IOP Conf. Series: Journal of Physics: Conf. Series **841** (2017) 012028 doi:10.1088/1742-6596/841/1/012028

Heterogeneous nucleation of ice in the atmosphere

A Nicosia[1,2,3], **M Piazza**[1], **G Santachiara**[1] **and F Belosi**[1]

[1] Institute of Atmospheric Sciences and Climate (ISAC-CNR), Bologna, Italy
[2] Department of Physics and Earth Sciences, University of Ferrara, Ferrara, Italy
[3] Laboratoire de Météorologie Physique (LaMP-CNRS), Université Blaise Pascal, Clermont-Ferrand, France

E-mail: a.nicosia@isac.cnr.it

Abstract. The occurrence of ice-nucleating aerosols in the atmosphere has a profound impact on the properties of clouds, and in turn, influences our understanding on weather and climate. Research on this topic has grown constantly over the last decades, driven by advances in online and offline instruments capable of measuring the characteristics of these cloud-modifying aerosol particles. This article presents different aspects to the understanding of how aerosol particles can trigger the nucleation of ice in clouds. In addition, we present some experimental results obtained with the Dynamic Filter Processing Chamber, an off-line instrument that has been applied extensively in the last years and that circumvents some of the problems related to the measurement of Ice Nucleating Particles properties.

1. Introduction

Laboratory experiments have shown that the freezing of very pure water droplets occurs at about -41 °C for droplets of 1 µm in diameter and at about -35 °C for droplets of 100 µm in diameter [1]. Hence, in the atmosphere, homogeneous freezing (i.e. the formation of ice crystals from pure water and haze droplets) is relevant only for high clouds, as for example cirrus. For mixed phase clouds, the formation of ice crystals is mainly related to the presence of a low concentration of aerosol particles called Ice Nucleating Particles (INP). These nuclei provide a substrate capable to lower the energy barrier between the supersaturated water vapour or the supercooled droplet (metastable liquid) and the thermodynamically stable crystalline phase. These particles may act as "deposition nuclei" (direct passage from the vapour state to the solid state) or as "freezing nuclei" (passage from the liquid intermediate phase to the solid phase). Three additional sub-cases are distinguished for the freezing nuclei: (i) the direct freezing of supercooled water by a nucleus contained within the droplet (immersion case); (ii) the condensation of water vapour on the nucleus surface and the subsequent freezing (condensation-freezing mode); (iii) the collision between a nucleus and a supercooled droplet with the subsequent freezing (contact-freezing mode).

Which process -among deposition, immersion freezing, condensation freezing and contact freezing- is the most relevant, may depend on the meteorological conditions and the specific nucleus, its chemical composition and dimension.

Particles with a crystallographic structure similar to that of ice crystal lattice (which has a hexagonal arrangement) tend to be effective as ice nuclei, although this condition is neither necessary nor sufficient. Traditionally, it has been thought that good heterogeneous ice nuclei should be insoluble solids, but extensive researches have shown that also soluble species can act in the formation of the solid phase in both the immersion [2, 3] and the deposition mode [4].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

The capability of an INP species to nucleate ice in a specific mode is influenced mainly by the temperature T and the supersaturation with respect to water S_w or ice S_i.

A parameter used to classify the ice nucleating capabilities of a species is the activation fraction, f_{IN}, calculated as the ratio of the number of ice crystals detected, to the total particle number concentration. The activated fraction can be used to identify the activation region which is peculiar to a certain species in relation to the parameters T, S_w and the specific nucleation mode.

Some inorganic particles (e.g. clay particles, volcanic ash, soil dust) present the highest activation fraction in a region of temperatures above -25 °C and for this reason they are considered to play an important role in cloud ice phase. Some recent studies have shown that also organic materials (such as bacteria, pollen, lichen, fungi, decaying vegetation material, marine bacteria associated with plankton) can be effective ice nucleators at fairly high temperatures (below -4 °C), but the activation fraction seems to be lower compared to clay particles. In recent years, focus on anthropogenic aerosol has asserted that also soot and metallic oxides can play a role in the INP population [5]. Eventually, further data are needed to clarify the significance of biogenic aerosols (as pollens, bacteria and cellulose), marine aerosol contributions or new possible INP sources. More generally, it is essential to investigate the composition and concentration of INP in different regions in order to predict the impact of natural and anthropogenic aerosol particles on cloud properties and to improve our understanding on weather and climate.

Research on this topic has grown constantly over the last decades but the study still presents some critical aspects that make its analysis and parameterization difficult. First of all, the small number concentration of INPs. It should be considered that no existing ice nucleus measuring system is capable of detecting ice formation by all known mechanisms simultaneously, then different techniques should be considered. Lastly, processes in the atmosphere, as the coating, may reduce the ice nucleating capabilities of INP species and these aging effects should not be neglected.

The instruments commonly used to investigate INP are: mixing chambers [6], expansion cloud chambers [7], continuous flow diffusion chambers [8], filter processing methods [9-11], immersion mode cooling chambers [12] and immersion mode offline methods [13].

Among these techniques, the filter processing is the most versatile one and has been largely used for its convenience and simplicity. Actually, aerosol particles can be easily collected on membrane filters, everywhere, and then conserved and transported. Inside the laboratory, a number of methods and instruments exist to process the filter, induce the activation of the INPs present, and distinguish them from the remaining aerosols collected.

The Dynamic Filter Processing Chamber (DFPC) is one of these instruments and it allows the control of the supersaturated water vapour S_w and the temperature T, in order to explore either the deposition or the condensation-freezing activation mode. We applied this instrument to a number of field campaigns [14-16] and we show the benefit obtained with respect to other techniques, and the INP concentrations obtained.

2. The dynamic filter processing chamber

The DFPC is a replica of the Langer dynamic developing chamber [11], housed in a refrigerator and used to detect and determine the concentration of aerosol particles active as INP at different supersaturations S_w and temperatures T.

The experimental method used to measure the INP activated fraction comprises three main steps. First the aerosol is collected on a filter through a common sampling line which combines a filter holder, a pump and eventually a cyclone or a particulate monitoring sampling head (as PM10 or PM1). The sampling is done in parallel with the monitoring of aerosol properties through an optical counter or a Scanning Mobility Particle Sizer (SMPS). Secondly, the filter is pretreated at the laboratory, by filling its pores with paraffin. More specifically, the filter is placed on a metallic support covered with a smooth layer of paraffin. Then the paraffin is slightly heated and rapidly cooled in order to penetrate deeper

inside the filter pores. The main goal of this pretreatment is to enhance the thermal conductivity between the filter and the supporting substrate. Lastly the filter is processed inside DFPC.

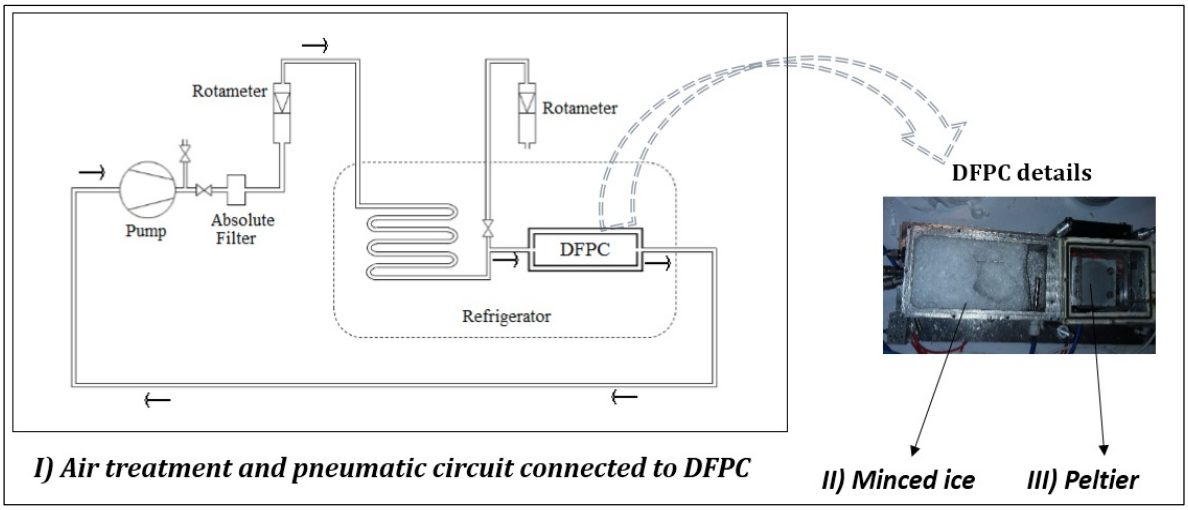

Figure 1. DFPC scheme (left) and view from above (right).

Fig. 1 reports the instrumental set-up which can be divided into three sections: the air pneumatic circuit (section I), the supersaturation control level (section II) and the filter temperature control (section III).

In section I, the air is filtered and forced by a pump to flow through the remaining sections in a closed loop. Section II is filled with minced ice, which is cooled by the base plate, while section III allocates a Peltier plate, where the filter is placed. When air spreads into the ice bed (section II), it becomes saturated with respect to ice, and then enters in the following section (III) and borders on the filter. The values of T and S_w are measured before approaching the filter with a thermo-hygrometer (model HD 9216, DeltaOhm). Supersaturations are calculated theoretically from vapour pressures of ice and water at the considered temperatures [17]. By varying the different temperatures inside the chamber and the vapour supersaturation with respect to liquid and/or ice, it is possible to activate the INP both in the deposition and in the condensation-freezing modes. Ice can form by deposition provided that the air is supersaturated with respect to ice and the temperature is low enough [1] such as, for example, at S_w = 0.92 and T = -18 °C. Ice can form by condensation-freezing if the air is supersaturated both with respect to ice and water such as, for example, at S_w = 1.02 and T = -18 °C.

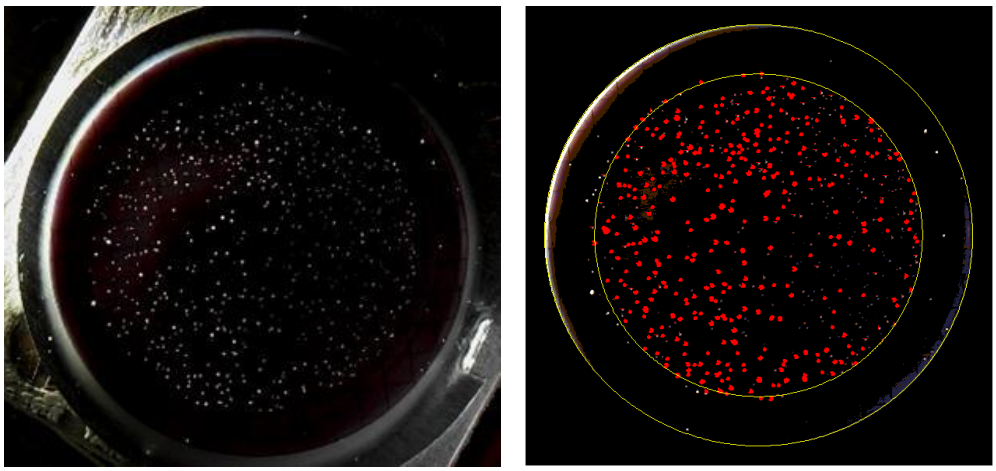

Figure 2. Activation of INP (left) and counting of the ice crystals through the software (right).

Finally, the INP activated fraction can be derived from the number of crystals grown on the filter and the initial sampling conditions (i.e. the volume of sampled air and the concentration measured by an optical counter or a SMPS). To count the number of ice crystals, a photograph of the filter is taken with a high resolution camera sensor (model DP-M17 USB digital microscope from Conrad electronic international) and analysed with an algorithm that runs under the Image Processing Toolbox of Matlab. The code has been conceived at ISAC-CNR and it excludes the external corona of the filter (which is pressed by the filter holder during the aerosol sampling and in which the air does not pass through). Fig. 2 reports an example of the ice crystals grown on the filter and the subsequent image processing and counting of the software.

3. Ice nucleating particles concentrations

The DFPC has been employed for the measurements of Ice Nucleating Particle concentrations [14-16] in the framework of BACCHUS (FP7-603445) and AIR-SEA LAB (CNR funded) projects between 2014 and 2016 at the following sampling sites: San Pietro Capofiume (SPC) in the north of Italy; Mace Head (MH) in Ireland; and the Global Atmospheric Watch station of Monte Cimone (MC) in Italy.

The first site, SPC, is considered a rural background site and the measurements were performed during a winter campaign (SPC1) and a spring campaign (SPC2). The second site, MH, is exposed to the North Atlantic Marine Boundary Layer and the campaign was performed during summer. The third site, MC, is the highest peak of the north Italian Apennines (2165 m a.s.l.) and it hosts the Italian Climate Observatory "O. Vittori". MC is a mountain site and it is considered representative of the free tropospheric conditions of the Mediterranean basin/southern Europe (MB/SE) during the cold months. In this last site two campaigns were performed, one in spring (MC1) and another one in autumn (MC2).

Aerosols were collected using a parallel PM1 - PM10 sampling system and the filters were then processed inside the DFPC at -22 °C (for the MH site) and -18 °C (for the other sites). The supersaturation level with respect to water S_w was fixed to 0.96 and to 1.02 to explore both the deposition and the condensation freezing activation mode. Fig. 3 and 4 show the box chart plot of the INP concentration values obtained at the different sites for respectively PM1 and PM10 aerosol size fraction (S_w of 1.02). The boxes indicate the 25th-75th percentiles, while lower and upper bars show the minimum and the maximum, respectively.

The coastal site MH appears with the lowest median INP concentration value (both in the PM10 and PM1 analysis). Nevertheless the INP concentration variability could reflect not only the different site but also the particular air masses which are affected by short and long-term transport of crustal and anthropogenic components.

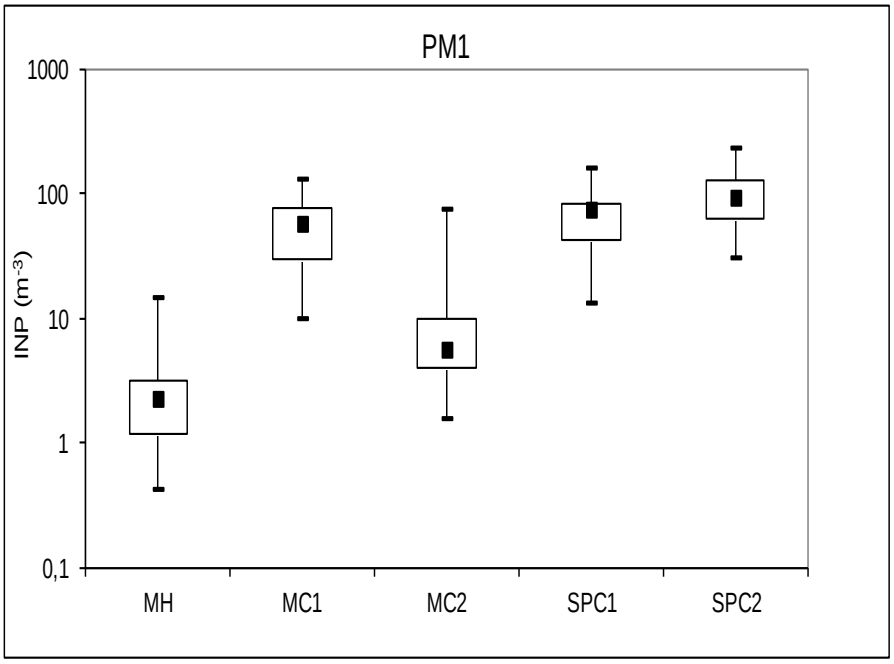

Figure 3. INP concentration (m^{-3}) from PM1 samplings at different sites: MC1 and MC2 refer to Monte Cimone (spring 2014 and autumn 2015); SPC1 and SPC2 refer to San Pietro Capofiume (winter 2014 and spring 2014, respectively); MH refers to Mace Head (summer 2015).

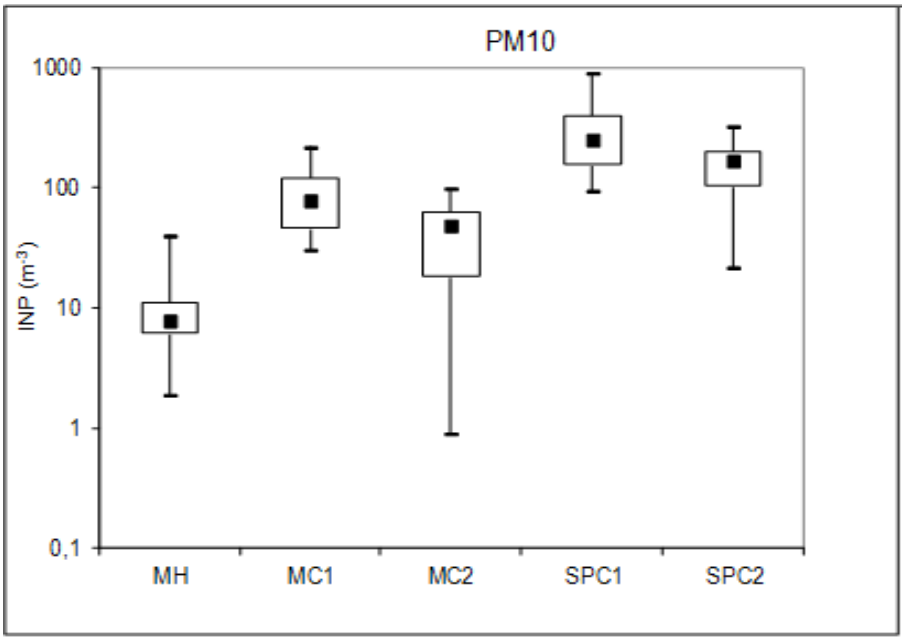

Figure 4. INP concentration (m^{-3}) from PM10 samplings at different sites.

Saharan dust transport episodes were observed during the campaigns of SPC2 and MC1. These episodes are generally characterized by increased INP concentration in the PM10 size range, particularly at S_w of 1.02, and an enhanced concentration of particles in the fine and coarse fractions. However, our observations show a decrease of the activated fraction during these events. This could depend on the aging processes (e.g. coating with sulphate or sea salts) during the long range transport of aerosol, as explained by [18]. Considering SPC1 in Fig. 3, the reduced nucleation activity of PM1 particles -with respect to SPC2- can be reasonably attributed to the enhance contribution of carbonaceous particles from

biomass burning (which are poor ice nuclei), characterizing the site during the cold months. On the other hand, the higher activation of super-micrometer particles observed in winter (SPC1 in Fig. 4) suggests different nucleating properties for the coarse aerosol populations in the two campaigns. Unfortunately, the lack of chemical/mineralogical composition data does not allow testing this hypothesis.

INP PM1/PM10 ratios are included between 0.2-0.3 at SPC1 (winter campaign) and 0.6 at MC and SPC2 (spring campaign). Then, not only different locations but also various periods of the year should be monitored to obtain reliable INP concentrations. Our results highlight also the need of measuring the freezing activity of the total aerosol population, and not only the fine fraction, as reported by [19].

4. Conclusions

We presented some aspects related to the characterisation of INP and their measurement. The DFPC is one of the instruments that are used to investigate the ice nucleation capabilities of aerosol particles collected onto a filter. Its goal is mainly the characterisation of INP when the deposition and the condensation-freezing modes are explored. We applied this instrument to evaluate the INP concentrations of several field campaigns and we showed the benefit obtained with respect to other techniques. In particular, the DFPC can investigate all the size spectrum of particles up to 10 μm, while on-line measurement devices allow measurements of particles up to about 2 μm. Results show that coarse aerosol particles (size range 1-10 μm) contribute significantly to the total INP concentration. We could find a case with the prevalence of INP in the coarse fraction -with respect to PM1 size fraction- during winter in San Pietro Capofiume. In addition, Saharan dust transport events were observed in a few measurement campaigns and related to the variability of the INP concentration. The measurement of INP properties achieved with the DFPC instrument could be crucial in the search for a better understanding of the aerosol-cloud interactions.

References

[1] Mason B J 1971 *The physics of clouds* (Oxford Univ. Press: Oxford) p 160
[2] Zuberi B, Bertram A K, Koop T, Molina L T and Molina M J 2001 *J. Phys. Chem. A* **105** 6458
[3] Zobrist B et al 2006 *Atmos. Chem. Phys.* **6** 3115
[4] Shilling J E, Fortin T J and Tolbert M A 2006 *J. Geophys. Res.* **111** D12204
[5] Salam A, Lesins G and Lohmann U 2008 *Air Qual. Atmos. Health* **1** 135
[6] Bundke U, Nillius B, Jaenicke R, Wetter T, Klein H and Bingemer H 2008 *Atmos. Res.* **90** 180
[7] Tajiri T, Yamashita K, Murakami M, Orikasa N, Saito A, Kusunoki K and Lilie L *2013 J. Meteor. Soc. Japan* **91** 687
[8] Rogers D C, DeMott P J, Kreidenweis S M and Chen Y 2001 *J. Atmos. Oceanic Technol.* **18** 725
[9] Bigg E K, 1996 *Tellus* **48B** 223
[10] Klein H, Haunold W, Bundke U, Nillius B, Wetter T, Schallenberg S and Bingemer H 2010 *Atmos. Res.* **96** 218
[11] Langer G and Rodgers J 1975 *J. Appl. Meteor.* **14** 560
[12] Kohn M, Lohmann U, Welti A and Kanji Z A 2016 *J. Geophys. Res. Atmos.* **121** 4713
[13] Budke C and Koop T 2015 *Atmos. Meas. Tech.* **8** 689
[14] Santachiara G, Di Matteo L, Prodi F and Belosi F 2010 *Atmos. Res.* **96** 266
[15] Belosi F, Santachiara G and Prodi F 2014 *Atmos. Res.* **145–146** 105
[16] Belosi F, Rinaldi M, Decesari S, Tarozzi L, Nicosia A and Santachiara G 2017 *Atmos. Res.* **186** 116-126
[17] Perry J H 1963 *Chemical Engineers' Handbook* (McGraw-Hill Company: New York)
[18] Levin Z, Teller A, Ganor E and Yin Y 2005 *J. Geophys. Res.* **110** D20202
[19] Mason R H et al. 2016 *Atmos. Chem. Phys.* **16** 1637