Dr. Ottmar Möhler

Editor ACP

Dear Dr. Ottmar Möhler,

Thank you for the reviews of manuscript entitled *"Influence of the ambient humidity on the activation of natural deposition ice nuclei"*. We really appreciate the positive comments from the three reviewers. They help us to improve the final version of the manuscript.

The paper has been rewritten with substantial changes as suggested by all the reviewers. We hope that this revised version will be acceptable for publication in ACP.

Sincerely,

María Laura López - Eldo Ávila

Answers to the reviewers' comments:

The answers to Reviewers are in red.
The added sentences and words are emphasized in *Italic*.

Reply to Reviewer #1

Specific Comment 1:
In the discussion of possible reasons behind the observed trend of IN concentrations with RHamb, two hypotheses are presented in the paper. The authors discuss the hypothesis that (1) nucleation below water saturation may take place in pores and cavities, as per Marcolli (2014) and (2) that the observations may be related to increases in bioaerosol concentrations. However, only a mention of the first hypothesis is raised in the abstract---why? Is this seen as the authors as being the more likely explanation?
The available information is insufficient to favor any of the hypotheses. Then, the second hypothesis was included in the abstract.

"The role *of biological-IN* and nucleation occurring in pores and cavities *were* discussed as possible mechanism to explain the increase on the IN concentration during high ambient relative humidity events."

Specific Comment 2:
Further to the first point above, the study does not appear to provide a means to suggest that either hypothesis (1) or (2) above is a more likely explanation. Accordingly, in relation to

the impacts of bioaerosols, the discussion of possible impacts of relative humidity /precipitation on ice nucleating biological particles is too short (e.g. at Page 16703 Line 25---29). For instance, why might biogenic IN levels be increased due to changes in RH and precipitation? Numerous references to results from recent important papers with relevance to this discussion are absent. These include T.P. Wright et al. (2014) Aerosol Science and Technology, 48:11, Hader et al. (2014) Atmos. Chem. Phys., 14, 5433–5449 and Bigg et al. Atmos. Chem. Phys. (2015), 15, 2313–2326.

We agree with the Reviewer that the hypothesis of bioaerosols has been poorly described in the manuscript. We extended the description of this hypothesis in the revised manuscript, including the references suggested by the Reviewer.

"Prenni et al. (2013), *Hader et al. (2014) and Bigg et al. (2015)* presented evidence that the rising of IN concentration during rain events can be related to the increase of microorganisms and other biological particles concentrations. *It has been shown that biological particles can be released during precipitation through mechanical mechanisms. For instance, winds produced by storms can release biological particles from leaf surfaces and soil. The release of these biological particles include biological IN (bacteria, fungal spores, and pollen) which can impact the IN population.* This assumption was supported by different studies reporting both: the release of biological particles during rain events and the role of these particles as sources of IN (Huffman et al., 2012, 2013*). Furthermore, Wright et al. (2014) suggested that high relative humidity may also trigger the release of IN at ground level. They provided observational evidence that a fraction of the biological particles released during high RH can serve as immersion mode IN while droplets cool during ascent.*

It is important to remark that unlike the present study, where the deposition nucleation mode was examined, the previous studies examined condensation and immersion freezing modes. We have no evidence, so far, that the increase of IN concentration in the present work can be analyzed in terms of biological particles. The role of the biological particles acting as deposition ice nuclei need to be studied in more detail.

Specific Comment 3:

Page 16703 Line 25--30. Were the nucleation modes probed by Prenni et al. and Huffman et al. the same as that probed here? Possible differences should be mentioned.

Prenni et al. and Huffman et al. have employed the continuous flow diffusion chamber for the measurements of IN concentrations. These measurements were made above water saturation (103–106% RH with respect to water). Instead, the measurements in the current work were made below water saturation. It was clarified in the last paragraph of the Specific Comment 2.

Specific Comment 4:

Page 16704 Line 22: I think the phrase "support the idea that the deposition nucleation can be a pore condensation and freezing" is a little bit too strong here, even with the preceding caveat in the sentence. In the absence of further evidence, I suggest weakening this

statement slightly and inserting a phrase like "may support…", or "could support", given that other, different, hypotheses exist to explain the observations.
The phase was changed as suggested by the Reviewer.
"…the results presented in this work *may* support the idea that the deposition nucleation can be a pore condensation…"

Specific Comment 5:
Page 16698 Line 26: The definition of immersion mode freezing here states that the particle must "penetrate" the droplet, suggesting that the lines between immersion and condensation freezing are unambiguously different. I suggest the definition should be simply "suspended in the droplet", as per Vali (1985).
The phase was changed as suggested by the Reviewer.
"During the immersion-freezing mode, *a particle suspended in the droplet* initiates freezing."

Technical comments:
Page 16698 Line 13:"was discussed as a possible…"
Page 16699 Line 19: of the atmosphere, not "on the atmosphere"
Page 16700 Line 1: Change "Then, the study…." to "Furthermore, the study…."
Page 16701 Line 20: "a size large enough…"
Page 16703 Line 24: "or known at this time" is redundant in this sentence. Remove.
Page 16703 Line 29: "Even though" doesn't really make much sense here. I suggest changing to "While in the present work…."
Page 16705 Line 15: "too scarce to make an analysis"
Page 16706 Line 16: change to "to differentiate between these mechanisms"
All the technical comments were taken into account.

Reply to Anonymous Referee #2
This paper presents experimental results on a very important topic of atmospheric research, the ability of aerosols on deposition ice nucleation. Among the ice nucleation modes probably deposition ice nucleation is of least understood. The authors try to find correlation between IN concentration and relative humidity of air. In general the paper is clearly written, well organized and scientifically sounds, however a clear statement of the major goal of the study is missing.
The major goal of this work is the study of the factors that regulate the effectiveness of aerosols on deposition ice nucleation. It was included in the revised manuscript.

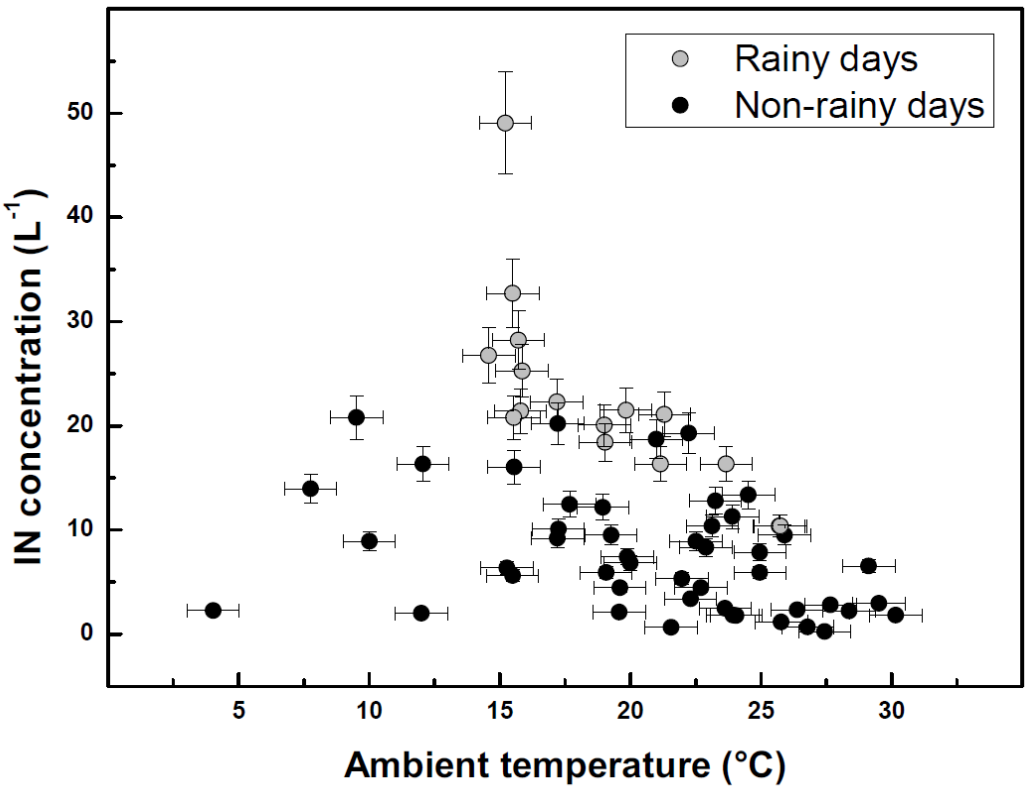
"Particularly, studies on anomalies in atmospheric ice nucleus concentration are important, since they will give us clues for solving problems on the origin and the nature of atmospheric ice nuclei. *The major goal of this work is the study of the factors that regulate the effectiveness of aerosols on deposition ice nucleation*. Regarding the possible …."

I recommend the paper for publication in the Atmospheric Chemistry and Physics.

Nevertheless, I list some comments and questions that can be taken into account for a revision before publication:

- "The experiments are clearly described, however it would probably be interesting to know also the ambient temperature."

We found that the ambient temperature (Ta) do not influence the IN concentration. The Figure below displays the IN concentration as a function of Ta. The temperature of the measurements varied between 5°C and 30°C and the results do not seem to indicate that there is any particular tendency of the IN concentration values with the ambient temperature variations.



- "Furthermore, the usage of relative humidity is ambiguous throughout the manuscript, therefore I suggest the use of RHw and RHi."

Agreed. This change was implemented.

p. 16701 line 10: "The increasing of the relative humidity *over ice* inside the cloud chamber (RH_i) is explained…"

p. 16701 line 11: "..with different *relative humidity* and temperature (Curry and Webster, 1999)."

p. 16701 line 12: "The supersaturation is achieved starting with a RH_i slightly lower…"

p. 16701 line 14: "Since the increase of RH_i for each air injection…"

p. 16701 line 15: " … even once the vapor is supersaturated over ice. Once the…"
p. 16701 line 27: "In order to determine RH_i and T in the cloud chamber the Testo 435-4 multifunction measuring instrument was used. This instrument measures *relative humidity* in the temperature range [−50,150] C. When RH_i is measured at temperatures below 0C, the resolution is 0.1 %."
p. 16702 line 5: "..variability in the RH_i increase between the injections…"
p. 16702 line 6: "…and accuracy of the *humidity* sensor."

- p. 16699 line 10: should read "ice-nuclei content _of_ the atmosphere"
Agreed. This change was implemented.

- p. 16700 line 26 to p. 16701 line 5: What in the present and in the previous work was done is not really clear, this part should be reorganized.
This paragraph was rewritten:

"*In a previous work we have quantified the IN-concentration (López and Ávila, 2013) in deposition nucleation mode at ground level in Córdoba, for temperatures between −15 and −30 C, and ice supersaturation ranging between 2 and 20 %. In the present work the experiments were carried out following the same procedure as described by López and Ávila (2013) and a total of 63 measurements of IN concentration were carried out during 45 days, since 28 July 2014 until 10 December 2014 (winter and spring seasons).*"

- p. 16701 line 9: If the air is exchanged inside the chamber, I do not see why the number of aerosols should stay constant. It depends on the ambient aerosol concentration, isn't it? Thus, it can vary.
It is assumed that the aerosol concentration of the air inside the chamber is the same (or quite similar) as the aerosol concentration outside the chamber (ambient). In fact, the air within the chamber was renewed at the beginning of every experiment.

- p. 16701 line 20: "reach a size _large_ enough": how large is it? Can you please provide some numbers?
Figure 1 shows image of crystals once they grown on the sugar solution. Considering the scale shown in the photograph, it is possible to observe that the crystals reach mm sizes.

- p. 16702 line 15 to 18: This part should come to Experimental. Furthermore, the saturation conditions described here are meant inside the chamber, aren't they?
It was already mentioned in the Experimental section that the measurements were performed in deposition nucleation mode. We want to recall the readers the experimental conditions here.
Yes, the saturation conditions described here occur inside the chamber.

- p. 16702 line 23: What was the reason that the cold chamber could not reach the expected temperature? The too high ambient temp?
In general, the reason was that the cold chamber engine was not working properly.

- Figure 3 and its discussion are the most important parts of the study. The clear trend of IN concentration vs. RH indicates for me that the RH is the most relevant factor, not the rain itself. Therefore the statement near line 18 on p. 16703 can be revised.
We cannot assess that the RH is the most relevant parameter because the measurements of high IN concentration were obtained with high RH during rainy days. We did not measure IN concentration at high RH (> 70%) without rain; then, it is not possible to discard that both effects (rain and high RH) are required.

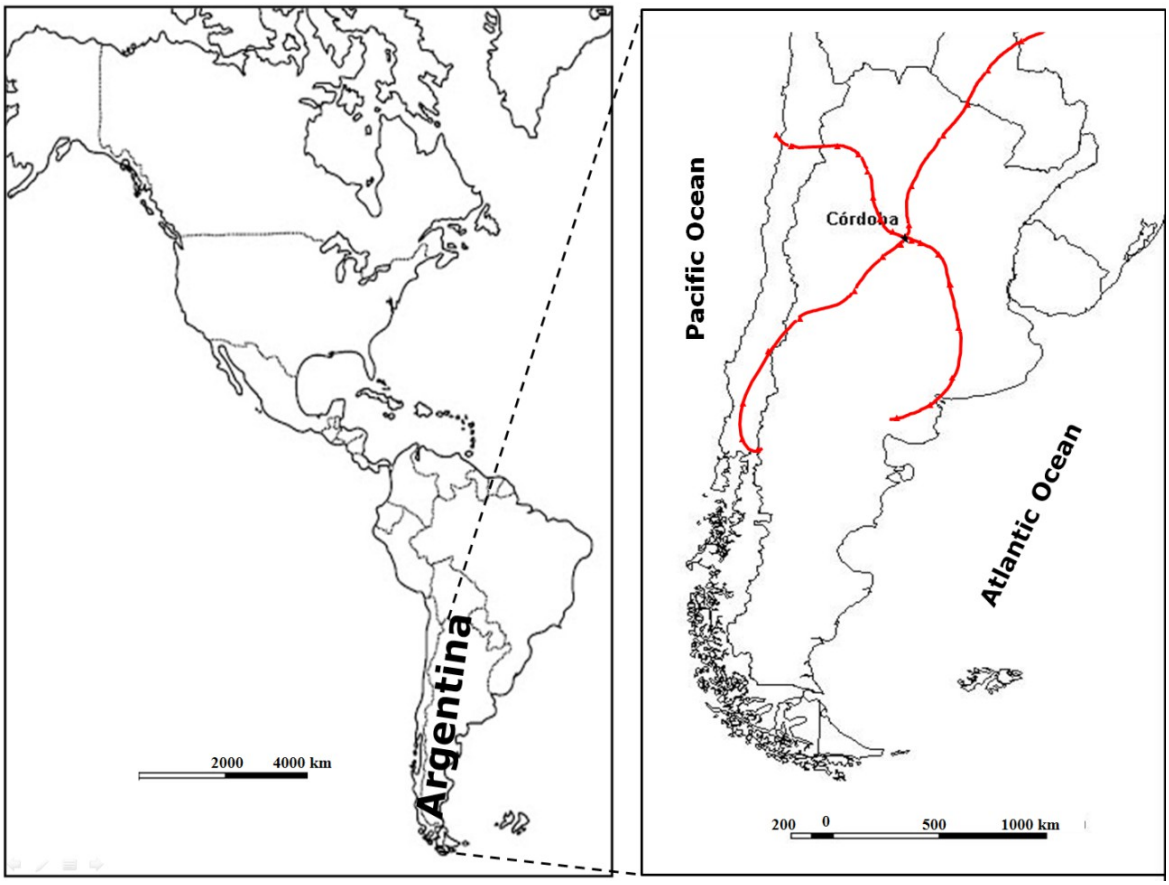
Actually, I do not see why a linear trend should be sought in the plot. Furthermore, I do not understand, why the IN concentration should depend on the RH. The discussion regarding pores and cavities provided by the authors seems to be plausible, but not regarding the IN concentration. I think one should ask himself/herself, what one exactly measures. I would say it is not the IN concentration which was measured, but the concentration of IN which were activated at -25°C and 15% ice supersaturation (i.e. the formulation in the paper for me is too loose). In this case the discussion provided by the authors is acceptable, since the nuclei had already been "prepared" (i.e. pre-processed) by the RH of the air. Actually this is somehow mentioned by the authors near line 19 on p. 16704.
We do not follow what the Reviewer points out in this comment. We think that in several parts of the manuscript (Abstract, Introduction, Experimental, Results and discussion sections) it was emphasized that we measured the IN concentration activated at -25°C and 15% ice supersaturation of ground level air.

- If the former issue holds, the concentration of effective IN is only relevant at the place of the measurement. So why is it important to make measurements on the ground? It should be measured inside the clouds, which would give some information about the generation of ice particles.
In the experiments, the thermodynamic conditions occurring in real clouds cannot be exactly reproduced; however, the measurements on the lab are relevant because in general the thermodynamic variables can be controlled or determined so that they allow for straightforward interpretation of the results. The lab experiments can add to understand the factors that govern the ice nucleation mechanisms. For instance, the findings of the current work would not be obtained from measurements inside clouds.

- The back trajectories provided in the manuscript should be discussed in more detail. It would be desirable to show a common map of the trajectories. I am not familiar with the geography of South-America so I could not really figure out from which part the air masses are coming. What more important could be is to identify the areas from which the air

masses are coming. It could give us some clues about the origin of the possible IN (e.g., whether they can be biological, mineral, etc).
The back trajectories Fig (see below) was changed as required by the Reviewer. The new Fig displays in more detail from which part of the continent the air masses are coming. As a consequence, the caption was rewritten as:
" Location of Argentina and air mass pathways of different quadrants: North-West quadrant, North-East quadrant, South-West quadrant and South-East."

Unfortunately, we do not have the information of the IN characteristic (biological, mineral, dust, etc) from the different trajectories. All we can say is that the enhancement of the IN concentration measured in lab is not linked to the origin of the air masses.



Reply to Anonymous Referee #3
This paper reports on an intriguing observed correlation between deposition ice nucleus concentration and the ambient relative humidity. By ambient the meaning is the environment from which the aerosol particles were sampled; the relative humidity at which ice nucleus concentration is measured is fixed at 15% with respect to ice at a temperature of -25 C. The finding is important for several reasons: the correlation itself adds understanding

to some prior observations (e.g., Prenni et al. 2013), the results are demonstrated to be independent of air mass origin, decreasing the possibility that geographical source is confused with relative humidity, the measurements are made using a very direct method that allows for straightforward interpretation, and although not mentioned in the paper, the results also provide valuable measurements from the southern hemisphere where such data are sparse (the authors may wish to point this out).
The last comment was included in the revised manuscript:
"This work provides valuable measurements of IN concentration from the Southern Hemisphere where the data of deposition ice nuclei are sparse."

I recommend that the paper be accepted after the following comment, as well as some minor points are considered:
More details on the air/aerosol sampling need to be included, and specifically, more information on residence time of the particles are needed to help with interpretation. Is it correct that the air is drawn continuously into the chamber from outside? Where does the air/aerosol sampling occur, and where is that located relative to the relative humidity sensor? Is there any cutoff filter or other size selection, or at least can an upper aerosol size be estimated for the sampling lines? Most importantly, what is the residence time of the air/aerosol within the sampling tube and then within the controlled relative humidity chamber? Presumably there is at least one, perhaps more than one, time scale associated with the response of aerosol particles to new ambient conditions. It seems to me that if that time scale is much less than the residence time in the cloud chamber, then one would not expect to observe any effect of outdoor relative humidity. The measurements therefore suggest that the time scale is of the same order or greater than the residence time in the chamber. This may be helpful in evaluating possible mechanisms, and therefore is important to discuss.
The reviewer makes a very good point here. Actually, there is not air drawn continuously into the chamber from outside; just the volume of air necessary to reach 15% supersaturation over ice is introduced in the chamber. There is no air/aerosol sampling neither cutoff filter nor other size selection. Once the system reaches the specific conditions (temperature and supersaturation), the natural IN are activated. The ice crystals grow at the expense of the water vapor. The amount of water vapor available in the chamber is given by the supersaturation of the system. It can be assumed that ice crystals grow until vapor density reaches the ice saturation. For this reason, the system is left for about 5 minutes for the ice crystals to reach a sufficient size to fall on the sugar solution.
We do not know how long the IN lies in the cloud chamber before being activated, but we agree with the Reviewer that if this time is short enough, then it could enable that the deposition nucleation can be influenced by the outdoor relative humidity.

Other suggestions and corrrections:
Line 9, abstract: "ability" probably should be "effectiveness". OK.

Line 10, abstract: I recommend deleting the sentence "These results are consistent with previous results." It is vague and may give some readers the impression that the measurements are repeating others already made. I do not think that is the case. OK.

Line 25, page 16698: I would say "can serve as IN" instead of "serve as IN". OK.

Line 21, page 16699: After "under thunderclouds" is a reference needed, or is this referring to the work cited on lines 24-25? Please clarify in the paper. OK. The references were moved to line 21.

Lines 28-29, page 16701: Is it verified that the instrument can measure at ice supersaturated conditions without artifacts?
Yes, the calibration can be verified by checking that a cloud of water droplet is formed when the ice supersaturation reaches the water saturation value.

Lines 7-9, page 16703: This statement seems unlikely to be correct, judging from the uncertainty bars on the data points. The points show scatter much greater than the bars. Can natural variability really be ruled out? If so, it needs to be shown.
The Reviewer is right, the variability of the results are related to both errors associated with the technique and the inherent variability in the IN concentration. This was clarified in the revised manuscript.
"...the dispersion of the experimental points is likely related to the natural variability in the IN concentration and to the inherent errors associated with the determination of T , Si, RHamb, and IN-number, which are present in each experiment."

References: I recently became aware of the following work by Wright et al. (Aerosol Sci Tech, 2014) that appears to be relevant to this paper. It should be cited and discussed. http://www.tandfonline.com/doi/abs/10.1080/02786826.2014.968244#.VbgxlflVhBc. OK.

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Influence of the ambient humidity on the concentration of natural deposition ice nuclei

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Abstract.

This study reports measurements of deposition ice nuclei (IN) concentration at ground level during the period July-December 2014 in Córdoba, Argentina. The measurements were carried out at temperature of $-25°\mathrm{C}$ and a 15 % supersaturation over ice. They were performed on days with different thermodynamic conditions, including rainy days. The effect of the relative humidity at ground level (RH_{amb}) on the IN concentration was analyzed. The number of IN activated varied from 1 L^{-1} at RH_{amb} of 25% to 30 L^{-1} at RH_{amb} of 90%. In general, a linear trend between the IN concentration and the RH_{amb} was found, suggesting that this variable must be related to the effectiveness of the aerosols acting as IN. From the backward trajectories analysis, it was found that the link between IN concentration and RH_{amb} is independent of the origin of the air masses. The role of biological-IN and nucleation occurring in pores and cavities were discussed as a possible mechanism to explain the increase on the IN concentration during high ambient relative humidity events. This work provides valuable measurements of IN concentration from the Southern Hemisphere where the data of deposition ice nuclei are sparse.

1 Introduction

Natural ice nuclei (IN) are considered important in atmospheric processes since they induce freezing in clouds, thus initiating an efficient mechanism for cloud particles to reach a precipitating size. Consequently, many studies have been undertaken to determine their absolute concentrations, their origin and their chemical composition (DeMott et al. (2011); Hoose and Möhler (2012)).

Homogeneous freezing of supercooled droplets occurs at temperatures near $-40°\mathrm{C}$, but at temperatures warmer than approximately $-36°\mathrm{C}$ heterogeneous nucleation occurs (e.g. Cantrell and

Heymsfield (2005)), which involves four different modes: condensation freezing, immersion freezing, contact freezing and deposition nucleation (Vali, 1985). Cloud condensation nuclei (CCN) can serve as IN at temperatures below $0^{\circ}\mathrm{C}$ during the condensation freezing mode. During the immersion-freezing mode, a particle suspended in the droplet initiates freezing. In the contact-freezing mode, ice is formed by the collision of cloud droplets with interstitial aerosols within the cloud. When the environment is supersaturated with respect to ice and subsaturated with respect to liquid water, ice deposits on the IN directly from the vapor phase. This last mode is known as deposition nucleation. Measurements performed in the regime below water saturation are important in the understanding of the deposition nucleation (DeMott et al., 2011).

Temperature and supersaturation ratio are the two main parameters determining the deposition nucleation. Several reports have provided measurements of IN concentration for different temperature and supersaturation conditions. Studies linking IN concentration to temperature have shown an exponential trend in the dependence of IN on temperature (e.g. Fletcher (1962); Hussain and Saunders (1984); Meyers et al. (1992); López and Ávila (2013)). This same correlation was found when studying IN concentration regarding supersaturation (e.g. Rogers (1982); Al-Naimi and Saunders (1985); Hussain and Saunders (1984); Cooper (1980); López and Ávila (2013)).

Although temperature and supersaturation are recognized as the two main parameters in the activation of the IN, a significant divergence among the results of IN quantification is found in the literature when IN measurements are carried out at around the same temperature and supersaturation conditions (DeMott et al. (2011); Hoose and Möhler (2012)). In general, the results show that the ice-nuclei content of the atmosphere varies considerably from day to day and from place to place. For instance, important anomalies of atmospheric ice nuclei were observed under thunderclouds (Isono and Tanaka (1966); Isaac and Douglas (1973)). Increments at ground level ice nucleus concentrations by a factor of 10 or higher have been measured during precipitation from convective storm precipitation. These anomalies were associated with downdrafts in and under the thunderclouds. Prenni et al. (2013) also studied the impact of precipitation at a forested site on the concentration and composition of IN. They showed that at ground level IN-concentrations increase during rain events.

Thus, our knowledge of ice formation through the nucleation modes is still scarce and limited. As a consequence, the ice nucleation processes are currently very poorly represented in global climate models (e.g. Hoose et al. (2010)). Furthermore, the study of ice cloud formation over a wide range of atmospherically relevant temperatures and humidity values is challenging (e.g. DeMott et al. (2011); Murray et al. (2012)). Particularly, studies on anomalies in atmospheric ice nucleus concentration are important, since they will give us clues for solving problems on the origin and the nature of atmospheric ice nuclei. The major goal of this work is the study of the factors that regulate the effectiveness of aerosols on deposition ice nucleation. Regarding the possible effect of precipitation on the IN-concentration, this study reports measurements of IN-concentration at ground level during

the period July-December 2014 in Córdoba, Argentina. The experiments were performed on days with different thermodynamic conditions, including precipitation days, and the effect of the relative humidity at ground level on the IN concentration was analyzed. IN-concentrations in deposition nucleation mode were determined at a temperature of approximately $-25°\mathrm{C}$ and supersaturation of approximately 15 % over ice. The ambient relative humidity at ground level was measured during all the experiments, in order to link this variable to the IN concentration.

2 Experimental

Measurements were carried out in Córdoba, a mediterranean city of Argentina, located in the center of the country, in a semiarid region (latitude $-31.4°\mathrm{C}$; longitude $-64.18°\mathrm{C}$; 470 m.a.s.l.). Córdoba is the second largest city in the country, with approximately 1.3 million inhabitants. The climate is sub-humid and the prevailing wind direction is NE. The annual average precipitation is close to 700 mm. However, the area is affected by severe and persistent dry periods that occur cyclically. Snowfalls are infrequent; thus, precipitations consist mostly of rain. Rainfall is highly seasonal, concentrated mainly in summer (December-February) having accumulated values higher than 400 mm, while the dry winter season (June-August) has a cumulative precipitation depth close to 20 mm.

In a previous work we have quantified the IN-concentration (López and Ávila, 2013) in deposition nucleation mode at ground level in Córdoba, for temperatures between $-15°\mathrm{C}$ and $-30°\mathrm{C}$, and ice supersaturation ranging between 2 and 20 %. In the present work the experiments were carried out following the same procedure as described by López and Ávila (2013) and a total of 63 measurements of IN concentration were carried out during 45 days, since 28 July 2014 until 10 December 2014 (winter and spring seasons). This procedure involves a cloud chamber of 46 L in volume placed inside a cold room. Controlled volumes of humid air were injected from the exterior (at ambient temperature) in order to increase the relative humidity in the cloud chamber. Since the same volume of air is removed while this air is injected, the number of aerosols and the pressure inside the chamber are kept around constant. The increasing of the relative humidity over ice inside the cloud chamber (RH_i) is explained according the adiabatic isobaric mixing of two masses of air with different relative humidity and temperature (Curry and Webster, 1999). The supersaturation is achieved starting with a RH_i slightly lower than 100% in the cloud chamber and introducing controlled air injections from outside. Since the increase of RH_i for each air injection is known, it is possible to estimate the increase produced by a known number of injections, even once the vapor is supersaturated over ice. Once the supersaturation is reached, the IN are activated and then grown at the expense of vapor until ice crystals fall down onto a dish placed on the floor of the cold chamber. This dish contains a supercooled aqueous solution of cane sugar. Once in the sugar solution, the ice crystals grow and reach a size large enough to be counted with the naked eye, as can be seen in Figure 1. For a more detailed description of the procedure, see López and Ávila (2013).

In all the measurements carried out in the present work the conditions of temperature (T) and supersaturation over ice (S_i) were settled at around $-25°C$ and 15%, respectively. These values were chosen because, under these conditions, the number of activated IN are significant and can be easily determined (López and Ávila, 2013). Furthermore, these T and S_i values are experimentally quick to reach, which facilitate carrying out the experiments. In order to determine RH_i and T in the cloud chamber the Testo 435-4 multifunction measuring instrument was used. This instrument measures relative humidity in the temperature range $[-50,150]°C$. When RH_i is measured over ice at temperatures below $0°C$, the resolution is 0.1%. The experimental uncertainty associated with the determination of T and S_i was $\pm$ 2°C and $\pm$ 2%, respectively. These errors arise from variations in the experimental conditions involved in each measurement, such as difference in the temperature between the beginning and the end of the air injections, variability in the RH_i increase between the injections, number of injections until reaching the particular S_i, and accuracy of the humidity sensor.

Thus, considering that T and S_i were the same for all the experiments (apart from the inherent errors), the IN concentration was studied as a function of the ambient relative humidity at ground level (RH_{amb}); this is the relative humidity of the air mass injected from the exterior. RH_{amb} was measured during all the experiments by using the instrument EE31 Series Model D (E+E Elektronik), which had a remote sensing probe for relative humidity measurements in the temperature range $[-40,180]°C$. The uncertainty in the determination of RH_{amb} was $\pm 1\%$.

3 Results and discussions

The experiments were all performed for a supersaturated atmosphere with respect to ice and subsaturated with respect to liquid water; thus, only the deposition IN were quantified. The IN concentration was determined at a temperature of approximately $-25°C$ and supersaturation of approximately 15% over ice. Figure 2 shows the temporal variations of the IN concentration values during the period under study. The grey points in the graph correspond to measurements performed during a rain event or immediately after rain had stopped. The error associated in the estimation of IN concentration did not exceed 10%. There are some time periods without experimental data mainly because the cold chamber was unable to achieve the expected temperature. The period of study is too short to perform a reliable statistical test showing a seasonal behavior of IN concentration; nevertheless, the results do not seem to indicate that there is any particular trend during this period.

In order to study the effect of the RH_{amb} in the IN concentration, Figure 3 displays the IN concentration as a function of the RH_{amb}. Again, the grey points indicate measurements performed on rainy days. IN concentration values can be seen to increase with RH_{amb}. The best linear fitting of the data yield values of 0.39 and -9.2 for the slope and ordinate, respectively, being the square of the correlation coefficient (R^2) equal to 0.71. The linear trend between the IN concentration and the RH_{amb} is remarkable and the dispersion of the experimental points is likely related to the natural

variability in the IN concentration and to the inherent errors associated with the determination of T, S_i, RH_{amb}, and IN-number, which are present in each experiment.

The number of IN activated varies from $\sim 1\ L^{-1}$ at RH_{amb} 25% to $\sim 30\ L^{-1}$ at $RH_{amb} \sim 90\%$. This variation is consistent with the results reported in López and Ávila (2013) on the same site, who found that IN concentration values varied between 2 and 35 L^{-1} at temperature of $\sim -25°C$ and $\sim$ 15% of supersaturation over ice. Thus, the variability in the IN concentration in the previous work could be related to the variability in RH_{amb} at the time the measurements were carried out (this variable was not recorded in such experiments). Current results are also in agreement with those reported by Prenni et al. (2013), who showed that, at ground level, the IN concentration rises by a factor of up to 40 during rain. Actually, here we observe that not only rainy days are required for increasing IN concentrations but also high relative humidity is needed, as shown in Figure 3 during rainfall events with low humidity.

A variety of insoluble particles such as volcanic ash, mineral dust, soot, metallic particles, or primary biological particles have been suggested as IN. However, the requirements needed for a surface to be an efficient IN are not completely understood (Pruppacher and Klett (1997); DeMott (2010); Hoose et al. (2010)). Prenni et al. (2013), Hader et al. (2014) and Bigg et al. (2015) presented evidence that the rising of IN concentration during rain events can be related to the increase of biological particle concentration. It has been shown that biological particles can be released during precipitation through mechanical mechanisms. For instance, winds produced by storms can release biological particles from leaf surfaces and soil. The release of these biological particles include biological IN (bacteria, fungal spores, and pollen) which can impact the IN population. This assumption was supported by different studies reporting both: the release of biological particles during rain events and the role of these particles as sources of IN (Huffman et al. (2012);Huffman et al. (2013)). Furthermore, Wright et al. (2014) suggested that high relative humidity may also trigger the release of IN at ground level. They provided observational evidence that a fraction of the biological particles released during high RH can serve as immersion mode IN while droplets cool during ascent.

It is important to remark that unlike the present study, where the deposition nucleation mode was examined, the previous studies examined condensation and immersion freezing modes. We have no evidence, so far, that the increase of IN concentration in the present work can be analyzed in terms of biological particles. The role of the biological particles acting as deposition ice nuclei need to be studied in more detail.

Mineral dust aerosols seem to play a relevant role in deposition nucleation. They have active sites which are able to start ice nucleation. These active sites are linked to surface defects, like cracks, capillaries, pores or cavities which allow water vapor to condense in them under vapor pressures below saturation (Fukuta (1966); Fletcher (1969)). Water vapor condenses in a capillary of a wettable particle under a pressure below water saturation (p), according to Kelvin equation

$$RTr \ln\left(\frac{p}{p_b}\right) = -2\gamma\nu_l \quad (1)$$

R is the gas constant, T the absolute temperature, r the radius of the curved water surface, p_b the water vapor pressure over a flat water surface, γ the surface tension of water and ν_l the molar volume of liquid water. Recently, Marcolli (2014) hypothesized that ice nucleation below water saturation occurs predominantly in water confined between closely spaced surfaces, such as cavities and pores that may form in aerosol particles. In this sense, it is plausible to expect that as the RH_{amb} increases, more water molecules from the surrounding environment can be adsorbed in cavities and pores. As a result, the condensation and the subsequent freezing can occur in the cavity when the relative humidity is lower than 100% outside. Considering this fact, a significant enhancement in ice nucleation efficiency should be expected at higher ambient relative humidity, which is consistent with the results reported here. Even though further work is needed to test and corroborate this hypothesis, the results presented in this work may support the idea that the deposition nucleation can be a pore condensation and freezing which occur in the defects on the surface of some aerosol particles as proposed by Marcolli (2014).

In order to relate the origin of the air masses to the behavior of IN measurements regarding RH, backward trajectories were calculated for all days when IN concentration measurements were carried out. Back trajectories were calculated by the NOAA HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory model) (Draxler and Rolph , 2003). Air mass back trajectories were calculated at 1000 m above mean sea level (AMSL), 48 h before the arrival time to the sampling site. NOAA trajectories were calculated every day of IN concentration measurements. The air mass back trajectories were subdivided into four groups, regarding the quadrants from the Compass Rose. As an example, Figure 4 shows of air mass back trajectories representative of the four studied sectors, which will be referred as North-West quadrant (example: Figure 4a), North-East quadrant (example: Figure 4b), South-West quadrant (example: Figure 4c) and South-East quadrant (example: Figure 4d). The lower sample number was obtained coming from NW quadrant (7.5%), while the highest numbers of IN measurements were obtained coming from NE quadrant (42.5%). Trajectories coming from SE and SW quadrants were 22.5% and 27.5%, respectively. Figure 5 shows the IN concentration measurements grouped following the previous classification of the origin of air masses. Observe that the number of IN measurements from NW quadrant is too scarce to make an analysis. However, the analysis from the three remaining quadrants show the increase of IN concentration with the increase in RH_{amb}, in the same way that it was observed in Figure 3. Results show that, from the studied period, variations in RH_{amb} are not explained because of the origin of the air masses. This is to say that, the relation between IN concentration and the ambient relative humidity is independent from the origin of the air masses. This fact discards the possibility that the increase in IN concentration is due to changes in the sources of the aerosols acting as ice nuclei. Thus, HYSPLIT results seem to be consistent with the previous assumption regarding to the importance of the ambient relative humidity on the ability of aerosols to act as IN.

4 Summary and concluding remarks

Studies of heterogeneous ice nucleation with natural aerosols under a broad range of thermodynamic conditions are important, because they can provide clues for solving problems regarding the origin and the nature of atmospheric IN. This study reports measurements of deposition IN concentration at ground level during the period July-December 2014 in Córdoba, Argentina. The experiments were carried out at temperature $(-25 \pm 2)^{\circ}\mathrm{C}$ and supersaturation $(15 \pm 2)\%$ over ice. The effect of the relative humidity at ground level on the IN concentration was analyzed and a linear trend between the IN concentration and the RH_{amb} was found, suggesting that this variable must be related to the ability of the aerosols acting as IN. This assumption seems to be corroborated by the analysis of the backward trajectories of the air masses, which shows that the relation between IN concentration and the ambient relative humidity is independent from the origin of the air masses. Therefore, the variability observed on IN concentration cannot be explained regarding the changes in the sources of the aerosols acting as ice nuclei.

The role of biological-IN and nucleation occurring in pores and cavities (as suggested by Marcolli (2014)) was discussed as a possible mechanism to explain the increase on the IN concentration during high ambient relative humidity events. More ice nucleation studies should be carried out to address the differentiation between these mechanisms.

This work contributes to the study of the factors affecting the IN-concentration. Laboratory studies of heterogeneous ice nucleation with natural aerosols are important for the possibility to transfer the results into parameterizations for numerical models of clouds and climate. Furthermore, this work provides valuable measurements of IN concentration from the Southern Hemisphere where the data of deposition ice nuclei are sparse.

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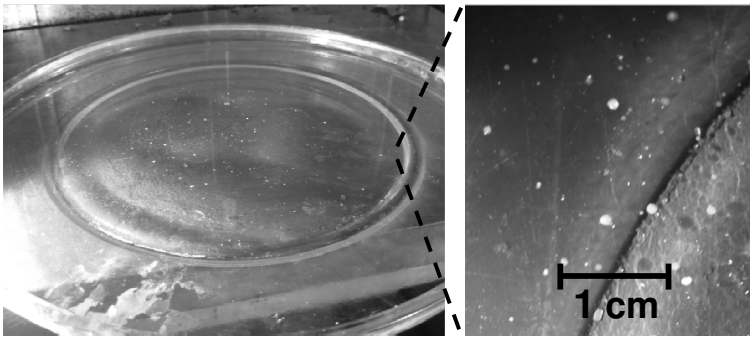

Fig. 1. Images of crystals once they grown on the sugar solution.

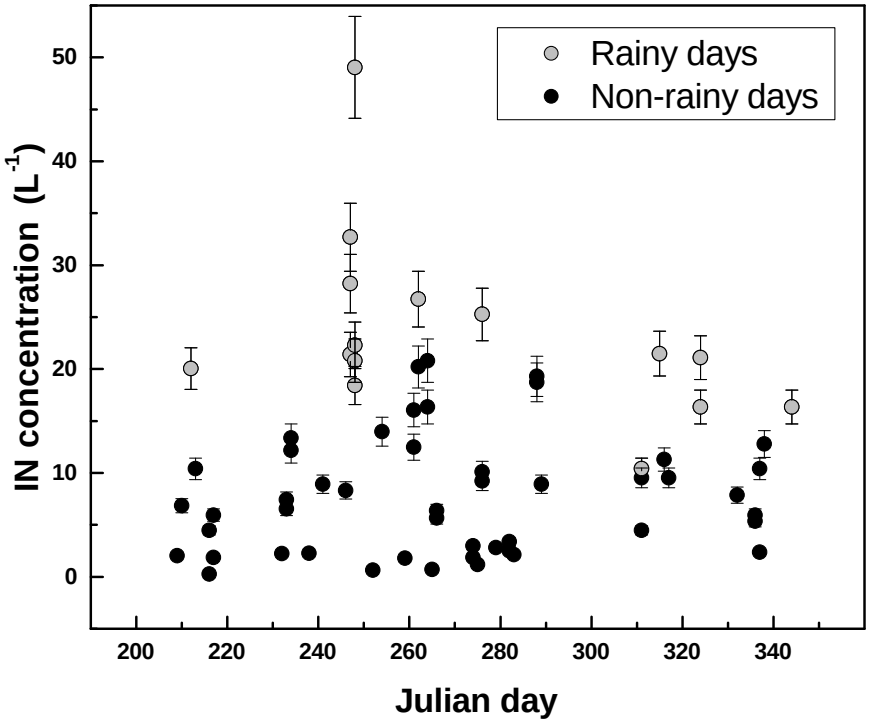

Fig. 2. Data of IN concentration measured throughout the period studied.

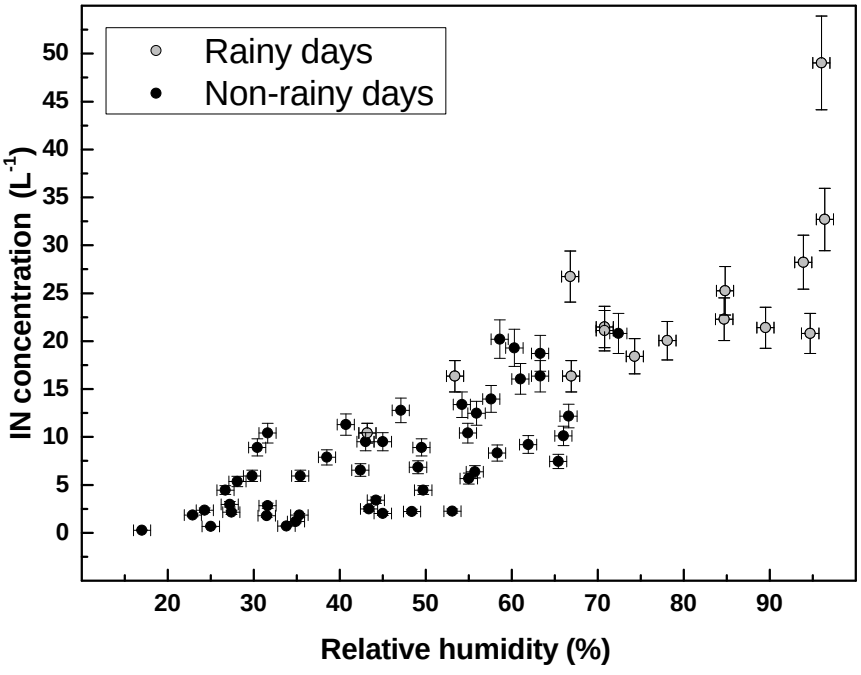

Fig. 3. Data of IN concentration at different ambient relative humidity.

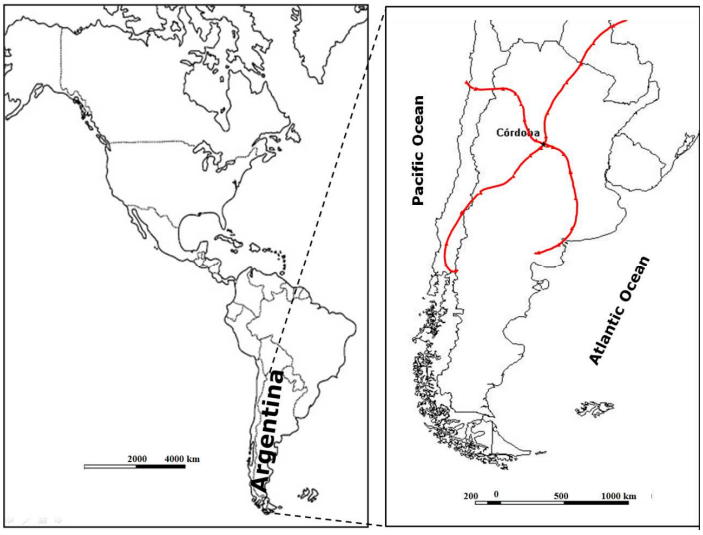

Fig. 4. Location of Argentina and air mass pathways of different quadrants: North-West, North-East, South-West and South-East.

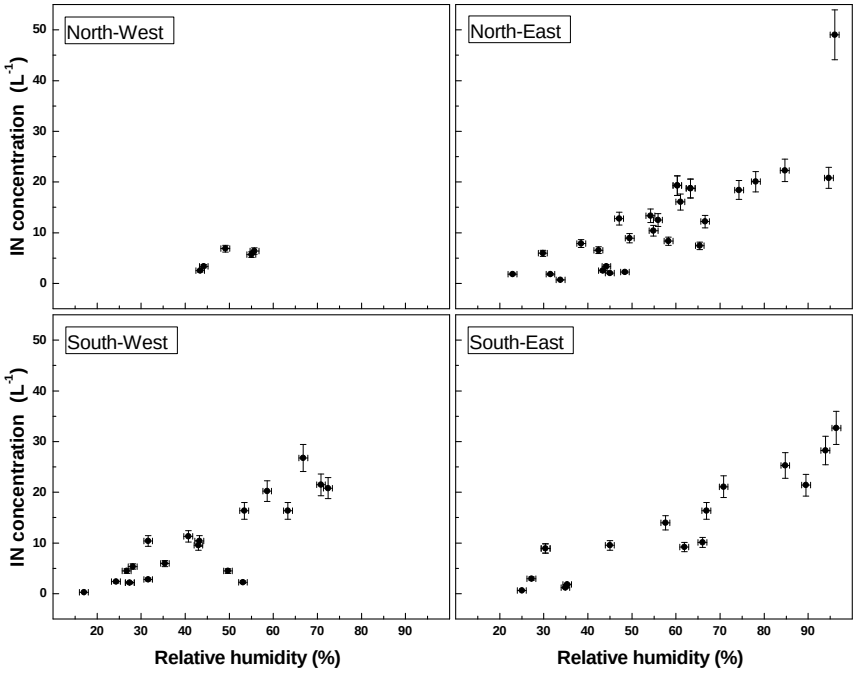

Fig. 5. IN concentration at different ambient relative humidity for the different origins of the air masses.