

Experimental Study on the Dependency of Ice Nucleation Active Surface Site Density on ATD Aerosol Size

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Abstract

In light of the percentage of Earth's cloud coverage, heterogeneous ice nucleation in clouds is the most important global-scale pathway. More recent parameterizations of ice nucleation processes in the atmosphere are based on the concept of ice nucleation active surface site density (n_s). It is usually assumed that n_s is independent of time and aerosol size distribution, *i.e.* that the surface properties of aerosols of the same species do not vary with size. However, the independence of n_s on aerosol size for every species has been questioned. This study presents the results of ice nucleation processes of ATD laboratory-generated aerosol (particle diameters of 0 - 3 μm). Ice nucleation in the condensation mode was performed in a Dynamic Filter Processing Chamber at temperatures of -18°C and -22°C , with a saturation ratio with respect to water of 1.02. Results show that n_s increased by lowering the nucleation temperature, and was also dependent on the particle size. The n_s of particles collected on the filters, after a 0.5 μm D_{50} cut-off cyclone, resulted statistically higher with respect to the values obtained from the particles collected on total filters. The results obtained suggest the need for further investigation of n_s dependence of same composition aerosol particles with a view to support weather and climate predictions.

Keywords

Ice Activated Fraction, Ice Nucleation Active Surface Site Density, Condensation Freezing

1. Introduction

Ice particles in the atmosphere can be formed via homogeneous ice nucleation in liquid water or heterogeneous ice nucleation triggered by relatively rare aerosol

particles. It is well accepted that homogeneous ice nucleation is a time and temperature dependent stochastic process [1] [2] [3]. There is, however, ongoing debate as to whether heterogeneous ice nucleation is only temperature dependent or both temperature and time dependent [4]. Several published papers and theoretical considerations have evidenced that time plays a much weaker role than temperature [4] [5]-[11].

There is general agreement on the increasing efficiency of aerosol particles to nucleate ice with increasing aerosol size [12] [13] [14] [15]. Many heterogeneous ice nucleation parameterizations relate ice crystal number concentrations simply to water supersaturation [16] or to temperature [17] [18], or to both temperature and supersaturation [12] [19]. Increased knowledge of ice nucleation from field and laboratory studies has led to the development of several different model representations of heterogeneous ice nucleation that take into account the fact that different types of aerosols can act as ice nucleating particles (INPs) with different nucleating efficiencies also depending on aerosol size [20]-[25]. More recent ice nucleation parameterization processes in the atmosphere are based on the concept of ice nucleation active surface site density (n_s). The $n_s(T)$ parameter represents the number of ice nucleation active sites per unit surface area of a solid sample on cooling from 0°C to the temperature considered [26].

It depends on the temperature, water saturation ratio, mineralogical composition, surface morphology and coating [27] [28] [29]. In addition it is usually assumed that n_s is independent of time and aerosol size distribution, *i.e.* that the surface properties of same-species aerosol do not vary with size, thus facilitating comparison of the ice nucleating ability of different aerosol particles. Starting from the density of active sites, one can calculate what fraction of the particles will nucleate ice at a certain temperature, *i.e.* the amount of ice in supercooled and mixed-phase clouds. In the presence of different aerosol species, the different active site density for every species must be defined in order to account for each species' different nucleating ice ability.

Errors in the assumed INP concentration will influence the simulated amount of ice in mixed-phase clouds, leading to errors in top-of-atmosphere radiative flux and the climate sensitivity of the model. However, the independence of n_s on aerosol size for every species has been questioned since although widely accepted, this assumption is poorly supported experimentally. A review of the main field and laboratory results will be presented.

In terms of field results, Si-Meng *et al.* [30] investigated INPs at three coastal marine sites in Canada, sampling aerosol with a micro-orifice uniform deposit impactor (MOUDI). At all three sites, activated fraction (AF) and n_s were found to be dependent on particle size, larger particles being more efficient at nucleating ice. The n_s dependence on the particle size was attributed to different types of aerosol in the size ranges considered.

Porter *et al.* [31] conducted measurements at Longyearbyen (Svalbard) and Leeds (UK) of size-resolved aerosol collected from a balloon, performing im-

mersion mode droplet freezing assays on the sampled aerosols. In the temperature range $-15 \div -28^\circ\text{C}$, the authors obtained the lowest AF and the highest n_s for particles in the size range $> 1 \mu\text{m}$ at Leeds. In contrast, in Longyearbyen the highest n_s value was obtained for aerosol in the $0.5 - 1.0 \mu\text{m}$ range.

At Leeds ($T = -25^\circ\text{C}$) AFs were about 2×10^{-4} in the lowest size range and 5×10^{-2} in the highest size range (Figure 10a of their paper). The opposite trend was observed for n_s , which was 10^9 m^{-2} for the lowest size bin and 10^8 m^{-2} for the largest one. In Longyearbyen (Figure 10b of their paper), while the same AF trend was found as in Leeds (about 4×10^{-3} and 2×10^{-1} respectively), n_s was lower in the lowest size bin (about 10^8 m^{-2}) with respect to largest one (about 10^9 m^{-2}).

Paramonov *et al.* [29] examined surface-collected dust from three different locations around the world with respect to its n_s in both the deposition nucleation and condensation freezing modes. The n_s of the 200 nm untreated, heated and washed particles was larger than for the 400 nm samples. The author concluded that it was not possible to directly determine the reasons behind this observed difference (larger particles might contain more soluble material and/or small particles may contain more IN-active material on their surface, e.g. bacteria or active minerals). Reicher *et al.* [32] characterized the ice nucleation properties of size-segregated mineral dust sampled during dust events in the eastern Mediterranean.

Larger particles were more active INPs, exhibiting higher INP concentrations and a higher number of nucleating sites per surface area at lower temperatures. Two parameterizations were derived for super-micron and sub-micron particles. Yadav *et al.* [33] characterized the size-resolved ice nucleation active site density for 200 - 600 nm particles of Thar Desert Dust (India). The lowest and highest values of AF were observed for 200 and 600 nm, respectively. Moreover n_s showed a similar pattern in both sizes and was found to increase with the particle diameter.

In terms of laboratory experiments, Zolles *et al.* [34] examined untreated alpha quartz samples and found higher n_s in smaller particles than in larger ones. An increase was also observed for milled compared to untreated samples, this result being attributed to higher defect density caused by mechanical milling. A similar result was obtained by Hiranuma *et al.* [35], who observed that n_s for milled hematite was an order of magnitude higher in AIDA immersion mode freezing experiments. Generally speaking, milling of dust samples in the laboratory or by natural mechanical weathering processes can lead to more surface inhomogeneities and also to an enrichment of more ice nucleation-active minerals, such as quartz. However, milling can also lead to a decrease in the ice nucleation ability in case of polymineralic samples [36].

Steinke *et al.* [37] found that for Arizona Test Dust (ATD) consisting of milled desert dust, the n_s in the deposition mode does not vary with the shift of median diameter from $d_{\text{med}} = 0.23 \mu\text{m}$ to $d_{\text{med}} = 0.35 \mu\text{m}$. Hartmann *et al.* [38]

investigated the impact of n_s for size-selected kaolinite particles (300, 700 and 1000 nm mobility diameter; one particle per droplet), concluding that different size kaolinite particles show similar ice nucleation properties if correction for multiply charged particles is made. In conclusion, a few published papers show a dependence of n_s on particle size.

These results call for deeper investigation of the widely accepted view that n_s is independent of particle size even for aerosol of the same composition. Indeed, in order to accurately model the global INP population there is a need to assess the size dependence of ice-nucleating particles. This paper aims to provide a contribution to this topic, reporting the results of laboratory experiments with ATD aerosol particles separated into two size classes by means of a cyclone.

2. Experiments

The fraction of aerosol particles acting as INPs and n_s as a function of aerosol size were investigated with laboratory-generated ATD aerosol. Commercial ATD particles (Powder Technology Inc.) with particle diameters of nominally 0 - 3 μm were used. ATD is composed of a mixture of different minerals, mainly silicates, calcite, and clay minerals [39] and can be considered a proxy for natural mineral dusts of desert origin [40] [41] [42] [43].

ATD aerosol was generated by nebulizing a 10 $\text{g}\cdot\text{L}^{-1}$ suspension with high-purity air, as the carrier gas, in a home-made Collison atomizer (Figure 1). A magnetic stirrer (ARE-6, Velp Scientifica) was used to maintain the mineral particle suspended during the atomization process. After nebulization, the wet aerosol in the carrier gas was dried by flowing it through a silica gel column, after which samples were collected on black-gridded cellulose nitrate membrane filters (Millipore HABG04700, porosity 0.45 μm) for ice nucleating particle assessment. The filters have a collection efficiency > 99% at 0.3 μm (most particle penetrating size), at a flow rate of 2 lpm [44]. INP losses due to filter penetration can therefore be excluded. Aerosol sampling took place with two parallel lines: one with a total filter holder, the other with a cyclone (SCC 0732, BGI Incorporated) in front of the filter holder. The SCC 0732 cyclone belongs to the Sharp-Cut Cyclone family Kenny and Gussman [45] [46]. Simultaneous sampling of aerosol particles by means of an Optical Particle Counter (Grimm OPC, model 11-A) was carried out to obtain particle concentration and size distribution. We assumed that the particles were spheres and therefore used the diameter of the OPC midpoint of the different channel size bins as the particle diameter. ATD particles are not as spherical as monodisperse polystyrene latex (PSL) used to calibrate the OPC. Therefore, the obtained size information could not be simply related to the geometric equivalent particle sphere diameter. However, the aim of our work was to measure n_s of a submicron particle fraction with respect to the total particles with the same composition. Since the conversion from geometric to aerodynamic particle diameter is not essential for our results, we will show our findings only in terms of optical diameter.

The fractional efficiency curve was obtained by measuring ATD particle size distribution and concentration with the OPC before and after the cyclone. **Figure 2** shows the cyclone penetration curve at 2 lpm flow rate. Vertical bars give one standard deviation of the three repeated tests. **Figure 2** also shows the interpolation curves obtained through a polynomial fitting of the experimental efficiency curves. The resultant geometric D_{50} cut point at 2 lpm flow rate was $0.45 \mu\text{m}$ ($\text{PM}_{0.5}$ from here on).

INP concentrations were detected by the membrane filter technique [47] [48] following the procedure reported by Santachiara *et al.* [14]. The following is a summary of the main points. Filters were inserted into a metal plate, previously covered with a smooth surface of Vaseline. The Vaseline was then heated slightly and rapidly cooled in order to fill the filter pores. A Dynamic Filter Processing Chamber (DFPC), deployed in several experimental campaigns [49] [50] [51] was used to determine the concentration of aerosol particles active as INPs at different supersaturations with respect to ice and water (**Figure 3**).

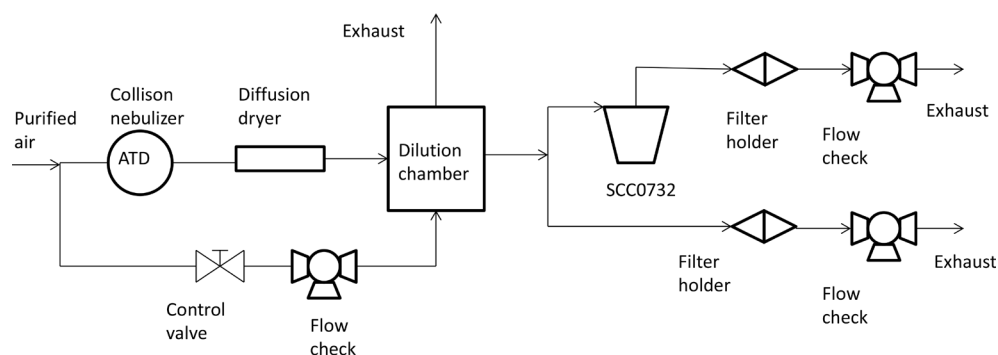


Figure 1. Scheme of the experimental set-up. ATD aerosol was generated by nebulizing a suspension in a home-made Collision atomizer. After nebulization, the wet aerosol in the carrier gas was dried by flowing it through a silica gel column, after which samples were diluted with clean air. Aerosol sampling took place with two parallel lines: one with a total filter holder, the other with a cyclone (SCC 0732, BGI Incorporated) in front of the filter holder.

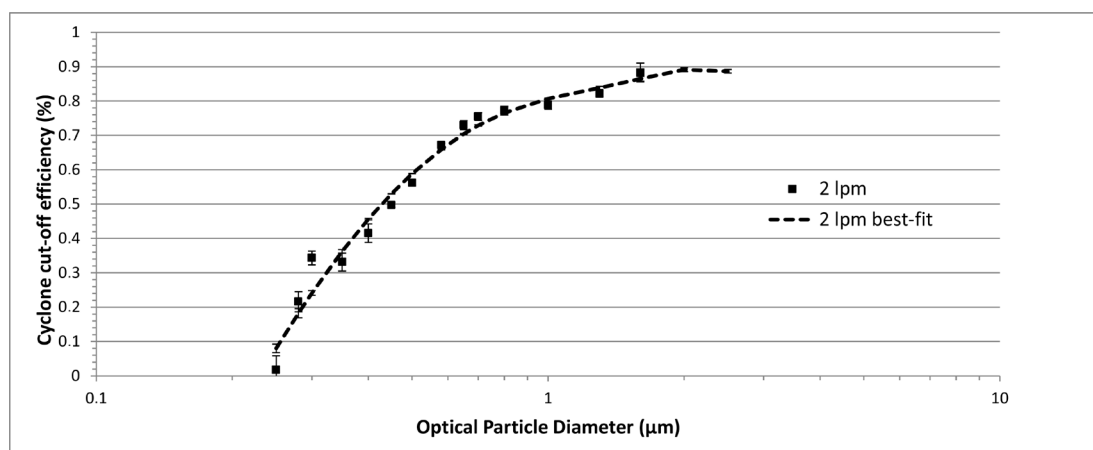


Figure 2. Experimental aerosol particles efficiency curves of the SCC 0732 cyclone for ATD particles obtained at 2 lpm. Vertical bars represent one standard deviation. Continuous curves show the best fit obtained with polynomial interpolation function scheme of the experimental set-up.

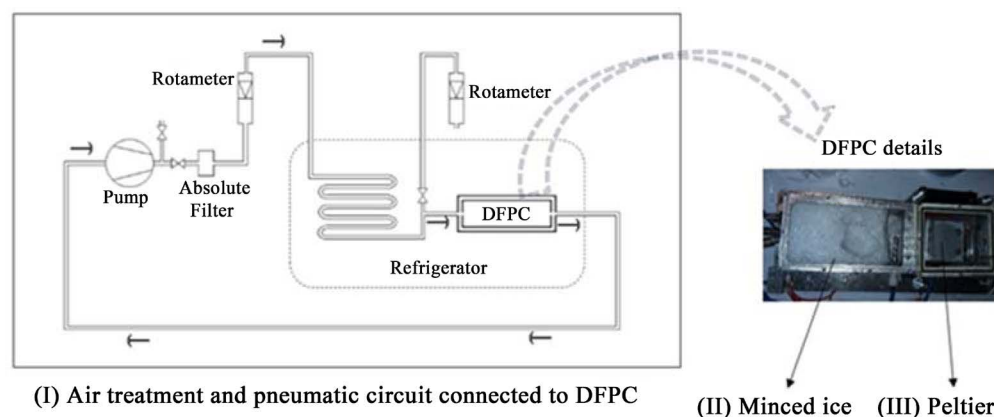


Figure 3. Left (I): DFPC scheme; right (II and III), view from above (from [52] Nicosia *et al.*, 2016).

The chamber is housed in a refrigerator. Filtered air is forced by a pump through the chamber in a closed loop. Air enters the chamber through a perforated plate into the minced ice. By varying the temperature inside the chamber and the vapour supersaturation with respect to liquid and/or ice, INPs can be activated both in the deposition and condensation-freezing modes.

The experiments were performed only at water saturation ratio $S_w = 1.02$, *i.e.* at 2% water supersaturation. A saturation ratio in the 1.02 - 1.04 range has been considered in many published papers, especially when a continuous flow diffusion chamber device is used [53] [54] [55]. A saturation ratio $S_w = 1.02$ allows measurements of ice nucleating particles in conditions comparable to those of immersion freezing.

AF was calculated by the ratio between the INPs and the aerosol particle number given by the OPC, while n_s was obtained from the ratio between the INPs and the total particle surface. The surfaces of the aerosol particles collected from the filters placed downstream of the cyclone were obtained by multiplying the aerosol size distribution with the corresponding cyclone penetration curve (best fit of the experimental penetration curve). Three replicas of each parallel aerosol sampling experiments were considered.

In the field campaigns, atmospheric PM_1 and PM_{10} aerosol fractions were sampled on the same filters type as those used in the laboratory. The aerosol fractions were sampled by inserting different sampling heads (1 μm , and 10 μm cut-point-Standard EN 12341, TCR Tecora) in front of the filter. Particle number concentration was measured with an Optical Spectrometer (Mod.1.108, Grimm Aerosol Technik). INP concentrations were detected by the membrane filter technique as in the laboratory runs.

3. Results

Figure 4 gives the ice AF for the fine ($AF_{PM_{0.5}}$) and coarse fraction (AF_{coarse}) of ATD aerosol in laboratory experiments at $T = -18^\circ\text{C}$ and -22°C , $S_w = 1.02$.

$AF_{PM_{0.5}}$ is given by the ratio between the activated INP and the aerosol particle number on the filter after the cyclone ($AF_{PM_{0.5}}$). AF_{coarse} was obtained by sub-

tracting the INP counted on the filter after the cyclone from the total INP, divided by the difference between the particle number sampled on the total filter and the cyclone (see Equation (1))

$$AF_{\text{Coarse}} = \frac{IN_{\text{PT}} - INP_{\text{PM0.5}}}{N_{\text{pT}} - N_{\text{pPM0.5}}} \quad (1)$$

where IN_{PT} and $INP_{\text{PM0.5}}$ are the ice nucleating particle numbers obtained from the total filter and the filter after the cyclone, respectively, and N_{pT} and $N_{\text{pPM0.5}}$ the total and the $\text{PM}_{0.5}$ particle number. Results show a small increase of AFs from fine to coarse aerosol size fraction, which, however, was not statistically significant due to large variability in the measurements (**Figure 4**).

Table 1 is a compilation of ice AFs obtained from several field campaigns at different sites performed by sampling aerosol on filters with different sampling heads, with subsequent activation as indicated in the experimental part above [49] [51] [56] [57].

Data from **Table 1** show a higher increase in the $AF_{\text{PM}_{10}\text{-PM}_1}$ aerosol fraction with respect to AF_{PM_1} , compared with laboratory experiments. This may depend on the fact that in the laboratory experiments the diameter of ATD particles in the coarse fraction is in the range 0.5 - 3 μm , while in the experimental campaign, the range is 1 - 10 μm . It is known that AF generally increases with aerosol size [41] [58]. In addition, the field campaigns were performed in sites with different characteristics: coastal site (Capo Granitola, South Sicily, CGR), mountain site (Mt. Cimone, 2165 m a.s.l., southern border of the Po Valley), rural site in the eastern Po Valley (S. Pietro Capofiume, SPC), remote marine area (Mace Head Research Station). In addition to aerosol size, heterogeneous ice activation efficiency of the particles depends on several other parameters: surface chemistry (e.g. the presence of functional groups able to bind water molecules), local surface features such as steps, cracks chemical composition (organic and/or inorganic compounds, soluble and/or insoluble compounds), and on freezing mode [28] [59] [60].

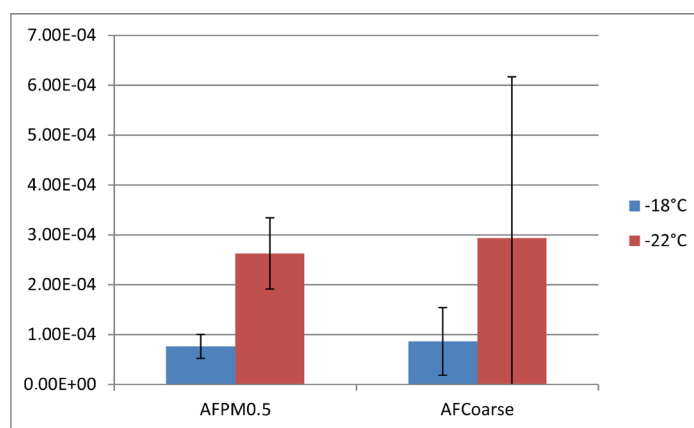


Figure 4. $AF_{\text{PM0.5}}$ and AF_{Coarse} obtained with ATD particles, in laboratory experiments at two temperatures and $Sw = 1.02$. The bars are not related to measurement uncertainties but to the variability in the AF of the three replicas.

Table 1. Ice AFs in the coarse and fine aerosol fraction obtained in several field campaigns: (SPC1, San Pietro Capofiume, Italy: February 10-21, 2014; SPC2, San Pietro Capo Fiume, Italy, May 19-30, 2014; CGR, Capo Granitola, Italy: April 8-25, 2016; MCH Mace Head, Ireland: August 5-29, 2015; MC1, Monte Cimone, Italy: May 19-29, 2014; MC2, Monte Cimone, Italy: October 5-12, 2015.

Sampling Site	INP Conditions	AF (PM ₁)	AF (PM ₁₀ -PM ₁)
MC1	-18°C, S _w = 1.02	$3.4 \times 10^{-6} \pm 5.1 \times 10^{-6}$	$9.4 \times 10^{-6} \pm 1.3 \times 10^{-5}$
MC2	-18°C, S _w = 1.02	$2.3 \times 10^{-6} \pm 3.4 \times 10^{-6}$	$5.9 \times 10^{-4} \pm 9.4 \times 10^{-4}$
SPC1	-18°C, S _w = 1.02	$9.8 \times 10^{-6} \pm 7.6 \times 10^{-6}$	$2.9 \times 10^{-4} \pm 3.8 \times 10^{-4}$
SPC2	-18°C, S _w = 1.02	$3.3 \times 10^{-5} \pm 2.2 \times 10^{-5}$	$5.5 \times 10^{-5} \pm 8.7 \times 10^{-5}$
CGR	-18°C, S _w = 1.02	$7.1 \times 10^{-7} \pm 6.1 \times 10^{-7}$	$8.3 \times 10^{-6} \pm 8.7 \times 10^{-6}$
CGR	-22°C, S _w = 1.02	$8.9 \times 10^{-7} \pm 7.0 \times 10^{-7}$	$1.2 \times 10^{-5} \pm 0.94 \times 10^{-5}$
MCH	-22°C, S _w = 1.02	$2.8 \times 10^{-7} \pm 4.5 \times 10^{-7}$	$2.7 \times 10^{-6} \pm 4.2 \times 10^{-6}$

Table 2. Averaged ice nuclei surface site n_s obtained from the tests at 2 lpm. The surface site nucleation density, n_s , is given in m⁻². In brackets the averaged standard deviation.

Temp.	Flow rate (lpm)	n_s (m ⁻²) Total filter	n_s (m ⁻²) PM _{0.5} (Cyclone filter)
-18°C	2	1.6×10^8 (0.3×10^8)	2.2×10^8 (0.3×10^8)
-22°C	2	5.2×10^8 (1.0×10^8)	7.6×10^8 (1.4×10^8)

Table 2 summarizes the n_s values obtained in the laboratory experiments with ATD, at T = -18°C and -22°C. Results are given for total and cyclone filters (PM_{0.5}). The standard deviation (in brackets) is obtained through the averaged standard deviation of each test (each made of three runs).

The n_s values obtained from the particles collected on the filters after the cyclone were statistically higher with respect to the n_s obtained from the particles collected on total filters. That means a higher surface density of ice nucleating sites on the surfaces of the smaller particles. In addition, n_s increases with the decrease of the ice nucleation temperature.

Figure 5 and **Figure 6** are the scatter plots between n_s and AF at -18°C and -22°C, respectively. Data refer to ATD particles without (total filter) and with the cyclone (PM_{0.5}), parallel samplings.

We observed that at the same given AF the active surface site density is higher in the fine aerosol fraction at both temperatures.

4. Conclusions

The paper shows the results of AF and n_s obtained from ATD particles generated by nebulizing a 10 g·L⁻¹ suspension with high-purity air in a home-made Collision atomizer. Aerosol was sampled on black-gridded cellulose nitrate membrane filters with two parallel lines. One line sampled the total aerosol (ATD with nominally 0 - 3 μm diameter), the other the aerosol after it had flowed through a

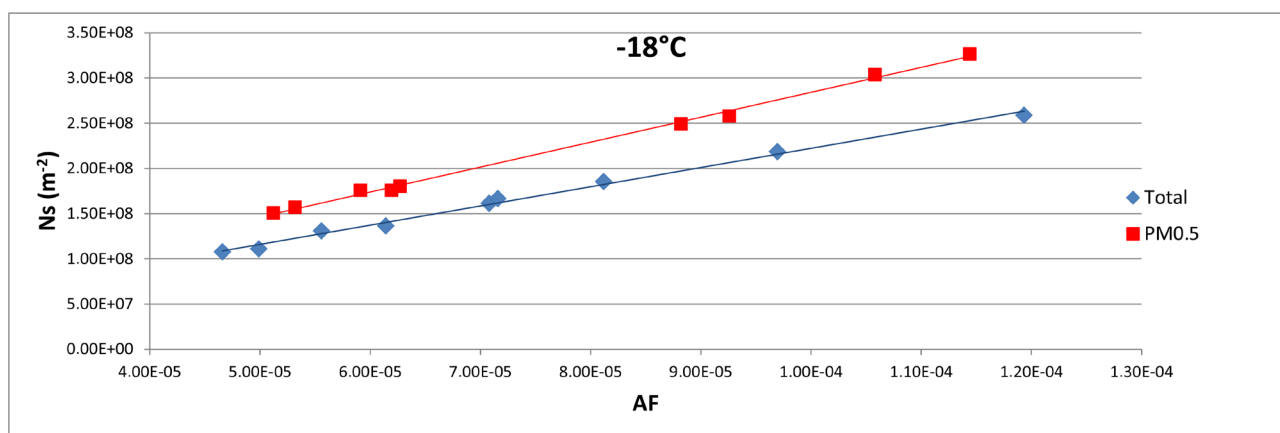


Figure 5. N_s versus AF from runs carried out at 2 lpm flow rates. Temperature -18°C .

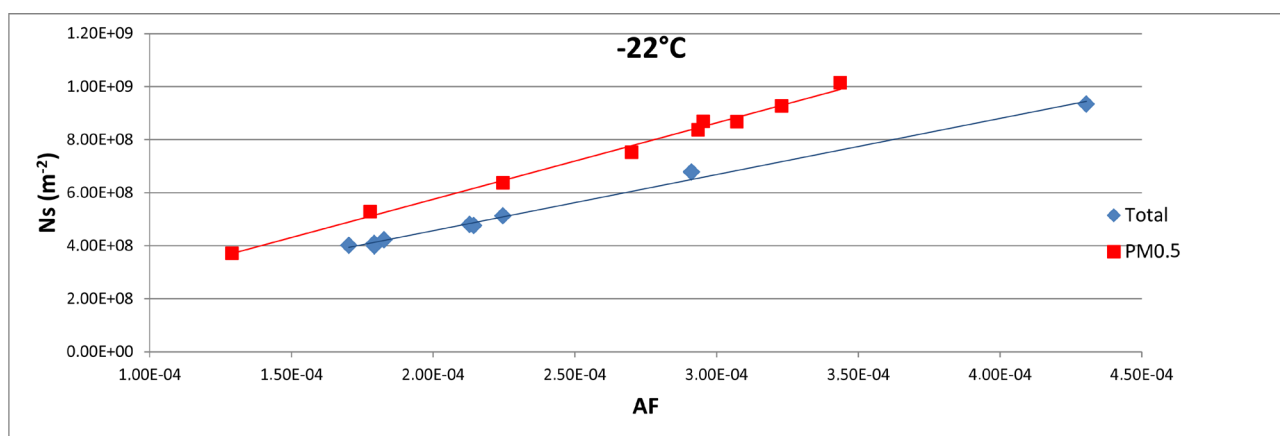


Figure 6. N_s versus AF from runs carried out at 2 lpm flow rates. Temperature -22°C .

cyclone with a 50% cut-point at about $0.5\ \mu\text{m}$. Simultaneous sampling of aerosol particles by means of an Optical Particle Counter (Grimm OPC, model 11-A) was carried out to obtain particle concentration and size distribution. Ice nucleation experiments of sampled aerosol was performed with a DFPC device, at $T = -18^\circ\text{C}$ and $T = -22^\circ\text{C}$.

The aerosol activated fraction increased when the nucleation temperature was decreased, and was seen to be weakly dependent on particle size. Results showed a small (not statistically significant) increase of AFs from the fine to coarse aerosol size fraction, which, however, was lower than the values obtained from several field campaigns carried out at different sites (coastal, mountain and rural sites, remote marine areas), using particles of PM_1 and PM_{10} size fractions. It is known that AF generally increases with aerosol size.

As regards the n_s parameter, it is usually assumed that n_s is independent of time and aerosol size distribution, *i.e.* that the surface properties of same-species aerosol do not vary with size. However, the independence of n_s from aerosol size for every species has been called into question. We indicate several papers reporting n_s variations in field campaigns [29]-[33], and in laboratory experiments [34] [35] [36]. The n_s dependence on particle size found in field campaigns was

attributed to different types of aerosol in the considered size ranges, and in laboratory experiments to mechanical treatment of the aerosol (e.g. milling).

In our experiment, the n_s values of particles collected on the filters after the cyclone were observed to be statistically higher with respect to the n_s obtained from the particles collected on total filters. This would signify higher surface density of ice nucleating sites on the surfaces of the smaller particles. In our investigation of coarse and fine particles, the n_s parameter was seen to increase from 1.6×10^8 ($\pm 0.3 \times 10^8$) to 2.2×10^8 ($\pm 0.3 \times 10^8$) at $T = -18$ and from 5.2×10^8 ($\pm 1.0 \times 10^8$) to 7.6×10^8 ($\pm 1.4 \times 10^8$) at $T = -22^\circ\text{C}$, respectively.

As we carried out size separation unaided by any mechanical operation, we cannot rule out that n_s dependence is simply correlated with particle size. Moreover, we did not use electrostatic aerosol classifiers in light of uncertainties concerning multiple charge correction. Lastly, we observe that our results might be influenced by a different ATD particle composition ranging from submicrometric to supermicrometric size ranges. Our results therefore call for deeper understanding of n_s dependence on particle size with the aim of enhancing the accuracy of evaluations of ice nucleating particle concentration throughout the atmosphere, and therefore the accuracy of weather and climate predictions.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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