

## Ice Nucleation in Clouds

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### **ABSTRACT**

*The formation of ice in clouds is very important to the precipitation development in the cold and mixed-phase clouds and also for the radiative budget of clouds. Understanding the process of ice nucleation and predicting the ice concentration poses a major challenge. This challenge arises due to the fact that there are large gaps in our understanding of the ice nucleation and ice multiplication processes occurring inside natural clouds. Although the observations of ice nuclei in the atmosphere began about 70 years ago, globally the measurements are very sparse. The quantification of the types of ice nuclei in the atmosphere is also not to the desired levels. The ice nucleation at warmer temperatures by the ice nuclei present in the atmosphere is not well understood. This comes from the fact that there are several orders of magnitude difference between the observed concentration of ice nuclei in the atmosphere and the ice particle concentration in clouds. Whether the proposed mechanisms of secondary ice multiplication processes can explain this discrepancy is still not proven. There are several gaps that need to be addressed to quantify correctly the ice formation in clouds.*

**Keywords:** *Aerosol, Dust, Ice Nucleation, Ice Nuclei, Cold & mixed phase clouds, and Parameterization.*

### **1. Introduction**

There are two types of clouds which produce precipitation, namely, warm clouds and cold clouds. Warm clouds do not cross the freezing level and the precipitation consists of liquid droplets (cloud droplets, drizzle drops and rain drops). The cold clouds can be categorized into mixed phase and glaciated type. The mixed phase which dominates the tropical convective clouds consists of ice (pristine ice, graupel and hail) and supercooled droplets which are found till  $-40$  °C. The glaciated type will contain only ice and are found in clouds whose temperatures are colder than  $-40$  °C. More than 50% of the mid-latitude precipitation is produced via cold clouds (involving Ice) processes, whereas this proportion in tropical regions is about 30% (Lau and Wu 2003). A look at the cloud top temperatures on a typical monsoon day would show that a sizeable fraction of clouds has cloud top temperatures that have crossed  $-40$  °C. Therefore, mixed-phase clouds (involving ice) are very important in producing rainfall during the monsoon season. The ice when it falls and crosses the freezing level will melt and will also reach the ground as rain. There are various cloud properties

which will control the way clouds contribute to the radiative transfer. Therefore, the size distribution of ice crystals and the Ice Water Path of Clouds are very important in quantifying the contribution of the clouds towards the radiative budget at the top of the atmosphere and the surface of the earth.

At temperatures lower than  $-38$  °C and high ice supersaturation, the ice nucleation happens through homogeneous nucleation. Ice Nucleation at temperatures warmer than  $-38$  °C can happen via a heterogenous ice nucleation process. Once an Ice Crystal has formed, it can grow further through the process of vapor deposition, aggregation, or accretion of supercooled droplets. Snow crystals or flakes can form through the process of vapor deposition or aggregation. The accretion process can result in the formation of rimed crystals and when the crystal shape can no longer be recognized it will be graupel and the extreme growth of graupel results in hail.

In a mixed-phase cloud, the Wegener-Bergeron-Findeisen process shows that the Ice crystals would gain mass by vapor deposition at the expense of liquid drops that would lose mass by evaporation

(Wallace and Hobbs, 2006). This is due to the fact that the equilibrium vapor pressure of water vapor with respect to ice is less than that with respect to liquid water at the same subfreezing temperature.

The heterogeneous Ice Nucleation process requires an Ice Nucleating Particle (INP), Molecule (INM) or Entity (INE). These are material, substance, object, item, unit or others, that are assumed to be the agents responsible for observed heterogeneous nucleation Vali et al. (2015). The four major possible modes of heterogeneous ice nucleation are Deposition Nucleation, Freezing Nucleation, Contact Freezing and Condensation-Freezing. In the deposition nucleation mode, Ice Nucleation can happen when the saturated water vapor can directly deposit on an INP and form ice without the formation of liquid. Freezing nucleation can happen when an INP embedded inside a supercooled droplet can activate and cause the ice nucleation to happen. Contact Freezing can happen when an INP comes in contact with a liquid droplet and can initiate ice nucleation. In Condensation-Freezing Mode the liquid droplet formation is first initiated on a Cloud Condensation Nuclei with the concurrent freezing of the droplet. In addition, there could be other modes of ice nucleation possible like electro-freezing, evaporation freezing, mechanical shock freezing and collision freezing (Vali et al., 2015). Temperature and Ice supersaturation are the main factors that control ice nucleation.

## 2. Ice Nucleating Particles (INPs)

The INPs are basically aerosol particles and their ability to become INPs is based on their crystal structure, size, surface features, solubility and chemical coating. Generally, INPs are water-insoluble particles and the solid surfaces provide sites for ice nucleation whereas, soluble particles get disintegrated under the action of water and prevent the Ice nucleation (Pruppacher and Klett, 1997; Lohmann et al. 2016). Those particles whose crystal structure closely matches the crystal structure of ice crystal will be favourable to act as INPs. In the deposition mode, the ice nucleation happens on “active sites” (Pruppacher and Klett, 1997; Lohmann et al. 2016) which are surface features or imperfections on the surface of INP like cracks, pores and steps. During long-range

transport, the aerosol particles are exposed to pollutants of varying concentrations and thus can be coated with chemicals. Such coatings can significantly increase or decrease the ice-nucleating ability of an INP depending upon the chemical with which it is coated.

The main groups of Ice nucleating particles are mineral dust, biomass burning aerosols, biological aerosols, sea salt and others. Numerous studies in the laboratory have been attempted to quantify the ice nucleation ability of different particles and have been reviewed by Hoose and Mohler (2012). In general, the laboratory experiments show that the deposition/ condensation ice nucleation by bioaerosols (bacteria, fungal spores, pollen and diatoms) can happen at higher temperatures and lower ice saturations. The deposition/ condensation ice nucleation by organics and black carbon requires lower temperature and higher supersaturations. Laboratory results of mineral dust show that larger particles tend to nucleate at lower supersaturations and higher temperatures. On the other hand, for submicron particles, there seems to be a tendency of natural desert dust to activate at higher supersaturation. For soot, several studies have reported no ice nucleation within the investigated conditions, but these disagree with several other experiments. Recent airborne observation by Schill et al. (2020) showed that between  $-36^{\circ}\text{C}$  to  $-11^{\circ}\text{C}$ , black carbon from biomass burning contributes, at most, 10% to INP. Soot particles vary in composition depending on the organic carbon content. The qualitative overview presented by Hoose and Möhler (2012) indicates that soot is generally a worse ice nucleus than mineral dust. Among bio-aerosols, in particular bacteria, the ability to nucleate is selective. Only a small number of bacterial strains and fungal species have been identified as Ice Nuclei at temperatures higher than  $-10^{\circ}\text{C}$ . For Cirrus cloud type of conditions, crystalline ammonium sulfate particles have been observed to nucleate ice efficiently under water-subaturated conditions. Hoose and Möhler (2012) have also reported ice nucleation activity of organic acids under cirrus conditions. There could be a number of other particles which could act as INP like Volcanic ash and sea salt. Vonnegut (1947) found that Silver Iodide (AgI) particles are

very efficient as Ice Nuclei and these are being used for artificial cloud seeding.

### 3. Groups of INP Particles

#### 3.1 Dust

Dust, in general are water-insoluble and solid surfaces provide sites for ice nucleation. Condensation of water molecules on rigid surfaces allows the ice embryo to reach a critical radius with a smaller number of water molecules, whereas the soluble ones get disintegrated under the action of water and prevent ice nucleation (Pruppacher and Klett, 1997). The surface area of aerosol and the number of active sites per unit area are very important for the aerosol particle to act as INP, especially for deposition mode Ice Nucleation. The active sites are imperfections on the surface of INP, such as cracks, pores and steps (Pruppacher and Klett, 1997). DeMott et al. (2010) suggested that the predominant role of mineral dust particles as INP suggests that particles greater than 0.5  $\mu\text{m}$  which are mineral dust and soil dust are dominant in the free troposphere. Since ice nucleation is a localized phenomenon, the number of active sites required for nucleation is not enough in smaller particles (Niedermeier et al., 2015). Hence, particles less than 0.5  $\mu\text{m}$  are not efficient as INP. However, biogenic aerosols of size less than 0.2  $\mu\text{m}$  can be active as INP in the immersion freezing mode (Wilson et al., 2015).

The crystal structure of the aerosol particle is very important for the water molecule to form an ice lattice on the particle. In the case of ice-nucleating bacteria, the protein layer on the bacteria has a resemblance to that of an ice lattice (Lohmann et al., 2016). The elemental composition of aerosols is therefore important in determining the ability of the aerosol particle to act as an INP. Desert dust is one of the major contributors to the ice nucleation by aerosol particles. Klein et al. (2010) reported that 90% of the particles that acted as INP during the Saharan dust episodes are Silicates or Calcium Carbonates.

The elemental analysis of aerosol particles which acted as INP during the CAIPEX ( Cloud Aerosol

Interactions and Precipitation Enhancement Experiments) campaign of 2009-2011 over the Indian region shows that most of the samples contained Fe, Mn, Cu and Zn (Patade et. al., 2014). The measurements at high altitude locations over India by Wagh et al. (2017) showed the presence of Si, Al, Na and Cl also.

The aerosol particles at any given place are a combination of ones that are produced locally and ones that have arrived there by long-range transport. The ones that arrive through long-range transport are exposed to different pollutants and are generally internally mixed and complex in nature. A few researchers have observed that mineral dust coated with sulfuric acid or soot particles activated as INP only at higher ice supersaturation (Möhler et al., 2005, Cziczo et al., 2009, Niedermeier et al., 2011). Similar observations were also reported from Ulaanbaatar in Mongolia, where they found that ice nucleation activity was lowest when the fraction of particles containing Sulfur was highest Hasenkopf et al. (2016).

Kanji et al. (2013) observed that when mineral dust was oxidized or aged by exposure to ozone its Ice Nucleation Activity (INA) increased. Some contradictory results were also reported of no change in INA of mineral dust when exposed to sulfuric acid and ozone by Salam et al. (2008). INA of coated aerosols is very important but difficult to study.

#### 3.2 Biomass burning and fossil fuel combustion aerosol

Carbonaceous and non-carbonaceous particles of both organic and inorganic in nature can be emitted during combustion. Biomass-burning Aerosols (BBA) sources are ash and soot which can be emitted during wildfires and agriculture residue burning, from wood stoves and some industrial activities also. A major source of soot is from incomplete combustion of fossil fuels Kanji et al. (2017). BBA can be a complex mixture of organic carbon, black carbon (often called soot) and inorganic substances (Jahn et al., 2020). Several studies show that soot and ash particles activate as deposition INP at  $T < -40\text{ }^{\circ}\text{C}$  (Kanji et al., 2017).

In the immersion-freezing mode, ash from biomass burning and coal combustion can exhibit higher nucleation ability than clay but less than mineral dust particles (Kanji et al., 2017). Hence, most of the studies related to the Ice Nucleating ability of BBA have been done in immersion freezing mode (Jahn et al., 2020; Levin et al., 2016). Biomass burning produces carbonaceous and non-carbonaceous aerosols and although there are several reports of an increase in INP associated with biomass burning, it cannot be attributed to any particular type. Levin et al., (2016) from laboratory experiments on biomass combustion indicated that refractory Black Carbon particles contribute to INP concentrations, especially those from burning marsh grasses.

New crystalline mineral phases have been recently discovered during biomass combustion which are the major sources of INP and can activate at higher temperatures of  $-13\text{ }^{\circ}\text{C}$  (Jahn et al., 2020). In the vast majority of studies involving biomass burning only freshly emitted aerosols have been investigated for their INP property. As the plume dilutes the BBA experiences chemical aging which can significantly alter the INP activity of BBA. Jahn et al. (2021) have found that the ice nucleation ability can be an order of magnitude higher under chemical aging.

Observations of deposition mode INP during the Winter Fog Experiments (WiFEX) of December 2016 and January 2017 at the Indira Gandhi International Airport, New Delhi, show a significant correlation between the number of INP and Black Carbon (BC) under foggy conditions (Wagh et al., 2021). Significant correlations between the number of INP with Biomass Burning and Fossil Fuel were also observed under foggy conditions. The back-trajectory analysis showed that the air mass originated from the adjoining regions and analysis by Scanning Electron Microscopy (SEM) showed that the particles were a mixture of mineral dust, metallic elements and soot (Wagh et al., 2021).

### 3.3 Bioaerosols

Bioaerosols are airborne biological particles like bacteria, fungal spores, pollen, viruses,

phytoplankton, lichens, marine exudates and plant fragments, which are emitted by vegetation, soils, oceans, lakes and living organisms (Kanji et al., 2017).

Among bacterial INP, the most common is the *Pseudomonas Syringae*, the other species being *Pseudomonas fluorescens* and *Erwinia herbicola*. They have been found to nucleate ice at temperatures between  $-2\text{ }^{\circ}\text{C}$  to  $-10\text{ }^{\circ}\text{C}$ . Fungi, both free-living and lichen fungi were found to nucleate ice at very high temperatures like  $-1\text{ }^{\circ}\text{C}$ . Pollen of various plant species has been found to nucleate ice at temperatures as high as  $-10\text{ }^{\circ}\text{C}$  and reach very high active fractions at  $-18\text{ }^{\circ}\text{C}$  (Despres et al., 2012). Based on a field campaign over Amazon, Patade et al. (2021) showed that biological INP (mostly bacteria and fungi) account for most of the total ice nucleation activity at temperatures warmer than  $-20\text{ }^{\circ}\text{C}$ . At colder temperatures than this, dust and soot become favored INPs. However, the overall role of bioaerosols that act as INP is very limited in altering the microphysical properties of continental deep convective clouds (Patade et al., 2022).

Although the bioaerosol number concentrations are orders of magnitude smaller than dust particles, their ability to freeze at higher temperatures than dust can have an impact on the formation of ice particles through secondary ice production (Kanji et al., 2017).

### 3.4 Marine aerosols

Most of the earth is covered by Ocean and they dominate the Southern Hemisphere. INPs over oceans could come from marine biogenic particles or sea spray aerosols. Schnell and Vali (1976) after looking at observations proposed a marine biogenic source as INP. Ice Nucleation activity of biogenic particles is mostly investigated in the immersion mode. Over the oceans relative to dust the marine biogenic INPs are found to play a dominant role (Burrows et al., 2013). The marine biogenic particles could be primarily cellular matter such as microorganisms and fungal spores (Despres et al., 2012). In addition, it could also include exudates of marine organisms (Burrows et al., 2013). Laboratory experiments have shown that organic

matter can be strongly enriched during sea spray aerosol (SSA) formation by bubble bursting. A strong increase in SSA INP emissions in association with Phytoplankton bloom has been shown in laboratory simulations (DeMott et al., 2016). Simulations show that marine biogenic INP are most likely to play a dominant role in remote marine locations which are less affected by the transported continental dust (Burrows et al., 2013).

#### 4. Instruments for Measuring Ice Nucleating Particles

The early measurements of INP were done by using the expansion chambers. Large volumes of moist air would be suddenly cooled to below the freezing temperatures and Ice Crystals that were formed would be counted to arrive at the number of INPs. Cwilong (1945) using Wilson cloud chamber conducted experiments using dust particles. In these expansion chambers, the challenge was to measure the ice crystal concentration, as counting was done by crystals falling on the bottom to supercooled water. Bigg (1957) modified the technique of Cwilong (1945) and replaced the supercooled water at the bottom of the chamber with a strong aqueous solution. Ice crystals falling into these would not freeze the solution and would grow as individual crystals. Using the expansion chamber Bigg (1957) measured the INP at the coast of Carnarvon in Western Australia.

In the 1960s, methods were made to determine the INP concentration on filter papers by sampling large volumes of air on which the aerosol particles were collected. The filter papers were then processed inside a Static Thermal Gradient Diffusion Chamber (S-TGDC) where the temperature and supersaturation could be controlled. The technique followed is that a layer of ice is first formed on two plates that face each other and are separated by a small distance usually around 10 to 12 mm and the filter paper exposed to atmospheric aerosols is kept at the center of the plates. The plates are then closed and the chamber is made airtight. The temperature of the top and bottom plates is kept different and the vapor inside the S-TGDC is at ice supersaturation. The supersaturation inside the chamber can be

calculated from the temperatures of the two plates (Hussain and Saunders 1984; Patade et al., 2014). The vapor will deposit on the aerosol particles which can act as an INP. The S-TGDC is opened and the ice crystals which have formed on the filter paper are counted using a magnifying glass to give the number of INPs. By varying the temperatures of the top and bottom plates the ice supersaturation inside the S-TGDC can be varied. The INPs activating through deposition and condensation-freezing modes can be determined using the S-TGDC. At a temperature below freezing and for any ice supersaturation, if the air in the chamber is below water saturation then the deposition mode INP will activate and if it is above water saturation then the condensation-freezing mode INP will activate.

In a series of workshops held in the 1960s and 1970s to intercompare the different instruments a major thing noticed was the divergent number of INPs measured by different instruments. The ice supersaturation was recognized as a major factor (DeMott et al., 2011). During these workshops, the need for portable equipment making continuous measurement of INPs from aircraft was recognized. Two designs emerged during the development of Continuous Flow Diffusion Chamber (CFDC) one was the parallel plate design similar to that of Hussain and Saunders (1984), and the other was a cylindrical wall design (Rogers 1988). Air is sampled continuously through the CFDC and aerosols which activate as INP by forming Ice particles while passing through the chamber in a short time of 10s is counted by the optical method when they exit the chamber. In early 2000 the commercially developed INP instrument for measurement using an aircraft platform called the SPectrometer for Ice Nuclei (SPIN) became available. A new Ice Nuclei measurement Instrument called the Continuous Flow Mixing Chamber (CFMC) was developed by Bundke et al., (2008) in which supersaturation is created by mixing aerosol streams with warm, humid and cold, dry airstreams. This design permits a higher sampling volume than the CFDC.

The contact-freezing mode INP is measured using a different technique. Svensson et al. (2009) used

**Table 1. History of development of different INP measuring instruments.**

Period of Development	Measurement Technique
1940's and 50's	Expansion Cloud Chamber
1960's and 70's	Static Thermal Gradient Diffusion Chamber (S-TGDC) Collecting aerosols on filter paper and processing it in S-TGDC. (Deposition and Condensation-Freezing Modes)
1970's	Diffusion and Settling chambers (for use in aircraft where supersaturation is controlled by injecting Cloud Condensation Nuclei [CCN])
1970's (Mid 70's)	Continuous Flow Diffusion Chamber (CFDC). Followed a cylindrical design for 20 years. Parallel plate geometry (Vertical and Horizontal) for mid-2000's. (Inability to measure Contact-Freezing Modes due to less sampling time of 1-2 L/min)
2000 (~2008)	Continuous Flow Mixing Chambers (CFMC). Permits higher sampling volumes (~10 L/min). Supersaturation is created by mixing aerosol stream with warm, humid and cold dry air stream.
2000 (~2009)	Electrodynamic Balance (EDB) for Contact-Freezing Modes

Electrodynamic Balance (EDB) to study the freezing of previously immersed INP in a droplet. Table 1 gives the history of the development of different INP measuring instruments.

### 5. Field Observations

The INP count at any particular location is closely related to the type of air mass, the origin and transport of this air mass before they arrive at the observation location. Large spatial and temporal variations in INP concentrations have been observed worldwide. Globally INP concentration has been found to vary from about  $0.001 \text{ L}^{-1}$  to about  $13 \text{ L}^{-1}$  in the temperature range  $-5$  to  $-20 \text{ }^\circ\text{C}$  (Bigg 1973; Meyers et al., 1992; DeMott et al., 2003; Richardson et al., 2007; Prenni et al., 2009; Lopez and Avila 2013; Jiang et al., 2014). The higher number concentration of INP  $40 \text{ L}^{-1}$  and  $53 \text{ L}^{-1}$  have been reported by Smith et al. (2009) and Ardon-Dryer et al. (2011) at temperatures lower than  $-30 \text{ }^\circ\text{C}$ .

Over the Indian region, Patade et al. (2014) have reported INP observations varying from  $0.276$  to  $5 \text{ L}^{-1}$  with an average concentration of  $1.12 \text{ L}^{-1}$  in the temperature range  $-13.5$  to  $-18.5 \text{ }^\circ\text{C}$  at Ice Supersaturations varying from 6% to 26%. These observations were made using the CAIPEEX aircraft over different parts of India. INP concentration can vary significantly with altitude

over the same location. Although, some observations show that there is not much change in INP concentration up to 5 km altitude. Generally, the INP concentration decreases with height in response to the aerosol variation. Studies have shown that the most effective INP originates at the surface or by long-range transport in the boundary layer. Patade et al. (2014) have shown that over the Indian region the concentration is higher in the boundary layer and there is not much influence of the long-range transport above the boundary layer.

There are limitations in making observations using aircraft as a platform. The sampling time is very small and the measurements are highly variable in space and time. To overcome these limitations, researchers carry out long periods of continuous observations on the land surface or mountain tops. At Jungfrauoch (3463 m above sea level (a.s.l)) in Switzerland, Chou et al. (2011) observed that the INP number concentration increases with the concentration of larger-sized particles, and found an INP number concentration of  $> 25 \text{ L}^{-1}$  on dusty days, and an average of  $14 \text{ L}^{-1}$  on the non-dusty day. Mineral dust aerosols that are suspended in the air during dust storms, especially from the Sahara Desert get transported over a wide range in the northern hemisphere (Klein et al., 2010). Klein et al. (2010) made measurements at a central European Mountain site on Mt. Kleiner Feldberg, a

low mountain range (825m a.s.l.) in Central Germany, approximately 25 km north of the city of Frankfurt am Main. During dust episodes, they have recorded INP concentrations of 200 – 312 L<sup>-1</sup> at -18 °C. Jiang et al. (2016) observed over North-Western China that during dust episodes the INP was several hundred per liter, whereas on non-dusty days the INP concentration was only about 11 L<sup>-1</sup> at -20 °C at an ice supersaturation of 22%. In the Guangmingding peak in Huangshan Mountains in China, whose maximum altitude is 1864 m a.s.l. Jiang et al. (2015) observed INP in the range 0.27 to 7.02 L<sup>-1</sup>. Their temperatures varied from -15 to -23 °C with ice supersaturation varying from 5 to 25%. Bertrand et al. (1973) during advection of Saharan dust particles over Abidjan in the Ivory Coast found that INP increased from 10 L<sup>-1</sup> to 50 L<sup>-1</sup> at -20 °C. Boose et al. (2016) at the Izana Observatory (2373 m a.s.l.) in Tenerife, Spain, observed INP concentrations in the range 0.2 to 2500 L<sup>-1</sup> at -33 °C and 105% relative humidity w.r.t water. These observations were made when the air was under influence of Saharan desert dust.

Wagh et al. (2017) reported observations carried out at two high altitude locations in India during the period 2011-2014. The first location was at IUCAA Girwali Observatory (IGO) near Pune at an altitude of 1005 m a.s.l, where the observations were done during April 2011 and 2013, and March 2014. The second location was the Radio Astronomy Center (RAC) in Ooty at an altitude of 2240 m a.s.l. where observations were done during January 2013 and 2014. The average INP concentration at IGO was 1 L<sup>-1</sup> with an activation factor of 1 INP in 10<sup>4</sup> aerosol particles to 1 INP in 10<sup>6</sup> aerosol particles. At RAC the average INP concentration was 1.6 L<sup>-1</sup> with a higher activation factor of 1 INP in 10<sup>3</sup> aerosol particles. At RAC they found the presence of rare earth elements like Mo, Ru, La, Ce and Zr which could be the probable reason for the higher average number of INP and a higher ratio of activation factor.

Anil Kumar et al. (2020) carried out observations using the commercially available SPIN during August-December 2018 at the High-Altitude Cloud Physics Laboratory (belonging to Indian Institute of Tropical Meteorology, Pune) at Mahabaleshwar

which is at an altitude of 1353 m a.s.l. Their observations showed a systematic increase of INP from less than 1 L<sup>-1</sup> at -25 °C to about 10 L<sup>-1</sup> at -34 °C. Their results at -25 °C are in good agreement with that of Wagh et al. (2017) and Patade et al. (2014) for the Indian region.

As there are hardly any long-term measurements of INP, there is not much knowledge of geographic and seasonal variations of INP. Measurements were therefore carried out for at two year period from May 2015 to January 2017 at four different locations globally. The locations were in the Amazon, Caribbean, Central Europe and Arctic (Schrod et al., 2020). These sites featured diverse geographical climates and ecosystems that are associated with dissimilar transport patterns, aerosol characteristics and different levels of anthropogenic impact. Two modes of INP activation i.e the Deposition mode and Condensation-Freezing modes were determined at -20 °C, -25 °C and -30 °C. Their observation is that the INP concentrations do not differ greatly from site to site, but usually fall well within the same order of magnitude.

## 6. Secondary Ice Production

The average number concentration of INP in the atmosphere is about 1 per liter. However, the observed number of ice particle concentrations in clouds is a factor of 10<sup>4</sup> more than the INP concentration. There must be a range of secondary ice production (SIP) mechanisms operative in the clouds responsible for this large discrepancy. In the past decade, several SIP mechanisms have been proposed based on laboratory experiments and well summarized in a recent review article by Korolev and Leisner (2020). SIP mechanism can enhance the mass and number concentration of ice particles in the clouds which in turn can affect cloud macro- and microphysical properties including cloud lifetime, rate of precipitation formation, glaciation time, and cloud electrification (Crawford et al., 2012; Lawson et al., 2015; Phillips et al., 2017b, 2018, 2020; Phillips and Patade, 2022; Sotiropoulou et al. 2021a,b). The changes in cloud properties due to SIP can also affect the global hydrological cycle and climate (Zhao and Liu, 2021).

Historically, the first mechanism proposed was droplet fragmentation during freezing (Lagham and Mason 1958). A drop begins to freeze from the outside and liquid water is trapped inside this ice shell. During further cooling when this liquid water also begins to freeze it expands and pressure is created on the inside resulting in the cracking of the ice shell. The ice splinters that result from this shattering will serve as secondary ice particles on which further growth can take place. Phillips et al. (2018) proposed an empirical formulation for of raindrop freezing mechanism based on laboratory data available in the literature. They implemented this formula into a parcel model and found that raindrop freezing fragmentation can explain ice number concentrations of up to 500 per liter in growing maritime cumulus clouds.

Hallett and Mossop (1974) proposed the ice multiplication during the riming process. Riming is a process that happens in mixed-phase clouds where supercooled droplets and ice coexist. This is the most implemented SIP mechanism in cloud models. When the supercooled droplets collide with the ice crystals they freeze on the surface of the ice crystals, a process which is called riming. Hallett and Mossop (1974) and Mossop and Hallett (1974) observed splinter formation during the riming process in a cloud chamber with a liquid water content of  $1 \text{ gm}^{-3}$  and droplet concentration of  $500 \text{ cm}^{-3}$ . They found splinter production in the temperature range  $-3$  to  $-8 \text{ }^\circ\text{C}$  with a pronounced production rate at an impact velocity of  $2.5 \text{ m/s}$ . This mechanism is referred to as the Hallett-Mossop mechanism and is operative only in a narrow temperature range under select conditions.

Langmuir (1948) had proposed that the collision of ice particles may result in mechanical fragmentation. This hypothesis of secondary ice production was confirmed by airborne observations reported by Hobbs and Farber (1972). The analysis of literature done by Korolev and Leisner (2020) suggests that the efficiency of fragmentation during ice-ice collision depends on a number of factors like (a) properties of ice, like size, mass, shape, density (b) crispness of ice which depends on temperature and (c) the relative fall velocity between two ice particles. Parametrization of the

secondary ice production due to fragmentation is difficult due to the lack of laboratory experiments. In an attempt to parameterize the SIP due to ice-ice collision Phillips et al. (2017a) proposed a physically-based formulation. It can predict the number of generated fragments based on collisional kinetic energy and can also account for the size and habit of colliding ice particles as well as their rimed fraction. A few modeling studies have highlighted the importance of SIP due to ice-ice collisions (Fridlind et al., 2017; Yano and Phillips, 2011; Phillips et al., 2017a).

Koenig (1963) suggested that when a supercooled droplet freezes on the ice crystal (riming process) there will be the release of latent heat which will increase the surface temperature of the ice. This can cause a thermal shock at the location where the droplet is freezing on the ice crystal and cause ice to crack due to differential expansion of ice. Dye and Hobbs (1968) in their lab experiments found that on occasions when such drop freezing occurred, the ice crystal would break into 5 pieces.

Fragmentation of sublimating ice particles can occur when the ice enters the sub-saturated regions of the cloud. Oraltay and Hallett (1989) observed the fragmentation of dendritic ice crystals when the Relative Humidity w.r.t ice was less than 70% but did not observe any sublimation breakup for ice crystals with column and plate shapes. In a recent study, Deshmukh et al. (2021) proposed an empirical formulation for sublimation break-up of graupel and dendritic snow. In their formulation, the total number of the ejected fragments is proportional to the square root of the sublimated mass. Korolev and Issac (2004) during in situ observations of the metamorphosis of shapes of sublimating ice in clouds concluded that fragmentation of ice during sublimation does not play a major role in secondary ice production in clouds.

## 7. Effect of Electric Field

All clouds are electrified to some level above the standard fair-weather electric field of  $-100 \text{ V/m}$ . Ice crystal splinters from the freezing of charged drops peaking at  $-10 \text{ }^\circ\text{C}$  have been reported by Lauber et al. (2018). Mandal and Pradeep Kumar (2000) from their laboratory experiments have

demonstrated that ice nucleation occurs during electric discharge (similar to lightning). They have also observed an enormous increase in ice crystal size when they grow in a very high electric field. However, for such high electric fields to occur in clouds the basic requirement is that the cloud should contain both ice crystals and graupel (Saunders, 2008). Therefore, a high electric field may not play a major role in primary ice production in clouds. However, there is a need to conduct more experiments to understand the role of strong and weak electric fields in clouds on ice nucleation.

### 8. Parametrization of INP

INP parameterization can be done either as a function of temperature and/or ice supersaturation. A parameterization equation with temperature was prescribed by Fletcher (1962) as follows:

$$N = N_o \exp(-aT_{sup}) \quad (1)$$

Here  $N$  is the number of INP per liter and  $T_{sup}$  is the degree of supercooling which can be taken as  $T - T_o$  where  $T_o = 273.16$  K. The parameters 'a' and  $N_o$  are empirical regression parameters. This equation has been widely used the world over to predict the INP concentration. The range of values used for North China for 'a' is  $0.11-0.42 \text{ } ^\circ\text{C}^{-1}$  and  $N_o$  between  $0.011 \text{ L}^{-1}$  and  $5.01 \text{ L}^{-1}$  (Yin Jinfang et al., 2012).

Huffman (1973) had given an equation for INP concentration with ice supersaturation based on the measurements for natural aerosols at Laramie, Wyoming, USA. To a good approximation he observed that the INP concentration ( $N$ ) was independent of temperature and obeyed the power law as follows:

$$N = CS^\alpha \quad (2)$$

Where  $C$  and  $\alpha$  are constants and  $S$  is supersaturation over ice. The slope factor  $\alpha$  was found to increase from 3 over rural northeast Colorado to 4.5 over urban Laramie.

Cotton et al. (1986) combined the temperature-dependent equation of Fletcher (1962) and Huffman (1973) to obtain a hybrid equation in which INP concentration  $N$  depends on both temperature and supersaturation.

$$N = N_o [(S_i - 1) (S_o - 1)^{-1}]^b \exp(aT_{sup}) \quad (3)$$

In this equation  $a = 0.6 \text{ } ^\circ\text{C}^{-1}$ ,  $b = 4.5$ ,  $N_o = 10^{-5} \text{ L}^{-1}$ ,  $T_{sup}$  is the degree of supercooling as given in Equation (1).  $S_i - 1$  is the fractional ice supersaturation and  $S_o - 1$  is the fractional ice supersaturation at water saturation at  $T_{sup}$ .

Meyers et al. (1992) tested a new INP parameterization scheme in an explicit cloud model using Regional Atmospheric Modelling System (RAMS) on wintertime precipitation events over Sierra Nevada region in the USA. The parameterization scheme which they used for determining INP concentration  $N$  in deposition and Condensation-Freezing mode from the measurements using CFDC is as follows:

$$N = \exp \{a + b[100(S_i - 1)]\} \quad (4)$$

Here  $a = -0.639$  and  $b = 0.1296$ .

DeMott et al. (2010) predicted global ice nuclei distributions using an ice parameterization which included Temperature, Ice Supersaturation and Aerosol number concentration for particles larger than  $0.5 \text{ }\mu\text{m}$  in diameter. The expression they have used is,

$$N_{IN,T_k} = a(273.16 - T_k)^b (N_{aer,0.5})^{[c(273.16 - T_k) + d]} \quad (5)$$

Here  $a = 0.0000594$ ,  $b=3.33$ ,  $c=0.264$ ,  $d=0.0033$ ,  $T_k$  is cloud temperature in degree Kelvin,  $N_{aer,0.5}$  is the aerosol number concentration of particle diameter greater than  $0.5 \text{ }\mu\text{m}$  ( $\text{cm}^{-3}$ ) and  $N_{IN,T_k}$  is the INP concentration at  $T_k$ . DeMott (2010) implemented Equation (5) in the global climate model and found that it strongly alters the cloud liquid water and ice water distributions. This could mean that there will be a net radiative forcing increase of  $\sim 1 \text{ Wm}^{-2}$  for each order of magnitude increase of INP concentration.

### 9. Summary

It has been increasingly recognized that proper representation of the Ice process in numerical Models improves the forecasting skills of the model. Hazra et al. (2015) conducted numerical experiments of ECHAM-5 for simulating Indian Summer Monsoon Rainfall (ISMR). They showed

that by using the formulation of Ice Nucleation as a function of ice supersaturation, there was a considerable improvement in the simulation of the total rainfall during ISMR. Hazra et al. (2017) using coupled Global Climate Model used Ice and no Ice experiments to look at the circulation. They observed that using Ice microphysics improved the strength of the Hadley Circulation and improved the contribution of cloud fraction.

While it is recognized that the understanding of ice nucleation processes is very important in weather and climate models, there are major shortcomings in our ability to treat this process reliably in the models. In order to produce more accurate ice nucleation parameterization in models we need more extensive continuous measurements of INP concentrations in all the modes of Ice Nucleation.

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