ice nucleation approaches during ZAMBIS allows for observations of INP concentrations over a wide temperature range. Environmental conditions such as meteorology, pollen concentrations and the abundance of bioaerosol particles driving the INP concentration are discussed.

In Chapter 4, the PIMCA-PINC setup is compared in laboratory experiments during the Leipzig Ice Nucleation chamber Comparison (LINC) in the immersion mode. Furthermore, a comparison with two CFDC instruments, PINC and SPIN, is presented and discussed for possible differences between measurements in the immersion and condensation freezing mode. The summary of the research in this thesis is presented in Chapter 5 and lastly this thesis is concluded with an outlook for future work.
Chapter 2

Immersion mode ice nucleation measurements with the new Portable Immersion Mode Cooling chAmber (PIMCA)

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Immersion mode ice nucleation measurements with the new Portable Immersion Mode Cooling Chamber (PIMCA)

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Abstract The new Portable Immersion Mode Cooling chamber (PIMCA) has been developed for online immersion freezing of single-immersed aerosol particles. PIMCA is a vertical extension of the established Portable Ice Nucleation Chamber (PIN). PIMCA immerses aerosol particles into cloud droplets before they enter PINC. Immersion freezing experiments on cloud droplets with a radius of 5–7 μm at a prescribed supercooled temperature (T) and water saturation can be conducted, while other ice nucleation mechanisms (deposition, condensation, and contact mode) are excluded. Validation experiments on reference aerosol (kaolinite, ammonium sulfate, and ammonium nitrate) showed good agreement with theory and literature. The PIMCA-PINC setup was tested in the field during the Zurich Ambient Immersion Freezing Study (ZAMBIS) in spring 2014 in Zurich, Switzerland. Significant concentrations of submicron ambient aerosol triggering immersion freezing at T > 236 K were rare. The mean frozen cloud droplet number concentration was estimated to be 7.22 · 10⁵ L⁻¹ for T < 238 K and determined from the measured frozen fraction and cloud condensation nuclei (CCN) concentrations predicted for the site at a typical supersaturation of SS = 0.3%. This value should be considered as an upper limit of cloud droplet freezing via immersion and homogeneous freezing processes. The predicted ice nucleating particle (INP) concentration based on measured total aerosol larger than 0.5 μm and the parameterization by DeMott et al. (2010) at T = 238 K is INP₀,₀₁₀ = 54 ± 39 L⁻¹. This is a lower limit as supermicron particles were not sampled with PIMCA-PINC during ZAMBIS.

1. Introduction

The Earth’s energy and radiation budget is strongly coupled to the presence of clouds, which influence the hydrological cycle by transporting water and are necessary for the formation of precipitation in the atmosphere. Hydrometeors like cloud droplets and, in particular, ice crystals which are found in cirrus and mixed-phase clouds influence the radiative budget by reflecting incoming solar radiation back to space and by absorbing outgoing (terrestrial) radiation from the Earth’s surface. These effects can lead to a cooling or warming of the atmosphere. The formation of primary ice crystals (ice nucleation) can significantly change the cloud physical properties. The ice phase in clouds is relevant for initiating precipitation and affects cloud cover and lifetime [DeMott et al., 2010; Lohmann and Feichter, 2005]. It is important to understand the processes leading to ice formation in the atmosphere to appropriately include them into global circulation models (GCMs).

Ice nucleation can take place in the atmosphere via different pathways. Homogeneous freezing occurs at temperatures below 235 K [Pruppacher and Klett, 1997]. Heterogeneous nucleation can take place where an aerosol particle called ice nucleating particle (INP) provides a surface for ice to nucleate upon, leading to ice formation at smaller supersaturations with respect to ice and supercooling (T > 235 K) than is required for homogeneous freezing [Vali et al., 2015]. Although homogeneous ice nucleation can be very active at low temperatures prevailing at high altitudes, the dominance of homogeneous freezing has been questioned recently by Cziczo et al. (2013) who found indications for heterogeneous ice nucleation at cirrus cloud conditions. Heterogeneous ice nucleation can occur via four mechanisms, where different phases of water are involved. Mechanisms are summarized in Vali [1985], and later, with more specific distinctions by Vali et al. [2015]. In summary, deposition nucleation occurs when water vapor directly deposits on an INP and forms an ice crystal without an intermediate liquid phase being involved. Immersion freezing occurs when an INP immersed in a supercooled droplet initiates freezing upon sufficient supercooling, while condensation freezing takes place when water vapor condenses on a supercooled INP followed by freezing during or immediately
after the condensation process. Lastly, contact freezing can occur when a supercooled cloud droplet collides with an INP. Recently, the distinction between the freezing modes has been challenged by some studies. Marcilli (2014) hypothesized that deposition nucleation may in fact be immersion freezing of trapped water in voids and cavities at subsaturated conditions with respect to water, which implies a pore condensation and freezing mechanism rather than deposition nucleation on the particle surface.

The ice nucleation activity depends on the physical and chemical properties of the aerosol particles, with insolubility, size, chemical bonding, active sites, and crystallographic structures being potential requirements [Pruppacher and Klett, 1997]. This knowledge has been challenged in the past, for example, by observation that crystalline ammonium sulfate acts as deposition mode INP [Abbatt et al., 2006] or glassy aerosols as immersion INP [Murray et al., 2010], which is in contrast to the necessity of a crystallographic structure or insolubility requirement.

Mixed-phase clouds, which consist of supercooled droplets and ice crystals, exist between ~236 K and 273 K [Murray et al., 2012]. Within the numerous studies on ice nucleation, the atmospheric importance of the four heterogeneous ice nucleation modes which can occur in mixed-phase clouds has not been well quantified. From lidar observations it has been found that supercooled droplets are present prior to the formation of ice crystals in mixed-phase clouds [e.g., Ansmann et al., 2009; Westbrook and Illingworth, 2011]. Liquid water droplets are a prerequisite for ice formation, and imply deposition nucleation in mixed-phase clouds plays a minor role [Murray et al., 2012]. Due to thermophoretic effects, which is the force exerted by a temperature gradient, contact freezing could be the favored nucleation process for evaporating droplets, but these droplets might even evaporate before freezing [Phillips et al., 2007]. Therefore, it is suggested that immersion freezing is the most important freezing mechanism in mixed-phase clouds.

Investigation of ambient INPs is feasible with various methods: INP concentration measurements of aerosol particles collected on filters [e.g., Bigg, 1967; Klein et al., 2010; Conen et al., 2012; Ardon-Dryer and Levin, 2014] or in solutions [e.g., Hader et al., 2014] have been conducted at various field sites. Recent studies of immersion freezing INP concentrations apply a droplet freezing array for which a number of aerosol particles are collected in a solution, on a filter or by taking samples of cloud, rain, or snow water [e.g., Hader et al., 2014; Stopelli et al., 2014; Wright et al., 2014; Conen et al., 2012, 2015; Joly et al., 2014; Mason et al., 2015a, 2016]. In these measurements, the abundance of active particles is investigated in suspensions, which contain multiple aerosol particles and with that multiple potential INPs. The measured freezing temperature belongs to the most active INP per sample volume. These methods can be used for ambient studies; however, they are not able to investigate the ice nucleation activity of single-immersed aerosol particles with a high temporal resolution.

To investigate the variability in INP concentration, continuous flow diffusion chambers (CFDCs) measure the ice nucleation activity for individual particles in real time. Originally, a cylindrical design is from the Colorado State University (CSU-CFDC) [Rogers, 1988]. Ambient aerosol is exposed in the chamber to a well-defined region between the inner and outer ice-coated chamber walls, which are the source for water vapor and held at different temperatures creating a temperature gradient and allowing control of the supersaturation conditions at a desired sample temperature. The concentration of INPs is obtained by counting the ice crystals downstream of the chamber. A parallel-plate design following the same experimental principle is the Zurich Ice Nucleation Chamber (ZINC) [Stetzer et al., 2008] and its portable version PINC for field studies [Chou et al., 2011], as well as the horizontal parallel-plate design by the University of Toronto (UT-CFDC) [Kanji and Abbatt, 2009]. Studies with CFDC instruments observe ice nucleation in the water subsaturated regime and a few percent in relative humidity (RH) above water saturation [e.g., Rogers et al., 1998; DeMott et al., 2010; Chou et al., 2011; Boose et al., 2016] but cannot isolate the immersion freezing mode with CCN activation prior to exposure to ice nucleation temperatures. To our knowledge, only four other instruments are able to activate single aerosol particles into cloud droplets prior to further supercooling at which ice nucleation is studied. These techniques are the Immersion Mode Cooling chAmber (IMCA) [Liünd et al., 2010; Welti et al., 2012] coupled to ZINC and the Leipzig Aerosol Cloud Interaction Simulator (LACIS) [Stratmann et al., 2004; Niedermeier et al., 2010; Hartmann et al., 2011]. Two other instruments utilizing the technique of cloud expansion chambers, the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) cloud chamber [Niemand et al., 2012] and Manchester Ice Cloud Chamber (MICC) [Conolly et al., 2012] are able to investigate immersion freezing of single-immersed particles while achieving water drop activation at supercooled conditions prior to freezing.
CCN activation of aerosol is achieved at temperatures above the freezing point of water in IMCA, the vertical extension of ZINC. Cloud droplets with single-immersed aerosol particles are subsequently cooled prior to ice nucleation in ZINC. LACIS is a laminar flow tube with a total length of 7 m, where water vapor is sourced from humidified sheath air. The aerosol is exposed to supersaturation conditions by controlled cooling of prehumidified air. Additional cooling results in immersion freezing of supercooled cloud droplets at the ice nucleation temperature. By contrast, the AIDA cloud chamber and the MICC are not continuous flow diffusion but expansion chambers. Aerosol particles are dispersed into the chamber prior to an expansion experiment already at supercooled temperatures. The aerosol vessel is evacuated to reduce the pressure, which allows a controlled further decrease in temperature in the chamber and leads to supersaturation conditions resulting in the formation of a liquid cloud in which ice nucleation can occur. All four methods are laboratory instruments and are stationary.

In this work, we present the newly developed Portable Immersion Mode Cooling chAmber (PIMCA) instrument as an extension to PINC, allowing activation of aerosol particles to cloud droplets for immersion mode experiments on single-immersed aerosol particles. PIMCA is portable and can be deployed in the field and to other laboratories for measurement campaigns. We introduce the advanced design and discuss adaptations in comparison to the laboratory chamber IMCA [Lüönd et al., 2010]. Validation experiments coupled to PINC [Chou et al., 2011] are presented. Droplet evolution calculations and validation experiments support calculations of residence time, droplet size, and comparison to reference aerosols, respectively. Data obtained during the first field study with PIMCA-PINC conducted in spring 2014 at an urban-forest site in Switzerland are presented. The atmospheric implications of the experiments are discussed.

2. Experimental Method
The experimental method used for this study comprises of three main devices to measure immersion mode ice nucleation, namely, PINC (section 2.1), its vertical extension for immersion mode experiments, PIMCA (section 2.2) and for ice detection, the Ice Optical DEtector, IODE (section 2.3). A schematic of the instrumental setup is shown in Figure 1. In the immersion freezing mode conducted in this work, aerosol particles are first activated and grown to cloud droplets in PIMCA. Droplets containing one immersed particle are supercooled before freezing occurs at isothermal conditions in the main chamber of PINC at water saturation. Ice crystals and cloud droplets are detected at the bottom of the chamber with IODE to obtain a frozen fraction (FF).

2.1. PINC
PINC has previously been described in detail by Chou et al. [2011]. Briefly, it is a continuous flow diffusion chamber, and its measurement principle follows the CSU-CFDC [Rogers, 1988]. PINC can be operated for sampling in the temperature range 231−265 K. At the extreme ends of the temperature range, the instrument can be run from below water saturation to a maximum relative humidity with respect to water, RHw = 100%. For intermediate temperatures RHw up to 108% can be achieved depending on set sample T. The instrument is a vertical chamber consisting of two temperature controlled parallel walls. Prior to an experiment, a thin ice layer is generated on the inner chamber walls. To achieve supersaturation conditions with respect to ice, a (horizontal) temperature gradient is applied between the chamber walls. This results in a parabolic ice supersaturation profile between the two chamber walls with its peak saturation closer to the colder wall. The sample aerosol flow is layered within a particle-free sheath air flow on either side of the aerosol layer to ensure well-defined temperature and relative humidity conditions in the sample layer. The lowest section of PINC is an evaporation section, whose walls are both held at the same temperature as the warm wall of the PINC main chamber to maintain ice saturation but water subsaturation causing small droplets to evaporate. This feature is needed for deposition nucleation/condensation freezing experiments, for which an optical particle counter (OPC) distinguishes ice crystals from unactivated aerosol only by a size threshold. More details on PINC experiments on a variety of aerosol samples and field studies can be found elsewhere [Chou et al., 2011; Kanji et al., 2013; Hiranuma et al., 2015; Wex et al., 2015; Boose et al., 2016].

2.2. Portable Immersion Mode Cooling chAmber (PIMCA)
The design of PIMCA follows the same parallel plate geometry as PINC but with a narrower plate distance in the upper droplet creating section for good control of T and RH. Both walls are temperature controlled in order to apply a lateral temperature gradient between the plates. Additionally, a vertical temperature gradient along each wall is applied in order to gradually transition the droplets to the subzero temperatures in PINC. As a source of water vapor and to create supersaturation with respect to water in the chamber, continuously wetted filter papers are mounted to the inner walls of PIMCA (Figure 1, blue layer on PIMCA inner walls).
Figure 1. PIMCA-PINC instrumental setup. (left) The three main chamber sections and the two detection devices (IODE and the optical particle counter (OPC)—the latter is used for the PINC-mode only) in frontal view. (right) A vertical cross section of the chamber illustrates the particle trajectory during the experiment. IODE is positioned at the evaporation section, and the laser beam is indicated as orange line. A horizontal temperature gradient ("cold" and "warm") as well as a vertical temperature gradient is applied to the chamber walls. The color code represents the temperature of the chamber walls. PIMCA has a cold (purple) and warm (red) chamber wall at $T > 273$ K. In PINC, wall temperatures are cold (dark blue) and warm (blue) at $T < 273$ K. The evaporation section in PINC is held at the PINC warm wall temperature without applying a horizontal temperature gradient (blue). Inner chamber walls are lined with humidified filter paper in PIMCA (dark layer) and with an ice layer in the lower section of PIMCA and PINC (light grey layer).

The PIMCA-PINC setup has a total height of 2.1 m (net chamber size 1.52 m). In the upper part of the chamber, a wall temperature difference $\Delta T = 25$ K is controlled by heating and cooling units for a sample temperature of $T = 313$ K after the aerosol particles have entered the chamber through a vertical and preheated sample inlet ($T = 313$ K) into the droplet activation and growth section. In this section the wall distance is 5 mm, and flow rates are kept at 0.6 lpm for the sample air and 2.2 lpm for each of the particle-free sheath air flows, generating an aerosol layer with a width of less than 0.5 mm calculated based on the buoyancy flow profile in the chamber. The thermostatic "zero line" cooling unit, which separates the warm and the cold section of PIMCA (273 K line) and the lower cooling unit are independently controlled by Peltier-cooling modules with air ventilation. The chamber below the zero line is a transition region where the droplets are supercooled and brought to a temperature closer to the experimental conditions in PINC with chamber walls covered with a thin ice layer (Figure 1, light grey layer in the lower section of PIMCA and on PINC inner walls). In this region, the plate distance is increased to 10 mm to adjust to the PINC dimensions. By increasing the chamber width, the flow velocity in the lower part of PIMCA and in PINC is reduced, which gives droplets more time to equilibrate to the colder temperatures before entering PINC. An advantage of keeping the flow rates in PINC at 0.6 lpm/4.4 lpm (sample/sheath) flow rate setting is a longer residence time of supercooled cloud droplets under ice nucleation conditions (cf. section 2.4).

2.3. Detection of Freezing

IODE is used to detect and distinguish between ice crystals and water droplets. The detector is placed at the evaporation section of PINC, 0.15 m below of the main chamber (Figure 1, orange line). This leads to partial evaporation of the droplets due to the subsaturated conditions with respect to water in the evaporation section of PINC (see section 2.4 for more details).

The ice nucleation activity of aerosol particles is obtained as a FF of droplets containing the aerosol as described in detail by Nicolet et al. [2010] and Liuönd et al. [2010]. Briefly, IODE uses linear polarized laser light, which is horizontally directed through the PINC chamber at the end of the ice growth section. To distinguish between ice crystals and water droplets, backscattered light intensity is detected in a parallel
and a perpendicular channel (angle of 3° of the horizontal plane). A wavelet peak detection algorithm is used to find the intensity peaks from individual particles in the backscattered signal, which allows single peak detection [Lüönd et al., 2010]. The depolarization ratio $\delta$ is obtained from the signal intensities from the parallel and the perpendicular channel, according to Nicolet et al. [2010],

$$\delta = \frac{I_{\perp}}{I_{\parallel} + I_{\perp}},$$

with the signal intensities $I_{\parallel}$ and $I_{\perp}$ being the parallel and perpendicular channel, respectively. Ice crystals, which are aspherical return a higher depolarization signal (depolarization ratio) than the spherical cloud droplets. Lüönd et al. [2010] found that to a certain extent even small spherical water droplets return a perpendicular signal, making it impossible to distinguish their depolarization signal from the signal of ice crystals. To account for this effect, they experimentally determined a minimum depolarization threshold of $\tau_\delta = 0.07$, which is applied so that water droplets are not falsely detected as ice crystals. Based on experiments reported by Nicolet et al. [2010], unactivated aerosol particles generate a small signal, which is not detected as a peak in the analysis algorithm [Lüönd et al., 2010]. For mineral dust aerosol, particles up to a size of about 800 nm remain undetected due to their low scattering signal [Nicolet et al., 2010; Lüönd et al., 2010].

Before each measurement, the background in the backscattered signal is determined using particle-free sample air. The background is subtracted from the signal. Main sources of the background are reflections from the chamber ice-coated walls or frost particles in the chamber. The input particle concentration is diluted to 20–100 cm$^{-3}$, which allows for distinguishable single-intensity peaks and prevents coincidence of multiple particles in the laser beam. The FF is given by the ratio of ice crystals to the total particle number detected by IODE:

$$FF = \frac{N_{\text{ice}}}{N_{\text{ice}} + N_{\text{droplets}}},$$

where $N_{\text{ice}}$ is the number of ice crystals and $N_{\text{droplets}}$ is the number of water droplets detected per experiment. The error in FF is based on measurement uncertainties of the detector, which arise due to electronic noise in the signal intensities of $I_{\parallel}$ and $I_{\perp}$. Error propagation on equation (1) leads to the error in the depolarization ratio $\Delta \delta$ as reported in Lüönd et al. [2010]:

$$\Delta \delta = \frac{1}{(I_{\parallel} + I_{\perp})^2} \sqrt{I_{\parallel}^2 (\Delta I_{\parallel})^2 + I_{\perp}^2 (\Delta I_{\perp})^2},$$

for which the standard deviations of the mean background in the parallel and perpendicular channels are used for the measurement errors $\Delta I_{\parallel}$ and $\Delta I_{\perp}$ of the signal intensities in both channels. For experiments with depolarization ratios close to the threshold $\tau_\delta$, a misclassification of the particle is possible. Thus, a particle with $\delta > \tau_\delta$ and $\delta - \Delta \delta < \tau_\delta$ is classified as an ice crystal but could be a potentially miscounted ice peak. The ratio of such peaks and the total particle number is indicated as the lower error bar and vice versa for potentially misclassified water droplets as the upper error bar. For better counting statistics, each data point shown in the plots hereafter is based on two to five individual measurements, each of at least 1000 individual (particle) intensity peaks detected at the same $T$. In addition to the measurement uncertainty from IODE, the statistical uncertainty is added. The statistical error $\Delta FF_{\text{stat}}$ is obtained as

$$\Delta FF_{\text{stat}} = \frac{FF_{\text{max}} - FF_{\text{min}}}{2 \sqrt{N}},$$

where $FF_{\text{max}}$ and $FF_{\text{min}}$ are the maximum and minimum values from the averaged data and $N$ the number of measurements per temperature averaged. FF values presented in the following are shown as averaged data per temperature.

2.4. Simulation for Droplet Evolution in PIMCA-PINC

To ensure that cloud droplets in PIMCA grow to sizes large enough to reach the detector, computational fluid dynamics (CFD) simulations with FLUENT 14.0 [ANSYS, 2011] were conducted. The simulations were setup in a vertical cross section taking into account chamber wall humidification and ice layers. A 2-D simulation is considered valid, because particles are only injected over a width of 0.27 m into the chamber with a 15 mm particle-free region on either side adding up to a total width of 0.3 m (Figure 1, left, frontal view). This means
Figure 2. Simulation of the droplet evolution in PIMCA-PINC. The calculations are based on $T = 243\text{ K}$ in PINC. Sample layer conditions were obtained based on simulated particle trajectories [ANSYS, 2011] to calculate diffusional growth and evaporation of cloud droplets in the setup along the path length of the PIMCA-PINC setup, given as (a) the temperature, $T$; (b) the residence time, $t_{\text{res}}$; (c) the saturation ratio, $S_w = \frac{\text{RH}_w}{100\%}$; and (d) the droplet radius, $r$. The detection device IODE (green vertical line) is positioned 1.43 m after the sample air inlet. Purple arrows indicate the position where the experimental conditions for ice nucleation conditions are reached.

Table 1. Properties and Experimental Parameters Under Typical Operation Conditions of the PIMCA-PINC Setup Compared to the Laboratory Version IMCA-ZINC

<table>
<thead>
<tr>
<th></th>
<th>PIMCA(-PINC)</th>
<th>IMCA(-ZINC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Application</td>
<td>Field and lab</td>
<td>Lab only</td>
</tr>
<tr>
<td>Flow rate sample</td>
<td>0.6 lpm</td>
<td>1 lpm</td>
</tr>
<tr>
<td>Flow rate total</td>
<td>5 lpm</td>
<td>5 lpm (10 lpm in ZINC)</td>
</tr>
<tr>
<td>Droplet size $r$</td>
<td>5 – 7 $\mu$m</td>
<td>10 $\mu$m [Welti et al., 2012]</td>
</tr>
<tr>
<td>Residence time $t_{\text{res}}$</td>
<td>7 s</td>
<td>10 s [Welti et al., 2012]</td>
</tr>
<tr>
<td>Length immersion chamber</td>
<td>0.65 m</td>
<td>0.72 m</td>
</tr>
<tr>
<td>Dimensions setup (net chamber)</td>
<td>2.1 m (1.52 m)</td>
<td>2.8 m (2.47 m)</td>
</tr>
<tr>
<td>Cooling system</td>
<td>Peltier elements (compressors)</td>
<td>Ethanol cooling system</td>
</tr>
<tr>
<td>Sheath air humidification</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

*4Droplet size and residence time refer to periods of ice nucleation conditions in the experiment.*
that the interaction of the sample flow with the side walls of the chamber can be neglected (see Lüönd et al. [2010] for similar simulations for IMCA). Temperature input parameters for the CFD simulation of the chamber were obtained experimentally along the PIMCA-PINC setup. The trajectories of spherical cloud droplets with the radius of 6 μm are derived from the CFD simulation. Diffusional growth and evaporation of droplets are calculated along the trajectory based on the simulated conditions in the sample lamina (temperature, saturation ratio with respect to water, and velocity) starting with a droplet size of \( d = 400 \text{ nm} \) once water saturation is reached (0.075 m downstream of the aerosol inlet). In Figure 2 the conditions are shown along the droplet path after entering the PIMCA-PINC setup including diffusional growth and evaporation. The dry sample aerosol and particle-free sheath air enter the chamber at \( T = 303 \text{ K} \). After 0.05 m, heating units on each wall increase the temperature in the sample layer to a droplet activation temperature (\( T = 313 \text{ K} \)) reaching water saturation conditions after 0.025 m along the particle trajectory. Activated particles nucleate and grow to cloud droplets with \( r = 8 \text{ μm} \) after exposure to the maximum RH_{water} > 115% in the chamber. Humidified inner walls in the warm section of PIMCA are indicated as “water layer” by a dashed line in Figure 2. Cloud droplets are subsequently cooled down before entering the subzero temperature region of PIMCA. At the “zero line” position, both chamber walls are set to identical temperatures. Below this section, the plate distance is widened from 5 mm to 10 mm to adjust to the chamber dimensions of PINC. An additional Peltier-based cooling unit in the lower part of PIMCA provides further supercooling and supersaturation with respect to ice prior to encountering conditions in PINC. In PINC the droplet with an immersed aerosol particle is exposed to the experimental conditions for ice nucleation (for this CFD example, \( T = 243 \text{ K} \) at water saturation) for \( ~7 \text{ s} \) (indicated by purple arrows) before entering the evaporation section. On average, a droplet reaching ice nucleation conditions is simulated to grow to a droplet radius between 5 μm and 7 μm depending on \( T \) in PINC. According to the calculated evaporation processes in the lower section of PINC, droplets reach a radius of \( r \approx 4 \text{ μm} \) at the position of IODE (path length = 1.43 m) and confirms the detectability of droplets at the position of the detector (see section 2.3). This theoretically confirmed the feasibility of the new design.
2.5. The PIMCA-PINC Specifications

Although the experimental principle is unchanged from the IMCA-ZINC laboratory version (cf. Lüönd et al., 2010), a major redesign was necessary to adapt to portable dimensions. The differences of the portable PIMCA-PINC setup to the laboratory version are summarized in Table 1.

An advantage of PIMCA is the Peltier-controlled cooling system, which allows the temperature control independently from PINC and does not require cooling liquid nor compressors. PIMCA-PINC can be operated in the immersion mode from 233 K to 263 K ensuring at least RH_w = 100% in PINC to prevent evaporation of cloud droplets. The given temperature range is limited by the cooling power of PIMCA-PINC and by the temperature of the warm wall in PINC to ensure that the ice layer on the chamber wall does not melt. The shorter chamber dimension of PIMCA-PINC (1.52 m net chamber size) allows easy transport and shipping and allows the possibility for deployment in remote measurement stations, e.g., in a measurement trailer or participation in lab campaigns internationally. The flow rates are set to lower flows to allow enough time for particles to grow to detectable cloud droplet sizes. In recent studies, IMCA-ZINC has been used at a total flow rate of 10 lpm by adding additional sheath air in the transition zone between IMCA and ZINC [Welti et al., 2012] or without additional sheath air at 5 lpm [Lüönd et al., 2010]. Because PINC is shorter than ZINC, it has a residence time of only 4–5 s at 10 lpm total flow. When operated with PIMCA, a total flow rate of 5 lpm is used in the PIMCA-PINC setup. This increases the available ice nucleation time to ~7 s and thereby reduces the residence time effects on the measured FF. Cloud droplet sizes reach r = 5–7 μm and are smaller compared to r = 10 μm in ZINC. The reason is the different water-subsaturated transition zones between droplet activation and ice nucleation conditions in the lab and in the portable chamber where droplets shrink. Based on the limitations of the cooling power in the lower section of PIMCA in transitioning to T in PINC, more evaporation results in smaller droplet sizes entering PINC in comparison to IMCA-ZINC. In addition to the humidification of the chamber walls, in IMCA the sheath air is humidified via nanofiber humidifiers. This was not done in the portable setup after obtaining an insignificant decrease in droplet size (from droplet evolution simulations) without additional humidification of the sheath air. To improve the particle transmission efficiency, the horizontal aerosol inlet is replaced by a vertical version.

3. Instrument Validation Experiments

3.1. Setup for Laboratory Studies

Validation and test experiments of the PIMCA-PINC setup were conducted under controlled laboratory conditions to calibrate RH and T as well as cloud droplet size. Particles were generated either by atomization of an aqueous solution or by dry dispersion (Figure 3). Aqueous solutions were aerosolized with a home-built atomizer for experiments with ammonium sulfate (NH₄)₂SO₄ and ammonium nitrate (NH₄NO₃) dissolved in Milli-Q water (18.2 MΩ cm purity) in a 1 wt % solution. Solution droplets produced by the atomizer are dried in a series of two 1 m diffusion dryers and passed through an impactor to narrow the size distribution prior to size selection with a Differential Mobility Analyzer (DMA, Electrostatic Classifier, TSI Model 3081), which selects particle diameters based on electrostatic mobility. A Condensation Particle Counter (CPC, TSI Model 3772) measured the particle concentration entering the PIMCA-PINC setup. A dilution stage was used in the sample line to adjust the particle concentration in the sample flow. Dilution was necessary to avoid coincidence...
errors while ensuring appropriate counting statistics. For dry particle aerosolization of mineral dust particles (Kaolinite Fluka, Sigma-Aldrich), the sample material was dispersed with a Fluidized Bed Generator (FBG, TSI Model 3400A). Two cyclones ($D_{50} = 3 \mu m$ (integrated in FBG) and an additional one ($D_{50} = 1 \mu m$)) were used upstream of the DMA.

### 3.2. Homogeneous and Heterogeneous Freezing on Well-Defined Aerosol Samples

Homogeneous freezing experiments were performed to characterize the instrument. Ammonium sulfate and ammonium nitrate were used as seed particles for cloud droplet formation to study the freezing of supercooled dilute aqueous droplets. Figure 4 summarizes the experimental results (FF as a function of $T$), where each aerosol type was evaluated in three independent measurements (i–iii) using 200 nm size-selected aerosol particles. Data are binned per temperature and experiment and compared to the theoretical predicted freezing curve for homogeneous freezing of $r = 6 \mu m$ droplets and a residence time of $t_{res} = 7$ s (cf. section 2.4) shown as a black line in Figure 4. The theoretical line is based on the homogeneous nucleation rate reported by Earle et al. [2010] taking into account $t_{res}$ and droplet volume. The experimental data coincide with theory and have a good reproducibility between three independent experiments. A heterogeneous freezing signal was not expected for these experiments and was not observed. Small FF for heterogeneous freezing temperatures ($T > 236$ K) are in the background (low signal-to-noise ratio) of the detector of FF $= 0.1$.

For comparison with the laboratory setup, IMCA-ZINC, the experiments were conducted with kaolinite. Particles were dry dispersed and size-selected at 200 nm, 400 nm, and 800 nm for comparison. Figure 5 shows an overview of PIMCA-PINC (filled symbols) with two independent measurements per particle size including best fit curves with 95% confidence intervals and the IMCA-ZINC literature data (open symbols; 400 nm and 800 nm data for $T < 245$ K from Welti et al. [2012]). The grey area represents the temperature regime where homogeneous freezing is expected [Earle et al., 2010]. This region extends to about 0.5 K warmer temperatures for IMCA-ZINC measurements due to longer residence time and larger droplet sizes (see Table 1). The homogeneous freezing regime in IMCA-ZINC experiments is indicated by the light grey line in Figure 5.

The PIMCA-PINC data show a heterogeneous freezing signal with a clear size dependence showing a higher freezing efficiency for larger kaolinite particles. This is in agreement with previous results in which a comparable setup for particle generation was used [Lüönd et al., 2010; Welti et al., 2012]. The median freezing temperatures $T_{50}$, where 50% of the droplets are frozen, is found to be 236.8 K for the 200 nm particles and 238.0 K and 239.2 K for the 400 nm and 800 nm particles, respectively. Error bars are not shown for clarity (cf. Figure 6). $T_{50}$ from Lüönd et al. [2010] and Welti et al. [2012] from the laboratory version IMCA-ZINC at the same sample conditions are about 1 K higher. This discrepancy can arise, e.g., from the longer residence time in IMCA-ZINC. In Figure 6, exemplary time dependence during ice nucleation conditions are compared for 400 nm particles using data from Welti et al. [2012]. Shorter droplet residence time of $t_{res} = 6$ s (purple) instead of $t_{res} = 10$ s (orange) reduced FFs in Welti et al. [2012] to values within the uncertainty of PIMCA-PINC data obtained with $t_{res} = 7$ s. The lower limit in FF at warmer temperatures is slightly higher in PIMCA-PINC compared to Welti et al. [2012]. A possible reason is a smaller droplet size resulting in a lower signal-to-noise ratio.
Figure 6. Heterogeneous freezing of size-selected kaolinite particles with PIMCA-PINC from this study (blue triangles) with $t_{\text{res}} = 7$ s. Data from Welti et al. [2012] for the same sample as orange circles ($t_{\text{res}} = 10$ s) and purple circles ($t_{\text{res}} = 6$ s). Also shown are data from Hartmann et al. [2016] ($t_{\text{res}} = 1.6$ s; without multiple charge correction) and Lüönd et al. [2010] ($t_{\text{res}} = 14$ s). The shaded area is calculated based on the homogeneous nucleation rate reported by Earle et al. [2010] for PIMCA-PINC. The grey lines represent the homogeneous freezing regime for Welti et al. [2012] with $t_{\text{res}} = 10$ s (solid) and $t_{\text{res}} = 6$ s (dashed), respectively.

Data from immersion freezing techniques on single-immersed aerosol particles with the same kaolinite sample (Fluka, Sigma-Aldrich) are reported by Augustin-Bauditz et al. [2014], Wex et al. [2014], and Hartmann et al. [2016]. Wex et al. [2014] and Augustin-Bauditz et al. [2014] did not observe a $T_{50}$ for particles of 700 nm or smaller for their reported $T > 237$ K. We compare to particle sizes which are closest to the size measured in this study. Hartmann et al. [2016] report $T_{50}$ between 235.5 and 236 K for particle sizes of 300 nm to 700 nm as shown by a selection of their data in Figure 6. The $T_{50}$ is 2–2.5 K lower compared to measurements from this study. The $t_{\text{res}}$ reported by Hartmann et al. [2016] is 1.6 s. The difference in observed $T_{50}$ between Hartmann et al. [2016] and the data from the current measurements could arise from the difference in residence time. The residence time of FF for this particular kaolinite sample has been shown by Welti et al. [2012]. A short residence time can lead to a lower FF and therefore lower $T_{50}$. Another reason could be that effective particle sizes could be larger in our study compared to those reported in Hartmann et al. [2016] due to multiply charged particles passing through the aerosol generation and size selection system.

4. Ambient In Situ Immersion Freezing With the PIMCA-PINC Setup During the ZAMBIS 2014 Field Study

4.1. Description of the Field Site and Instrumentation

In spring 2014 the Zurich AMBient Immersion freezing Study (ZAMBIS) was conducted to investigate the immersion freezing efficiency of urban aerosol particles during pollen season. The study was undertaken at an urban-forest site over a period of 6 weeks. The measurement site (47.406°N, 8.512°E, 540 m above sea level) was located in the northwestern periphery of the city of Zurich, Switzerland at an elevated area near the ETH Hönggerberg Campus. In situ ice nucleation measurements were conducted with PIMCA-PINC from within a mobile trailer on site. A schematic of the setup is shown in Figure 7. Aerosol inlet 1 was used for sampling aerosol for immersion freezing experiments. Bends in the sampling line allow mainly particles in the submicron size range to reach PIMCA-PINC (cf. Appendix C for characterization of particle losses). In addition, for experiments with PIMCA-PINC a dilution stage was used in the ambient sample line to avoid coincidence errors while ensuring appropriate counting statistics for particle detection with IODE. As shown in Figure 7, aerosol number concentrations after the dilution stage were measured with a CPC in parallel to measurements with PIMCA-PINC, similar to laboratory experiments. Measurements were taken as temperature scans approximately once to twice per day each with a sampling time of 1.5 – 2 hours. On the second total aerosol
Figure 7. Experimental setup for ambient measurements during ZAMBIS. Inlet 1 was used for in situ immersion measurements with PIMCA-PINC. A dryer and a dilution stage were installed upstream of PIMCA-PINC. Aerosol particle number concentration was measured after dilution (CPC) parallel to the immersion freezing experiments. Inlet 2 was used for measurements of the aerosol size distribution (SMPS).

Inlet 2, the aerosol size distribution was measured with a Scanning Mobility Particle Sizer (SMPS, custom built) [Wiedensohler et al., 2012] for a size range from 10 nm to 880 nm. Additionally, meteorological conditions were monitored at the institute’s weather station on site. Complimentary bioparticledetection, daily filters for particulate matter <10 μm (PM10), and liquid impaction for drop freezing assay experiments were also collected.

In this work we present and discuss the results from PIMCA-PINC.

4.2. Investigating the Frozen Fraction of Ambient Aerosol Particles

In situ ice nucleation experiments with PIMCA-PINC are analyzed to obtain the frozen fraction of activated particles. Temperature scans were started at homogeneous freezing temperatures with the first sample taken at \( T < 234 \) K and ended at warmer temperatures when FF did not show a further decrease with increasing temperature. Figure 8a summarizes the data throughout the period of the campaign with the date shown as one color per week. Each data point represents an average value of two to five measurements taken within a 5 min period at the same \( T \), representing an average of 3600±1500 individual (particle) intensity peaks analyzed per temperature. The temperature regime, which is dominated by homogeneous freezing, is indicated by the dark grey curve. Most data points are close to temperatures dominated by homogeneous freezing within a temperature uncertainty of \( dT = 0.4 \) K. The uncertainty in FF at warmer temperatures (\( T > 236 \) K) is increased due to smaller droplet sizes in ambient measurements. In field studies on polydisperse aerosol which can vary in composition and hygroscopicity, particles are activated to cloud droplets from the whole size distribution, which results in a wider distribution of droplet sizes compared to experiments on chemically similar and pure monodisperse aerosol. Therefore, the composition dependent hygroscopicity of the ambient aerosol can influence the droplet activation, growth, and the resulting droplet sizes. This effect leads to a higher uncertainty in the signal peak detection and therefore to a higher uncertainty in FF. To rule out possible miscounting (underestimation of droplets) due to small droplet sizes, which are not detectable by IODE, the total activation (acttot) is obtained. The acttot is the ratio of the particle number detected by IODE (Ntot)
Figure 8. (a) The measured frozen fraction (FF) as a function of temperature for each experiment during ZAMBIS 2014. Data have been averaged for all data points (2–5) at each measured temperature. The dark grey line represents the homogeneous freezing regime. The horizontal dashed line shows the detection limit. (b) Data from Figure 8a after adjustments considering undetected droplets in IODE as reported in section 4.2.

per interval (35 s) and the sampled aerosol particle number per sample interval after the dilution stage ($N_{CPC}$), which is measured upstream of PIMCA-PINC with a CPC. The $act_{tot}$ is then given by

$$act_{tot} = \frac{N_{tot}}{N_{CPC}}$$

and presented as a function of $T$ in Figure 9a. A temperature dependent decrease of $act_{tot}$ is observed. This indicates that activated particles did not grow large enough or that the droplets partly evaporated and remained at an undetectable size at warmer temperatures. During the experiment, the dilution of the ambient aerosol was reduced (thus increasing the sampled aerosol number) at higher temperatures to counteract the decrease in the detected particle number in IODE. The particle concentrations were measured after the dilution stage upstream of PIMCA-PINC and are shown in Figure 9d. A decrease in the number of detected particles with increasing temperature is not observed for experiments with size-selected particles in the laboratory (a comparison for polydisperse and monodisperse experiments can be found in Appendix B). As can be expected, the detected liquid fraction increased with temperature (Figure 9b) while the detected ice fraction decreased with increasing $T$ (Figure 9c). To consider undetected cloud droplets and therefore the potential to overestimate FF, the following adjustment is introduced, where $N_{tot}$ is adjusted based on $N_{CPC}$.

In the homogeneous freezing temperature regime, all droplets freeze and grow to large ice crystals which can be detected reliably. Therefore, at the coldest measured temperature, the highest number of frozen CCN activated particles will be counted by IODE. With this assumption, the maximum detected activation for each temperature scan is reached at the coldest temperature ($T_0$) measured at $T_0 < 234$ K and with that at $act_{tot}(T_0)$. Accordingly, the maximum possible counts detectable by IODE are:

$$max\ counts = act_{tot}(T_0) \cdot N_{CPC}$$

which leads to an adjusted frozen fraction $FF_{adj}$ including undetectable particles by IODE in the form:

$$FF_{adj} = \frac{N_{ice}}{N_{tot}} = \frac{N_{ice}}{N_{tot}} = \frac{N_{ice}}{N_{CPC}(T_0) \cdot max\ counts} = \frac{N_{ice} N_{CPC}(T_0)}{N_{CPC} N_{tot}(T_0)}$$

with $N_{nd}$ being the undetected number of aerosol particles based on the maximum fraction at the beginning of each experiment. The ratio of undetectable particles to the total sampled particle number per interval (Figure 9e) is given by

$$F_{nd} = \frac{N_{nd}}{N_{CPC}}$$
Figure 9. Activation of ambient aerosol in PIMCA-PINC. Detected aerosol particles are distinguished into (a) total activated particles, (b) droplets, and (c) ice crystals detected by IODE as a fraction to the entering aerosol. (d) Sampled interstitial aerosol concentration was measured with a CPC after the dilution stage for the ambient sample parallel to the PIMCA inlet. (e) The fraction of undetected particles by IODE is given.

Depending on the experiment and measured temperature, the fraction of undetected particles $F_{nd}$ can range up to 30% of $N_{tot}$ and increases with increasing temperature. This indicates that a substantial fraction of cloud droplets are too small to remain at a detectable size at the position of the detector. Major differences are found between experimental days which can arise from differences in the ambient particle size distribution and composition, where the latter may influence the hygroscopicity and therefore the ability to grow. This could be the case for, e.g., freshly emitted soot from traffic or wood fires.

The adjusted frozen fraction $F_{adj}$ is given in Figure 8b. Compared to the raw data (Figure 8a), the $F_{adj}$ lie close to the temperatures which are dominated by homogeneous freezing. Some exceptions are found in the week of 14 April 2014 to 21 April 2014. The number concentration measured with the CPC (Figure 9d, cyan) during this period was higher at $T < 234$ K. Changes in the particle concentration during the period could be due to local influences. Overall, $F_{adj}$ for $T > 236$ K are found to be low, which supports the assumption of ice overestimation before the adjustment. The measurement uncertainty is lowered by applying this adjustment. $F_{adj}$ larger than 0.1 are reliable measurements within the instruments uncertainties and is the typical lower limit found for laboratory studies (see section 3.2). Day-to-day variations in the freezing curves are within the uncertainty of $dT = \pm 0.4$ K of the experiment. However, data taken at the beginning of April (before 7 April 2014, dark blue) indicate a more ice nucleation active aerosol. Parallel size distribution measurements (Figure 10) show a higher concentration of particles with a diameter larger than 100 nm,

Figure 10. Measured ambient size distribution during PIMCA-PINC measurement periods.
possibly from a local source. Larger aerosol particles are typically more efficient INP and therefore are expected to contribute to a higher FFadjtot compared to smaller aerosol particles. Even though no distinct heterogeneous freezing signal could be detected for the majority of the data points within the instrumental uncertainty, it is likely that bursts of particles are found to be active immersion freezing nuclei. Concentration of ambient particles triggering heterogeneous nucleation are expected to be some orders of magnitudes smaller than CCN active particles (only 1 in $10^6$ of the total aerosol particles at $T = 253$ K) [Seinfeld and Pandis, 2006] and therefore below the detection limit of the measurement method with IODE for $T > 236$ K.

4.3. Atmospheric Implication of Observed Ice Nucleation With PIMCA-PINC

Experiments in PIMCA are obtained at RHw > 115% in order to activate each aerosol particle to a cloud droplet. In the atmosphere, typical supersaturations for CCN activation in the polluted boundary layer are found to usually remain below 0.3%, but can reach 1.0% in clean and convective conditions [Ditas et al., 2012; Hammer et al., 2014; Hudson and Noble, 2013]. Therefore, it has to be taken into account that under atmospheric conditions not all aerosol particles activate to cloud droplets, like in PIMCA due to the higher supersaturation. Immersion freezing in the atmosphere depends on the number of cloud droplets available. The number of particles activating into cloud droplets during ZAMBIS is estimated using typical atmospheric supersaturations (0.3–0.4%). The CCN concentration during ZAMBIS was not measured on site (e.g., with a CCN counter) and is therefore estimated as follows.

The CCN activated fraction ($A_{CCN}$) is defined as the fraction of ambient aerosol acting as CCN and therefore represents the activation of cloud droplets under the given supersaturation conditions. Paramonov et al. [2015] proposed a function, representing the average CCN activated fraction from ambient aerosol, $A_{CCN,global}$ for eight field sites around the world as a function of supersaturation SS [%] given as

$$A_{CCN,global} = 0.22 \cdot \ln(SS) + 0.69.$$  \hspace{1cm} (9)

Assuming a typical atmospheric supersaturation SS = 0.3% in the boundary layer, the CCN activated fraction is $A_{CCN,global} = 0.43 \pm 0.12$. However, a global average for CCN activation may be incorrect for the local properties at the urban forest site. Andreae [2009] summarized various studies on polluted continental CCN properties and obtained an average $A_{CCN,poll} = 0.36 \pm 0.12$ at a supersaturation of SS = 0.4%. In a third study, Madonna [2009] reported CCN measurements at a polluted urban location in the city of Zurich and found for SS = 0.3% $A_{CCN,ZH} = 0.18 \pm 0.09$ corresponding to CCN concentrations of $\sim 1700$ cm$^{-3}$ for measurements during their study in Zurich. For the three cases, the CCN concentration $N_{CCN}$ during ZAMBIS with the total ambient aerosol concentration, $N_{amb}$, between 10 nm and 880 nm is calculated:

$$N_{CCN} = N_{amb} \cdot A_{CCN}.$$  \hspace{1cm} (10)

Table 2. CCN Concentrations for ZAMBIS Aerosol Particle Concentrations Measured From 10 nm to 880 nm for Typical Ambient Supersaturations SS Based on the CCN Activated Fraction $A_{CCN}$ from Paramonov et al. [2015], Andreae [2009], and Madonna [2009]

<table>
<thead>
<tr>
<th>SS (%)</th>
<th>Mean $N_{CCN}$ (cm$^{-3}$)</th>
<th>Minimum to Maximum $N_{CCN}$ (cm$^{-3}$)</th>
<th>$A_{CCN}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global average [Paramonov et al., 2015]</td>
<td>0.3 3450 916–11040 0.43 ± 0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polluted continental conditions [Andreae, 2009]</td>
<td>0.4 2992 776–9352 0.36 ± 0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban/ZH [Madonna, 2009]</td>
<td>0.3 1461 388–4676 0.18 ± 0.09</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. CCN Concentrations $N_{CCN}$ (cm$^{-3}$) and Activated Fraction $A_{CCN}$ of the Total Ambient Aerosol $N_{amb}$ (cm$^{-3}$) for Zurich (April 2010) in the Size Range of $d = 10$–1000 nm From ECHAM6-HAM2 for Typical Ambient Supersaturations SS

<table>
<thead>
<tr>
<th>SS (%)</th>
<th>Mean $N_{CCN}$ (cm$^{-3}$)</th>
<th>Minimum to Maximum $N_{CCN}$ (cm$^{-3}$)</th>
<th>$A_{CCN}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>434 ± 246 37–1406 0.21 ± 0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>451 ± 262 39–1511 0.22 ± 0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>503 ± 289 59–1663 0.24 ± 0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2220 ± 1404 314–7567</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 11. (a) CCN concentrations ($N_{CCN}$) predicted for a global average (global) [Paramonov et al., 2015], for polluted continental aerosol (poll) [Andreae, 2009], and for a polluted urban location (ZH) [Madonna, 2009] are given in colors, and the CCN concentration taken from ECHAM6-HAM2 is shown in black. (b) The total aerosol number concentrations from ECHAM6-HAM2 (black) and measured aerosol number concentration during ZAMBIS ($N_{amb}$, grey) are shown. Points indicate mean values and bars the range of concentrations.

The resulting CCN concentrations for the three cases are given in Table 2. A comparison of the three CCN estimations to typical aerosol properties obtained with the ECHAM6-HAM2 global aerosol-climate model is presented for model specifications in Neubauer et al. [2014] to identify which estimation for CCN describes measurements during ZAMBIS the best. $N_{CCN,ECHAM}$ (Table 3) is calculated for the surface aerosol in spring in Zurich (3 h instantaneous data for April 2010, interpolated to the coordinates of Zurich) and representative for the typical aerosol size distribution, number, and composition as can be expected during ZAMBIS. $N_{CCN,ECHAM}$ is on average $434 \pm 246 \, \text{cm}^{-3}$ at SS = 0.3% (451 ± 262 cm$^{-3}$ at SS = 0.4%) corresponding to $A_{CCN,ECHAM} = 0.21 \pm 0.08$ (0.22 ± 0.08 at SS = 0.4%). $N_{CCN}$ from the three estimations discussed above including the total aerosol number concentration from ECHAM6-HAM2 and the measured $N_{amb}$ during ZAMBIS are shown in Figure 11. At SS = 0.3% and SS = 0.4%, estimated mean $N_{CCN}$ are significantly higher than $N_{CCN,ECHAM}$ (factor 3.4–7.9 for SS = 0.3% and factor 6.5 for SS = 0.4%). $N_{amb}$ is $2.2 \cdot 10^3$ cm$^{-3}$ to $2.6 \cdot 10^4$ cm$^{-3}$ for the investigated size range of 10–880 nm (Figure 11b, grey). A discrepancy between the measured and the modeled total number concentration obtained from ECHAM6-HAM2 for a comparable size range of ambient aerosol is found to be a factor of 3.7 (Figure 11b). This indicates that the local number concentration of the ambient aerosol during ZAMBIS is underestimated by the model output from ECHAM6-HAM2 for the surface aerosol. This could be due to local influences at the site, e.g., pollution from traffic or wood fires. However, the discrepancies between $N_{CCN,ECHAM}$ and the three cases for $N_{CCN}$ are significantly larger. Best agreement is found for $N_{CCN,ZH}$ (factor 3.4 for SS = 0.3%), which suggests that the aerosol measured during ZAMBIS is best described by an urban aerosol measured in the same area by Madonna [2009].

$N_{CCN}$ only represents estimations for the surface aerosol. Typically, cloud droplet number concentrations in the atmosphere at altitudes relevant for ice nucleation may be significantly lower due to sedimentation and scavenging of the surface aerosol. Therefore, we suggest these numbers used for following calculations to be an upper limit for available cloud droplet numbers in the atmosphere where ice nucleation takes place via immersion freezing.

The frozen cloud droplet number concentration (FCDNC), which is the fraction of cloud droplets that can potentially freeze, is given as

$$FCDNC(T) = FF_{\text{adjtot}}(T) \cdot N_{amb} \cdot A_{CCN,ZH},$$

where $FF_{\text{adjtot}}$ is taken from Figure 8b. The resulting FCDNC as a function of $T$ is given in Figure 12 with FCDNC between $5.4 \cdot 10^4$ and $4.1 \cdot 10^6$ L$^{-1}$.
(mean FCDNC = 7.22 \times 10^5 \text{L}^{-1}, \text{SS} = 0.3\%). These values are only calculated for FF \text{adj}_{\text{tot}} > 0.1. The measurement uncertainties given as error bars are discussed in Appendix A.

The FCDNC presented gives the number of available cloud droplets in the atmosphere which are based on ground level CCN activation for conditions in the polluted boundary layer. Freezing of the droplets is measured with PIMCA-PINC as a frozen fraction during ZAMiBS and applied to the available number of cloud droplets. Therefore, FCDNC can be seen as an upper limit of cloud droplets in the atmosphere at altitudes where immersion freezing can occur. We note that most measurements were performed at temperatures dominated by homogeneous freezing. Therefore, an aerosol particle is only required for the CCN activation but not for homogeneous freezing at temperatures \( T < 236 \text{ K} \) in PIMCA-PINC.

Most experiments during ZAMiBS showed FF \text{adj}_{\text{tot}} < 0.1 for temperatures \( T > 236 \text{ K} \), where ice primarily forms due to heterogeneous ice nucleation. The exception was the first week of April, when heterogeneous freezing for \( T > 236 \text{ K} \) was measured. For comparison with previous studies on ambient observations of INPs, the INP concentrations for measurements during ZAMiBS is predicted based on the parameterization by DeMott et al. [2010] (hereafter: D10). They found a good correlation between the INP concentration and the measured ambient particle concentrations for sizes larger 0.5 \( \mu \text{m} \) based on a comprehensive data set from airborne and ground-based experiments measured with a CFDC above water saturation. According to equation (1) by DeMott et al. [2010] and the measured \( N_{\text{amb}} > 0.5 \mu \text{m} \) \((\text{cm}^{-3})\) during ZAMiBS, the INP\text{D10} is \( 54 \pm 39 \text{ L}^{-1} \) at \( T = 238 \text{ K} \). This is the coldest temperature the parameterization is valid for and does not cover the temperature range where heterogeneous ice nucleation was observed during ZAMiBS. Concentrations summarized from observations in DeMott et al. [2010] range from 0.01 stdL\(^{-1}\) to 400 stdL\(^{-1}\) for temperatures 238–264 K. Because measurements during ZAMiBS were obtained at \( T < 238 \text{ K} \) a direct comparison of the FCDNC to INP concentrations by DeMott et al. [2010] is therefore not applicable as a change in temperature by 2 K could result in a significantly higher ice nucleation activity. The FCDNC (mean 7.22 \times 10^5 \text{L}^{-1} for \( T < 238 \text{ K} \) and INP\text{D10} \((54 \pm 39 \text{ L}^{-1} \) at \( T < 238 \text{ K} \) give the upper and lower limit possible for INP concentrations in this atmosphere in this temperature regime that would be possible from measurements with PIMCA-PINC during ZAMiBS.

The calculation presented here only considers aerosol particles larger than 0.5 \( \mu \text{m} \) for the INP concentration. In addition, the INP concentration in this work was only derived for the submicron size range of the atmospheric aerosol size distribution (cf. Appendix C). Mason et al. [2016] reported size-resolved INPs measurements for various ground sites. They found about 40–95% of the observed INP being larger than 1 \( \mu \text{m} \) and 20–65% larger than 2.5 \( \mu \text{m} \) at 248 K. This suggests that supermicron and coarse-mode particles are a significant fraction of the INP population. In summary this could result in underestimated INP\text{D10} concentration, because we neither sampled supermicron particles nor considered aerosol particles smaller than 0.5 \( \mu \text{m} \) in the derivation of INP\text{D10}. Compared to previous studies on immersion mode INPs, the investigated temperatures during ZAMiBS are close to the homogeneous freezing regime making it difficult to directly compare to other immersion freezing measurements which are reported for \( T \gg 236 \text{ K} \) [e.g., Conen et al., 2012, 2015; Hader et al., 2014; Mason et al., 2015b].

In summary, the calculation of the INP concentration from measurements of frozen fraction is difficult, as assumptions have to be made when referring to aerosol numbers and sizes sampled. In offline methods this is not crucial as such methods refer to the most ice nucleation active aerosol particle per sample unit. Because the sample volumes in offline methods contain polydisperse aerosol particles, activation already occurs at warmer temperatures compared to single-immersed methods.

5. Conclusions and Outlook

In this work we introduced the portable immersion freezing instrument, PIMCA, for online measurements of single-immersed aerosol particles. PIMCA extends PINC vertically and is controlled independently from PINC. PIMCA-PINC can be deployed in the field and remote laboratories. Sample temperatures as low as 233 K can be reached to obtain the freezing behavior of the sample aerosol as a frozen fraction (FF). The design is based on the laboratory instrument IMCA-ZINC [Lüönd et al., 2010] but has been adapted based on the constraints of a portable setup. Particle detection and discrimination between ice crystals and cloud droplets is achieved by measuring the depolarization intensity of plane polarized light and leads to FF as a function of temperature. The most important changes are a thermoelectric, Peltier-module-based cooling system without the requirement of a cooling liquid and a reduced total sample/sheath flow rate. The new total flow rate of 5 lpm in the PIMCA-PINC setup leads to cloud droplets with a radius of 5–7 \( \mu \text{m} \) which have an ice nucleation time...
of ∼7 s. Homogeneous freezing experiments were used to validate the freezing conditions in PIMCA-PINC. Immersion freezing experiments of size-selected kaolinite particles agree well with previously published data measured with IMCA-ZINC but exceed FFs of measurements reported by Hartmann et al. [2016]. The reasons for the discrepancy are likely due to longer residence times and possibly larger effective particle sizes in the current work leading to a larger particle surface area available for ice nucleation. Simultaneous measurements to compare different immersion freezing experiments, such as LACIS and the portable PIMCA-PINC, will help to confirm the influence of particle size selection and residence time.

Ambient in situ experiments were conducted during the ZAMBIS campaign in spring 2014 at an urban-forest site in Zurich, Switzerland. Due to the polydisperse aerosol with a large fraction of small aerosol particles, it was necessary to account for undetected aerosol particles during the experiments leading to an adjusted frozen fraction (FFadj). Experiments from a period of about 6 weeks resulted in data with the majority of experiments in the temperature regime where homogeneous freezing is expected to dominate. Yet a smaller fraction of heterogeneous freezing which is not quantifiable by the PIMCA-PINC sensitivities in the current state is possible for the measured atmospheric aerosol.

The cloud condensation nuclei (CCN) concentration was estimated to predict the available number of cloud droplets for immersion freezing in the atmosphere. CCN activated fractions for urban aerosol measured in the city of Zurich (A_{AEROSOL}) by Madonna (2009) agreed best to aerosol properties during ZAMBIS. They were chosen by comparison to aerosol data from ECHAM6-HAM2. By applying the measured frozen fraction to the available CCN, the FCDNC was obtained. The FCDNC is an upper limit of ice crystals which can be formed in the atmosphere based on the primary ice nucleation processes of homogeneous nucleation and immersion freezing for T < 238 K. In the heterogeneous freezing regime, the parameterization by DeMott et al. [2010] was used to estimate the INP concentration at T = 238 K. With the mean observed aerosol number concentration larger 0.5 μm during ZAMBIS, INP_{0.5} is 54 ± 39 L^{-1} at T = 238 K. We suggest this as a lower limit for the investigated temperatures in an urban environment.

At the present state the PIMCA-PINC setup can be used for laboratory studies and instrument intercomparison [e.g., Hiranuma et al., 2015; Wex et al., 2015] as it is the only portable instrument to measure immersion freezing of single-immersed aerosol particles that excludes other ice nucleation mechanisms. To study ambient immersion freezing in a broader temperature regime more relevant for mixed-phase clouds, the detection limit has to be lowered. Ambient ice nucleation experiments on size-selected single-immersed aerosol particles can be used if these are available in sufficiently large concentrations. Similar studies have been presented recently for droplet freezing studies on dilute solution droplets [e.g., Hader et al., 2014; Mason et al., 2016] but not yet for individual aerosol particles. Conducting field studies with size-selected particles would reduce the challenge of small aerosol particles activating into droplets in PIMCA causing a FF below the detection limit of the current experiment. Additionally, size resolved information on the chemical composition of the ambient aerosol particles would be helpful to better understand which components predominantly act as INPs.

A reduction in the uncertainty from particle misclassification in IODE would be possible in an experimental setup without the evaporation section to increase the signal intensity by keeping droplets at a larger size. This could be achieved when IODE is positioned in the main ice nucleation chamber or if the evaporation section can be used as an extended main chamber. For both options major changes in the cooling circuitry of PINC would be necessary. Furthermore, a chamber without an evaporation section would allow the use of a more sensitive detector to distinguish the particle phase downstream of PIMC. This will be addressed in future developments of PIMCA-PINC. For future analysis of aerosol particles, sampling of ice residuals could be achieved via isolation of large ice crystals through a device such as a Pumped-Counterflow Virtual Impactor (P-CVI) [Kulkarni et al., 2011] coupled downstream of PIMCA-PINC. Ice crystals separated by a P-CVI could be collected onto substrates for further analysis. After sublimation of the ice crystals, the residuals can be analyzed, for example, via scanning electron microscopy with energy-dispersive X-ray (SEM-EDX) microanalysis in order to obtain information about their composition [Worringen et al., 2015].

Appendix A: Evaluation of Measurement Uncertainties for PIMCA-PINC Experiments

The applied temperature gradient between the chamber walls of PINC leads to a supersaturation profile in the chamber. Validation experiments for PINC by Chou et al. [2011] showed a resulting uncertainty in RH of ±2% based on ammonium sulfate studies on deliquescence [Kanji and Abbatt, 2006; Braban et al., 2001] and
Figure A1. Typical flow profile for PINC at a total flow rate of 5 lpm and a target temperature of 243 K at water saturation. The red line indicates the temperature between the chamber walls (position 0 cm is the warm wall, position 1 cm is the cold wall). The laminar flow profile is shown in blue and in green the buoyant flow (takes into account convection). In comparison to the laminar flow, consideration of buoyancy shifts the sample lamina (grey lines) toward the colder chamber walls according to the maximum flow velocity.

homogeneous freezing (based on theoretical calculations by Koop et al. [2000]). The uncertainty of the thermocouples measuring the temperature at different positions along the chamber is ±0.1 K. The variation of temperature in the sample layer was estimated to be 0.8 K [Kanji et al., 2013]. The velocity profile and the sample position in PIMCA-PINC is calculated for the flow rate of 2.2 lpm of sheath air on each side and a sample flow of 0.6 lpm. Consideration of convective forces due to the temperature gradient results in a shift of the sample layer closer to the colder chamber wall. Figure A1 shows the shift in the sample position, the flow velocities, and the linear temperature gradient between the warm wall (position: 0 cm) and the cold wall (position: 1 cm) in PINC. The position of the sample layer is indicated as dash-dotted lines located at a position of 2.5–3 mm from the cold wall for \( T = 242.7 \) K at \( \text{RH}_w = 101\% \) (equivalent to \( \text{RH}_w \geq 100\% \) throughout the whole sample layer). The flow profile and the position of the sample layer depend on set points of ice nucleation temperature and \( \text{RH}_w \). The corresponding saturation profile is shown in Figure A2.

Error bars in FCDNC (Figure 12) arise from error propagation based on the measurement uncertainty for size distribution data of 10% and the reported uncertainty obtained from \( \text{FF}_{adj,tot} \) (cf. section 2.3). In addition, the uncertainty in \( A_{\text{CCN,ZH}} \) is considered in the error propagation for the calculation of FCDNC.

Figure A2. Typical saturation profile for PINC with respect to ice (\( S_i \)) and water (\( S_w \)) at a total flow rate of 5 lpm and a target temperature of 243 K. Temperature conditions in the chamber cross section are shown in red. The position of the sample layer is indicated with grey vertical lines.
Appendix B: Particle Activation in PIMCA-PINC

As discussed in section 4.2, a correction for the activation of particles in PIMCA-PINC is applied. In Figure B1 particle activation is compared for two studies. The case of size-selected 400 nm illite particles is compared to the field case of 3 April 2014 during ZAMBIS. Particle counts per measurement of ice crystals, droplets, and total counts of IODE are shown in the top row in Figure B1 and the particle concentration measured upstream of PIMCA-PINC in the bottom row in Figure B1. The case of size-selected 400 nm particles is compared to the field case of 3 April during ZAMBIS. Particle concentrations are controlled by a dilution system to prevent coincidence in the detector. The experimental temperatures of the data shown increased with time, which leads to a decrease in ice and an increase in the liquid droplet fraction. In the illite experiment the total IODE counts remain constant while the aerosol particle concentration was held between 15 and 30 cm$^{-3}$. During the field study to find a constant number of detected particles in IODE, the sampled aerosol concentration had to be increased as higher experimental temperatures were accessed. This indicates that polydisperse particles sampled from the ambient were not always detectable as cloud droplets at the position of IODE due to smaller droplet sizes and evaporation before the detector. This behavior is not found for size-selected aerosol.

Appendix C: Particle Losses in the Aerosol Inlet System

Particle losses were considered between the sample inlet and the PIMCA-PINC setup. A total flow rate 1.6 lpm was used in a 6 mm tube with an approximate length of 5 m consisting mostly of a horizontal sample line and some 90° bends. Particle loss calculations showed losses of 10% for 1 μm particles and 50% loss for particles $d > 2 \mu m$. Considering the ambient size distribution and that the large majority of the particles have diameters $< 1 \mu m$, it can be assumed that a possible depolarization signal arising from unactivated large aerosol particles is negligible.

For measurements of the ambient aerosol size distributions, the SMPS sample line was positioned on a separate, however, identical inlet positioned 1.5 m from the PIMCA-PINC inlet on the measurement trailer. A total flow rate of 2 lpm and nearly vertical tubing of about 1.5 m result in a particle loss smaller than 0.5% for the entire aerosol size distribution and for aerosol diameters $< 1 \mu m$ even smaller (less than 0.02%).

References


Chapter 2. Immersion mode ice nucleation with the new PIMCA


Chapter 3

Investigating the effect of pollen and meteorological conditions on INP concentration: Results from the ZAMBIS campaign

with data contributions from: James D. Atkinson\textsuperscript{1} (impinger analysis) and Kevin Kilchhofer\textsuperscript{1} (PM\textsubscript{10} filter analysis), Andreas Pauling\textsuperscript{2} (pollen concentration, \textit{MeteoSwiss} station), Emre Toprak\textsuperscript{3}, Claudia Linke\textsuperscript{3} and Martin Schnaiter\textsuperscript{3} (FBAP concentration)

3.1 Motivation

Aerosol particles of biological origin contribute to about 25\% of the total atmospheric aerosol both by concentration or by volume in urban and rural air masses (Matthias-Maser and Jaenicke, 1995) and 10 – 20\% in remote marine air masses (Gruber et al., 1998). The potential relevance of primary bioaerosol particles (PBAP), such as pollen, bacteria, viruses, fungal spores, plant fragments and algae (Dichl et al., 2001, 2002; von Blohn et al., 2005), for processes in the atmosphere has been recognized for many years (e.g., Pöschl, 2005; Schnell and Vali, 1972). Aerodynamic diameters of PBAP have large size ranges from a few nanometers (e.g. viruses, cell fragments) up to a few hundred micrometers (e.g. pollen and plant debris) (Cox and Wathes, 1995; Hinds, 1999; Jaenicke, 2005; Pöschl, 2005). The different sizes largely influence the distribution and, therefore, the atmospheric relevance of PBAP.

In the past, numerous studies showed that mineral dust particles act as relatively efficient ice nucleating particles (INPs). However, particles nucleating ice at the highest subzero temperatures were observed to be of biological origin (e.g., DeMott, 1990; Despres et al., 2012; Hoffer, 2012; Hoffer, 2012; Hoffer, 2012; Hoffer, 2012).
1961; Pitter and Pruppacher, 1973). Even though bacteria and pollen belong to the species with the highest freezing onset temperatures, their INP concentrations are a few orders of magnitudes smaller than those of other INP species (Fig. 19, Murray et al., 2012). Due to the large variations in local emissions, the horizontal and vertical distribution of different biological aerosols varies significantly. Thus, an impact on cloud droplet and ice formation on a regional scale is possible rather than on the global scale (e.g., Sesartic et al., 2012, 2013).

Pollen, for instance, are among the largest aerosol particles in physical size and vary between 10 and 100 µm in diameter. In addition to whole pollen grains, fragmented pieces can also be found in the atmosphere, which are produced by rupturing of the grains due to high humidities (Despres et al., 2012). These fragments were found to range between 30 nm and 5 µm in size (Miguel et al., 2006; Taylor et al., 2002, 2004). Generally, pollen concentrations decrease with height. However, they have been observed to be lifted into the upper atmosphere by convection (e.g., Monin and Obukhov, 1954; Taylor et al., 2004), making pollen grains potential candidates for ice nucleation in the atmosphere. During the pollination season, pollen concentrations can reach peaks of about several particles per liter (Vogel et al., 2008). Peak pollen concentrations of $1 \times 10^{-2}$ L$^{-1}$ at the surface have been observed in a study by Noh et al. (2013), but the accompanied LIDAR measurements only indicated the presence of pollen up to 2 km above the ground. This makes long-range transport of whole pollen grains into the free troposphere solely by dispersion unlikely. Nevertheless, depending on their size, smaller fragments of pollen grains can be more easily distributed in the atmosphere.

Diehl et al. (2001) found different pollen species with particle diameters of 25 to 70 µm to be inefficient INPs in the deposition nucleation mode at $T = 240$ K and $RH_i = 135\%$. As for the condensation freezing mode, ice nucleation took place at relatively warm temperatures at an onset temperature of $T = 261$ K and at a mean condensation freezing efficiency of 50% for birch pollen. Meanwhile, several studies have shown pollen to be efficient INPs in the immersion mode. Diehl et al. (2002) reported initiating (median) freezing temperatures of 262 K (259.2 K) for birch pollen and 257 K (257.2 K) for pine pollen. Further investigations on birch and pine pollen were done by Pummer et al. (2012) using a cryo-stage method with the pollen suspended in a water-oil matrix. The study showed birch and pine pollen to nucleate at the warmest temperatures with median freezing temperatures of 254 K to 253 K. In the past, the ice nucleation (IN) ability of pollen has been explained by surface structures like the roughness and the porosity of the pollen surface (Diehl et al., 2001) that could act as possible active sites for ice nucleation. Comparing the behavior of pollen grains and their filtered washing waters showed a large similarity, which led to the conclusion that ice nucleating macro-molecules (INMs) on the surface of the pollen are responsible for initiating freezing (Pummer et al., 2012). These INMs were suggested to consist of polysaccharides. Laboratory experiments of single-immersed 500 nm and 800 nm particles have been presented by Augustin et al. (2013) for birch pollen washing waters (southern sample, Czech Republic). They found the ice fraction increased logarithmically with decreasing temperatures between 255 K and 238 K. However, below a temperature of 250 K the ice fraction levels off suggesting a saturation behavior in the immersion freezing process arising from the fact that not every
droplet contained an INM. Their highest frozen fractions did not exceed 70% \( (T = 237 \text{ K}) \) for the largest aerosol diameter of 800 nm and their experiments indicate that the grains are not necessary a carrier for an INM to induce freezing. A release and distribution of the INM from pollen in the atmosphere could increase their IN ability drastically, because the INMs are small and a single pollen grain can release a large number of INMs that can easily be distributed in the atmosphere \( (\sim 10^4 \text{ per grain}, \text{ Augustin et al., 2013}) \).

A study by Huffman et al. (2013) observed an increase in the INP concentration and an increase in bioaerosol concentration by an order of magnitude or more after periods of high surface wetness suggesting an effect of high relative humidity on INP concentration. Similar to the exposure of pollen by preparing the pollen washing waters, high \( RH \) in the atmosphere may lead to the release of INMs e.g. by rupture of the grains. However, the relationship between the presence of pollen and INP concentration has not yet been conducted.

Due to the low supercooling required for pollen to nucleate ice, a measurement technique which is able to observe INP concentrations at relatively warm subzero temperatures and low atmospheric abundance is ideal for such observations. In addition, differences in the sampled particle sizes to distinguish the potential effect of whole pollen grains compared to those only referred to INMs is of advantage. A method introduced by Conen et al. (2012) used \( PM_{10} \) filters to collect aerosol for subsequent ice nucleation measurements for the first time. This technique allows for measurements of INP concentrations with a very low detection limit due to the high volume of air sampled. In contrast to continuous flow diffusion chambers (CFDCs), this filter method allows for measurements at warmer subzero temperatures due to bulk sampling and therefore the possibility to investigate ice nucleation onset conditions in the ambient atmosphere potentially driven by aerosol particles with a low abundance such as pollen. This method does not capture whole pollen grains with sizes larger than 10 \( \mu \text{m} \). In contrast, an additional method based on aerosol sampling by liquid impaction as presented by Hader et al. (2014) allows for sampling of large coarse mode particles such as pollen, whereas submicron particles smaller than an aerodynamic diameter of 0.5 \( \mu \text{m} \) are not sampled. Therefore, a combination of different IN techniques is advantageous for measurements of pollen and their potentially released INMs in the ambient air.

3.2 Objectives of the Zurich AMBient Immersion Freezing Study (ZAMBIS)

Ambient in-situ measurements are necessary to investigate the distribution of INPs in the atmosphere. They allow for estimating the atmospheric relevance of pollen grains and their potential release of INMs as well as meteorological factors driving the INP concentration in the atmosphere. The ZAMBIS campaign was conducted to measure INP concentrations in the immersion mode using three different methods in order to capture all aerosol size modes during the ice nucleation experiments for the ground-based experiments performed and allows for INP observations over a wide range of atmospheric temperatures within the limitations
of the methods. The instruments were PIMCA-PINC for measurements on single-immersed aerosol particles and two drop freezing arrays using aerosol sampling by liquid impaction (impinger) or standard \( PM_{10} \) filter sampling. Due to the low fraction of pollen in the total aerosol number, the peak season of birch pollen was chosen to conduct the measurements in order to estimate possible local and regional effects. With the measurements conducted, we tested if INMs were released in the atmosphere during the pollen season by measuring the INP concentration for which an increase is expected in the size range for small particles and if such an increase can be related to the abundance of INMs. Due to their small size, the distribution of INMs can be much higher as compared to those of pollen grains. Therefore, the presence of INMs inducing ice nucleation may significantly contribute to cloud formation on a regional and possibly also on larger scale.

3.3 Description of ZAMBIS and instrumental methods

3.3.1 Field site for ZAMBIS

The ZAMBIS campaign was performed at an urban-forest site in the surroundings of the city of Zurich, Switzerland and a brief description is given in Kohn et al. (2016). The site is located in the northwestern-periphery of Zurich at an elevated area nearby ETH Hönggerberg Campus on a site of the Institute for Atmospheric and Climate Science (IAC, 47.406°N, 8.512°E, 540m above sea level, Fig. 3.1). The site is specified as an urban-forest environment with both anthropogenic and biogenic aerosol. Birch trees north of the site were in their pollen season during ZAMBIS leading to a high concentration of birch pollen. Measurements during ZAMBIS were conducted from 01.04.2014-15.05.2014.

3.3.2 Instrumental setup

Instrumentation was located in a mobile trailer and ambient aerosol was fed through 2 individual inlets from the roof of the trailer. Accompanying measurements were situated outside of the trailer as shown in Figure 3.2.

On inlet 1, in-situ immersion freezing measurements were performed with the PIMCA-PINC setup: The Portable Immersion Mode chAmber (PIMCA) which is an extension to the Portable Ice Nucleation Chamber (PINC) allowing for in-situ ice nucleation measurements on single-immersed aerosol particles. The aerosol number concentration entering PIMCA-PINC was measured with a Condensation Particle Counter (CPC, TSI, Model 3772) after a dilution stage, which is necessary for good peak detection with the setup. Connected to inlet 2 for aerosol number and size distribution measurements were a Scanning Mobility Particle Sizer (SMPS, custom-built, Wiedensohler et al., 2012) for a size range from 10 nm to 880 nm and an Aerodynamic Particle Sizer (APS, TSI, Model 3321) for the size range of 0.5 – 20 \( \mu \)m.
For the second half of the campaign, fluorescent biological aerosol particles (FBAP) were detected with the Wideband Integrated Bioaerosol Sensor (WIBS-4, Healy et al., 2012a,b; Kaye et al., 2005), which allows for classification of the ambient aerosol by size (0.6 – 13 μm) and FBAP concentrations via three fluorescence channels giving indications on the abundance of bioaerosol particles.

Particle inlets were chosen in order to sample the whole size distribution on inlet 2, while measurements on inlet 1 were set up in a way to significantly reduce supermicron particles (see Chapter 2 or Kohn et al., 2016, Appendix C, for more details). At the IAC weather station meteorological data including air temperature, dew point temperature, relative humidity, rain fall, wind speed and direction were taken continuously. Pollen concentrations were measured with a Burkard spore trap (Hirst-type, Hirst, 1952) and the sample was changed every 7 days to obtain a daily time resolution. Dyed pollen were counted optically via a standardized microscope routine in collaboration with MeteoSwiss. In addition to the pollen concentration at the measurement site, measurements from the MeteoSwiss station ZH-Zurichberg located approx. 7 km south-east of the field site were used to provide additional information about the pollen species and concentrations.

Aerosol particles with aerodynamic diameter smaller than 10 μm (PM$_{10}$) were collected daily by a high volume sampler (Model DH-77, Digitel Elektronik AG, 8604 Hegnau, Switzerland).
Chapter 3. Investigating the effects on INP concentration: Results from ZAMBIS

Figure 3.2: Setup of instrumentation in the trailer for in-situ ice nucleation measurements with PIMCA-PINC, number and size distributions and bioparticle detection. At the field site, monitoring of the meteorological conditions and the pollen concentration took place. Aerosol sampling on daily PM filters as well as with a liquid impinger was conducted for the determination of the INP concentration by two drop freezing methods.

on quartz fiber filters with 150 mm diameter. From 07.05.2014 to 11.05.2015, filters were changed twice per day to investigate possible diurnal variations of the particle mass. For some days at the end of the campaign, the inlet of the sampler was modified allowing for the sampling of PM$_{2.5}$ instead of PM$_{10}$. Filters were subsequently weighed to obtain the PM mass per volume of air ($\mu$g m$^{-3}$). Additionally, sections of the filters were used for ice nucleation measurements with the drop freezing experiment described in Section 3.3.3.2. Aerosol sampling in liquid impingers next to the trailer were conducted for selected days of the campaign and a detailed description of the drop freezing procedure used is given in Section 3.3.3.1.

3.3.3 Ice nucleation methods

3.3.3.1 Drop freezing with impingers

Ambient particles of 500 nm and larger in aerodynamic size were collected for analysis of their ice nucleating ability in a process similar to Hader et al. (2014). A known volume of ambient air was pumped through a biosampler (SKC Inc., USA), which collects particles by impaction on a liquid surface. A 0.9 wt% NaCl solution (18.2 MΩ cm Milli-Q water) was used
3.3. Description of ZAMBIS and instrumental methods

3.3.1 Biosamplers

To reduce the impact of any osmotic stress upon any biological particles collected (Stopelli et al., 2014). The biosamplers were run between 30 and 95 minutes, corresponding to $\sim 375$ and $\sim 1225$ liters of air, respectively. The sampling times were used to ensure a sufficient separation between the observations and blank experiments. For longer sample runs the biosampler liquid level was maintained within recommended limits ($\sim 20$ ml) by the periodic addition of pure water. The analysis of the samples began within two hours of collection. The biosamplers were cleaned by soaking in an acid bath for several hours and then rinsing with pure water and ethanol. Experimental analysis of the collected samples followed a process similar to Conen et al. (2012). Up to 54 of 200 µl aliquots of the collected liquid were inserted into micro-centrifuge tubes and suspended in the top of a cooling bath allowing for the whole sample to be immersed in the cooling bath liquid (Lauda Alpha Cooling Thermostat, model RP845). The bath was then gradually cooled by 0.5 K intervals starting at 266 K at which none of the aliquots froze. The temperature of freezing of individual aliquots was noted. The concentration of INPs at each temperature was then estimated with the widely used relationship (Vali, 1971):

$$INP_{\text{IMP}}(T) = \ln \left( \frac{N_{\text{tubes}}}{N_{\text{liq}}(T)} \right)$$ \hspace{1cm} (3.1)

The INP concentration $INP_{\text{IMP}}$ is for aerosol samples collected with impingers. $N_{\text{tubes}}$ is the total number of aliquots in the experiment, $N_{\text{liq}}(T)$ is the number of remaining unfrozen aliquots at a particular temperature and $V_a$ is the volume of air that the aerosol in the aliquot originated from, calculated using total volume sampled and the ratio of the aliquot mass and total liquid sample mass. Blank experiments were performed each day, giving a cutoff temperature between 256 K and 257 K. The cutoff temperature was determined when 10% of the tubes froze at the given temperature during the blank test. Data colder than the cutoff temperature were discarded because of the low signal to noise ratio.

3.3.3.2 Drop freezing of PM filters

$PM$ filters were collected from 01.04.2014 – 15.05.2014 as daily samples ($\sim 23$ h) at a flow rate of $30$ m$^{-3}$h$^{-1}$ starting at 10 am and were analyzed to obtain the INP concentration $INP_{\text{PMF}}$ similar to Conen et al. (2012) as briefly explained in the following. A total of 108 cut-outs with 2 mm diameter were taken from each filter and individually placed into 100 µl Milli-Q water (18.2 MΩcm purity). Sealed aliquots were placed in a tray in an ethanol cooling bath (Lauda Alpha Cooling Thermostat, model RP 845). A total of two batches (each 54 tubes) for each sample was measured in a way that the liquid in the tube was fully immersed by the cooling bath liquid. The experimental starting temperature was typically 269 K at which freezing did not occur and was gradually decreased in steps of 0.5 K. Frozen tubes at each temperature were visually detected until all tubes were frozen. Blank experiments were taken for each sample from the edge of the filter where no particles were sampled and analyzed as a
half batch (27 tubes). \( INP_{PMF} \) as a function of temperature was obtained via Equation 3.1 according to Vali (1971), where \( V_A \) is the volume of air that passed through the filter cut-out of 2 mm. It is derived by the flow rate of the sampler, the sample time and the fraction of the surface area of the 2 mm cut-out in comparison to the surface area of the whole 150 mm filter (see Kilchhofer, 2015, for details).

### 3.3.3.3 Ice nucleation on single-immersed aerosol particles with PIMCA-PINC

Ice nucleation measurements of single-immersed aerosol particles were measured with PIMCA-PINC. The portable setup allows for measuring at remote sites and was deployed in the field for the first time during this campaign. An adjustable dilution was applied after drying the aerosol particles in a diffusion drier. The dilution is necessary so as to not oversaturate the detection of ice crystals in PIMCA-PINC. The particle concentration after dilution varies during the experiment and is measured in parallel downstream of the dilution stage just before particles are sampled by PIMCA-PINC. In PIMCA, aerosol particles are activated to cloud droplets (at \( RH_w > 115\% \)) after which droplets composing of a single-immersed aerosol are supercooled prior to exposure to ice nucleation conditions when the cloud droplets enter PINC. The IN ability is obtained by measuring the frozen fraction (\( FF \)) with the IODE detector, where the ice crystals are distinguished from the unfrozen droplets by depolarization. The measured \( FF \) is then applied to the total ambient aerosol concentration. The frozen cloud droplet number concentration (\( FCDNC \)) is evaluated based on the particle number available for cloud condensation nuclei activation in the atmosphere based on more realistic supersaturations reported from previous studies (compared to \( RH_w > 115\% \) here). Due to the limit of detection of IODE, valid measurements of \( FCDNC \) were usually close to the homogeneous freezing temperatures. We note that a direct measurement of INP concentrations is not possible without making major assumptions of the ambient aerosol and their ability to activate to cloud droplets under typical atmospheric conditions. The \( FCDNC \) can be understood as the upper limit of cloud droplets freezing at temperatures, which can be dominated by homogeneous freezing. For detailed explanation of results obtained from PIMCA-PINC measurements during ZAMBIS we refer the reader to Chapter 2 (Kohn et al., 2016).
3.4 Results and discussion

3.4.1 Observed INP concentrations

An overview of all collected data obtained from immersion freezing from daily PM$_{10}$ filters (PMF method) is shown in Figure 3.3a as a function of $T$. Freezing was observed between 260 K and 269 K with concentrations ranging from $6.62 \cdot 10^{-5}$ L$^{-1}$ to $6.67 \cdot 10^{-2}$ L$^{-1}$ and all samples froze within 8 – 9 K. Background concentrations from the filter fringe were found to be on average a factor of 36 times lower compared to the sample concentrations at the observed temperatures with an average concentration of $3.94 \pm 0.08 \cdot 10^{-3}$ L$^{-1}$ (Kilchhofer, 2015). INP concentrations observed from the blank experiments are subtracted from the samples. The cooling rate during the experiments was not explicitly controlled and temperature was approached by small iterative changes of the cooling bath temperature for intervals of the sample temperature of 0.5 K. Differences of 1 – 1.5 orders of magnitude are found for observed temperatures within the time series of about 6 weeks (colorbar). A lower IN ability was found at the beginning of the campaign (blues) and the highest values at the end of April (greens). This shows that the INP concentration varied by up to an order of magnitude for instance at 263 K over the course of the campaign suggesting differences in the chemical and physical properties of the aerosol particles or changes in the environmental conditions. Onset of immersion freezing was observed at relatively warm subzero temperatures suggesting the presence of bioaerosols acting as INPs as these are the only class of aerosols known to nucleate ice at such warm temperatures (Murray et al., 2012, and references therein). PMF measurements were performed on daily filters with interruptions on some weekend days where no filters were sampled. After 07.05.2014, filters were sampled twice per day and analyzed accordingly. This is visible from the higher upper limit of INP concentration due to a lower sample volume on the filter (Fig. 3.3a, orange data points). The upper and lower limits of detection (beginning/end of each curve) are based on the sample volume of the filter at which all tubes are frozen.

INP concentrations obtained from the impinger samples are presented in the same way in Figure 3.3b. $INP_{\text{IMP}}$ were found in a range from $9 \cdot 10^{-4}$ L$^{-1}$ to $9 \cdot 10^{-1}$ L$^{-1}$ for the temperatures between 256 K and 268 K (Fig. 3.3b). The upper and lower limits of detection vary due to the differences in aerosol sample time which varied from sample to sample more than for the PMF measurements and the limits of detection for the two methods differed by about one order of magnitude. Those for impinger samples were on average approximately one order of magnitude higher in INP concentration and found at about 3 K colder in $T$ compared to the PMF method. For example for temperatures between 260 K and 263 K the span in the data is on the order of 1 – 1.5 orders of magnitude. IMP data were not taken as frequent as for PMF measurements, but with multiple measurements (1 – 3) for days when a sample was taken. For an overview of the frequency of the collected data and the INP concentrations shown as timeseries for all temperatures, we refer the reader to Figure 3.A1. The variation
in INP concentration is of a similar extent as found for PMF samples. In contrast to PMF data, IMP samples indicated the highest IN ability in the first week during ZAMBIS (dark blue) as seen in the highest INP concentrations observed at 257.5 K. In the period from the end of April and beginning of May, a scattering in the data is observed indicating changing properties of the sampled aerosol or the environmental conditions within the period of 1 − 2 weeks.

With the differences found for the onset freezing conditions, data sets between PMF and IMP methods show a good agreement for a range of temperatures. One can also interpret the PMF data by observing that for the INP concentration to reach $10^{-2} \text{L}^{-1}$ a temperature of 261 to 265 K has to be reached (Fig. 3.3a). For impinger measurements in Figure 3.3b an INP concentration of $10^{-2} \text{L}^{-1}$ is reached when the temperature is between 260 and 266 K showing agreement between the two methods. Differences in the range of INP concentrations observed between the two methods arise from differences in the sample volume of ambient air sampled and the higher sample volumes contain more aerosol particles and, thus potential INP induce freezing at warmer temperatures. Differences pointed out for individual sample times may also be affected by the particle size investigated with the methods, where only particle sizes between 0.5 and 10 µm were sampled with both methods. Particles smaller than 0.5 µm were only subject to measurements of PMF samples and those larger than 10 µm for IMP samples.

For measurements on single-immersed aerosol particles measured with PIMCA-PINC, droplets froze at much lower temperatures and usually below 238 K. This is a consequence of individual aerosol particles immersed in the droplets thus providing a smaller surface area or number of sites per droplet in comparison to PMF and IMP measurements. The $FCDNC$ for all
3.4. Results and discussion

Table 3.1: Aerosol particle sizes sampled for ice nucleation measurements and temperature range of resulting INP concentration and FCDNC conducted during ZAMBIS.

<table>
<thead>
<tr>
<th>IN technique</th>
<th>Particle size</th>
<th>Temperature range</th>
<th>INP, FCDNC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIMCA-PINC</td>
<td>yes</td>
<td>&lt; 0.5 µm</td>
<td>(yes, ≤ 1 µm)</td>
</tr>
<tr>
<td>Drop freezing PMF</td>
<td>yes</td>
<td>0.5 – 10 µm</td>
<td>yes</td>
</tr>
<tr>
<td>Drop freezing IMP</td>
<td>–</td>
<td>&gt; 10 µm</td>
<td>yes</td>
</tr>
</tbody>
</table>

samples measured is found between 5.4 · 10⁴ L⁻¹ and 4.1 · 10⁶ L⁻¹ and below 238 K. We refer to Chapter 2 or Kohn et al. (2016) for more details on the immersion freezing results from PIMCA-PINC.

With the combination of the three ice nucleation techniques, INP concentrations were obtained over a range from 233 K (homogeneous freezing) up to 269 K for measurements in the immersion freezing mode. An overview of IN techniques with their investigated particle size range and the temperatures at which the INP concentrations are observed are summarized in Table 3.1. In Section 3.4.2 and 3.4.3 the effect of particle size and variations in the atmospheric conditions possibly triggering the INP concentration are discussed in detail.

3.4.2 The influence of atmospheric conditions on the INP concentration in ground-based measurements

3.4.2.1 Correlations with ambient conditions

A number of factors can influence the INP concentration in the atmosphere and possible factors triggering the INP concentrations are discussed in the following section. Time series data are used from PMF data (daily average) to find possible correlations with the measured ambient conditions. An overall correlation based on the IMP data is limited due to the infrequent measurements. Environmental conditions measured during the campaign as well as INP concentrations with the PMF and the IMP method are summarized as an overview in Figure 3.6 and Figure 3.7 to which we refer the reader for our discussion already.

Pollen

Measurements of pollen concentrations were conducted during ZAMBIS at the site for which data from a selection of days are available, but no continuous measurements were made (Fig. 3.6g). Given we had pollen measurements from two different sites we first conducted a correlation to see how well these sites agreed for the pollen concentration. Excellent agreement was found between the two locations at the ZAMBIS site and at the MeteoSwiss station (R² = 0.99, Fig. 3.A2) which allows for the use of continuous pollen measurements at MeteoSwiss instead of those measured on site. For a correlation between the INP concentration and
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Table 3.2: Correlations ($R^2$) between INP concentrations measured with PMF (or else if indicated as IMP) and different environmental conditions such as the pollen concentrations, bioaerosol particles (FBAP), relative humidity, precipitation and PM$_{10}$ mass for the time series of the campaign and daily averaged values.

<table>
<thead>
<tr>
<th></th>
<th>$T = 261$ K</th>
<th>$T = 263$ K</th>
<th>$T = 265$ K</th>
<th>$T = 266$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pollen $[L^{-1}]$</td>
<td>0.10</td>
<td>0.01</td>
<td>0.22</td>
<td>0.21</td>
</tr>
<tr>
<td>Pollen and $INP_{IMP}$ $[L^{-1}]$</td>
<td>0.14</td>
<td>0.02</td>
<td>0.01</td>
<td>(0.77)</td>
</tr>
<tr>
<td>FBAP $[L^{-1}]$</td>
<td>0.40</td>
<td>0.16</td>
<td>0.22</td>
<td>0.23</td>
</tr>
<tr>
<td>Relative Humidity [%]</td>
<td>0.00</td>
<td>0.01</td>
<td>0.38</td>
<td>0.34</td>
</tr>
<tr>
<td>Precipitation (acc., [mm d$^{-1}$])</td>
<td>0.49</td>
<td>0.16</td>
<td>0.14</td>
<td>0.21</td>
</tr>
<tr>
<td>$PM_{10}$ mass $[\mu g m^{-3}]$</td>
<td>0.03</td>
<td>0.03</td>
<td>0.45</td>
<td>0.42</td>
</tr>
</tbody>
</table>

The pollen concentrations daily averages for $INP_{IMP}$ and $INP_{PMF}$ were used to obtain the correlation. Values for $R^2$ between $INP_{PMF}$ and pollen concentrations were found to range between 0.01 – 0.22 for example temperatures of 261 K, 263 K, 265 K and 266 K as summarized in Table 3.2. These temperatures were selected to obtain results to cover a wide range of temperatures measured with both IMP and PMF methods as can be seen in Figure 3.3a and 3.3b. The low correlation values between PMF samples and pollen concentration is caused because only aerosol particles smaller than 10 $\mu m$ are sampled on the filters compared with the abundant pollen species typically being larger than 20 $\mu m$. In contrast to PMF samples, pollen larger than 10 $\mu m$ are collected in IMP samples. For the INP concentration of the IMP samples and the pollen concentration an $R^2$ is found to be 0.01 – 0.77. At 266 K only three data points were subject to the comparison leading to $R^2 = 0.77$. Discarding this temperature due to statistical insignificance, $R^2$ is only found in the range between 0.01 and 0.14 for the other temperatures tested. We point out that diurnal variations in the pollen concentration can effect this correlation, because the sample periods for the IMP method was short (30 – 95 minutes) and may be influenced by the diurnal cycle of pollen release.

A possible reason for the low correlations of the INP and pollen concentration is that the IN ability of pollen may not be directly related to the number of pollen grains but rather to the abundance of INMs, which can be released in large numbers from a single pollen grain as reported by Augustin et al. (2013) for birch pollen on the order of 10$^4$ per grain. The effect of INMs on the INP concentration can therefore inhibit a correlation with the pollen grains itself for the case that a single pollen grain can release INMs in differing numbers. Another reason is that pollen concentrations in the atmosphere may be too low in comparison with other aerosol particles such as mineral dust particles or particles of biological origin and therefore are not detected with the sampled methods used for the detection of INPs. We note that the environmental conditions varied significantly over the course of the campaign, therefore, an effect of pollen as INPs at times of peak pollen concentrations or certain ambient conditions may still be observable on a smaller time scale.
Bioparticles, precipitation and relative humidity

A study by Huffman et al. (2013) found increasing INP concentrations and bioaerosol concentration after a rain event. A correlation for ZAMBIS measurements is obtained between the INP concentration and precipitation, relative humidity or the number concentration of FBAP for daily mean values (PMF data). For the same temperatures as tested for pollen concentrations, the correlations are given in Table 3.2 (note: FBAP concentrations were only observed in the second half of the campaign). Over the entire campaign, no significant correlation was found between the INP concentration and detected bioparticles, relative humidity or the amount of precipitation. Short term responses could not be captured with this method because of the daily averages of INP concentration, although do not exclude the possibility for a relationship on smaller time scales.

The relationship between INP concentration and $PM_{10}$ mass

$PM$ filter sampling is used globally for monitoring the air quality with a high spatial and temporal resolution. An ice nucleation technique allowing for measurements from such filters is therefore very convenient. As only a section of the filters is used for the PMF technique, samples from standardized measurements can be used without additional sampling effort. To which extent the INP concentrations can be obtained from the mass of the aerosol particles in the ambient was first studied by Conen et al. (2012). Larger aerosol particles are more likely to act as INPs due to the larger surface area. Due to their size, even a small number of large aerosol particles may contribute to a large fraction in the $PM$ mass. A correlation between the INP concentrations obtained from PMF measurements and the $PM_{10}$ mass is tested and the results are shown for selected temperatures in Figure 3.4. The colored lines show a linear fit on the data resulting in no correlation between the measures ($R^2 = 0.03$ to $R^2 = 0.45$ for temperatures between 261 K and 266 K, Tab. 3.2). This indicates that the higher INP concentrations during ZAMBIS did not directly relate to the mass of $PM_{10}$ and allows for speculations that the freezing was not only related to aerosol particles for which the IN ability scales with mass such as mineral dust. Instead, it suggests that specific aerosol species with unique properties led to the ice formation observed. For example small aerosol particles such as bacteria known to induce ice nucleation at low supercooling can therefore be of more relevance in our study. Bacteria can occur in larger number concentrations in the atmosphere for which mean concentrations over land were found to be at least $1 \cdot 10^4$ cells m$^{-3}$ (Bauer et al., 2002) and typical particle sizes are below $\sim 1 \mu m$ (Despres et al., 2012) thus not contributing to a large $PM_{10}$ mass.

In Figure 3.5 the measured INP per unit mass of $PM_{10}$ (in $\mu g^{-1}$) is given. The INP per unit mass range for example from $2 \cdot 10^{-2} - 4.2 \mu g^{-1}$ at $T = 265$ K. At the beginning of April (01.04.2014–03.04.2014) the lowest values were found while the largest values of INP per unit mass were found between 26.04.2014 and 02.05.2014. This shows that over the course of the
Figure 3.4: Correlation between INP concentrations and $PM_{10}$ mass for daily measurements for four selected temperatures indicated by the color (circles). Lines show linear fit curves to the data with the correlation ($R^2$).

Figure 3.5: INP per unit mass sampled on $PM_{10}$ filters in a time series for the campaign. Different colors indicate the difference between some of the observed ice nucleation temperatures.

campaign, the properties of the aerosol must have changed by large extent. The mentioned periods are distinct in the amount and frequency of precipitation as well as the total $PM_{10}$ mass and also the pollen concentration, which influences the distribution of INP per mass according to the properties of the sampled aerosol particles (size, aerosol type, abundance) (cf. Fig. 3.6:d/f/g and Fig. 3.7d).
3.4. Results and discussion

3.4.2.2 Determination of case study periods

As seen in the last section, conditions and properties of aerosol particles differed a lot throughout the campaign. Therefore, different cases during ZAMBIS are analyzed based on the time series of INP concentrations and corresponding environmental conditions in order to investigate potential sources of INP and under which conditions they were relevant. In Figure 3.6 and 3.7 INP concentrations of PMF and IMP experiments are shown in a time series for selected temperatures as well as parallel measurements of meteorological conditions and auxiliary measurements such as number and size distribution of aerosol particles, $PM_{10}$ mass, pollen concentration and FBAP concentrations.

For this study, we focus on three measurement periods of interest to discuss possible environmental conditions driving the ice nucleation ability of the ambient aerosol. The periods are indicated in Figures 3.6 and 3.7 by red vertical lines (A, B and C). The times and the determination of the periods for the case studies are as follows:

- **Period A**: 01.04.2014–03.04.2014
  Period A is a fair weather period with high pollen concentrations. An increase in the INP concentration related to the peak of the pollen season is tested to draw conclusions on the atmospheric relevance of pollen grains as potential INPs.

- **Period B**: 27.04.2014–02.05.2014
  Period B is characterized as a wet and humid period accompanied by heavy precipitation. This time period is used to investigate the potential relationship between INP concentrations and high relative humidity and precipitation.

- **Period C**: 07.05.2014–11.05.2014
  In period C, PMF samples were taken twice per day. This allows for the investigation of possible diurnal variations or the investigation of short term responses on environmental conditions. Such responses can include changes in the bioaerosol concentration and INP concentration triggered by short precipitating periods and changing $RH$ conditions.
Figure 3.6: Overview of INP concentration from a) $PM_{10}$ filters and b) impinger samples for selected temperatures. Other measurement time series given: c) relative humidity where the light color denotes hourly mean values and the thick black line the daily mean; d) accumulated precipitation per hour (yellow) and per day (black bars); e) FBAP concentrations measured with the WIBS as hourly and daily mean values as of 24.04.2014; f) $PM_{10}$ ($PM_{2.5}$) mass from daily measurements; g) daily mean pollen concentrations measured on site (red, ZAMBIS) and at the MeteoSwiss station (MCH station, ZH-Zurichberg). Times without data denotes times when no sampling took place or technical interruptions occurred. Red markers indicate the time periods A, B and C, which are discussed as case studies.
Figure 3.7: Overview of INP concentration as in Fig. 3.6 and c-d) number concentration in the sub- and supermicron size range (hourly and daily mean); e-g) meteorological conditions: ambient air temperature (black) and dew point temperature (blue), wind speed and direction as hourly and daily mean values. Red markers indicate the time periods A, B and C (see text).
3.4.2.3 Period A: Pollen peak period

During period A from 01.04.2014-03.04.2014 high INP concentrations were measured with the IMP method, which coincided with the highest pollen concentrations. The period was dominated by fair weather without precipitation and therefore low RH. INP concentrations were $1 \cdot 10^{-2} - 5 \cdot 10^{-2} \text{L}^{-1}$ at $T = 263 \text{K}$ obtained with the IMP method. Meanwhile, PMF data was in a medium range with $1.6 - 1.9 \cdot 10^{-2} \text{L}^{-1}$ with higher values later in the campaign. The high INP concentrations obtained with IMP samples in the pollen peak period indicate an influence of pollen grains on the INP concentration, which are not sampled on the PMF samples. The highest pollen concentrations were found with daily concentrations exceeding $2.9 \text{L}^{-1}$ on 02.04.2014. The major pollen species was birch pollen contributing to as much as 60% of the total pollen concentration besides white beech, beech, ash, plane, oak, grasses, spruce and pine (Fig. 3.8). Birch pollen are found to serve as efficient INPs in laboratory experiments, when investigated using washing water or whole pollen grains (median freezing temperature 255 K for washing water and 254 K for whole pollen grains, respectively, Pummer et al., 2012). Onset freezing temperatures of birch pollen can be as warm as 264 K in the immersion freezing mode (Diehl et al., 2002). Therefore, a contribution of pollen to the INP concentrations observed and in the temperature regime investigated is possible and the high INP concentrations from IMP samples measured support this suggestion. A pronounced INP concentration measured during the pollen period is in contrast to findings by Hader et al. (2014) who did not observe a correlation between IN ability and the abundance of pollen. We note that the correlation over the course of the whole campaign did also not show correlation to the pollen concentration, but an effect on smaller time scale at which a pollen burst was observed is found in period A and can be related to a certain pollen type. Hader et al. (2014) studied primarily pine pollen, whereas birch pollen were most abundant during period A and are more IN active based on previous laboratory studies (e.g., Pummer et al., 2012).

Pollen concentrations are much lower than total aerosol number concentrations. Therefore,

![Figure 3.8: Daily measurements of pollen concentration and species at the MeteoSwiss station (ZH-Zurichberg) during April and May 2014 in Zurich, Switzerland. Data source: MeteoSwiss.](image)
their impact can be small and possibly only of local and seasonal scales. The release of INMs for pollen into the atmosphere can increase the number of potential INPs and, thus the impact of pollen significantly as the small particles and large numbers can be distributed easily in the atmosphere. Due to their small size, they can also be sampled on \( PM_{10} \) samples when not attached to the pollen grain (or a different carrier larger than 10\( \mu \)m). With the PMF method INP concentrations were not observed to be extraordinarily high in this period and were exceeded later during the campaign by up to an order of magnitude (cf. Fig. 3.6a, period B). The measurement of INPs did not give indications on INMs inducing freezing without pollen grains as their carrier or at least not in a sufficiently large number to dominate the INPs from other sources during period A. The weak southerly winds (Fig. 3.7f-g) and the dry fair weather period without precipitation (Fig. 3.6d) enhanced the emission of pollen grains mainly consisting of birch species. These dry conditions were possibly not ideal for the separation of INMs from their carrier.

Also characteristic for period A are the relatively large amounts of \( PM_{10} \) mass (32−49\( \mu \)g m\(^{-3}\), Fig. 3.6f). A high aerosol mass can reduce the relative importance of pollen due to the high number concentrations of aerosol particles with sizes smaller than 10\( \mu \)m. This sized aerosol particles can be e.g. of mineral dust origin, which are found to nucleate ice well below 248 K, which is in the temperature regime not investigated by the PMF and IMP methods. The freezing onset at much warmer temperatures point to the abundance of other, possibly biological, contents. Minerals dust mixed with biological material were observed to adapt the IN ability of the biological material in immersion freezing experiments (e.g. study on illite with birch pollen washing water, Augustin-Bauditz et al., 2016). Such mixtures or coating of particles with biological material can potentially also occur in the atmosphere and associate the IN ability of the biological material to other carrier particles.

The INP per unit mass as shown in Figure 3.5 for period A is very small compared to later dates during the campaign. This indicates that aerosol particles measured were fairly large and of a high density contributing to the large mass in the size range below 10\( \mu \)m as pollen grains are not sampled on the \( PM_{10} \) filters. This is also visible in the high concentration of supermicron particles measured with the APS (Fig. 3.7d, daily average: 10−20 cm\(^{-3}\)) indicating the presence of aerosol particles below 20\( \mu \)m. Back trajectories for 7 days (cf. Fig. 3.A3) indicate Mediterranean air masses. Mixing with aerosol from desert regions of North Africa is possible, which could explain the enhanced \( PM_{10} \) mass concentration in the first days of April. The abundance of mineral dust such as a Saharan dust event can lead to an increase in the INP concentrations due to the measured size range of 0.5−10\( \mu \)m with both methods, but it was not observed. In addition, during long range transport aerosol particles can age leading to an increase or decrease in the IN ability. This can also include a possible coating with biological material. Due to the absence of an increased INP concentration from the PMF samples a contribution from the large particles (larger than 10\( \mu \)m) such as pollen grains from the site is more likely. Mineral dust (also with biological content) of sizes beyond the upper limit of the \( PM_{10} \) filters are rare.
3.4.2.4 Period B: High INP concentrations accompanied by humid conditions

In the last days of April and beginning of May, the highest INP concentrations were found in the PMF measurements. The weather situation was significantly different from period A. In the period B between 27.04.2014-02.05.2014 heavy rainfall with up to 20 mm per day (accumulated) occurred and humid conditions with mainly south-easterly winds were observed. Pollen concentrations decreased drastically due to wash out and small release from the vegetation due to cooler ambient temperatures ($T_{\text{amb}} < 10^\circ\text{C}$) measured at the IAC weather station at the site. The birch pollen season was approaching its end, which contributed as a major species to the total pollen concentration in period A. An associated decrease is also found in the $PM_{10}$ mass during this period.

Measurements with PMF result in INP concentrations exceeding $1 \cdot 10^{-2} \, \text{L}^{-1}$ for $T = 265 \, \text{K}$ (Fig. 3.6a) and are much higher compared to period A. In period B, no samples were taken for IMP measurements. Even though pollen concentrations as well as $PM_{10}$ mass were low (Fig. 3.6f-g), INP concentrations during period B were the highest observed with the PMF method. Measurements on all FBAP particles during period B were measured in parallel and are between 14 and 47 $\text{L}^{-1}$ as a daily average (Fig. 3.6e). Hourly mean values show a significant variation within the days (Fig. 3.6c, thin line). The variations were less pronounced for days with little or no rain (e.g. 04.05.-07.05.2014). On a daily average no correlation between FBAP and INP concentrations for period B was observed. While the INP concentration did not change significantly during period B, the FBAP concentration decreased significantly (Fig. 3.6a/e). The absent correlation indicates, that the INP concentration was not dominantly driven by the concentration of FBAP detected by the WIBS (0.6 – 13 $\mu\text{m}$), but does not exclude a correlation with certain species not distinguished with the WIBS. A possible aerosol source are smaller INPs such as bacteria or fungal spores. We do not exclude the INMs to potentially induce freezing in this respect, but low pollen concentration decrease the potential for freezing induced INMs washed off from the pollen grains as such were not abundant in a large number. Pollen grains sedimented on the surface may release INMs particularly in humid conditions although it is unknown in which number.

In Figure 3.9 the time series for FBAP concentrations and precipitation are shown in a hourly time resolution in order to examine short term responses. FBAP concentrations often increased after precipitation set in, which is in agreement with findings by Huffman et al. (2013) (Fig. 3.9, black lines). However, the time lag at which the increase is observed varies and is typically on the order of one hour. In addition, a significant increase in the observed FBAP concentration is observed at the end of rain events (cyan) suggesting possible sources of FBAP related with precipitation. An increase of bioparticles with the occurrence of rain on short time scales and high INP concentrations in rainy conditions is in agreement with findings for a forest ecosystem in the Amazon (Huffman et al., 2013; Prenni et al., 2013; Tobo et al., 2013). However, we do not capture short term burst of the FBAP concentration and a related increase in the INP concentration. High $INP_{\text{PMF}}$ were measured during rainy periods, a humidity dependent source is likely for the INPs and may be linked to precipitation.
3.4. Results and discussion

**Figure 3.9:** Time series of concentrations of fluorescent biological aerosol particles (FBAP) and precipitation. FBAP concentrations are shown as an hourly average concentration (green) and precipitation (rain) is accumulated hourly (blue). Black lines show the beginning of a rain event. An increase in the FBAP concentration is found immediately after the rain event (no marker) or with a short time lag on the order of one hour later (red lines). Times at which the FBAP concentration increased significantly after precipitation ended (decreased significantly) are shown as cyan lines.

Events thus FBAP concentrations. Relatively low $PM_{10}$ and supermicron aerosol number concentrations compared to period A rather suggest smaller and lighter particles to induce freezing (Fig. 3.6g and 3.7d). However, FBAP concentrations were not much higher compared to those later in the campaign with less precipitation (Fig. 3.6e). The particles inducing ice nucleation can possibly be below the detection size limit of the WIBS. For example bacteria and fungal spores may have contributed to the high INP concentration as they are much smaller in size, which is indicated by the increased number concentration of FBAP during and after rain events. Fungal spores have a typical size range of $2 - 6 \mu m$ and bacteria are even smaller. During rainfall, these particles can be released by mechanical agitation by raindrops from the surrounding vegetation (e.g., Allitt, 2000; Boyer, 2008; Hirst, 1953). The high relative humidity and leaf wetness can be an additional source of bioparticles e.g. via the active wet ejection of fungal spores (e.g., Despres et al., 2012; Elbert et al., 2007). A third mechanism are aerosol particles which have been precipitated from a cloud during rainfall (e.g., Christner et al., 2008; Morris et al., 2004). After rain, bioaerosol particles may also be emitted from active biota of the wet local surface (Elbert et al., 2007). Due to the small size and low density of bacteria, they do not contribute to the large mass but rather to the number possibly emitted by the ecosystem at the observed humid conditions. As the pollen concentrations were low during period B, freezing induced by INMs from pollen cannot be directly deduced, although due to the number of molecules released from a single grain it is possible that not a high abundance of pollen grains in the atmosphere is necessary to induce freezing by INMs e.g. from bursting pollen sedimented on the surface. A possible contribution of small particles is also indicated by the INP per unit mass as discussed previously (cf.
Fig. 3.5). The INP per unit of mass was very high indicating that the occurrence of a single INP was associated with a small mass, thus supporting our speculation.

### 3.4.2.5 Period C: $PM_{10}$ filter sampling twice per day under changing meteorological conditions

In period C (07.05.2014-11.05.2014), $PM_{10}$ filters samples were taken twice per day to increase the temporal resolution of INP measurements and to investigate possible diurnal variations and short term responses related to the environmental conditions (cf. Fig. 3.A5 and 3.A6 for time resolved data).

Period C shows average INP concentrations for PMF and enhanced concentrations with the IMP method in comparison to the overall findings during the campaign. The weather conditions varied the most during this period with heavier precipitation every second day. According to the daily back trajectories, air mass origins were from different directions and regions (cf. Fig. 3.A7). The daily average in relative humidity changed according to precipitation events and varied between 60 and 80%. Pollen concentrations increased due to the pine pollen season setting in which contributed significantly to the pollen concentrations after 03.05.2014 (cf. Fig. 3.8). Concentrations of FBAP increased from $22 \text{ L}^{-1}$ to $35 \text{ L}^{-1}$ in Period C. $PM_{10}$ filters were measured twice per day starting at 10 am and 10 pm. Data points for INP concentrations from PMF are given at the mid-point of the sample time in Fig. 3.A5 and 3.A6. A diurnal cycle in the INP concentration was not found, which is possibly also related to the still coarse time resolution. For $RH$ a clear diurnal cycle is found with driest conditions in the afternoon (Fig. 3.A5c). FBAP concentrations anti-correlate with the $RH$ in hourly averaged data (thin lines) or else, correlate with a time lag of half a day with highest FBAP concentrations at mid-day as can be seen in Figure 3.A5c/e. A response in the INP concentration (PMF) is neither observed for any other environmental condition in this period nor a diurnal trend is observed.

### 3.4.3 The influence of aerosol particle sizes sampled with different ice nucleation techniques

All three techniques for IN measurements during ZAMBIS have a specific range of aerosol particles investigated, which were introduced in Table 3.1. PIMCA-PINC measurements were mainly obtained for submicron particles, with the PMF method aerosol particle sizes smaller than $10 \text{ µm}$ were sampled and with the IMP method particles larger than $0.5 \text{ µm}$ were probed. Thus, an overlap in the particle size range for the two drop freezing methods is found between $0.5 - 10 \text{ µm}$. The different size ranges allow for the exploration of particle sizes relevant for the INP concentrations observed in this study.

To investigate the effect of particle sizes measured with the different techniques, IMP and PMF measurements were compared. PIMCA-PINC is excluded from this comparison due to
3.4. Results and discussion

Figure 3.10: Correlation between the INP concentration from sampling aerosol particles on PM$_{10}$ filters (PMF) or by liquid impaction with an impinger (IMP). Data are binned by the date of the campaign to distinguish possible differences from the source of the aerosol particles. The grey line shows the one to one line.

the low temperature range in which the IN ability was quantified. The correlation between the INP concentration measured at the temperature and time for PMF and IMP is shown in Figure 3.10. A general agreement between the methods is found indicated by the distribution of the data in comparison to the one to one line. The difference in the INP concentration between the two methods can be observed at different times during ZAMBIS as indicated by the color bar. In the first week of the campaign, which was subject of period A (dark blue), the IMP technique observed at the same temperature significantly higher INP concentrations than with PMF, whereas at the beginning of May measurements with the PMF method were higher for some measurements although a scattering is found. Due to the overlap in the sampled aerosol particle size range, this suggests that particles larger than 10 $\mu$m sampled only with the IMP method contributed significantly to the INP concentrations at the beginning of April (see Section 3.4.2.3), which is in agreement with a possible contribution of pollen grains during period A. In contrast, in the second last week of the campaign a large scattering in the data can be observed. At the beginning of May (orange), small particles below 0.5 $\mu$m must have contributed to the ice nucleation for some days, which were not captured with the impingers visible from higher INP$_{PMF}$. This is the part of the campaign where rain events occurred at least every other day and PM$_{10}$ masses were low (cf. Fig.3.6f/g). This is inline with suggestions made about the potential source of very small aerosol particles such as bacteria acting as INP. However, the scattering indicates, that between 05.05.2015 and 12.05.2014 the aerosol properties must have changed a lot, too. A linkage to changing conditions between rainy and dry days and thus a different size and chemistry of the ambient
aerosol is given. For days at which the IMP method measured higher INP concentration, a contribution from (pine) pollen, for which the concentration increased after the first days of May is possible, but not certain (cf. Fig. 3.8). Thus, a combination of the two methods for INP expands conclusions about the source of the aerosol particles acting as INPs according to their size. The findings with respect to the aerosol size are in agreement with findings at different environmental conditions found in the case studies A and B.

3.4.4 INP concentrations measured during ZAMBIS in a global context

Results from ZAMBIS are compared to previous studies in the immersion mode at different locations and measurements techniques. In Figure 3.11 results from various studies including the INP concentrations from ZAMBIS with IMP samples (green) and PMF (blue) are shown. The mean INP concentration for the whole campaign as a function of temperature is shown as a green and blue line accordingly. The \( FCDNC \) obtained from measurements with PIMCA-PINC are shown in red.

During ZAMBIS, PMF resulted in average INP concentrations of \( 6.9 \cdot 10^{-3} \text{ L}^{-1} \), \( 1.4 \cdot 10^{-2} \text{ L}^{-1} \) and \( 2.7 \cdot 10^{-2} \text{ L}^{-1} \) at 265 K, 263 K and 261 K, respectively. Measurements on the Jungfraujoch (JFJ) in the Swiss Alps conducted by Conen et al. (2012) obtained with the same PMF technique observed INP concentrations which are well within the range of results from the present study, while sample volumes of ambient air were similar (Fig. 3.11, red area). All of their samples showed INPs active at 266 K and colder. Average concentrations were \( 3.3 \cdot 10^{-3} \text{ L}^{-1} \), \( 1.1 \cdot 10^{-2} \text{ L}^{-1} \) and \( 1.7 \cdot 10^{-2} \text{ L}^{-1} \) at 265 K, 263 K and 261 K, respectively (Conen et al., 2012). Observations by Conen et al. (2012) are on average a factor of two smaller compared to measurements during ZAMBIS. Differences in the ice nucleation ability can be for a variety of reasons. Typically, number concentrations of atmospheric aerosol are low on JFJ as the station is often in free-tropospheric conditions (for example below \( 450 \text{ cm}^{-3} \) for the size range of \( 0.01 \text{ - } 3 \mu \text{m} \), Boose et al., 2016), whereas during ZAMBIS, an urban-site was investigated with number concentrations of \( 10^3 \text{ - } 10^4 \text{ cm}^{-3} \) for submicron aerosol particles (cf. Fig. 3.7c). This is in agreement with INP concentrations being lower during ZAMBIS than at JFJ due to the differences in the ambient aerosol number concentration. However, the discrepancy of a factor of two in the INP concentration between the two locations is small suggesting that relative to the aerosol number concentrations the fraction of INPs in the total aerosol was much smaller for the ground-based measurements during ZAMBIS. This could be an effect of the source of the aerosol itself and local influences. Additionally, aging and coating processes in the atmosphere can increase or decrease the ice nucleating ability of aerosol particles transported to JFJ.

The yellow shaded area in Figure 3.11 is reported by Petters and Wright (2015) as a summary of studies on rain, cloud and snow samples (with data from Christner et al., 2008; Hader et al., 2014; Hill et al., 2014; Joly et al., 2014; Stopelli et al., 2014; Vali, 1966, 1971; Wright et al., 2014, and their own study calculated with an assumed cloud water content of 0.4 g m\(^{-3}\)).
3.4. Results and discussion

Figure 3.11: Ambient immersion freezing from various studies in a global context. Impinger samples (green) and PM$_{10}$ filter freezing (blue) from this work are shown by the data points. The mean INP concentration as a function of temperature is given by the green and blue lines for the IMP and PMF method, respectively. The frozen cloud droplet number concentration (FCDNC) is given in red (data: Kohn et al., 2016). INP concentrations from snow, cloud and rain water samples are given for a cloud water content of 0.4 g m$^{-3}$ (Petters and Wright, 2015, and references therein). Measurements from Hader et al. (2014) are taken during a pollen season.

Data from ZAMBIS fit well in the range given by Petters and Wright (2015). We note that measurements with both drop freezing methods (PMF and IMP) were investigated in the upper range of INP concentrations for the warmer temperature regime (above 255 K) in comparison to those reported by Petters and Wright (2015). This gives indications that ambient aerosol measured in ground-based measurements contained in general a comparable INP concentration to those from precipitation. However, a higher INP concentration than those from precipitation samples is given on average and leads to the suggestion of more local sources contributing to the INP concentrations during ZAMBIS. These local sources may not reach altitudes at which cloud droplet and ice formation occurs and can consist of particles e.g. produced by construction work or anthropogenic emissions. However, for the comparison with studies summarized by Petters and Wright (2015), the differences in sample location and the type of the hydrometeors (snow, hail, rain) or cloud water has to be considered. In addition to precipitation samples Hader et al. (2014) performed INP measurements during
the pollen peak season in North Carolina similar to the IMP method in this study (purple lines, Fig. 3.11). Their data agree well with the present study and extend to colder temperatures. Except one of their samples disagreed, which was directly taken after a rain shower and thought to contain a distinct mode of active INPs not present in the other samples. In contrast to the PMF and IMP results, measurements with PIMCA-PINC rarely overlap with temperatures in the summary of Petters and Wright (2015). FCDNCs are found to be up to two orders of magnitude higher at the same temperatures compared the precipitation samples in Petters and Wright (2015) between 235 K and 236 K. This gap can be of two reasons. On the one hand, it can be understood as the discrepancy between homogeneous and heterogeneous ice nucleation in the atmosphere. On the other hand, it gives indications that ground based measurements had a significantly larger number of particles activating to cloud droplets and froze at relatively cold temperatures close to homogeneous freezing conditions. For the determination of FCDNC the CCN concentration was estimated for the surface aerosol. Sedimentation and scavenging processes prior to precipitation can change the properties of the aerosol. This could lead to an overestimation of the FCDNC at altitudes relevant for precipitation formation or else gives indications that not all cloud droplets subject of the determination of FCDNC grow to precipitable size and the contributing INPs are therefore not measured in precipitation samples.

For ambient measurements, a number of empirical parameterizations have been developed. Early studies report temperature dependent parameterizations such as Fletcher (1962), while others include the dependence of supersaturation (Cooper, 1986; Meyers et al., 1992). In Figure 3.11 a comparison of our data with the mentioned parameterizations is shown. Drop freezing measurements (PMF and IMP) show an agreement to parameterizations by Fletcher (1962) for lower INP concentrations and some of the data points are in the range of the parameterization given by Cooper (1986). The predicted INP concentrations by Meyers et al. (1992) is not agreeing with our measurements. Average values during ZAMBIS are in better agreement with the parameterization by Fletcher (1962) in particular for the warmer temperatures investigated. However, a strict exponential agreement is not found in our data sets. A similar finding was reported by Hader et al. (2014) who did not find a strict exponential agreement in all their samples taken with impingers (in particular not the sample obtained after a rain shower). However, the INP concentration in most of their samples could be parameterized with the Fletcher (1962) curve. The scattering in our data throughout the campaign was explained by large differences in the aerosol properties and environmental conditions (cf. Sect. 3.4.2). At a temperature of 263 K INP concentrations were in average $INP_{\text{MP,263K}} = 1.9 \cdot 10^{-2} \text{L}^{-1}$ and $INP_{\text{MP,263K}} = 1.4 \cdot 10^{-2} \text{L}^{-1}$ which is a factor of 4.8 and 2.5 higher compared to the predicted values from Fletcher (1962). At a temperature of 261 K the agreement was slightly better with $INP_{\text{MP,261K}} = 4.7 \cdot 10^{-2} \text{L}^{-1}$ and $INP_{\text{MP,261K}} = 2.7 \cdot 10^{-2} \text{L}^{-1}$ resulting in a difference of a factor 3.5 and 2.0 higher for IMP and PMF data, respectively. FCDNC with PIMCA-PINC extend the ranges for which the parameterizations are valid. However, an exponential relationship on $T$ is found to be on a similar joint slope for the three IN techniques used. The slope of this curve is also similar to the parameterization.
3.5 Summary of the ZAMBIS field campaign

INP concentrations were observed with three ice nucleation techniques during the Zurich AMBient Immersion freezing Study (ZAMBIS) over a period of six weeks and the measurements were obtained between 233 K and 269 K. During ZAMBIS, observations concerning the meteorology, number and size distribution as well as pollen and bioparticle detection gave indications about the sources of the INPs. Over the course of the campaign, daily measurements of INP concentrations obtained from the PMF method were compared to the concentrations of FBAP, relative humidity, the pollen concentration and precipitation without finding correlations. In contrast, analysis of shorter time periods led to findings related to the environmental conditions:

of Fletcher (1962), although we note, that the Fletcher (1962) parameterization is not valid for temperatures at which the \( FCDNC \) was observed.

3.5.5 Benefits and limitations of the used ice nucleation techniques

The combination of three ice nucleation techniques deployed during ZAMBIS provides the opportunity for measurements over a wide temperature and aerosol size range. Although, each of the instruments has its limitations as discussed here. PIMCA-PINC experiments allow for measuring in a high temporal resolution and in-situ, but only for temperatures close to where homogeneous freezing can be dominating due to the detection limit of the instrument. A drop freezing array with PMF or IMP sampling allows for INP concentrations to be obtained at small supercooling. Thus, they are able to detect onset freezing conditions e.g. for bioaerosol particles. In addition, large sample volumes allow for low detection limits and the observations of much smaller INP concentrations in comparison to established in-situ methods (PIMCA-PINC or CFDCs for deposition nucleation/condensation freezing). However, ice nucleation techniques with sampling on filters or in suspensions are offline bulk measurements, in which only the freezing onset is observed at which the most efficient INP (per observed droplet volume) induces the ice formation. Therefore a potential less efficient INP is not observed when distributed in the same sample volume (droplet) with a more efficient INP. Another caveat of the drop freezing methods is the storage of samples, which can potentially reduce the IN ability of the sample to a certain extent. IMP samples were evaluated immediately after sampling. In contrast, \( PM_{10} \) filters were stored prior to analysis for up to one year. A slight decrease in the ice nucleation ability of stored samples was found for snow water samples (Stopelli et al., 2014). This points out, that in particular for bioaerosol particles and organic material, which are more sensitive to storage, a degradation of the INP concentration cannot be excluded as they may lose their viability, leading to a possible reduction in the ice nucleation ability.
The first period of interest (period A) was during a fair weather period accompanied by high pollen concentrations and a large \( PM_{10} \) mass load. The high concentrations were observed from IMP measurements, whereas those from PMF were only at an average concentration obtained during the campaign. An increase of INP concentration during the pollen peak in this period could not be observed with the PMF method suggesting that INP were larger than the cutoff size of 10 \( \mu \text{m} \) \( (D_{50}) \) of \( PM_{10} \) samples. Due to the good efficiency of (birch) pollen to act as INPs and their large sizes of 20 \( \mu \text{m} \) and more, a potential source of INP can be pollen grains. INMs, are small ice active macro-molecules from pollen and can be captured on \( PM_{10} \) samples due to their small size. From INP measurements we could not conclude on the presence of INMs during the peak of the pollen concentrations i.e. were at least not dominating the INP concentration. Also, the contribution of the high \( PM_{10} \) mass was not the major driver for the INP concentration due to the discrepancy between the two methods (PMF and IMP), which both sampled aerosol particles of large overlapping particle size range (0.5 – 10 \( \mu \text{m} \)). However, a smaller contribution from this size range is still possible, but can not be separated from other effects in this study.

For period B low pollen concentrations and \( PM_{10} \) mass were typical. INP concentrations from the PMF method showed the highest values during ZAMBIS and showed little variation within period B. This suggests small particles to be a major source of INPs. Parallel measurements of FBAP concentrations identified an increase of bioaerosol particles during and after rain events, which may be related to the release of bacteria or fungal spores from local sources. The abundance of high numbers of efficient biological INPs can explain the high INP concentration found. However, on a daily average a correlation between INP and FBAP concentrations was not found and is possibly due to the time scale of investigation or particle sizes below the detection limit of WIBS which induced freezing. The comparison between the INP concentration of PMF compared to the IMP method supported our assumptions on the particle sizes of INPs made for the case studies.

The observed INP concentrations fit well in the context of other immersion freezing measurements of cloud, rain and snow water samples from different locations (Petters and Wright, 2015, and references therein), impinger measurements performed in the pollen season (pine pollen) in North Carolina (Hader et al., 2014) and a study using the same PMF method on JFJ (Conen et al., 2012). PIMCA-PINC measurements, which investigated the \( FCDNC \) at temperatures potentially dominated by homogeneous freezing exceeded the other measurements by two orders of magnitude. The parameterization by Fletcher (1962) underestimated our measurements by as much as a factor of 5, but showed the best agreement for the three parameterizations tested. Differences and scattering in the data can be explained by differences in the sample location compared to other studies and prevailing ambient conditions as the latter has been found to have a major effect on the measured INP concentration in the present study.

The atmospheric relevance of pollen on ice formation is still poorly understood. With this study, it has been shown that pollen concentrations may contribute to a small extent to the
INP concentration observed during the peak of the birch pollen season. To act as an INP in the atmosphere pollen grains have to be lifted to altitudes at which ice formation occurs. High relative humidity or immersion into a droplet can release the INMs for subsequent ice nucleation. Due their low number concentrations and additionally the large size of pollen grains in contrast to other aerosol species, this effect is likely to be rather small and seasonal. A distribution of INMs attached to other carriers, such as mineral dust particles, is possible. However, this would also require a release in the atmosphere first. Measurements on the chemical composition of the ambient aerosol may give further indications on the presence of INMs during a pollen season. For future studies, these should be combined with observations of INPs to gain further insight into the relevance of INMs from pollen on atmospheric ice formation.
3.A Appendix: Supplementary data ZAMBIS

Figure 3.A1: INP concentrations obtained from PM$_{10}$ filters (PMF) and with impinger samples (IMP) for the full temperature range investigated. Gaps in the time series indicate days where no samples were taken.
**Figure 3.A2:** Correlation between pollen concentration measured at MeteoSwiss station and ZAMBIS site. Data points are given for all days at which both data sets were available.

**Figure 3.A3:** Daily back trajectories for period A from 01.04.2014 to 03.04.2014. The location during ZAMBIS (Zurich, Switzerland) is shown as a red circle. The back trajectories are calculated for a duration of 7 days and starting at noon 20 m above the ground. Spacing of data points is one hour. Sources of the air masses for the studied period are the Mediterranean with possible influences from North Africa. Trajectories were obtained by the HYSPLIT model.
Figure 3.A4: Daily back trajectories for period B from 27.04.2014 to 02.05.2014. The domain and setup of the back trajectories is the same as in Figure 3.A3. Back trajectories show air masses from the North Atlantic reaching Zurich, Switzerland. Trajectories were obtained by the HYSPLIT model.
Figure 3.A5: Overview of INP concentration from a) PMF and b) IMP for selected temperatures in Period C (07.05.2014-11.05.2014). All parameters as in Figure 3.6 for the short time period.
Figure 3.A6: Overview of INP concentration from a) PMF and b) IMP for selected temperatures in Period C (07.05.2014-11.05.2014). All parameters as in Figure 3.7 for the short time period.
Figure 3.A7: Daily back trajectories for period C from 07.05.2014-11.05.2014. The domain and setup of the back trajectories is the same as in Figure 3.A3. Air mass sources are not consistent and reach the measurement location (Zurich, Switzerland) from north-easterly, south-westerly and westerly directions. Trajectories were obtained by the HYSPLIT model.
Leipzig Ice Nucleation chamber Comparison (LINC): Inter-comparison of four online ice nucleation methods

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Abstract

Ice crystal formation in atmospheric clouds has a strong effect on precipitation, cloud lifetime, cloud radiative properties and thus global energy budget. The formation of ice above 235 K is initiated by nucleation on seed aerosol particles called ice nucleating particles (INPs). Instruments that measure the ice nucleating properties of aerosol particles in the atmosphere need to be able to accurately quantify ambient INP concentrations. In the last decade the number of instruments to measure these properties has increased rapidly. Therefore, there is a need for inter-comparisons to ensure instrument differences are not interpreted as scientific findings.

In this study, we inter-compare a total of four online ice nucleation chambers in parallel measurements. Seven different aerosol types are used including untreated and acid treated mineral dust (K-feldspar and kaolinite), as well as birch pollen washing waters. Experiments exploring heterogeneous ice nucleation above and below water saturation are performed to cover the

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whole range of thermodynamic conditions that can be obtained by the inter-compared chambers. The Leipzig Aerosol Cloud Interaction Simulator (LACIS) and the Portable Immersion Mode Cooling Chamber coupled to the Portable Ice Nucleation Chamber (PIMCA-PINC) perform measurements in the immersion freezing mode. Additionally two continuous flow diffusion chambers (CFDCs) PINC and the Spectrometer for Ice Nuclei (SPIN) are used to perform measurements below and just above water saturation nominally presenting deposition nucleation and condensation freezing.

The results of LACIS and PIMCA-PINC agreed well over the whole range of measured frozen fractions \( (FF) \) and temperature. In general PINC and SPIN compared well, too. Observed differences between PINC and SPIN can be explained by ice crystal growth and residence time in the chamber. Consideration of the latter resulted in an improved agreement. To study the mechanisms responsible for ice nucleation in the four instruments, \( FF \) (for LACIS and PIMCA-PINC) and activated fraction, \( AF \) (for PINC and SPIN) were compared. For simultaneously conducted experiments \( FF \) was up to a factor of three higher than \( AF \) and was not consistent for all aerosol types and temperatures investigated. It shows that measurements from CFDCs cannot be assumed to produce the same results as those exclusively measuring immersion freezing, but instead the need to apply a scaling factor to CFDCs operating above water saturation to allow comparison with immersion freezing devices has to be taken into account. Apart from insights on the capabilities of the individual instruments, the results further provide awareness on factors such as the importance of quality of particle size distributions and dispersion methods for inter-comparing instruments. Investigation of the method’s advantages in particular for instruments used for observation of ambient INP concentrations help to improve the data quality which are used for implementation and validation of modeled atmospheric ice formation.

4.1 Introduction

Ice crystal formation in the atmosphere changes cloud physical and optical properties, thus influencing the lifetime of clouds and is important for precipitation formation (Lohmann and Feichter, 2005). Ice nucleation mechanisms and the properties of aerosol particles acting as so-called INPs, which are seed particles necessary for ice nucleation to occur on, are not sufficiently understood, yet demand further investigation to accurately parameterize atmospheric ice formation in models for weather and climate. Laboratory measurements on well-characterized aerosol particles and observations in the ambient environment improve our understanding of atmospheric ice nucleation in general and help us to understand and quantify the role of different INPs on cloud formation and conditions commonly found in the atmosphere.

Ice nucleation can take place by different mechanisms, either homogeneously at temperatures \( (T) \) colder than 235 K (Pruppacher and Klett, 1997), or heterogeneously – catalyzed by an INP which provides a surface for ice to nucleate on at temperatures warmer than 235 K.
For heterogeneous ice nucleation, several pathways are distinguished: Deposition nucleation, during which water vapor directly deposits on an INP to form ice in liquid subsaturated conditions; contact freezing where freezing is due to a supercooled cloud droplet colliding with an INP; condensation freezing in which water vapor directly deposits on an INP to form ice in liquid supersaturated conditions with the existence of water expected but not explicitly observed; and immersion freezing, when an INP is immersed in a droplet and has attained sufficient supercooling to freeze (e.g., Vali, 1985). Recently, Marcolli (2014) even suggested that deposition nucleation might in fact be immersion freezing of water trapped in pores and cavities at water subsaturated conditions. Which ice nucleation pathways exist and under which conditions they are relevant for the atmosphere is not yet fully understood. However, there is no reason to believe that in the atmosphere a difference in the freezing mechanism would be relevant, as ice formation is invoked via the liquid phase in both cases.

Instruments developed to explore ice nucleation for different formation pathways and to measure the concentration of atmospheric INPs fall into two broad categories: Offline measurements of aerosol collected on filters (e.g., Bigg, 1967; Conen et al., 2012; Klein et al., 2010b) or in suspensions (e.g., Hader et al., 2014), which operate on hour to day timescales, and online measurements which are capable of real-time detection of INP concentration with a higher temporal resolution. Some of the online instruments are portable reporting INP concentrations for both ground-based (e.g., DeMott et al., 2010; Garcia et al., 2012; Tobo et al., 2013) and airborne measurements (DeMott et al., 2003a/b, 2010; Rogers et al., 2001a).

Inter-comparing instruments in the laboratory under controlled conditions is necessary to characterize their performance also for field studies and compare quantitative reproducibility. Some studies have already investigated the comparability of a number of online and offline instruments on selected aerosol types (DeMott et al., 2011; Hiranuma et al., 2015; Wex et al., 2014, 2015). Ice nucleation measurements were conducted with LACIS (Hartmann et al., 2011; immersion mode) in parallel to the Colorado State University (CSU)-CFDC (Rogers et al., 2001b; condensation mode) on size-selected kaolinite particles including samples coated with soluble material (Wex et al., 2014). Lower FFs were measured in LACIS compared to the CSU-CFDC, and good agreement was found when particle residence times were accounted for. Wex et al. (2015) reported measurements on size-selected Snomax® particles with seven instruments including LACIS and PINC (Chou et al., 2011). They examined both droplets formed on single particles and droplets taken from suspensions containing Snomax®. The varying particle concentrations used by the different instruments was accounted for, and the results agreed within a factor of three below 263 K for all instruments. The PINC measurements in liquid supersaturated conditions showed an activation onset temperature of 2 K lower than LACIS showing less ice activity observed in PINC than immersion freezing with LACIS. What factors cause this deviation is not yet fully known. DeMott et al. (2015) presented a comparison of a CFDC to the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) cloud chamber and found agreement only when an empirically determined factor of three was applied to the CFDC data for their measurements of mineral dust at a relative humidity with
respect to water ($RH_w$) of 105%. A previous study on immersion freezing observed differences in the ice nucleation active site density ($n_s$) between LACIS and the Immersion Mode Cooling chAmber coupled to the Zurich Ice Nucleation Chamber (IMCA-ZINC, Lüönd et al., 2010) when the same particle type and size was tested at different times/locations. An offset of about one order of magnitude in $n_s$ or a temperature shift of $5−6\,K$ for kaolinite particles was found (Hartmann et al., 2016). Differences in the aerosol sample can be ruled out for some of the studies as an identical aerosol sample was used in these inter-comparisons. The same aerosol particles were used in a comprehensive inter-comparison of 17 ice nucleation instruments on illite NX showing an even larger deviation of $8\,K$ or three orders of magnitude in $n_s$ between the instruments (Hiranuma et al., 2015). So far it has not been possible to decipher whether these discrepancies are based on the instruments used or other factors such as the particle generation techniques and size-selection, because the instruments were often also not operated in parallel. The discrepancies found in previous studies with a selection of different instruments and aerosol types emphasizes the importance of parallel measurements for a direct comparison of ice nucleation instrumentation. Selection of specific particle sizes can be used to identify any discrepancies that arise from the ice nucleation methods itself as other factors such as different aerosol samples, particle generation methods or particle sizes can be ruled out.

We present a comparison of four online ice nucleation instruments performed during the Leipzig Ice Nucleation chamber Comparison (LINC) in September 2015, which was hosted by TROPOS, Leipzig. Seven different types of size-segregated aerosol particles were tested for their immersion freezing properties, four were additionally tested for condensation freezing and deposition nucleation. The samples were two different mineral dusts (K-feldspar and kaolinite), nitric or sulfuric acid treated K-feldspar particles and birch pollen washing water of a samples from the Czech Republic and from Sweden. As coating of aerosol particles with atmospherically relevant substances such as sulfuric acid can cause a temporary or permanent change in the physicochemical properties of the particles and can decrease the ice activity, an acid treatment of K-feldspar particles was chosen in the present study to investigate a permanent change after treatment and removal of the acid. The selection of aerosol types allows for comparison over the full range of detectable frozen/activated fractions over the entire temperature range possible with the instruments.

A simultaneous comparison of LACIS and PIMCA-PINC (Kohn et al., 2016) is presented for the first time as well as the direct comparison between PINC and SPIN (Garimella et al., 2016) on size-selected aerosol particles providing the ability to investigate instrument specific differences. Further, observations with the four instruments allow for a comparison of measurements of immersion freezing of droplets containing a single aerosol particle (LACIS and PIMCA-PINC) and experiments using dry particles above water saturation (SPIN and PINC), where it is not possible to distinguish between deposition nucleation, immersion and condensation freezing.
4.2. Materials and methods

4.2.1 Aerosol samples and treatment

The kaolinite sample used in this study is a commercially available product from Fluka (same as from Sigma-Aldrich). The K-feldspar sample is mainly composed of microcline and is from Minas Gerais in Brazil. It was provided by the Technical University Darmstadt within the framework of the Ice Nucleation research UnIT (INUIT). 2.5 g of the respective powder material was suspended in 30 ml of double deionized water (Milli-Q, 18.2 MΩ cm) for the purpose of wet aerosolization. For the acid treatment, 2.5 g K-feldspar powder was suspended in 30 ml of 1 M sulfuric or nitric acid solution for about twelve hours. To remove the acid, the suspension was centrifuged at 17000 rpm for ten minutes. The supernatant was removed from the sample, its pH level determined, and the sample diluted with Milli-Q water. This step was repeated several times until the pH of the supernatant reached the same pH as untreated deionized water (pH ∼ 5). The pollen washing water was made from two birch pollen samples belonging to the species *Betula pendula*. One birch pollen sample originated from the Czech Republic (Pharmallerga®, referred to as birchS) and the other one from Sweden (AllergonAB®, referred to as birchN). The sample preparation of the pollen washing water followed the procedure described by Pummer et al. (2012). One gram of the pollen was suspended in 20 ml of Milli-Q water. After one night (about 12 h) in the refrigerator, the pollen grains were removed from the suspension by gravitational filtering (round filter, Schleicher and Schüll Selecta 595, pore size 4−7 µm).

4.2.2 Instrumental setup, particle generation and size-selection

A schematic of the instrumental setup is shown in Figure 4.1. All particles were aerosolized from suspension using a home-built atomizer (design similar to TSI, Model 3076). Droplets of the suspension containing particles were produced and passed through a diffusion dryer creating agglomerates from the residuals of the droplets (Fig. 4.1), which are size-selected in a Differential Mobility Analyser (DMA, type Vienna medium, Knutson and Whitby, 1975). To remove multiple-charged larger particles, a cyclone was operated at 41 min⁻¹ downstream of the DMA (D₅₀ = 500 nm, 50% efficiency). As shown in Fig. 4.1, downstream of the cyclone an aerosol distributor supplied the aerosol (RHₘ below 1%) to all instruments including a Condensation Particle Counter (CPC, TSI, Model 3010), a Cloud Condensation Nucleus Counter (CCNC, Droplet Measurement Technologies, Roberts and Nenes, 2005), an Ultra High Sensitivity Aerosol Spectrometer (UHSAS, Droplet Measurement Technologies), SPIN, LACIS and either PINC or PIMCA-PINC (see Sect. 4.2.3 for description of ice nucleation chambers). Impactors upstream of the sampling devices were not used for any of the experiments to exclude biases from particle losses and were not necessary for the size-selected particles used. Size distribution and hygroscopicity as indicators for acid treatment residue
Figure 4.1: Schematic of the inter-comparison setup at the Leipzig Aerosol Cloud Interaction Simulator (LACIS) facility. Components include a Differential Mobility Analyzer (DMA), Condensation Particle Counter (CPC), Cloud Condensation Nucleus Counter (CCNC), Ultra High Sensitivity Aerosol Spectrometer (UHSAS), the Portable Immersion Mode Cooling Chamber (PIMCA), the Portable Ice Nucleation Chamber (PINC) and the Spectrometer for Ice Nuclei (SPIN).

were monitored after the DMA. UHSAS measurements (not shown) indicate a substantial reduction in the number of multiple-charged particles by the cyclone but not complete removal. Table 4.1 summarizes the selected particle sizes and the fraction of multiple-charged particles during the experiments. It was found that the fraction of multiple-charged particles remained constant in time during each experiment for all particle types investigated. Therefore, the measurements of identical samples at different times have been averaged. The fraction of multiple-charged particles is important when making comparisons to other studies on size-selected particles. CCNC measurements (not shown here) showed complete removal of soluble salt residues from the acid treatment by the applied procedure of repeated rinsing of the sample in a lower hygroscopicity compared to untreated particles.
Table 4.1: Size and fraction of single- or multiple-charged particles (labeled with 1, 2, 3 and 4) of the resulting aerosol after size-selection and the cyclone. Selected sizes and the resulting particle size corresponding to the mean particle surface area corrected by the fraction of multiple-charged particles measured are given in the right column.

<table>
<thead>
<tr>
<th>Substance</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>Selected size [nm]</th>
<th>Measured size [nm]</th>
</tr>
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<tr>
<td>K-feldspar</td>
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<td>324</td>
<td>439</td>
<td>552</td>
<td>200</td>
<td>277</td>
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<tr>
<td>Stokes size [nm]</td>
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<td>0.307</td>
<td>0.086</td>
<td>0.014</td>
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<tr>
<td>K-feldspar</td>
<td>300</td>
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<td></td>
<td></td>
<td>300</td>
<td>342</td>
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<td>0.003</td>
<td></td>
<td></td>
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<tr>
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<td>342</td>
<td></td>
<td></td>
<td>300</td>
<td>347</td>
</tr>
<tr>
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<td>0.017</td>
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<td></td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td>300</td>
<td>342</td>
</tr>
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<td></td>
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</tr>
<tr>
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<td>500</td>
<td>506</td>
<td></td>
<td></td>
<td>500</td>
<td>506</td>
</tr>
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<td>Stokes size [nm]</td>
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<td>0.012</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BirchS</td>
<td>500</td>
<td>534</td>
<td></td>
<td></td>
<td>500</td>
<td>534</td>
</tr>
<tr>
<td>Stokes size [nm]</td>
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<td>0.065</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BirchN</td>
<td>300</td>
<td>329</td>
<td></td>
<td></td>
<td>300</td>
<td>329</td>
</tr>
<tr>
<td>Stokes size [nm]</td>
<td>0.893</td>
<td>0.105</td>
<td>0.002</td>
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<td></td>
</tr>
</tbody>
</table>

4.2.3 Description of ice nucleation chambers

4.2.3.1 PINC

PINC is a portable parallel-plate vertical chamber with two individually temperature controlled walls. Prior to an experiment, a thin ice-layer is applied to the chamber walls to provide a source of water vapor. A difference in temperature (ΔT) is applied to the walls that generates a parabolic supersaturation profile with a peak saturation close to the center of the chamber. Sample aerosol is introduced with a flow rate of 1 l min⁻¹ and layered between two particle-free sheath air flows (4.5 l min⁻¹ on each side) ensuring a narrow sample lamina. After a residence time (t_res) of 4 – 5 s, the aerosol enters the evaporation section of the chamber where the chamber is isothermal set to the warm wall temperature, creating a subsaturated environment with respect to liquid water causing small cloud droplets to evaporate and ice crystals are maintained at ice saturated conditions until detection. At the
bottom of the chamber exiting aerosol particles and ice crystals are counted by an optical particle counter (OPC, Lighthouse R5104). Particles greater than a set size threshold are classed as ice crystals. Ice nucleation below water saturation ($RH_w < 100\%$) is classified as deposition nucleation and above water saturation ($RH_w \geq 100\%$) as condensation freezing. The uncertainty of the temperature sensor is $\pm 0.1\,\text{K}$ and is including the variation of temperature across the sample lamina $\pm 0.4\,\text{K}$. This corresponds to an uncertainty in $RH_w$ of $\pm 2\%$ (Chou et al., 2011; Kanji et al., 2013). For data presented in this study, the INP concentration is obtained by considering a size threshold of 2 $\mu$m for ice. Experiments consist of a scan in $RH_w$ at a prescribed $T$ and are conducted from ice saturation to above water saturation up to an $RH$ at which droplets cannot be distinguished from ice crystals based on size (droplet breakthrough). Before and after each scan, background concentrations in the chamber are obtained by sampling filtered air and this background signal is then linearly interpolated between the two filter periods and subtracted from the sample signal. The $AF$ is determined by the ratio of ice crystals detected with the OPC to the number of total aerosol particles measured with the CPC. Its uncertainty is 14\%, resulting from 10\% uncertainty in both the OPC and CPC.

### 4.2.3.2 PIMCA-PINC

The PIMCA-PINC setup is the portable version of the laboratory design IMCA-ZINC (Lüönd et al., 2010; Stetzer et al., 2008) and allows for measurements in the immersion freezing mode. PIMCA is a vertical extension of PINC in which aerosol particles are activated to cloud droplets at about 303 K, prior to supercooling the droplets to the desired ice nucleation temperature. $RH_w$ in PINC is set to water saturation conditions to maintain cloud droplets at a radius of 5 – 7 $\mu$m. Flow rates are set to 0.61 l min$^{-1}$ sample air with 2.21 l min$^{-1}$ of sheath air on either side of the aerosol lamina. This gives a residence time of $\sim 7\,\text{s}$ at ice nucleation conditions in PINC. Ice crystals and cloud droplets are distinguished via depolarization with the ice optical detector IODE (Nicolet et al., 2010). Unlike the detection system used in the PINC configuration, IODE only observes a small volume of the sample lamina. The frozen fraction derived is the ratio of ice crystals to the total particles detected in this subset of the sample. More details on the specifications of the PIMCA-PINC setup can be found in Kohn et al. (2016). In a typical experiment a temperature scan is performed, starting at homogeneous freezing conditions at $T < 233\,\text{K}$. Temperature is then increased until the detected $FF$ is not distinguishable anymore from the experimental background. Each reported data point consists of an average of two to five individual measurements at the same $T$. This adds up to more than 3000 individual (particle) intensity peaks analyzed per data point shown. For cases of which the temperature scan is repeated in an individual experiment, results for the same aerosol samples are averaged at a given $T$ (see Kohn et al., 2016, for details). Error bars in $FF$ indicate the measurement uncertainty from the classification of ice crystals and cloud droplets and the statistical error using standard error propagation and uncertainty in
temperature is ±0.4 K due to variation throughout the sample lamina and uncertainty in the thermocouple of ±0.1 K (see Kohn et al., 2016 and references therein).

4.2.3.3 SPIN

The SPIN geometry is equivalent to PINC but with almost double the residence time. It is the first commercially available ice nucleation chamber (Droplet Measurement Technologies, Inc.) and was recently described by Garimella et al. (2016). The SPIN chamber allows for an experimental residence time of 8 – 10 s depending on the $T$ and $RH$ set points of the experiment. Additionally, the temperature and supersaturation conditions in the evaporation section can be controlled independently from the ice nucleation section and temperatures as low as 228 K can be reached. Similar to PINC, ice crystals are discriminated from non-activated aerosol particles by a size threshold. For this study a threshold size of 2.5 µm is used. This threshold size is somewhat larger compared to PINC and chosen to clearly distinguish ice crystals from background counts. Background counts from frost particles are measured by sampling filtered air before each $RH$ scan and are subtracted from the ice counts. The AF is obtained in the same way as for PINC. Uncertainty in $AF$ is 14% due to a 10% uncertainty in both the SPIN OPC and the CPC.

4.2.3.4 LACIS

LACIS (Hartmann et al., 2011) is a laminar flow tube where, in contrast to ice coated CFDCs, humidified sheath air is the source of water vapor and the tube walls are water vapor sinks. LACIS consists of seven one-meter long tube sections with an internal diameter of 15 mm with each tube section separately temperature controlled by a thermostat. The aerosol surrounded by humidified particle free sheath air enters LACIS in an isokinetic fashion. This leads to the formation of a particle beam with a diameter of 2 mm at the center of the flow tube. All particles moving along the center-line of the laminar flow tube experience the same humidity and temperature conditions, which depend on the inlet dew point and temperature as well as the wall temperature of the tube sections. Detailed information can be found in Hartmann et al. (2011). In this study LACIS was operated in the immersion mode with aerosol particles activated to droplets which subsequently grew before freezing. The ratio of frozen droplets to the total is determined after a residence time of 1.6 s. This $FF$ is derived from measurements with the Thermo-stabilized Optical Particle Spectrometer for the detection of ice (TOPS-Ice, Clauss et al., 2013) installed underneath LACIS evaluating a change in polarization to distinguish between frozen and unfrozen droplets.
4.3 Results and discussion

4.3.1 Ice nucleation ability of investigated aerosol types

In the following, the ice nucleation ability of the tested samples are compared to previous studies for immersion freezing (Sec. 4.3.1.1) and deposition/condensation nucleation (Sec. 4.3.1.2) in which only measurements from PIMCA-PINC and PINC are shown for clarity. Additional measurements with LACIS and SPIN are discussed in Section 4.3.2 and 4.3.3.

4.3.1.1 Immersion freezing with PIMCA-PINC

A total of seven aerosol samples were investigated during LINC for immersion freezing experiments. Figure 4.2 summarizes size-segregated measurements with PIMCA-PINC for mineral dusts and pollen washing waters given as symbols. For comparison with previous LACIS measurements, model calculations using the Soccer Ball Model (SBM) were made with correcting for the number of multiple-charged particles and particle sizes from this study (Table 4.1). Parameters used for the SBM calculations are based on fits to previous LACIS measurements (Table 4.2, Augustin et al., 2013; Augustin-Bauditz et al., 2016; Hartmann et al. 2016; Niedermeier et al., 2015) and respective curves are shown in Fig. 4.2.

For size-selected K-feldspar the temperature at which half the cloud droplets freeze ($T_{50}$) is between 244 K and 244.5 K for 200 nm and 300 nm particles and the SBM modeled $T_{50}$ are between 243 and 244.5 K (200 and 300 nm). The increase in FF with decreasing $T$ is well reproduced by the model calculations, but for $T < 240$ K the model results underestimate the measurements. PIMCA-PINC data shows a higher ice activity for both particle sizes and the modeled plateau does not occur, in which FF doesn’t change with temperature. Parameters for the SBM taken from Niedermeier et al. (2015) are based on measurements for which the number of multiple-charged particles was taken into account for FF. Correcting the FF from PIMCA-PINC with the fraction of multiple-charged particles as done by Niedermeier et al. (2015) does improve the agreement to the model below 240 K, however, does not produce a plateau in FF in the measurements (see Appendix 4.A for multiple-charge corrected data).

It should be noted that the recent study of Niedermeier et al. (2015) examined dry dispersed particles, while in the present study particles were generated from aqueous suspensions. In contrast to our comparison with Niedermeier et al. (2015), Harrison et al. (2016) observed a decrease of the mean freezing temperature by 2 K when the K-feldspar was kept in water for 16 month. A decrease in the freezing temperature was observed on other mineral dusts, too, when the sample was suspended in water (e.g., Koehler et al., 2010, Arizona test dust in subsaturated conditions).
4.3. Results and discussion

Figure 4.2: Summary of immersion mode experiments with PIMCA-PINC. Results are shown for untreated and nitric or sulfuric acid treated mineral dusts (panel A) and for birch pollen washing waters of two sources (birchS and birchN, panel B). Curves show results of the SBM using fit parameters from literature (see text for details). The grey shaded area represents homogeneous freezing for PIMCA-PINC (Kohn et al., 2016). $T_{50}$, where half of the droplets have frozen, is indicated by the horizontal black dashed line; different symbols correspond to independent experiments. Error bars show the uncertainty due to the ice identification technique and the uncertainty in $T$.

Compared to K-feldspar, 500 nm kaolinite particles were less efficient. Heterogeneous freezing between 235 K and 243 K was observed, but $T_{50}$ was not reached before homogeneous freezing $T$. Kaolinite from the same supplier has been used previously in studies with PIMCA-PINC and IMCA-ZINC (Kohn et al., 2016; Lüönd et al., 2010; Welti et al., 2012). Kohn et al. (2016) reported for 400 nm particles a $T_{50}$ of 238.0 K, which agreed well with IMCA-ZINC experiments by Welti et al. (2012) when taking time dependence into account ($T_{50} = 238.5$ K also for 400 nm). During LINC the freezing temperature of 500 nm kaolinite particles was found to be about 3 K lower than the 400 nm particles used by Kohn et al. (2016) with wet
Table 4.2: Parameters from literature used for Soccer Ball Model calculations shown in Fig. 4.2 with the fractions of multiple-charged particles as shown in Table 4.1. The mean, $\mu_\theta$, and standard deviation, $\sigma_\theta$, of contact angle distribution, lambda and $S_{\text{site}}$ are taken from literature.

<table>
<thead>
<tr>
<th>Aerosol type/Reference</th>
<th>$S_{\text{site}}$ [m$^2$]</th>
<th>$\mu_\theta$ [rad]</th>
<th>$\sigma_\theta$ [rad]</th>
<th>$\lambda$</th>
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<tr>
<td>K-feldspar 200 nm</td>
<td>$10^{-14}$</td>
<td>1.29</td>
<td>0.10</td>
<td>6.46 $\cdot$ 10$^{12}$ m$^{-2} \cdot S_p$</td>
</tr>
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<td>Niedermeier et al. (2015)</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>K-feldspar 300 nm</td>
<td>$10^{-14}$</td>
<td>1.29</td>
<td>0.10</td>
<td>6.46 $\cdot$ 10$^{12}$ m$^{-2} \cdot S_p$</td>
</tr>
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<td>Niedermeier et al. (2015)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite 500 nm</td>
<td>$10^{-14}$</td>
<td>1.87</td>
<td>0.25</td>
<td>n.a.</td>
</tr>
<tr>
<td>Hartmann et al. (2016)</td>
<td></td>
<td></td>
<td></td>
<td>$n_{\text{site}} = 10^{12} \cdot S_p + 0.0203$</td>
</tr>
<tr>
<td>BirchN 300 nm</td>
<td>$3.14 \cdot 10^{-16}$</td>
<td>1.016</td>
<td>0.08</td>
<td>(a) $3.3 \cdot 10^{12}$ m$^{-2} \cdot D_p^2$</td>
</tr>
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<td>Augustin-Bauditz et al. (2016)</td>
<td></td>
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<tr>
<td>BirchN 300 nm</td>
<td>$3.14 \cdot 10^{-16}$</td>
<td>1.016</td>
<td>0.08</td>
<td>(b) $6.65 \cdot 10^{11}$ m$^{-2} \cdot D_p^2$</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>BirchS 500 nm</td>
<td>$3.14 \cdot 10^{-16}$</td>
<td>1.016</td>
<td>0.08</td>
<td>$1.777 \cdot 10^{-6}$ nm$^{-2} \cdot D_p^2$</td>
</tr>
<tr>
<td>Augustin et al. (2013)</td>
<td></td>
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</table>

Dispersed kaolinite particles appearing to be less efficient compared to previous dry dispersed particle experiments. This is unexpected as larger particle sizes with larger surface area are sampled in this work. However, the produced SBM curves based on dry dispersed particles experiments by Hartmann et al. (2016) yielded an even lower $FF$ for the $T$ range of 235—243 K (Figure 4.2A, blue curve). As the ice activity of kaolinite particles observed during LINC within the range of previous measurements of dry dispersed particles, the dispersion method (wet vs. dry) does not fully explain the discrepancy found compared to previous studies, but suggests experiment specific discrepancies.

When the K-feldspar samples were treated with sulfuric or nitric acid, no quantifiable ice nucleation ability was exhibited by PIMCA-PINC. Augustin-Bauditz et al. (2014) found a significant decrease in the ice nucleation ability of the same particle type in the immersion mode when coated with sulfuric acid without removing the acid prior to the experiment. Our results indicate a permanent reduction in the ice activity of K-feldspar after treatment with acids and removing acid residuals from the particle surface. Homogeneous freezing occurs at colder temperatures for the acid treated K-feldspar samples and indicates a smaller droplet volume compared to experiments by Kohn et al. (2016) (grey area in Fig. 4.2). A reduction in the hygroscopicity of the aerosol particles due to the acid washing (see Section 4.2.2) and a resulting delay in the droplet activation in PIMCA can lead to smaller droplets explaining this effect.

The birch pollen washing waters birchS and birchN were active below 258 K (Fig. 4.2B). In comparison to the mineral dusts, the $FF$ showed a shallow temperature dependence. For birchN $FF$ levels off below 248 K, but not as clearly as for the birchS sample. Based on our SBM calculation using fit parameters from Augustin et al. (2013), the ice activity of the
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BirchS samples was expected to be higher than measured. However, the lower ice activity as measured in the current work could arise from the sample used being kept at room temperature for more than three years therefore experienced a reduction in ice activity during storage. The steep increase before homogeneous freezing is due to the distribution of ice nucleation active macro-molecules (INMs) which only a subset of the produced particles contain of as observed by Augustin et al. (2013). Using fit parameters from (Augustin-Bauditz et al., 2016) for the birchN sample reproduces the freezing curve within measurement uncertainty for most of the data points, although a plateau in FF with decreasing temperature was not clearly observable.

4.3.1.2 Ice nucleation ability of aerosol types in deposition and condensation mode

The ice nucleation behavior of K-feldspar (with and without nitric acid treatment), kaolinite and birch pollen washing water (birchN) were tested with PINC in the water sub- and supersaturated regime between 233 K and 253 K (Fig. 4.3). An efficient INP is indicated by high AF at low RH. Among the tested mineral dust samples, the untreated K-feldspar particles (300 nm) showed the highest AF for a given RH (Fig. 4.3A). The ice formation onset (here defined for convenience of discussion as \( \text{AF} = 10^{-3} \)) for untreated K-feldspar is observed at \( RH_w = 89\% \) (RH with respect to ice \( RH_i \) is 120\%) and the maximum \( \text{AF} \) ranges from \( 6 \cdot 10^{-1} \) to \( 3 \cdot 10^{-3} \) for 236—253 K. Earlier deposition nucleation studies on K-feldspar observed a similar range of \( \text{AF} \) (Emersic et al., 2015; Yakobi-Hancock et al., 2013; Zimmermann et al., 2008). Treatment of K-feldspar with nitric acid (Fig. 4.3B) resulted in a lower \( \text{AF} \) maximum of \( 10^{-2} \) when comparing temperatures of 233—243 K for untreated and nitric acid treated samples, implying a decrease in ice activity which was also observed in the immersion freezing experiments (see Sec. 4.3.1.1). Freezing onset conditions did not significantly change with acid treatment below 240 K (Fig. 4.3B), but at 243 K onset was observed at higher \( RH_w \).

Kulkarni et al. (2014) also reported a reduction in the ice nucleation ability after sulfuric acid coating of 200 nm K-feldspar particles. They found a maximum \( \text{AF} \) of \( \sim 0.3 \) at 238—248 K without treating and an about two orders of magnitude decrease in the deposition regime and up to one order of magnitude decrease in the condensation regime due to the sulfuric acid coating. A general reduction in the ice nucleation ability agrees with the immersion freezing measurements on K-feldspar after treatment with nitric acid presented in this work, but sulfuric acid treatment was not tested with PINC.

The ice nucleation activity of kaolinite (Fig. 4.3C) was tested at four temperatures. Similar onset freezing conditions to the K-feldspar samples were observed (Fig. 4.3A; \( \text{AF} = 10^{-3} \) onset conditions at \( RH_w = 90–98\% \)). For the lowest temperatures (236 K, 240 K and 245 K) a reduction in the increase in \( \text{AF} \) is found with increasing \( RH_w \) above water saturation indicating a saturation effect of ice nucleation occurring. This is not observed at 233 K because the
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Figure 4.3: Activated fractions measured with PINC as a function of RH$_w$ at selected temperatures for four aerosol types: A) K-feldspar untreated (300 nm) and B) K-feldspar after treatment with HNO$_3$ (300 nm), C) kaolinite (500 nm) and D) birch pollen washing water (birchN, 300 nm). Example measurement uncertainties are given for K-feldspar (A) at 248 K.

The experiment was stopped shortly after reaching water saturation as the limit of the supersaturation attainable by PINC (limited by the cooling power of the walls) at these temperature conditions was reached. The required RH$_w$ for an AF of 10$^{-2}$ at 233 K is approx. 20% higher compared to a previous study by Welti et al. (2009, 400 nm particles), even though larger particle sizes were tested in the present study. Compared to data reported on the same kaolinite sample by Wex et al. (2014) (300 – 700 nm particles, 239 – 243 K), in the present study 15 – 20% higher RH$_w$ was required to reach the same AF of 10$^{-3}$. This shows that kaolinite particles investigated during LINC were less active as INPs compared to previous studies. One difference between previous studies and the present work is that aerosol particles in Welti et al. (2009) and Wex et al. (2014) were dry dispersed and wet dispersion methods can reduce ice nucleating activity in some cases (Koehler et al., 2010). A possible explanation is that in suspension, a redistribution of soluble material can lead to covering ice active sites on the particles thus inhibiting freezing or the soluble material keeps the subcritical ice embryo in a stable condition thus inhibiting heterogeneous freezing due to the solute. These processes have already been suggested by earlier studies (e.g., Alpert et al., 2011; Koehler et al., 2010; Welti et al., 2014), but may be limited to the ice nucleation pathway. In contrast to immersion mode in which a possible redistribution of the solutes on the surface may not play a significant role since the solute re-mobilizes in the droplet, the ice activity in subsaturated conditions can be affected. Thus, the reduction in activity observed in the deposition nucleation regime
could point to, but does not limit to an effect of the wet dispersion. Birch pollen washing water (birchN sample, Fig. 4.3D) shows a steep increase and high maximum value in $AF$, suggesting uniformity among the particles responsible for ice nucleation. At 248 K, ice nucleation onset occurs at 94% $RH_w$ and at 233 K, the onset $RH_w$ is 85%. The temperature dependence of the maximum $AF$ value of the pollen sample is less pronounced than the K-feldspar sample suggesting that the threshold temperature required to freeze birchN is much warmer and a decrease in temperature results in only a marginal increase in freezing.

### 4.3.2 Comparison between PIMCA-PINC and LACIS

Immersion freezing experiments performed during LINC using PIMCA-PINC and LACIS are shown in Fig. 4.4. Experiments were repeated three times for untreated K-feldspar, once for kaolinite and twice for all other samples. When averaging the $AF$ in 1 K bins, within the experimental uncertainty a good agreement ($R^2 = 0.90$) is found between the two instruments (Fig. 4.5A). $FF$s measured with PIMCA-PINC tend to be slightly higher than those of LACIS at low $FF$ (warmer $T$) and vice versa at high $FF$. By using the Bland-Altman approach (Bland and Altman, 1999), the difference in $FF$ between PIMCA-PINC and LACIS as a function of their obtained mean $FF$ was calculated and shows no trend, implying no dependency of the smaller disagreements from $FF$ observed (Fig. 4.5B). This result suggests, that discrepancies found previously are not due to the ability of PIMCA-PINC and LACIS to accurately quantify immersion freezing. Instead, it points to differences in sample material, and treatment prior to measurements such as the dispersion method (wet vs. dry) and size-selection procedure in recent non-parallel instrument inter-comparison studies.
Figure 4.4: Comparison of FF observed with PIMCA-PINC (colored points) and LACIS (black crosses) for various aerosol types. A-B) untreated K-feldspar 300 nm and 200 nm, C-D) 300 nm K-feldspar with treatment with $H_2SO_4$ and $HNO_3$, respectively, E) kaolinite (Fluka) 500 nm, F) 500 nm birch pollen washing water (birchS) and G) 300 nm birch pollen washing water (birchN). The grey area is the same as in Fig. 4.2. Error bars show the uncertainty for distinguishing cloud droplets from ice crystals with the depolarization detector. The horizontal dashed line denotes the $T_{50}$, at which 50% of the droplets freeze.
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4.3.3 Comparison between SPIN and PINC

For the first time PINC and SPIN measurements were conducted using the same size-segregated aerosol particles. Experiments between 233 K and 253 K scanning RH from ice saturation up to above water saturation until droplet breakthrough were conducted for four aerosol types: untreated and nitric acid treated K-feldspar, untreated kaolinite and birch pollen washing water (birchN). In Fig. 4.6 SPIN and PINC data for all aerosol types and temperatures are shown. In general, the two instruments produce similar dependencies of AF on RH_w and temperature. Overall, SPIN detects higher AFs, with differences more pronounced at lower temperatures and RH_w. For the birchN, the difference at low temperatures is much less pronounced than for the mineral dusts, suggesting an aerosol specific behavior. The ice activity of particles influences the time for ice growth, with less efficient particles having a shorter available growth time due to non-instantaneous nucleation upon entering the chamber (see Section 4.3.3.3 for further discussion). The largest deviation between PINC and SPIN is observed for measurements on nitric acid treated K-feldspar, which showed a different behavior and lower AF measured with SPIN compared to those from PINC. Note that measurements on nitric acid treated K-feldspar were performed on two different batches of nitric acid treated samples, i.e. PINC and SPIN were neither sampling the same sample batch nor in parallel for this aerosol type. However, no differences in the size distribution after size-selection or the hygroscopicity of the particles in the two batches were observed, which could explain the differences in ice nucleation between the instruments.
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Collecting the data in $\pm 2\%$ $RH_w$ and 1 K temperature bins, $AF$s measured with PINC and SPIN can be compared (Fig. 4.7). Overall the instruments compared well ($R^2 = 0.74$). The lowest $AF$s shown are closer to the detection limits of SPIN and PINC and scattering is expected to be much larger as can be seen by the differences between SPIN and PINC as a function of their mean $AF$ (Fig. 4.7B). Reasons for the deviation from the 1:1-line may be related to $T$ and $RH$ uncertainties, different data analysis procedures or instrument design differences such as residence time or the method of detection of ice crystals. These differences are discussed below.
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Figure 4.7: A) Correlation of AF measured with PINC and SPIN differentiated for aerosol types and corresponding measurement uncertainties. Data is binned in ±2 % in RH_w to obtain the correlation. B) Differences in AF between PINC and SPIN as a function of their mean AF measured. The red dashed lines show the standard deviation (1σ) range.

4.3.3.1 Data analysis techniques

As described in sections 4.2.3.1 and 4.2.3.3, background counts obtained from sampled filtered air are treated differently for the ice nucleation counters. For PINC, the background is found to deteriorate during the RH scan. To estimate the background counts during the scan, a linear interpolation between the background measurement at the beginning (lower background counts) and at the end (higher background counts) of each RH scan is performed. For PINC a typical background concentration between the start and end of an RH scan was 3.01^{-1} obtained with a sample concentration of 6130 l^{-1} on average for example for an experiment on kaolinite at 248 K. This indicates that the ice crystal concentrations in the experiments were sufficiently large and the background counts only played a minor role. For SPIN the chamber background is determined at the beginning of each RH scan and subtracted from the ice counts during the experiment. Is is reasonable to assume that the background counts in SPIN also increase with increase in ΔT (and RH) as is the case in PINC. However, the lack of a high RH background measurement will result in higher ice crystal counts for SPIN than PINC at the highest RH. Even though background counts were treated differently in the two chambers the resulting change in AF with or without background correction (see Appendix 4.B for an example on PINC data) does not explain the discrepancies at high RH_w nor the large offset in onset conditions although contributing to differences observed at low RH_w.
4.3.3.2 Importance of particle size threshold for ice crystal identification

The experiment-specific size threshold to distinguish ice crystals from unactivated aerosol particles as is used for CFDCs complicates a direct comparison, especially at low $T$ and low $RH$ where ice growth is kinetically limited. The comparison between PINC and SPIN was performed with ice crystal size thresholds of 2 and 2.5 $\mu m$ respectively. The size thresholds were chosen such that ice crystals could accurately be counted while preventing unactivated particles being falsely counted as ice crystals. To demonstrate the effect of a change in the threshold size, Fig. 4.8 shows a comparison on the example of the ice nucleation scans on kaolinite using a 2 $\mu m$ ice crystal threshold for PINC and either 2.5 $\mu m$ or a 4 $\mu m$ size threshold for SPIN. Although the maximum $AF$ observed in SPIN did not change drastically with a change in the threshold size from 2.5 $\mu m$ to 4 $\mu m$, at low $AF$ there is a significant change observed with freezing onsets ($AF = 10^{-3}$) up to 3 – 4% $RH_w$ higher than for the 2.5 $\mu m$ threshold case. Increasing the ice threshold up to 4 $\mu m$ in SPIN gives a better agreement between the SPIN and PINC onset conditions, but not in the maximum $AF$ observed. Thus, changing the threshold size does not completely overcome the discrepancy in $AF$ between PINC and SPIN for kaolinite, which suggests that other factors such as time dependence of the aerosol sample may contribute to the discrepancy.

Figure 4.8: PINC and SPIN RH scans for size-selected kaolinite particles. PINC data is analyzed with an ice crystal size threshold of 2 $\mu m$. SPIN data is presented with the used ice threshold size of 2.5 $\mu m$ and a larger one of 4 $\mu m$. 
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4.3.3.3 Residence time in the ice nucleation chamber

Another factor to be taken into account is differences in the residence time between SPIN \( t_{\text{res}} \approx 9 \text{s} \) and PINC \( t_{\text{res}} \approx 5 \text{s} \). Longer residence time allows for ice crystals to grow to larger sizes, allowing crystals that do not nucleate immediately upon entering the chamber to still have enough time to nucleate and grow before being detected. In particular at low \( T \), where the growth rates are lower, this could explain the higher \( AF \) measured with SPIN compared to PINC. Following Rogers and Yau (1989) crystal growth by diffusion for spherical ice crystals and different temperatures were calculated using the typical residence times of PINC and SPIN (Fig. 4.9). The mass accommodation coefficient was set to 0.3 based on literature data by Rogers and Yau (1989) \((0.2 \text{ for small ice at } T > 263 \text{K})\) and Skrotzki et al. (2013) \((0.2 – 1 \text{ for } T = 190 – 235 \text{K})\) and the starting particle diameter used was 500 nm, the same as used for kaolinite experiments. Note, that \( t_{\text{res}} \) changes by 1–2 s depending on the experimental temperature and supersaturation. The growth rates show that for a threshold size of 2 \( \mu \text{m} \) at 233 K, PINC would detect an ice crystal at \( RH_w = 78.5 \% \), but for SPIN detection is possible at \( RH_w = 74 \% \) (solid black lines/symbols, Fig. 4.9) in both cases assuming nucleation occurs instantaneously upon the aerosol particle encountering the chamber conditions. The ice threshold size of 2.5 \( \mu \text{m} \) used for SPIN in this study accounts for this effect (grey lines), which reduced the observed difference in ice onset to \( \sim 1 \% \) \( RH_w \) between PINC and SPIN. While this resulting difference is small, it must be noted that the particles are exposed to an \( RH \) distribution across the aerosol sample lamina of \( \pm 2 \% \), which additionally varies with the nominal \( RH \) condition and \( T \) due to chamber flow dynamics. Therefore, the deviation in \( RH_w \) at which a fixed ice crystal size is reached may be underestimated. Further, it must be noted that this calculation assumes spherical ice crystal growth and also that nucleation is instantaneous and the entire residence time in the nucleation chamber is available for growth. If the latter two were not the case it would result in a reduction of available time for ice crystal growth, and therefore larger differences would be expected at the position of detection for the two chambers. More efficient INPs would rapidly freeze without a large time delay and support the hypothesis of ice growth effects and a weaker time dependence as can be observed for K-feldspar at lower temperatures and birchN (Fig. 4.6). Instead, less efficient aerosol particles such as kaolinite would spend part of the time in the chamber dry rather than growing as ice, and for the 5 s PINC residence time this dry period would take up a greater proportion of the growth time than in SPIN leading to generally lower ice activity being detected as can be observed at high \( RH_w \) and warmer temperatures (Fig. 4.6). In fact the same kaolinite sample as tested here has been shown to display time dependence towards ice nucleation in the immersion freezing mode in the work of Welti et al. (2012) supporting our observations that ice growth alone does not completely explain the discrepancy.

A commonly used ice nucleation model to account for time dependence (stochastic description, Murray et al., 2012), the heterogeneous nucleation rate coefficient \( (J_{\text{het}}) \) is determined
using the following relationship:

\[ J_{\text{het}} \left[ \text{s}^{-1} \text{m}^{-2} \right] = -\frac{\ln(1 - AF)}{A \cdot t_{\text{nuc}} \left[ \text{s} \right]} \]  

(4.1)

where \( A \) is the surface area of the sampled aerosol and \( t_{\text{nuc}} \) the nucleation time. Using this model improves the agreement between PINC and SPIN (Fig. 4.10). In particular, the offset at low \( AF \) is diminished by taking the residence time into account. A caveat when using \( J_{\text{het}} \) is that \( t_{\text{res}} \) is not the same as \( t_{\text{nuc}} \), but rather the sum of the time required for nucleation (\( t_{\text{nuc}} \)) and growth prior to detection. As such \( J_{\text{het}} \) should be treated as a lower limit to the true nucleation rate. The time after which an ice crystal is detected on one hand depends on how fast ice growth is occurring and on the other hand at which time in the chamber ice nucleation occurred after exposing the particles to the investigated ice nucleation conditions of interest. However, studying after which residence time in the chamber the ice nucleation occurs in order to accurately account for this effect cannot be obtained by the type of experiments conducted in this work.

**Figure 4.9:** Ice crystal growth calculations for the typical residence times of 5 s in PINC (circles) and 9 s in SPIN (crosses), according to Rogers and Yau (1989) using a mass accommodation coefficient of 0.3. Vertical black lines show the discrepancy in RH\(_w\) arising from ice crystals counted with the same ice threshold size of 2 \( \mu \)m in both SPIN and PINC. Grey lines indicate the ice threshold size used during LINC resulting in a much smaller discrepancy in onset RH\(_w\). The used ice threshold sizes for PINC and SPIN are indicated by the horizontal dotted lines. Markers on the line plots are spaced by 1 % RH\(_i\).
4.3. Results and discussion

Figure 4.10: A) Correlation for the heterogeneous nucleation rate coefficient for PINC and SPIN on different aerosol binned by ±2% in RH<sub>w</sub>. B) Differences in J<sub>het</sub> between PINC and SPIN as a function of mean J<sub>het</sub>. The red dashed lines show the standard deviation (1σ).

4.3.4 Comparing immersion and condensation freezing

In atmospheric mixed-phase cloud conditions it is suggested that the immersion mode is the dominant heterogeneous freezing pathway (e.g., Ansmann et al., 2008), which explains the raising interest in measuring atmospheric immersion freezing with in-situ instruments such as CFDCs. How well condensation freezing measurements in CFDCs compares with immersion freezing is not sufficiently investigated and was tested by comparing measurements from PIMCA-PINC and LACIS to those from SPIN and PINC (Fig. 4.11). PIMCA-PINC and PINC cannot be operated at the same time and therefore these experiments were performed on different days by running experiments with three out of the four instruments in parallel. Measurements on nitric acid treated K-feldspar were excluded as the aerosol was inactive in the immersion mode within the instruments detection limits. For the three tested aerosol types (K-feldspar, kaolinite and birchN), a clear offset is found for measurements with PINC and SPIN compared to immersion freezing, with a more pronounced discrepancy at lower T (Fig. 4.11). Maximum AF in PINC and SPIN did not exceed AF = 0.6, indicating that not all aerosol particles activated to ice crystals at the highest RH<sub>w</sub> before droplet breakthrough biases the results. In Fig. 4.12 a scatter plot for FF of PIMCA-PINC and the AF of PINC and SPIN are shown with respective lines for ratios of 1:1, 1:2 and 1:3 between the samples. LACIS data is excluded from the figure for clarity and not necessary for this discussion due to the good agreement found with PIMCA-PINC (Sec. 4.3.2).
Figure 4.11: Comparison of all instruments. PIMCA-PINC and LACIS experiments were performed with droplet activation prior to exposure to freezing conditions. Results from immersion freezing experiments are reported as $FF$. PINC and SPIN measured the activated fraction ($AF$) at ice nucleation conditions above water saturation and $RH_w$ up to droplet breakthrough, which is the limitation for the scan range. $RH_w$ is indicated by the color bar. The uncertainty in $AF$ for PINC and SPIN is 14\%.
Figure 4.12: Scatter plot showing of FF (immersion freezing) and AF (condensation freezing experiments above water saturation) showing discrepancies between the instruments. Lines show the 1:1, 1:2, 1:3 ratios (black, red, pink respectively) for three different aerosol types. PINC and SPIN data are binned by RH\(_w\) of ±2%.

For K-feldspar below 243 K FFs measured with PIMCA-PINC are a factor of 2 – 3 higher and more than a factor of three higher at warmer temperatures. A similar behavior is observed for kaolinite with scaling factors of three or larger required to achieve agreement with immersion freezing. This is in agreement with the scaling factor of three previously reported by DeMott et al. (2015) comparing experiments on mineral dust between CSU-CFDC and the AIDA cloud chamber. The offset between FF and AF is observed in all cases tested and it is noteworthy that the factor is not found to be constant across the different experimental temperatures and aerosol types tested during the present study. For the birchN sample, the scaling factor behaved differently with being less than two at 243 K and up to three for colder temperatures.

The disagreement in ice activity observed with four independent online instruments provides evidence that CFDCs should not be assumed to give the same results as the existing in-situ chambers exclusively measuring immersion freezing. The results raise the question what possible differences can lead to this discrepancy and whether these are of physical or instrumental nature. If the ice nucleation mechanism is the same in all instruments (i.e. ice forms from liquid at the surface of an immersed particle), the most fundamental difference between condensation and immersion freezing experiments is the additional need to create liquid water during condensation freezing starting with a dry aerosol particle. Recently, DeMott et al. (2015) showed that aerosol particles can in fact be activated inside the CFDC to a sufficiently large droplet size to investigate immersion freezing in the CFDC. However, at which time
in the chamber ice nucleation occurs and whether the residence time after droplet activation is sufficient is unclear. Common ice nucleation counters operate on different residence times and if the time is not sufficient for droplet growth in the instrument prior to freezing, a discrepancy is possible. The time lost nucleating and creating sufficient liquid within the growth section of the CFDC would cause a reduction in the observed condensation freezing, especially for INPs that show a time dependence for immersion freezing which is the case for the kaolinite sample used here (Welti et al., 2012). However, results reported by Wex et al. (2015) indicate not a strong time dependence in the immersion mode, but point to a possible limitation for high temperatures (above 263 K) and very short residence times. In addition to the time effect, the maximum $\text{RH}_w$ resulting from the instruments droplet breakthrough limits the maximum $\text{AF}$ before all particles nucleate ice and are detected. Changes in the dynamics of the CFDC at high $\text{RH}_w$ as indicated by Rogers (1988) and DeMott et al. (2015) with respective temperature gradients larger than $10–15\,\text{K}$ may be leading to undercounting of ice crystals in the CFDC and makes an improving agreement at higher $\text{RH}_w$ unlikely – even for instruments with a higher droplet breakthrough $\text{RH}_w$. An obvious instrumental difference between the CFDCs and the immersion mode instruments are the methods of ice crystals being detected using two completely different measures. While the CFDCs detect the ice crystals as an absolute concentration in the sample air volume via a size threshold (ratio of ice to total particle number entering the chamber), LACIS and PIMCA-PINC observe the fraction of frozen droplets via depolarization (ratio ice to total number of ice and droplets) in a subset of the sample. The latter assumes that the sample volume is representative of the total sample air, with the advantage of being less sensitive to particle losses in the chamber, inlet system and tubing compared to the detection with OPCs using a size threshold only. The decision on the experiment specific threshold size is an additional uncertainty in the absolute ice counts detected by the OPCs. Both setups have their advantages and the combination of depolarization detectors measuring the absolute number of ice crystals is advantageous for future studies, thus so far limited by measured particle size ranges and technical limitations of the instrument. For a final judgment on the effects leading to the observed differences or a difference in the freezing mechanism itself, disentangling of the mentioned instrumental effects will be necessary.

4.4 Summary and conclusions of the LINC instrument inter-comparison

Experimental results of four online ice nucleation devices were compared using size-selected aerosol particles as INPs. Two devices capable of measuring immersion freezing (PIMCA-PINC and LACIS) and two CFDCs measuring deposition nucleation and condensation freezing (PINC and SPIN) were used in this study. The investigated aerosol samples were K-feldspar untreated and treated with either sulfuric or nitric acid, kaolinite (Fluka) and two types of birch pollen washing waters, which allowed for measurements in the whole range of temperature (and $\text{RH}$) possible with the chambers. Parallel measurements with different experimental
setups using a variety of size-selected aerosol particles were used to validate the performance of individual instruments to each other and potential differences of the mechanisms can be investigated.

Immersion freezing measurements were compared to SBM calculations based on previous measurements in literature, which reproduced the increase in $FF$ with temperature well. However, a plateau in which the $FF$ does not change in temperature as given by the SBM calculation was not observed for the experiments of PIMCA-PINC on K-feldspar. Treatment of K-feldspar with sulfuric or nitric acid, where the acid was removed from the particles prior to experiments, destroyed the ice nucleation ability of the K-feldspar permanently and heterogeneous freezing was not quantifiable with PIMCA-PINC. Kaolinite particles were also underpredicted by the model in their ice nucleation ability although their freezing curves (i.e. $T_{50}$) showed a temperature difference of up to 3 K lower compared to previous studies (Kohn et al., 2016; Löönd et al., 2010; Welti et al., 2012). A possible reason is that aerosol particles during LINC were wet dispersed while those reported in previous studies were dry dispersed. However, this finding is inconclusive as contradictory results were found when SBM results were compared to previous measurements with LACIS (Hartmann et al., 2016) from dry disperse measurements. It has to be kept in mind that a direct comparison of dry and wet dispersed particles was not conducted during the present study and could be a topic for future work. Additional measurements on birch pollen washing waters showed ice nucleation occurring as warm as 258 K and the combination of all aerosol types investigated allowed for measurements in the whole temperature range possible with PIMCA-PINC.

Measurements of deposition nucleation and condensation freezing with PINC showed ice formation at higher $RH_w$ than previous studies, indicating that the particles were not very ice active in the water subsaturated regime and revealed lower ice nucleation efficiencies compared with previous studies on kaolinite (e.g., Welti et al., 2014; Wex et al., 2014). Treatment with nitric acid of K-feldspar led to a significantly reduced $AF$ between 233 and 243 K. In contrast, the birchN sample showed a steep increase on $RH_w$ and high maximum in $AF$ below 248 K compared to the tested mineral dusts.

A comparison of parallel measurements with LACIS and PIMCA-PINC, conducted for the first time with these instruments, showed good agreement ($R^2 = 0.9$) for investigated aerosol types. No instrument specific differences for immersion freezing experiments were found when compared in parallel suggesting other factors such as the particle size-selection and dispersion method contributing to any discrepancies found in previous studies when the same instruments are compared.

Measurements from the two CFDC instruments PINC and SPIN were compared in sub- and supersaturated $RH_w$ regime. In general, $AF$ showed good agreement ($R^2 = 0.74$). However, a direct comparison showed that SPIN detects higher $AF$, in particular at low temperatures (233 – 236 K) and $RH_w$. Calculations of ice crystal growth revealed that the chamber residence times, in addition to the selected ice crystal threshold sizes, explained any discrepancies. For higher $T$ and the parameters of $t_{res}$ and threshold size, this effect diminishes. Part of this difference in onset $RH_w$ between both chambers was already accounted for by adjusting
the instrument specific ice crystal threshold size used to classify unactivated aerosol and ice crystals (PINC 2 µm; SPIN 2.5 µm). In order to account for the residence time in the experimental results, calculating the heterogeneous nucleation rate coefficient produced a better agreement between the two instruments. This shows that differences in the chamber residence times of the instruments, and its effect on the reported results of a CFDC, cannot be ignored as well as differences on the ice growth rates, which depend on experimental temperature and RH.

Lastly, results from all four instruments were compared to investigate possible differences between immersion- and condensation freezing. Overall a clear discrepancy was found, with immersion freezing being up to a factor of three higher than condensation freezing for untreated mineral dust samples, which is a similar scaling factor as reported by DeMott et al. (2015), but was observed to vary with aerosol type investigated and temperature. When comparing CFDCs with the in-situ chambers exclusively measuring immersion freezing, it has to be kept in mind that different methods of ice detection are applied. While CFDC instruments measure absolute ice concentrations, which are normalized to unactivated particles, immersion freezing is obtained by self normalization using the ratio of ice crystals to the sum of ice and droplets directly. To determine to what extent CFDCs are able to measure immersion freezing, further investigations at very high RH allowing for full droplet activation within the residence time of the chamber as well as the evaluation of the comparability of the detection methods are desirable. An assessment of how all instruments measure the same mechanism (i.e. immersion freezing) cannot be made based on the present study. However, the finding stresses that CFDC measurements should not be assumed to produce the same results as experiments on immersion freezing while sufficient residence time for droplet activation is unclear and different methods are used for ice detection.

4.A Appendix A: Correcting the frozen fraction for multiple-charged particles

Previously, some studies have introduced the correction for multiple-charged particles in the size distribution of quasi-monodisperse particles to inter-compare independent studies on INPs in the immersion mode. According to Table 4.1, the $FF$ has been recalculated using the approach of Hartmann et al. (2016) and the measured fractions of single- and multiple-charged particles:

$$FF_{\text{calc}} = a_1 \cdot (1 - \exp(J_{\text{het}} \cdot A_1 \cdot t_{\text{res}})) + a_2 \cdot (1 - \exp(J_{\text{het}} \cdot A_2 \cdot t_{\text{res}})) + a_3 \cdot (1 - \exp(J_{\text{het}} \cdot A_3 \cdot t_{\text{res}})) + ...$$

(4.2)

with $a_i$ being the fraction of particles with $i$ charges and the particle surface area of $A_i$. $J_{\text{het}}$ is chosen to reach the minimum squared error for the difference between $FF$ and $FF_{\text{calc}}$. The
corrected frozen fraction $F_{\text{corr}}$ is then obtained by

$$F_{\text{corr}} = a_1 \cdot (1 - \exp(J_{\text{het}} \cdot A_1 \cdot t_{\text{res}})) \ (4.3)$$

as shown in Fig. 4.A1.

\[\text{Figure 4.A1: Frozen fraction for measurements obtained with PIMCA-PINC. The same data as Fig. 4.2 but here accounting for the fraction of multiple-charged particles in the quasi mono-disperse sample. Soccer Ball Model calculations (solid lines) were taken from Fig. 4.2.}\]
4.B Appendix B: Effect of instruments background correction on the activated fraction

Ice crystal counts in CFDCs are biased with background counts such as ice crystals falling off the iced chambers walls, which are falsely counted as ice crystals. The so called background counts are evaluated for PINC at the beginning and after each RH scan is measured, which is linearly interpolated and background counts are then subtracted from the sample counts. The background correction for SPIN was conducted in a different manner in the presented inter-comparison study by only taking the background measured at the beginning of the RH scan into account. In order to discuss possible differences between PINC and SPIN, the effect of the background in a typical experiment during this study is shown on the example of kaolinite (Fig. 4.B1). It shows that for high AF (high RH_w) the correction has a minor effect for the plots usually presented on the log-scale (data points are overlapping). For measurements presented here the treatment of the background between SPIN and PINC does not affect the main findings. The interpolation through the scan for PINC would in particular effect the values at high RH_w. However, for low AF closer to the freezing onset, the background correction reduces the AF. Thus, accounting for the background does not explain differences observed between PINC and SPIN. Instead, it supports that for particle concentrations used in this study, the accounting for the background counts does not have an influence on the findings. It is noteworthy that a stronger effect may be found for experiments with low AF or INP concentration such as measured in field studies for which the correction of the background has to be carefully considered.

Figure 4.B1: Activated fraction results of PINC as shown in Fig. 4.8 including background correction (circles) and raw data without accounting for background counts (crosses).
Chapter 5

Conclusions

5.1 Summary of the results

5.1.1 Development of a new portable device for in-situ detection of immersion freezing nuclei

A new portable instrument for both laboratory and field studies was developed and introduced. The Portable Immersion Mode Cooling chAmber (PIMCA), which is a vertical extension of the established Portable Ice Nucleation Chamber (PINC) allows for the investigation of the ice nucleating properties of individual aerosol particles. Aerosol particles are activated to cloud droplets and grow in PIMCA prior to supercooling in the transition to PINC. Supercooled cloud droplets with an immersed aerosol particle are directly fed into PINC in which freezing of the cloud droplets can occur at a prescribed ice nucleation temperature and at water saturation. Thus, the PIMCA-PINC setup allows for ice nucleation measurements exclusively in the immersion freezing mode.

In the design phase, computational fluid dynamics simulations were conducted to simulate residence time and cloud droplet size within the chamber. For the total flow rate of 5 lpm used in the PIMCA-PINC setup, a cloud droplet with a radius of 5 – 7 µm is exposed to ice nucleation conditions for about 7 s. It is crucial that the cloud droplets are large enough to survive the subsaturated transition regime between PIMCA and PINC and also for reliable determination between nucleated ice crystals and unfrozen cloud droplets with the ice optical detector (IODE). This is particularly challenging due to the partial evaporation of cloud droplets in the subsaturated regime with respect to water in the transition zone between PIMCA and PINC and in the lower section of PINC (evaporation section). Validation experiments for homogeneous and heterogeneous freezing on well-defined aerosol particles (ammonium sulfate, ammonium nitrate, kaolinite) are presented and agreed well with theory and literature within the uncertainty of the detector.
5.1.2 Ice nucleation measurements during ZAMBIS

The ZAMBIS campaign was conducted during the spring of 2014 in Zurich, Switzerland. Three ice nucleation techniques were used to obtain INP concentrations in the immersion mode at an urban-forest site and for the first time, over a wide temperature range between 233 K and 269 K.

During ZAMBIS, the first ambient measurements were successfully performed with PIMCA-PINC and are so far the only field observations of INPs in the immersion mode on single-immersed aerosol. Over a period of six weeks, ice nucleation measurements were conducted resulting in frozen cloud droplet number concentrations which were quantifiable close to homogeneous freezing temperatures in PIMCA-PINC and present the upper limit of cloud droplets frozen at the observed temperature in the atmosphere. The $F_{CDNC}$ below 238 K was between $5.4 \cdot 10^4 - 4.1 \cdot 10^6 \text{L}^{-1}$ derived by estimating typical CCN concentrations for urban aerosol at a supersaturation of 0.3%. Ice nucleation occurring warmer than $\sim 238$ K was not quantified with PIMCA-PINC due to the sensitivity of the IODE detector and the dominance of non-INPs. However, two additional ice nucleation methods were deployed for measurements in the warmer temperature regime to obtain ambient INP concentrations. Both of these drop freezing methods used are bulk measurements i.e. the aerosol particles were either sampled by liquid impaction (impingers) or by standardized $PM$ filter sampling using a high volume sampler. The drop freezing methods allowed for investigation of onset freezing temperatures and low INP concentrations in the immersion mode, which are typically not reached with CFDC measurements in either deposition nucleation or the condensation freezing regime at the same temperatures. INP concentrations measured were between $6.62 \cdot 10^{-5}$ to $9 \cdot 10^{-1} \text{L}^{-1}$ for temperatures between 269 K and 265 K. In comparison to the submicron aerosol particles investigated with PIMCA-PINC, the two drop freezing techniques allowed for measurements in two particle size ranges: Impinger samples collected aerosol particles above 0.5 $\mu$m and $PM_{10}$ filters sampled ambient aerosol particles smaller than 10 $\mu$m in aerodynamic diameter (both $D_{50}$). The difference in sampled sizes could indicate if particles larger than 10 $\mu$m or smaller than 0.5 $\mu$m played an active role in ice nucleation.

5.1.3 Pollen concentration and environmental conditions driving the ambient INP concentration

During ZAMBIS, a number of auxiliary measurements were performed to investigate which environmental conditions influence ambient INP concentrations. Different hypotheses were tested.

Pollen are known for their good ice nucleating properties inducing freezing at low supercooling. However, due to their low abundance and large particle size of typically larger than 20 $\mu$m, their atmospheric impact in terms of ice formation probably matters only regionally and at the peak of the pollen season. The abundance of highly active INMs which might be released
from the pollen grains in high number concentrations and of small sizes was investigated by measurements of ambient INP concentrations in parallel to pollen concentrations. The INMs can easily be distributed in the atmosphere due to their small size. During ZAMBIS, total pollen concentrations of up to \(3 \text{ L}^{-1}\) were measured. Measurements of INP concentration showed an increase during a period in which highest pollen concentrations were observed. This increase was found for impinger samples only, which suggests that particles larger than 10 \(\mu\text{m}\) contributed to the freezing. An increase in INP concentrations from the \(PM_{10}\) samples, including the small particle sizes not captured by impinger sampling during this pollen peak was not observed. However, we cannot exclude an influence of the smaller INMs. According to this result, we did not find clear indications for the abundance of the small INMs without pollen grains as their carrier by measuring the ambient INP concentration. High concentrations from the \(PM\) filters were observed during a humid period with heavy precipitation. Pollen concentrations and the mass concentration of ambient aerosol particles decreased significantly, while the INP concentrations were high for \(PM_{10}\) filters. Low pollen concentration decreased the probability for INMs to be present as they are thought to be observed with the presence of pollen grains. However, a secondary release of sedimented pollen grains exposed to high relative humidity and leading to emission of INMs is possible. Small aerosol particles induced the freezing suggesting the presence of either other INPs of biological origin or else mineral dust or maybe soot, which does not exclude a possible contribution from present INMs although we were not able to identify their presence. The opposite finding would have increased the atmospheric relevance of pollen drastically, because the INMs are much smaller compared to the coarse pollen grains and can easily be distributed in the atmosphere and lifted to altitudes in which ice nucleation prevails. For time series of INP concentrations from \(PM_{10}\) filter samples, the highest IN ability was found for high relative humidity conditions with precipitation. This is in agreement with a previous study by Huffman et al. (2013) observing high ice activity after rain. A correlation between bioaerosol particles and INP concentration was not clearly deducted from FBAP observations for daily measurements taken with the PMF method. In addition, bioparticle detection (diameter larger than 0.6 \(\mu\text{m}\)) did show large variation during rainy conditions, but not a drastic increase, which makes a firm conclusion impossible. A comparison to the dry period in terms of bioparticle measurements was unfortunately not possible with the available data.

5.1.4 Inter-comparing ice nucleation techniques in the immersion and other ice nucleation modes

Although indications exist that immersion freezing is the most relevant heterogeneous ice nucleation pathway in the atmosphere, many ice nucleation techniques measure different freezing modes according to the set points of the instrumentation or the analysis technique. Some portable ice nucleation devices, such as established CFDCs, are not able to explicitly distinguish which ice nucleation pathway occurs. In order to gain a better understanding on which
mechanisms are measured and how data can be compared, an instrument inter-comparison was performed within this thesis. Parallel measurements allow for constraining variables which can influence the experimental results such as the aerosol samples used, the particle generation method and the size-selection setup.

Immersion freezing on single-immersed aerosol particles obtained with PIMCA-PINC were compared in parallel measurements for the first time with the laboratory setup LACIS and led to an excellent agreement. This finding proves that former differences were not related to instrumental differences but rather to external factors such as sample preparation or size-selection.

In addition to the two immersion mode experiments, the CFDCs PINC and SPIN were compared for the first time on size-selected aerosol particles. SPIN is the first commercially available CFDC based on the measurement principle and design of PINC. The two instruments compared well. Observed differences were explained by ice crystal growth and differences in residence time in PINC and SPIN and consideration of the latter resulted in an improved agreement. These measurements were performed in the deposition nucleation/condensation freezing regime, where droplets are not explicitly activated prior to ice nucleation taking place.

For the investigation between measurements in the immersion freezing (droplet activation prior to freezing) and condensation freezing (possible droplet activation and growth during the freezing process), all four instruments were compared. A clear distinction was observed between immersion freezing results and the CFDCs. They were found to be a factor of $2 - 3$ apart, but differed with the aerosol sample used and experimental temperature. This shows that measurements with the CFDCs do not lead to the same results as those techniques observing immersion freezing alone. It is suggested that techniques to distinguish ice crystals from aerosol particles can contribute to this effect. However, this discrepancy does not prove a difference in the freezing mechanisms themselves. It rather points to the need for more investigations in this respect in order to exclude the possibility of experimental differences being falsely interpreted as differences in the ice formation mechanism and to quantify discrepancies as well as under which conditions they occur.
5.2 Outlook

5.2.1 Improvements for the PIMCA-PINC setup

Within the goals achieved during this work and the advantages of the portable setup developed, a number of improvements can be suggested for future projects with the PIMCA-PINC setup. These are in particular addressed for ambient immersion freezing experiments. At its present state ambient PIMCA-PINC measurements are only quantifiable at temperatures close to where homogeneous freezing prevails. In order to improve the temperature regime that PIMCA-PINC is capable of sampling in, the sensitivity of detection needs to be improved for quantitative measurements in the heterogeneous temperature regime for \( T \) significantly warmer than 238 K. Currently, the sensitivity of detection is a frozen fraction of \( \sim 0.1 \). Due to the low concentrations of INPs observed in ambient conditions reducing the background counts produced by the chamber due to the high humidity source (humidification system) in PIMCA, could greatly improve the capabilities of PIMCA-PINC. Moreover, a re-evaluation of the experimentally obtained depolarization threshold to distinguish the particle phase in the intensity peak algorithm or the use of a more sensitive detector can improve the quality of the results.

The decrease in droplet size in the evaporation section of PINC is a major problem in the current configuration as smaller droplet sizes lead to a higher probability of misclassification between ice crystals and cloud droplets by the IODE detector and therefore higher uncertainties in the measurements. Disabling the evaporation section by applying the same temperature gradient as in the growth section of PINC will prevent droplet evaporation and result in a better signal to noise ratio. Due to the necessity of the evaporation section for PINC in the deposition nucleation and condensation freezing modes without PIMCA, an extension of the growth section by decoupling the cooling circuit of PINC is not permanently possible. To achieve this, a major reconstruction of PINC would be required, with the ability of the cooling system to be run in two modes. A detector which can distinguish between the ice and the liquid phases downstream of the PINC chamber, such as the optical particle counter, but with the ability for depolarization, can be of advantage. However, humidification of the PIMCA chamber walls drastically increases the background of small particles, which are not detected by IODE, but may be observed by more sensitive detectors applied downstream of the chamber.

5.2.2 Increasing the detection sensitivity for ambient observations with PIMCA-PINC by size-selection of ambient aerosol

Given the limitations for ice detection in the current setup, for future ambient measurements it would be highly beneficial to select the particle sizes which are investigated in terms of ice nucleating properties. Often, the fraction of aerosol particles acting as an INP in the ambient
is on the order of 1 in $10^6$ requiring a sensitivity in frozen fraction of as low as $10^{-6}$ for quantitative measurements. A selection of a certain particle size range possibly acting as INP e.g. by size-selection or a reduction of small aerosol particles, which are only acting as CCN can be advantageous for measuring in the heterogeneous temperature regime. More remote locations such as the research station on Jungfraujoch being typical for lower ambient aerosol number concentration could be a first step for future studies. As IODE requires the dilution of the aerosol concentration ($<50 \text{ cm}^{-3}$) a low ambient aerosol number concentration such as found at remote sites are not a limitation. A number of techniques can be used to select a certain size range of aerosol particles in the sample air flow e.g. a pumped counter-flow virtual impactor for the selection of large particles (Kulkarni et al., 2011). However, their deployment with PIMCA-PINC is currently impossible as a pressure drop in the sample line is induced by these devices and large particles induce a depolarization signal thus can be falsely counted as ice crystals.

Parallel measurements of CCN concentrations to PIMCA-PINC observations are highly recommended for future studies. This allows for applying the measured frozen fraction from PIMCA-PINC to a measured CCN concentration, which represents the real atmospheric number of potential cloud droplets under typical atmospheric conditions without making assumptions on the hygroscopicity of the ambient aerosol tested.

5.2.3 Estimating the relevance of INMs in the atmosphere

For a quantitative estimation of the atmospheric relevance of INMs and if they are released directly into the atmosphere, further ambient measurements are needed in which measurements of the chemical composition are used to identify the presence of INMs in the ambient aerosol. For these measurements whole pollen grains need to be separated e.g. by size without applying an artificial relative humidity exceeding the ambient conditions or even washing of the pollen. Additional parallel observations on pollen concentration and INP concentration can then be used to estimate the atmospheric relevance of INMs separated from pollen grains quantitatively. Apart from pollen and their remains, other aerosol types such as mineral dust, fungal spores or bacteria can be distinguished by their size, fluorescence and number. For a quantitative conclusion about the effect of pollen grains, their potential release of INMs and their effect on atmospheric ice formation, additional observations are necessary including the peak season for other ice active pollen species with accompanying INP measurements.
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<td>Arizona test dust</td>
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<td>SMPS</td>
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<td>Thermo-stabilized Optical Particle Spectrometer for ice</td>
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\( \text{act}_{\text{tot}} \) - Total activation
\( A \) - \( m^2 \) Particle surface area
\( A_{\text{CCN}} \) - CCN activated fraction
\( AF \) - Activated fraction
\( d \) - \( m \) Particle diameter
\( D_{50} \) - \( m \) Cutoff diameter (50 % efficiency)
\( e_{\text{sat},i}, e_{\text{sat},w} \) - Pa Saturation vapor pressure over ice and water, respectively
\( G \) - \( J \) Gibbs free energy
\( f \) - Compatibility factor
\( F_{\text{nd}} \) - Fraction of undetected particles (IODE)
\( FBAP \) - \( L^{-1} \) FBAP concentration
\( FCDCN \) - \( L^{-1} \) Frozen cloud droplet number concentration
\( FF \) - Frozen fraction
\( FF_{\text{adjtot}} \) - Adjusted frozen fraction
\( FF_{\text{corr}} \) - Corrected frozen fraction (for multiple-charged particles)
\( FF_{\text{min}}, FF_{\text{max}} \) - Minimum/maximum value of frozen fraction
\( FF_{\text{stat}} \) - Statistical error of frozen fraction
\( ICNC \) - \( \text{cm}^{-3} \) Ice crystal number concentration
\( INP \) - \( L^{-1} \) Ice nucleating particle concentration
\( INP_{D10} \) - \( L^{-1} \) INP concentration from DeMott et al. (2010) parameterization
\( INP_{\text{imp}} \) - \( L^{-1} \) INP concentration from impinger samples
\( INP_{\text{PMF}} \) - \( L^{-1} \) INP concentration from \( PM_{10} \) filters
\( I_{\parallel} \) - \( \text{pW} \) Parallel signal intensity (IODE)
\( I_{\perp} \) - \( \text{pW} \) Perpendicular signal intensity (IODE)
\( J_{\text{het}} \) - \( \text{m}^{-2}\text{s}^{-1} \) Homogeneous nucleation rate
\( J_{\text{hom}} \) - \( \text{m}^{-2}\text{s}^{-1} \) Heterogeneous nucleation rate
\( k \) - \( \text{J K}^{-1} \) Boltzmann constant
### List of symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>m$^{-2}$s$^{-1}$</td>
<td>Kinetic constant</td>
</tr>
<tr>
<td>maxcounts</td>
<td>-</td>
<td>Maximum possible counts (IODE)</td>
</tr>
<tr>
<td>$n$</td>
<td>m$^{-3}$</td>
<td>Number density of water molecules</td>
</tr>
<tr>
<td>$N_{amb}$</td>
<td>cm$^{-3}$</td>
<td>Ambient aerosol number concentration</td>
</tr>
<tr>
<td>$N_{CPC}$</td>
<td>cm$^{-3}$</td>
<td>Particle concentration (after dilution stage)</td>
</tr>
<tr>
<td>$N_{CCN}$</td>
<td>cm$^{-3}$</td>
<td>Estimated CCN number concentration</td>
</tr>
<tr>
<td>$N_{droplet}$</td>
<td>-</td>
<td>Number of droplets (IODE)</td>
</tr>
<tr>
<td>$N_{ice}$</td>
<td>-</td>
<td>Number of ice crystals (IODE)</td>
</tr>
<tr>
<td>$N_{liq}$</td>
<td>-</td>
<td>Number of tubes liquid (drop freezing array)</td>
</tr>
<tr>
<td>$N_{nd}$</td>
<td>-</td>
<td>Number of undetected particles (IODE)</td>
</tr>
<tr>
<td>$N_{tot}$</td>
<td>-</td>
<td>Number of total particles (ice crystals and droplets) detected (IODE)</td>
</tr>
<tr>
<td>$N_{tubes}$</td>
<td>-</td>
<td>Number of tubes (drop freezing array)</td>
</tr>
<tr>
<td>$n_s$</td>
<td>m$^{-2}$</td>
<td>Surface density of active sites</td>
</tr>
<tr>
<td>$P$</td>
<td>-</td>
<td>Probability of freezing</td>
</tr>
<tr>
<td>$PM_{10}$, $PM_{2.5}$</td>
<td>µg m$^{-3}$</td>
<td>Particle mass larger 10/2.5 µm, respectively</td>
</tr>
<tr>
<td>$r$</td>
<td>m</td>
<td>Droplet radius</td>
</tr>
<tr>
<td>$r_c$</td>
<td>m</td>
<td>Critical radius of an ice embryo</td>
</tr>
<tr>
<td>$r_n$</td>
<td>m</td>
<td>Radius of a cluster</td>
</tr>
<tr>
<td>$RH_i$, $RH_w$</td>
<td>%</td>
<td>Relative humidity with respect to ice and water, respectively</td>
</tr>
<tr>
<td>$s$</td>
<td>m$^2$</td>
<td>Surface area</td>
</tr>
<tr>
<td>$S_i$, $S_w$</td>
<td>-</td>
<td>Saturation ratio with respect to ice and water, respectively</td>
</tr>
<tr>
<td>$S$</td>
<td>%</td>
<td>Effective supersaturation</td>
</tr>
<tr>
<td>$t$</td>
<td>s</td>
<td>Date/Time</td>
</tr>
<tr>
<td>$t_{nuc}$</td>
<td>s</td>
<td>Nucleation time</td>
</tr>
<tr>
<td>$t_{res}$</td>
<td>s</td>
<td>Residence time</td>
</tr>
<tr>
<td>$T$</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_{amb}$, $T_{dew}$</td>
<td>ºC</td>
<td>Ambient air and dew point temperature</td>
</tr>
<tr>
<td>$T_{50}$</td>
<td>K</td>
<td>Median freezing temperature</td>
</tr>
<tr>
<td>$V_a$</td>
<td>m$^3$</td>
<td>Volume of air sampled</td>
</tr>
<tr>
<td>$v$</td>
<td>m s$^{-1}$</td>
<td>Flow velocity</td>
</tr>
<tr>
<td>$\delta$</td>
<td>-</td>
<td>Depolarization ratio</td>
</tr>
<tr>
<td>$\Delta G^*$</td>
<td>J</td>
<td>Gibbs free energy barrier</td>
</tr>
<tr>
<td>$\Delta G_n$</td>
<td>J</td>
<td>Gibbs free energy for the formation of a cluster</td>
</tr>
<tr>
<td>$\mu_i$, $\mu_w$</td>
<td>J</td>
<td>Chemical potential of ice and water, respectively</td>
</tr>
<tr>
<td>$\nu_{ice}$</td>
<td>m$^3$</td>
<td>Volume of a water molecule in ice</td>
</tr>
<tr>
<td>$\nu_{drop}$</td>
<td>m$^3$</td>
<td>Volume of a droplet</td>
</tr>
<tr>
<td>$\sigma_{i,w}$</td>
<td>J m$^{-2}$</td>
<td>Surface tension of an ice-water interface</td>
</tr>
<tr>
<td>$\theta$</td>
<td>deg</td>
<td>Contact angle</td>
</tr>
<tr>
<td>$\tau$</td>
<td>-</td>
<td>Depolarization threshold</td>
</tr>
</tbody>
</table>


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DANKE!