Response to the Comments of Keith Bigg (Reviewer 1)

We would like to thank Dr Bigg for his helpful comments and suggestions. We address the individual comments point by point below.

General comment *This manuscript provides a potentially valuable long series of IN data for an area from which there have been no previous IN measurements that I am aware of. The topic is suitable for ACP and the methods used appear to be satisfactory, although there is a suspicion that concentrations may be underestimated. The language and presentation are clear and the few changes that seem desirable will be listed at the end of this review. This is a good paper and I hope that some of the following comments might be helpful. Where the authors disagree with those comments, I would be happy to enter into a debate.*
Summarising, I recommend publication after the authors have made any changes that appear to be appropriate.

Specific comments

1. ***Abstract:*** *The paragraph that shows no relation between bulk chemical composition and IN concentrations is not very useful in the main text and certainly not in the Abstract. At a site where sea salt particles will be dominant by mass and IN active at temperatures relevant to cloud formation represent about one particle in a million, no other result would be credible.*

   We agree with Dr. Bigg that no direct correlation of the IN composition to the bulk aerosol composition is to be expected due to the rarity of IN in the total aerosol number concentration. The idea of the presented analysis is to use changes in bulk chemical composition of the aerosol as a tracer for different sources. This way, even if only one in a million particles acts as IN we expected to see a proportional increase in concentration with the increase of one of the "tracer materials" for different sources. The finding that this is not the case could indicate that none of these sources (marine, continental, combustion) is the strong supplier of IN active in this temperature range or that IN are distributed independently of their sources main compounds, or that additional conditions affecting the IN content in these sources have to be met. The result confirms that a simple attribution of an ice active particle fraction to a certain source is not feasible.
   The section was removed from the abstract. We decided to keep the part in the main text as we think the implications of comparing to bulk chemistry, support the findings in the section about the air mass origin.

2. ***Introduction:*** *p1., line 21. Is there any firm evidence for concentrations as low as 0.01m^{-3} except in polar regions? In addition to the listed factors influencing the formation of precipitation, updraft velocities and liquid water content could be added. Cloud extent suggests horizontal extent – cloud depth would be better.*

   We could not find published measurements of such low ice crystal concentrations. The reason for the lack of measurements could be the lower detection limit of ~0.1ℓ^{-1} typical for instruments deployed for the task (e.g. 2D-S, Farrington et al., 2016). The description of the visual appearance of ice clouds containing different concentrations of ice crystals is removed from the manuscript because it was not essential.
   Updraft velocities and liquid water content are added to the list of factors influencing properties of glaciating clouds and "cloud extent" has been replaced by "cloud depth".

3. *p2 line 1: What concentration of ice crystals is necessary for ground-based detection? The presence of concentrations of IN in clouds at -10C will usually be similar to that of the concentrations in the air feeding the cloud of all biological IN capable of nucleation at that temperature. The list of potential IN from those sources continues to grow and concentrations must often exceed 100m^{-3}.*

   The lower limit of ice crystal concentrations detectable by ground based Lidar measurements are on the order of ~0.5ℓ^{-1} (A. Ansmann, personal communication). In-situ detectors like the 2D-S are sensitive to concentrations larger than ~0.1ℓ^{-1}.

Sesartic et al. (2013) reviewed measurements of bacteria and fungal spore concentration in the atmosphere and modeled their impact on clouds. Concentrations can be more than $1000m^{-3}$, but most bioaerosol seem to remain near their source of origin. Their presence is strongly coupled to vegetation and their ability to act as IN sometimes needs to be triggered by stress factors. It could be speculated that bacteria and fungi living in a subtropical habitat rarely encounter stress factors that they could counteract by expressing ice nucleating properties.
Because the importance of biological IN is circumstantial in the present study, no changes to the text were made in this context.

4. *P2. line 5. Insert reference here: Hallett and Mossop, Nature 249, 26-28, 1974 who were first to investigate the effect experimentally and define the conditions necessary for it to operate. Line 15 Hallett and Mossop defined that condition in 1974!*

   We now refer to Hallett and Mossop (1974) and added to the manuscript: "Hallett and Mossop (1974) suggested that marine cumuli contain large ice crystal concentrations for dynamical reasons. They usually have higher cloud top temperatures, therefore the contact of ice and supercooled droplet occurs at temperatures favorable for splintering."

5. *P2. Line 19-22. In Bigg's 1973 paper, 3 years of continuous measurements in the Southern Ocean, south Indian Ocean and south Pacific were summarised. The measurements were later used by Schnell and Vali (J. Atmos.Sci., 33(8), 1554-1564, 1976) to show that the measurements revealed a strong dependence on biological productivity. Their interpretation of biological IN rather than dust as the main factors in the measurements is much preferable to Bigg's.*
   This work brings up an important point in relation to your manuscript. The ocean measurements were made with membrane filters that are known to undercount the concentration of IN in a salt-laden atmosphere, yet concentrations in the biologically productive zones were considerably higher than those reported in your manuscript. Chlorophyll measurements in the vicinity of the Cape Verde is reported by Ramos et al. to indicate strong biological activity and significant biological IN should become airborne by bubble bursting. Am I right in assuming that your method only gives a "yes-no" answer for the presence of an active IN at temperature T? If so it needs to be pointed out that actual concentrations may be higher.

   We prefer to include both, the marine biological and the long-range transported desert dust IN interpretation. The evidence for marine biological IN being more important than other substances for ice formation at low supercooling, remains circumstantial. It could also be that biological IN adhere to desert dust and are transported with it (Conen et al., 2011).
   Biological particles exhibit a complex variety of dependencies of their activity as IN on environmental parameters. Research into the importance of organic marine aerosol, released from the sea surface microlayer by bubble bursting, has been conducted by Wilson et al. (2015). They reported a wide range of freezing temperatures, wherein samples from the Atlantic tend to freeze at lower temperatures than Arctic samples. The hypothesis would be, that marine bacteria in the subtropic ocean are less active IN than strains living at higher latitudes. See also comment 8 and 10.
   The measurement method does give a "yes-no" answer for each of the 103 subsamples. For the interpretation of the measurement, we use a non-stochastic view of the nucleation process. Under this premiss, the assumption that only one IN causes freezing in a freezing droplet, is justified in Vali (1971). A possible effect of long sampling times to deactivate IN by blocking active sites, is already mentioned in the introduction. We are not aware of other reasons why the method would under predict concentrations. No changes were made to the text.

6. *p.3 lines 3-4. A spectacular example of the changes in IN concentrations that can occur was published in J. Meteorol. 15, 561-562, 1958. This was later interpreted to be due to related to enhanced biological populations resulting from heavy rain, with a proportion becoming airborne. (Atmos. Chem. Phys., 15, 2313-2326, 2015).*

   The 20-30 day change in IN concentration following intense rainfall discussed in Bigg (1958); Bigg et al. (2015) is a spectacular example for the importance of biological IN under certain conditions, at places close to their origin. The fluctuations we refereed to in the manuscript are on shorter timescales. In Bigg (1961) you refereed to these events as "sudden onset storms". To include both, we changed the sentence to: "The concentration of potential IN measured

at a certain location and temperature can undergo large changes on timescales of days (Bigg, 1958) or hours (Bigg, 1961)." On Cape Verde rain events seem to be followed by prolonged low IN concentrations (at -8 °C). See Fig. 1 for a time series including precipitation events. Rain washes the IN out. This could indicate that biological IN active at this temperature are transported over long distances, eventually attached to larger particles like desert dust.

7. *p.3 line 11-12. Long sampling times aren't necessary. Membrane filters with pore sizes 0.45μm or larger can be sampled at >10l/min but sampling >300l leads to serious undercounts. For long-term measurements or simultaneous measurements at many sites, sampling at 300l/day avoided logistic difficulties but averaged out any short-term fluctuations.*

   The filter used in this study were collected with the intention to investigate the chemical composition of the aerosol at Cape Verde. We reused them to find out about the IN concentration. The sampling time of these filters was 1-3 days and before the time consuming IN-measurements, we estimated the concentration range for which the method would be sensitive to if we took subsamples of different sizes. The calculation showed that thanks to the long sampling time (large sampled air volume) we could use the smallest practical subsample size. This was important to minimize the background from the filter material of the subsample. Much shorter sampling times would not have allowed to use these filters for the measurement of IN concentrations. We agree that, when collecting filters with the purpose to measure IN concentrations, it would be better using the shortest possible sampling interval to reveal short-term fluctuations. We rephrased the sentence. "To measure the low concentration of IN, able to initiate immersion freezing above -20 °C, it is necessary to collect particles from a large enough air volume. The time required to collect this volume depends on the sample flow through the filter, which is influenced by its type (fiber or membrane), fiber or pore size, and the capacity of the pump. Long sampling times may be necessary."

8. *p3. Line 14. Reduction of the RH in the vicinity of a hygroscopic particle is a major factor. Allowing hygroscopic material from a $1m^3$ sample on a membrane filter to diffuse into an underlying wet filter, then drying the top filter and processing it, results in an IN count more than a factor of 2 higher than on a simultaneously sampled filter kept dry. (This work has not been published – use the information if you want to).*

   For the analysis of the filter samples we assume the IN are acting in the immersion freezing mode, residing in droplets. The method consists of immersing pieces of the filter in water drops and observe the freezing of those. The method is immune to water-vapour depletion effects and the water drops are large enough to prevent freezing point depression by the dissolved sea salt within the sensitivity of the temperature measurement. No changes were made to the text in this context.

9. *p.5, line2. At first I didn't understand this as all particles capable of forming IN at temperatures warmer than the test temperature will be activated. Does the answer lie in comment 5?*

   With decreasing temperatures the change in activity of single substances is steeper than the observed change in IN concentration. Consequently substances contribute only at high activity to the ambient IN spectrum (see response to comment 1 of Reviewer 2 and Appendix A).

10. *Figure 2. According to Ramos et al. chlorophyll is a maximum at the end of the year at Cape Verde. I don't see much evidence of a corresponding change in the -8C figure. As it is an important point in determining whether biological IN are effective at the site, running means of about 9 measurements at -8C shown on a diagram with a more extended scale might help. This procedure would be useful in reinforcing the surprising statement in lines 6 and 7 on p.8.*

    Concentration data at -8 °C for the years 2011, 2012 and 5 months of 2013 are shown in Fig. 1. The data show no clear signal corresponding to the maximum in chlorophyll, Ramos et al. found in Nov. and Feb. The increased IN-concentrations in Feb. 2011 and 2013 occurred several days after dust events. It has been reported that bacteria express ice nucleating properties as a response to environmental stresses. It can be speculated that during times of high biological productivity, bacteria have a good time as well and don't need to express ice nucleating properties.

    We didn't include Fig. 1 into the manuscript and no changes were made to the text.

11. *Bulk chemical composition. See comment 1.*

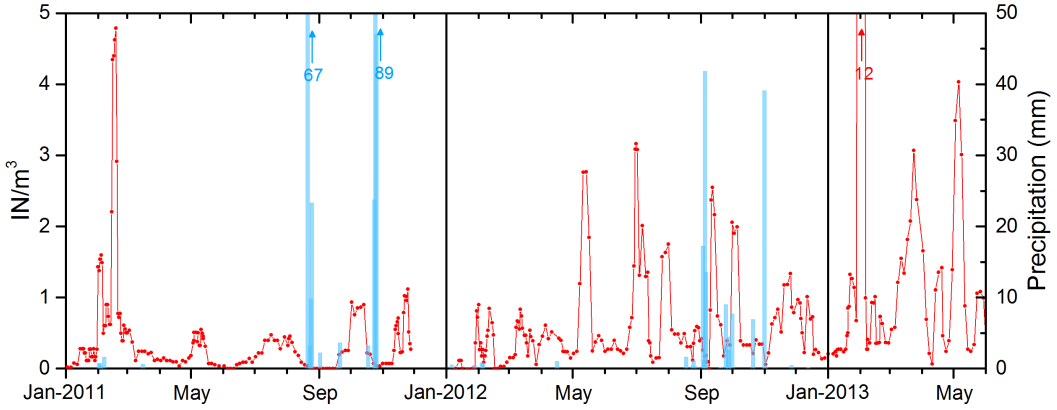

Figure 1. Time series of IN concentration at -8 °C is shown in red. Daily precipitation amount (right hand axis) is shown as blue bars.

We prefer to keep the section in the manuscript. See comment 1.

12. *Air mass origin. How many cases were involved in each of the 7 categories of figure 4? The sporadic rainy season from August-September would probably lead to much deeper atmospheric mixing at times and occasional scavenging of aerosol. How reliable are the 10-day trajectories to the site during that period?*

    The individual data points composing the box plots are shown on the left hand site of each box. This data points are color coded according to the quarter of the year in which they are observed. The number of individual data points is given in Tab. 1.

Table 1. Number of cases per air mass category. Categories are: 1. African coastal, 2. Atlantic marine, 3. North American, marine and coastal, 4. North American and marine, 5. dust and Europe, 6. dust (e.g. Saharan and Sahel region), 7. coastal and Europe.

Temperature	1.	2.	3.	4.	5.	6.	7.
-8 °C	74	11	19	40	47	55	30
-12 °C	111	12	28	54	76	93	44
-16 °C	109	13	28	51	73	92	41

How efficient wet deposition removes aerosol depends on rain intensity, raindrop size, aerosol size (Jung et al., 2013). The NAME model should be able to detect any deep atmospheric mixing (the UM met data should be able to track these events). Rainfall is a rare event on the Cape Verde island and often of very light intensity. The NAME model did the simulation for an inert tracer so as to detect the overall air mass transport, rather than act as a chemical transport model that tracks aerosol movement. An analysis separating the rainy season as suggested in comment 15 showed that IN concentrations do not generally change in this period.

13. *Frequency distribution, p.9 lines 7-9. Size distribution of particles produced by a common method frequently have a log-normal size distribution and this can be expected from a local source. An alternative to Ott's random dilution hypothesis might simply be preservation of the original distribution during transport.*

    If the size distribution is preserved, then we would not expect an effect on the concentration of IN over time. The change in concentration can have two causes. A change in the ice nucleation activity of the aerosol (e.g. due to size) or a change

in abundance. The change in activity with particle size can account for up to two orders of magnitude in concentration (cf. Fig.1 in the response to Reviewer 2). A connection of changes in the size distribution with abundance seems plausible e.g. lower wind speed, transporting less and smaller particles. However, if this would lead to a log-normal frequency distribution is unclear. It could be an additional factor besides random dilution that causes the large variation in IN-concentration. At this point, Ott's hypothesis seems the simplest explanation for the observed log-normal distribution. No changes were made to the text in this context.

14. *p.10, line 6. What is the minimum concentration of ice crystals needed for the lidar observations to detect them? It might be better to replace "to start" with "to be detected".*

    The sentence has been changed accordingly. The lower limit for Lidar to detect ice is in the range of ~$0.5\ell^{-1}$, see comment 3.

15. *Figure B1, p.14. It might be interesting to have a separate diagram for the "rainy" season of August and September and for the period of maximum productivity, October-December.*

    The extended Fig. B1 is shown below. No trend emerges from the rainy or biological active season. Fig. 2 is now included in Appendix B instead of former Fig. B1.

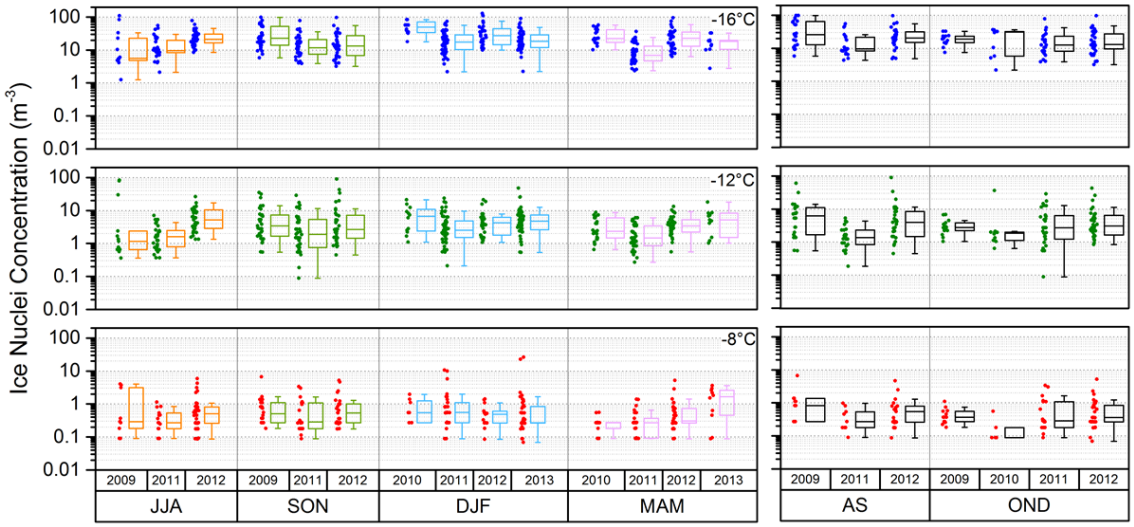

Figure 2. Fig. B1 extended by boxplots of the rainy season (Aug. and Sep.) and the season of high biological productivity (Oct.-Dec.)

Technical corrections

p.1 line 22 : change "cloud extend" to "cloud depth".
p.2 line 26. Change "consist to" to "consist of".
p.5 line 14 "exemplary shown". Change to "exemplified by". Change "year" to "years".
p.8. line 6. Change "effected" to "affected".
p.9 line 20. Change "to identify" to "identification of".
p.10. line 10. Change "to identify" to "in identifying". Line 19: change "must not" to "need not".

Done.

References

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Response to the Comments of Reviewer 2

We would like to thank Reviewer 2 for his comments and thoughtful suggestions. We reply to the individual comments below.

General comment *First of all, this is a very impressive set of measurements. The field of atmospheric ice nucleation is lacking long term data sets with which to compare models and test our understanding. Hence, a dataset comprised of 500 individual measurements over the course of 5 years is extremely valuable. Hence, I support its publication. However, I think there are some aspects of the paper which need to be improved prior to publication. I go through these in detail below:*

Specific comments

1. *P1. Ln 11. Why does an exponential change in INP concentration suggest that several groups of particles with different ice nucleating properties are contributing to INP populations? The exponential dependency on T could also just be explained by a distribution of sites across a surface, rather than particles of different composition or size.*

   The crucial point in our view is that the INP concentration is observed to exponentially increase by seven order of magnitude from -5 °C to -38 °C i.e. the steepness with which the concentration increases on a log-scale. This increase is shallower than the increase in ice nucleation activity of any pure substance, bringing us to the conclusion that several substances contribute to the ambient temperature spectra. To clarify, we rephrase in the manuscript: "Concentration of ice nuclei is found to increase exponentially by seven order of magnitude from -5 °C to -38 °C. Sample to sample variation in the steepness of the increase indicates that particles of different origin, with different ice nucleation properties (size, composition) are contributing to the ice nuclei concentration at different temperatures."
   Our interpretation of the temperature spectra is a central point of criticism of Reviewer 2, also in comment 7, 8 and 12. We attempted to illustrate our point of view in Appendix A in the manuscript. Below we try to clarify and support our conclusions by following the Reviewers suggestion to use active surface site distributions to explain the observed temperature spectrum. We show how the atmospheric INP spectrum compares to an INP spectrum that is constructed using concentrations of ice nucleation active surface sites (referred to as INAS or n_s) for desert dust and for Microcline.
   The temperature spectra (INP concentration as function of temperature) generated by a substance is the substance's ice nucleation activity (e.g. frozen fraction as function of temperature) multiplied by the number of particles of this substance. We assume one particle per droplet.
   Frozen fractions can be derived from n_s parametrizations by $FF = 1 - exp(-n_s \cdot A)$ with A being the particle surface area per droplet. The frozen fraction envelop in Fig. 1(a) is obtained by using A of spherical particles with diameter between 100nm and 1μm.
   Fig. 1(a) shows the calculated frozen fraction for n_s parametrizations, found for the K-feldspar, Microcline (Atkinson et al., 2013) and different desert dusts (Ullrich et al., 2017). Microcline is considered the most ice nucleation active dust identified so far (Atkinson et al., 2013), we come back to that in comment 7. Desert dust is not a pure substance but a mixture of different minerals and whatever sticks to the mineral dust particles (e.g. biological residues, Conen et al., 2011).
   Looking at Fig. 1(a) it can be seen that the ice nucleation activity of both, desert dust and Microcline is higher than that of a hypothetical substance that would correspond to Fletcher's curve. As pointed out by the Reviewer, using n_s results in an exponential dependency on temperature. However the slope of Microcline is steeper than the Fletcher curve. Based on laboratory measurements on other, seemingly pure substances (e.g Fig.1a, Atkinson et al., 2013) we argue that all pure mineral dusts exhibit a comparable or steeper slope than Microcline, i.e. activity increases more rapidly with decreasing temperature than that of a hypothetical substance that would correspond to the Fletcher curve. As a consequence, if only one mineral dust would contribute to the concentration of INP in the entire temperature spectra, the spectrum must have the same steepness as the frozen fraction of that mineral. Only Microcline, as an example, would produce the temperature spectrum shown in Fig. 1(a) with the right hand y-axis (calculated by $FF_{Microcline} \cdot N_{IN@233K}$). While INP concentrations between 263-268K would correspond to observational data, at 253K where typical INP concentration is ~$1\ell^{-1}$,

Microcline would produce ~1000ℓ^{-1}. This is not what is observed. The lower temperature dependence of the frozen fraction calculated using n_s of desert dust must result from a superposition of several steeper curves of all substances composing desert dust in their specific fraction.
Fig. 1(b) shows the temperature spectrum from multiplying desert dust's ice nucleation activity with a globally averaged dust concentration given in Atkinson et al. (2013). This represents observations well, in steepness and range. As mentioned above, we argue that the match in steepness stems from the contribution of different substances contained in desert dust.

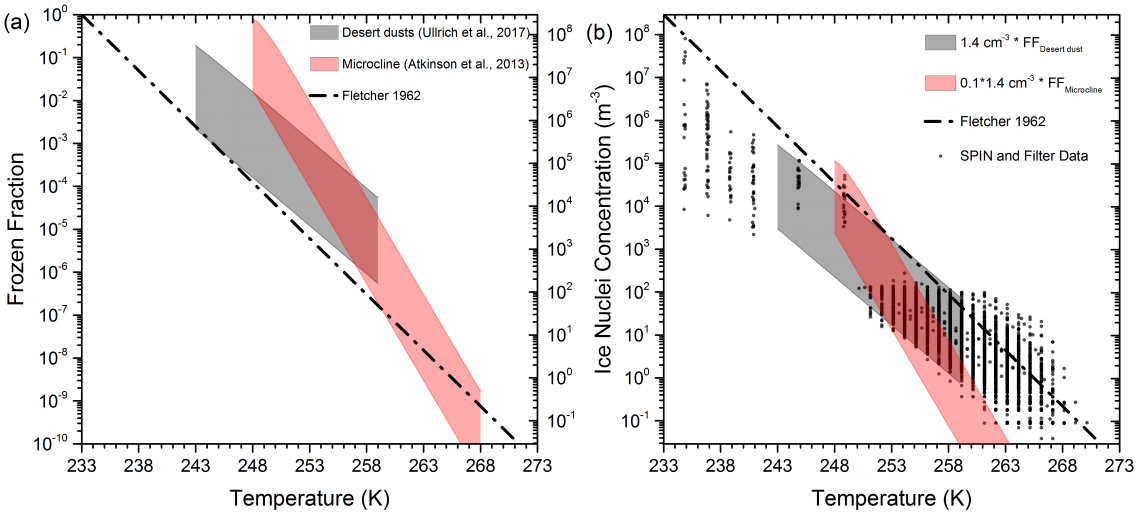

Figure 1. (a) Frozen fraction (left side axis) of of Desert dust, Microcline and ambient INP as function of temperature. Frozen fractions are calculated based n_s from Atkinson et al. (2013); Ullrich et al. (2017) for particle diameter between 100nm and 1μm, respectively by normalizing Fletcher's parametrization by the maximum predicted INP concentration (at 233K). Multiplying frozen fractions by the normalization factor leads to the corresponding ice nuclei concentrations (right hand axis).
(b) Temperature spectra including Fletcher's parametrization and n_s predicted concentration, scaled by globally averaged dust concentration for desert dust and 10% of globally averaged dust concentration for Microcline.

2. *Consider using the term 'ice nucleating particles; INPs' rather than ice nuclei (IN). Vali et al. [2015] in their recent definitions paper came up with some compelling reasons why this is a better and less confusing term.*

   As we are investigating filter samples and ice nuclei may be of various nature (particles, macro-molecules, ...) we rather prefer to stick to the classic abbreviation IN. We now state in the introduction that IN stands for "ice nucleating substance".

3. *P1 ln 24. Provide a citation for 100 L-1 INP leading to diamond dust. My understanding was that diamond dust was a relatively low concentration of ice crystals of relatively large size, i.e. in contradiction to the statement made here. In addition, I understand diamond dust tends to form in clear air, without the presence of a liquid cloud.*

   The sentence is inspired by the following report by Vincent Schaefer: "One late winter day in 1944, when I was climbing Mt. Washington by way of Tuckermans Ravine with Dr. Irving Langmuir, we approached the base of an orographic cap cloud which covered the cone of the mountain. He pointed out that the concentration of ice nuclei in the cloud was probably less than one per 1000 cubic meters, i.e. 1 x 10^{-6}/liter! He made his estimate using the horizontal and vertical distances of about 10 meters existing between the snow pellets which were falling from the cloud. We were also aware that at other times, what we call diamond dust, could be observed under similar temperature conditions with

concentrations as high as 100 per liter." (Schaefer, 1967).
The Reviewer is correct that the connection to ice formation in liquid clouds is not obvious without context. As no firm evidence could be found elsewhere, the sentence is removed from the manuscript.

4. *P2, ln 1. When discussing data like that of Ansmann et al. and making statements such as 'above -10 C ice containing clouds are rare', make sure it is stated what sort of clouds are being referred to. For example, in convective clouds ice formation above -10oC is common. Ansmann et al. deal with shallow clouds.*

   Ice formation via immersion freezing should occur at the same temperatures, independent on the dynamical conditions under which clouds form. The difference must be due to secondary ice formation, which is more effective in cumuli than in stratiform clouds.
   The cloud type in the studies cited is added to the manuscript.

5. *P2. Ln 3. This paragraph is very confused. Parts of it seem to be referring to ice formation in shallow cloud types (e.g. stratus), whereas it then morphs into a discussion about secondary production which is more relevant for deep clouds.*

   We have restructured and extended this part of the introduction to make it more organized. The cloud regime in which the measurements we refer to have taken place is indicated.
   It now reads: "Ambient measurements of IN-concentrations from various studies were compiled by Fletcher (1962) to derive a spectrum of the average IN-concentration as a function of temperature (curve shown in Fig. 1). Fletcher's curve has been found to match ice crystal concentrations measured in stratiform clouds and cold-based convective clouds but underpredict the concentration in deep convective clouds (e.g. Mossop, 1985; Cooper, 1986). Matching concentrations of ice crystals and IN indicate a direct influence of immersion freezing IN on cloud properties.
   At what concentration ice crystals exert a substantial influence on the properties of the cloud in which they form, has been addressed by Rangno and Hobbs (1988). From aircraft and mountaintop observations, Rangno and Hobbs (1988) identified the significant ice crystal concentrations able to produce precipitation to be on the order of $1\,\mathrm{L}^{-1}$ or more, cf. Fig. 1. In their data-set, such concentrations have been measured in cumulus clouds with top temperatures between -5 °C and -10 °C. At this temperature, this is a much larger concentrations than expected from the Fletcher curve and indicates secondary ice formation. Secondary ice formation mechanisms (most efficient at -5 °C) can increase the ice crystal concentration within a cloud by as much as four orders of magnitude above the number of IN present (e.g. Hallett and Mossop, 1974; Hobbs and Rangno, 1985; Mossop et al., 1970). Already few active IN ($0.01\,\mathrm{L}^{-1}$) can be enough to start the multiplication (Sullivan et al., 2017). In-situ evidence for secondary ice formation is reported in Hoffer and Braham (1962). They collected graupel from the top of cumulus clouds to melt and refreeze them under laboratory conditions. They found that every sample froze at substantially lower temperatures than the lowest temperature in the cloud from which they were collected, indicating that they did not contain IN active at the temperature the ice pellets froze in the cloud.
   Typical temperatures at which ice crystals are observed to form in numbers high enough to affect the properties of clouds have been measured by remote sensing. Satellite observations, averaging clouds globally (e.g. Carro-Calvo et al., 2016) and ground-based Lidar measurements, looking at shallow clouds (e.g. Ansmann et al., 2009), report that above -10 °C ice containing clouds are rarely detected and often cloud top temperatures below -20 °C are necessary for clouds to glaciate. Satellite data (Carro-Calvo et al., 2016; Rosenfeld et al., 2011) and aircraft observations (Rangno and Hobbs, 1991, 1994) agree on a land-sea contrast with the tendency of cloud glaciation at higher cloud top temperatures over sea. Carro-Calvo et al. (2016) offer the explanation that the presence of larger sized droplets in maritime clouds, which are required for effective secondary ice formation (Heymsfield and Willis, 2014) could play a role. Hallett and Mossop (1974) suggested that marine cumuli contain large ice crystal concentrations for dynamical reasons. They usually have higher cloud top temperatures, therefore the contact of ice and supercooled droplet occurs at temperatures favorable for splintering."

6. *P2. Ln 17-25. This discussion of marine INP is lacking reference to some more recent literature on the subject, e.g.: [Burrows et al., 2013; McCluskey et al., 2017; Vergara-Temprado et al., 2017; Wilson et al., 2015; Yun and Penner, 2013]. I appreciate the effort made to go back to much older studies, but the new work also needs to be discussed.*

We thank the Reviewer for pointing us to this recent studies. We included some of them at this point of the manuscript. "More recently, laboratory investigations (DeMott et al., 2016; McCluskey et al., 2017), modeling (Burrows et al., 2013; Vergara-Temprado et al., 2017) and ambient observations (Wilson et al., 2015) showed that under certain conditions, IN from marine sources can be abundant enough to significantly contribute to the total IN population, particularly in high latitudes."

7. *P2. Ln 25. The statement that 'From laboratory experiments it is established that dust particles tend to nucleate ice below -20C whereas biological particles can initiate immersion freezing at temperatures up to -5 C' is wrong. I can point to numerous studies showing dust can nucleate ice at much warmer temperatures; e.g. [Atkinson et al., 2013; Niemand et al., 2012; Ullrich et al., 2017]. Modeling suggests that dust is important in many locations at much warmer temperatures than -20 C [Vergara-Temprado et al., 2017].*

   We changed the sentence to:'From laboratory experiments it is established that dust particles tend to nucleate ice efficiently below -20 °C whereas some biological particles can efficiently initiate immersion freezing at temperatures up to -5 °C (Murray et al., 2012).'
   Modeling INP concentrations with only Feldspar suffers on over-predicting concentrations at low temperatures and under-predicting concentrations at warm temperatures, in agreement with what is demonstrated in Fig. 1, comment 1. The temperature of agreement between model output and observation shifts with the feldspar number concentration.

8. *P2-3. It is not possible to distinguish between dust and bio INP on the basis of an inflection at -16oC. It is false to claim that such an inflection would give you information about biological INP. In making this statement the authors are assuming they know what the ice nucleating spectrum of dust is and also that they know that biological INP nucleate around -16C. Neither can be assumed or are correct. Biological material has a huge diversity in its nucleating ability. There are exceptional ice nucleating materials from specific fungal and bacterial species and much less active materials associated with marine biology. Also, the work of DeMott et al. [2016] and Wilson et al. [2015] suggest that the slope of INP vs T for marine INP materials is quite shallow, in contrast to what is stated here.*

   There might be a misunderstanding. As shown in Fig. 1 comment 1, mineral dust contribute at temperatures lower than -16 °C, therefore changes in abundance of dust shifts the temperature spectrum up and down, below this temperature. Any inflection at warmer temperatures can be attributed to other INP species (which don't need, but could be biological). It is more difficult to differentiate between them on the basis of the temperature spectrum at lower temperatures.
   Shallow slope of any material must be due to its inhomogeneity. The largest inhomogeneity in marine INP is probably the diversity in composition i.e. various particle species in different concentrations and with differing activities. Laboratory results pointing in this direction can be found in McCluskey et al. (2017). They report that experiments when a phytoplankton bloom was provoked, caused a response at various temperatures during different stages of the bloom, suggesting a diverse marine INP population.
   The section was slightly changed to make it clearer. It now reads:"Two main sources for IN in maritime air have been proposed. Long-range transported continental aerosol (mainly dust) suggested by Bigg (1973) or marine organic ice nuclei of biogenic origin aerosolized with the sea spray (Schnell and Vali, 1975; Rosinski et al., 1987). Aerosol from both sources have been investigated (e.g. DeMott et al., 2003, 2016, and references therein). They found that marine-sourced IN are less efficient than IN from continental sources and can contribute IN in a broad temperature range. From laboratory experiments it is established that dust particles tend to nucleate ice efficiently below -20 °C whereas some biological substances can efficiently initiate immersion freezing at temperatures up to -5 °C (Murray et al., 2012). Joly et al. (2014) demonstrated that the particles initiating immersion freezing in cloud water samples collected at Puy de Dôme consist to an increasing fraction of biological IN (identified by sensibility to heat treatment) towards higher freezing temperatures. They estimate 77% biological IN at -12 °C increasing to 100% at -8 °C.
   The different temperature range in which dust or biological particles act efficiently as IN, can generate a specific signature in the concentration-temperature spectra if there is a change in abundance (cf. Sec. 4 and Appendix A). Some biological particles and in particular bacterial IN of one source tend to exhibit homogeneous ice nucleating properties. They initiate ice formation in a narrow temperature range seen as step like increase in concentration in a temperature spectra (e.g. Murray et al., 2012). In contrast, dust particles activate in a broader temperature range (e.g. due to inhomogeneities in

composition, surface structure and the influence of particle size on nucleation efficiency) seen as exponential increase in concentration towards lower temperatures (Bigg, 1961). If a strong marine source of biological origin exists it can be expected to be detectable as an inflection in IN-concentration at temperatures above -16 °C where the ice nucleating fraction of dust particles is small."

9. *P4. Ln 5. It would be helpful to see the control fraction frozen curves as well as the fraction frozen curves for the samples. These control experiments look better than those reported by Conen et al., why is this? What has been done differently?*

   We don't know what makes the difference. Fig. 2(a) shows the frozen fraction curves from the reported samples in comparison to three measurements of each the used water, fresh filter and field blanks of filters treated, stored and handled the same way as samples but removed from the Digitel before sampling. The contribution from sampled aerosol to the frozen fraction can be isolated from the background contribution of water and filter material. According to the 'At least one Rule' in probability calculus, freezing is caused by the aerosol, the background or both. Treating the frozen fraction as probability for a droplet to freeze we can calculate the probability for a droplet not to freeze:

$$(1 - FF_{BG}) \cdot (1 - FF_{Aerosol}) = 1 - FF_{Sample} \tag{1}$$

   Solving for $FF_{Aerosol}$ results in

$$FF_{Aerosol} = \frac{FF_{BG} - FF_{Sample}}{FF_{BG} - 1} \tag{2}$$

   where FF_{BG}, $FF_{Aerosol}$, FF_{Sample} denoting the frozen fraction only from the background, the aerosol and the measured frozen fraction of the sample. With FF_{BG} and FF_{Sample} known, Eq. 2 can be used to calculate the contribution which can only be attributed to the sampled aerosol. The result is shown in Fig. 2(b).

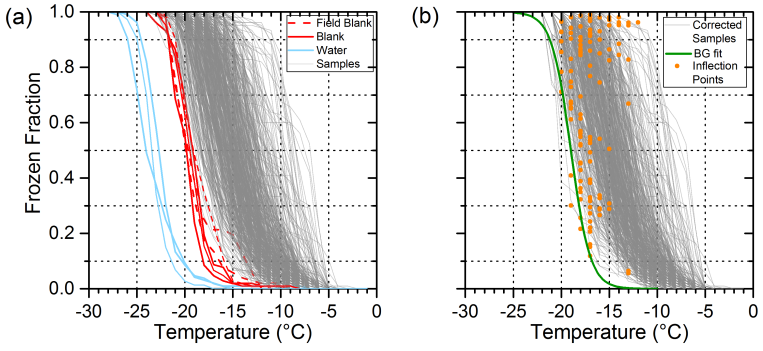

Figure 2. (a) Frozen fraction curves of filter samples (FF_{Sample}) in comparison to background measurements. (b) Minimal frozen fraction from sampled aerosol ($FF_{Aerosol}$). The FF_{BG} derived as a fit to blank measurements is shown in green. $FF_{Aerosol}$ curves are cut if their slope becomes negative and endpoints are marked in orange.

   For some measurements, isolating $FF_{Aerosol}$ in the way described above can lead to decreasing frozen fraction with decreasing temperatures. As this is unphysical, we cut such curves at their inflection point.
   The above analysis supports the temperature information given in the manuscript. We did not make changes to the text.

10. *Figure 1. Also show other INP parameterisations that are used in models in addition to Fletcher, e.g. Meyers et al, Cooper et al.*

    The two parametrizations from Cooper (1986); Meyers et al. (1992) have been added. In order not to overload the figure and distract from the actual measurements, no other additional parametrizations are shown. The temperature range of the

parametrization lines has been capped according to the validity range given in the original work. The parametrization lines are calculated according to Eqs. 3, 4, 5 and shown in the range of supercooling (ΔT) indicated:

$$\text{Fletcher 1962:} \quad N_{IN}[m^{-3}] = 10^{-2} \cdot exp(0.6 \cdot \Delta T), \qquad 10^\circ < \Delta T < 30^\circ \quad (3)$$

$$\text{Cooper 1986:} \quad N_{IN}[m^{-3}] = 10^3 \cdot 10^{(-2.35-0.135 \cdot -\Delta T)} = 10^{(0.65+0.135 \cdot \Delta T)}, \qquad 5^\circ < \Delta T < 25^\circ \quad (4)$$

$$\text{Meyers et al. 1992:} \quad N_{IN}[m^{-3}] = 10^3 \cdot exp(-0.639 + 0.1296 \cdot (100 \cdot (S_i - 1)))$$

$$= 10^3 \cdot exp(-0.639 + 0.1296 \cdot (100 \cdot (S_w \cdot \frac{p_{w,sat}(T)}{p_{i,sat}(T)} - 1))), \qquad 7^\circ < \Delta T < 20^\circ \quad (5)$$

11. *P10, ln 15-23. In this discussion of the conclusion that the authors see no evidence for marine INP, they need to cite other papers with similar conclusions. For example, Fig 5 of Vergara-Temprado et al. [2017] clearly shows that desert dust is much more important than marine organic INP in the Eastern Atlantic region. Similarly to the final statement referring to Burrows, Wilson et al. [2015] also conclude that marine INP might be important in the southern ocean. They do not make this conclusion on the basis that marine organics are particularly good at nucleating ice, they conclude this because the southern ocean atmosphere has very little desert dust in it and marine organics therefore define INP population.*

    We added Vergara-Temprado et al. (2017).

12. *P11, ln 15, Why are INP above -10 biogenic? This statement needs to be expanded upon or altered. As mentioned above, mineral dust can nucleate ice in this temperature regime.*

    In the course of improving the conclusion section the statement was deleted. However, we think there is evidence that it is true. See comment 1. We conclude this based on the observed INP-concentration, which is the product of activity and abundance of the substance. The activity of mineral dust at -10 °C is low and a high number of particles would be necessary to produce the INP-concentration observed in the atmosphere. At lower temperatures, the high abundance of dust particles would result in much more INP than observed (see the calculation example in comment 1 and Fig. 1b). This leads to two possible explanations. First, the explanation offered in our paper, that what makes the temperature spectra are the concentrations of different substances contributing in a temperature range where their activity is high . As the most active mineral dust known today is not active enough to explain the observed INP concentration at $T > -20\,^\circ\mathrm{C}$, another substance must be nucleating ice. Because Microcline is the most active mineral dust, no other mineral dust can be this more active substance. Natural substances with a higher activity are found in the class of biological aerosol. Alternative, there is a more active, very rare (low concentration) mineral dust that has not jet been identified or an entirely different source.

13. *P12. In this discussion of Ansmann et al., make it clear that this -20C number is for shallow clouds only, not deep convective clouds. In contrast the OSCIP from Rango and Hobbs is for cumulus clouds. Consequently I think the link between these ground level measurements and mid-level clouds is not as clear as the authors suggest.*

    Ansmann et al. (2009) measured alto cumulus clouds. This is now mentioned in the manuscript. The evidence is circumstantial, but the point is that an ice crystal concentration of $1\ell^{-1}$ is a benchmark concentration to clearly change mixed-phase cloud properties. In clouds where primary ice nucleation dominates ice crystal formation, this concentration is observed at -20 °C in agreement to our measurement of the INP-spectra at ground-level. We think this is an interesting agreement and kept it in the text. It could also be evidence that concentrations measured at ground are similar at cloud level.

14. *Conclusions: Some of these paragraphs are very short and there is a single sentence paragraph which seems to be floating and not connected to other statements. Hence, it reads more like a list of bullet points than a well-crafted conclusions section. This could be improved.*

We re wrote and condensed parts of the conclusion. It now reads:
"Typical IN-concentrations in the subtropic, marine environment are obtained from 500 particle filter samples collected over 4 years and from a 2-month field campaign with the SPIN instrument. Concentrations increase exponentially from $10^{-1}\,\mathrm{m}^{-3}$ to $10^{6}\,\mathrm{m}^{-3}$ between -5 °C to -38 °C. Over time, the concentration varies up to three orders of magnitude on a synoptic scale (filter samples) and up to four orders of magnitude on a higher resolution (SPIN measurements). The frequency with which certain concentrations are measured at a temperature T follows a log-normal distribution, characteristic for successive random dilution during long-range transport. The log-normal frequency distribution is found at all investigated temperatures. Parametrizations in numerical models should reproduce this feature.
For the long-term series of filter measurements, we find that random dilution during transport could account for larger fluctuations in IN-concentration than seasonal changes, changes in air mass origin and changes in the bulk aerosol composition. At Cape Verde, the later do not reveal a clear correlation to the measured IN-concentration. The only observable tendency is that continental air mass contain higher IN-concentrations than maritime air mass, in agreement to previous measurements (e.g. Bertrand et al., 1973) and model predictions (e.g. Burrows et al., 2013). The absence of an annual trend despite a dust and a biological active season is surprising and highlights the lack of knowledge about the nature of ice nucleating particles.
The diversity of the ice nuclei population manifests in the shape of the cumulative temperature spectra. The contribution of each source to the temperature spectra depends on the source strength, dilution during transport and the temperature range to which the source contributes efficient IN. Multiple sources, together with random dilution, could produce the appearance of an ubiquitous, almost constant background concentration of IN.
Assuming $10^{3}\,\mathrm{m}^{-3}$ to be a threshold IN-concentration to have a significant, primary effect on properties of supercooled clouds, temperatures below the range covered by the drop freezing experiment used in this study, need to be reached to have an effect. If the temperature dependent IN-concentration exponentially increases with the slope of the Fletcher (1962) approximation, a primary effect of ice nucleation by immersion freezing on cloud glaciation and precipitation formation can be expected at $-20\,^{\circ}\mathrm{C} \pm 5\,^{\circ}\mathrm{C}$, matching the -20 °C alto cumulus cloud glaciation temperature over Cape Verde reported by Ansmann et al. (2009). The SPIN data measured at temperatures below -24 °C support the temperature trend. Given that measurements of IN-concentrations at ground are representative for higher altitudes, the observation of cloud glaciation at $-20\,^{\circ}\mathrm{C}$ where IN-concentrations reach OSCIP support the importance of immersion freezing on cloud properties in a subtropical, marine environment."

Technical corrections
None.

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Concentration and variability of ice nuclei in the subtropic, maritime boundary layer

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Abstract. Measurements of the concentration and variability of ice nucleating particles in the subtropical, maritime boundary layer are reported. Filter samples collected in Cape Verde over the period 2009-2013 are analyzed with a drop freezing experiment sensitive to detect the few, rare ice nuclei active at low supercooling. The data-set is augmented with continuous flow diffusion chamber (SPIN) measurements at temperatures below -24 °C from a two month field campaign ~~at~~ in Cape Verde in 2016. The data set is used to address the questions: What are typical concentrations of ice nucleating particles active at a certain temperature, what affects their concentration ~~, what is their composition~~ and where are their sources?

~~To investigate what the most common ice nuclei are and to identify the sources, bulk chemical aerosol composition obtained from the utilized filter samples is tested for correlations with ice nuclei concentration. It is shown that no significant correlation between the rare ice nuclei and the bulk aerosol chemical composition, which could serve as tracer for a specific aerosol class e.g. of maritime origin, can be made.~~

Concentration of ice ~~nuclei~~ nucleating particles is found to increase exponentially ~~with decreasing temperature. It indicates that several groups of particles~~ by seven order of magnitude from -5 °C to -38 °C. Sample to sample variation in the steepness of the increase indicates that particles of different origin, with different ice nucleation properties (size, composition) are contributing to the ice nuclei concentration at different temperatures. The concentration of ice nuclei active at a specific temperature varies over a ~~wide range~~ range up to 4 orders of magnitude. The frequency with which a certain ice nuclei concentration is measured within this range is found to follow a log-normal distribution~~. The log-normal frequency distribution~~ , that can be explained by random dilution ~~associated with turbulent,~~ during long-distance transport.

To investigate the geographic origin of ice nuclei, source attribution of air masses from dispersion modeling is used to classify the data into 7 typical situations. While no source could be attributed to the ice nuclei active at temperatures higher than -12 °C, concentrations at lower temperatures tend to be elevated in air masses originating from the Saharan desert.

1 Introduction

Ice crystals form in ~~many ways in the atmosphere~~ the atmosphere in a number of different ways. If ice formation ~~initiates on ice nucleating particles~~ is initiated by an ice nucleating substance (IN) immersed in ~~supercooled cloud droplets~~a supercooled cloud droplet, the ice nucleation mechanism is ~~named~~ referred to as immersion freezing. The effect immersion freezing exerts on ~~cloud extend~~clouds (cloud depth, lifetime, radiative properties and rain formation~~depends~~) depends, beside updraft

velocities and cloud-drop spectra on the concentration of IN active at a particular temperature ~~(DeMott et al., 2010).Very high~~ (Hallett and Mossop, 1974; DeMott et al., 2010).

Ambient measurements of IN-concentrations ~~above 100~~from various studies were compiled by Fletcher (1962) to derive a spectrum of the average IN-concentration as a function of temperature (curve shown in Fig. ~~lead to the formation of numerous small floating crystals known as diamond dust, whereas low concentrations e.g. 0.01 would produce large ice crystals falling from a cloud in distances meters apart.Satellite observations (e.g. Carro-Calvo et al., 2016) and ground-based remote sensing (Ansmann et al., 2009) show that above -10 ice containing clouds are rare and often cloud top temperatures below -20 are necessary for clouds to glaciate.~~

~~Glaciation of supercooled clouds often initiates at the cloud top where ice is formed by immersion freezing (primary ice formation). Ice crystals growing at the expense of cloud droplets (see e.g. Korolev, 2007) settle by gravitation and upon contact with supercooled droplets, secondary ice formation mechanisms (most efficient at -5) multiply the ice crystal concentration within the cloud above the number of IN present (e.g. Heymsfield and Willis, 2014; Hobbs and Rangno, 1985; Mossop et al., 1970).Conditi within marine clouds make them susceptible to ice multiplication processes (Heymsfield and Willis, 2014) so that already few active ice nuclei could lead to the formation of many secondary ice crystals.~~ 1). Fletcher's curve has been found to match ice crystal concentrations measured in stratiform clouds and cold-based convective clouds but underpredict the concentration in deep convective clouds (e.g. Mossop, 1985; Cooper, 1986). Matching concentrations of ice crystals and IN indicate a direct influence of immersion freezing IN on cloud properties.

At what concentration ice crystals exert ~~significant~~ a substantial influence on the properties of the cloud in which they form, has been addressed by Rangno and Hobbs (1988). From aircraft and mountaintop observations, Rangno and Hobbs (1988) identified the significant ice crystal concentrations able to produce precipitation to be on the order of 1 L^{-1} or more, cf. Fig. 1. In their data-set, such concentrations have been measured in cumulus clouds with top temperatures between -5 °C and -10 °C.

~~Satellite~~ At this temperature, this is a much larger concentrations than expected from the Fletcher curve and indicates secondary ice formation. Secondary ice formation mechanisms (most efficient at -5 °C) can increase the ice crystal concentration within a cloud by as much as four orders of magnitude above the number of IN present (e.g. Hallett and Mossop, 1974; Hobbs and Rangno, Already few active IN (0.01 L^{-1}) can be enough to start the multiplication (Sullivan et al., 2017). In-situ evidence for secondary ice formation is reported in Hoffer and Braham (1962). They collected graupel from the top of cumulus clouds to melt and refreeze them under laboratory conditions. They found that every sample froze at substantially lower temperatures than the lowest temperature in the cloud from which they were collected, indicating that they did not contain IN active at the temperature the ice pellets froze in the cloud.

Typical temperatures at which ice crystals are observed to form in numbers high enough to affect the properties of clouds have been measured by remote sensing. Satellite observations, averaging clouds globally (e.g. Carro-Calvo et al., 2016) and ground-based Lidar measurements, looking at shallow clouds (e.g. Ansmann et al., 2009), report that above -10 °C ice containing clouds are rarely detected and often cloud top temperatures below -20 °C are necessary for clouds to glaciate. Satellite data (Carro-Calvo et al., 2016; Rosenfeld et al., 2011) and aircraft observations (Rangno and Hobbs, 1991, 1994) agree on a land-sea contrast with the tendency of cloud glaciation at higher cloud top temperatures over sea. Carro-Calvo et al. (2016) offer

the explanation that the presence of larger sized droplets in maritime clouds, which are required for effective secondary ice formation (Heymsfield and Willis, 2014) could play a role.

Hallett and Mossop (1974) suggested that marine cumuli contain large ice crystal concentrations for dynamical reasons. They usually have higher cloud top temperatures, therefore the contact of ice and supercooled droplet occurs at temperatures favorable for splintering.

Several studies (e.g. Hobbs and Locatelli, 1970; Bertrand et al., 1973; Borys and Duce, 1979; Castro et al., 1998) observed that IN-concentrations in maritime air masses are generally lower than in continental air, suggesting no important source for IN from the ocean. But Bigg (1961) or Soulage (1961) measured an increased IN-concentration in air of maritime and coastal origin, providing directly conflicting evidence for the importance of the ocean as IN source.

More recently, laboratory investigations (DeMott et al., 2016; McCluskey et al., 2017), modeling (Burrows et al., 2013; Vergara-Tempra ambient observations (Wilson et al., 2015) showed that under certain conditions, IN from marine sources can be abundant enough to significantly contribute to the total IN population, particularly in high latitudes.

Two main sources for IN in maritime air have been proposed. Long-range transported continental aerosol (mainly dust) suggested by Bigg (1973) or marine organic ice nuclei of biogenic origin aerosolized with the sea spray (Schnell and Vali, 1975; Rosinski et al., 1987). Aerosol from both sources have been investigated (e.g. DeMott et al., 2003, 2016, and references therein)~~and found to provide efficient IN~~. They found that marine-sourced IN are less efficient than IN from continental sources and can contribute IN in a broad temperature range. From laboratory experiments it is established that dust particles tend to nucleate ice efficiently below -20 °C whereas ~~biological particles can~~ some biological substances can efficiently initiate immersion freezing at temperatures up to -5 °C (Murray et al., 2012). Joly et al. (2014) demonstrated that the particles initiating immersion freezing in cloud water samples collected at Puy de Dôme consist to an increasing fraction of biological IN (identified by sensibility to heat treatment) towards higher freezing temperatures. They estimate 77% biological IN at -12 °C increasing to 100% at -8 °C.

~~Beside the~~

The different temperature range in which dust or biological particles act efficiently as IN, ~~they~~ can generate a specific signature in the concentration-temperature spectra if there is a change in abundance (cf. Sec. 4 and Appendix A)~~by which they can be identified. Biological~~. Some biological particles and in particular bacterial IN of one source tend to exhibit homogeneous ice nucleating properties. They initiate ice formation in a narrow temperature range seen as step like increase in concentration in a temperature spectra (e.g. Murray et al., 2012). In contrast, dust particles activate in a broader temperature range (e.g. due to inhomogeneities in composition, surface structure and the influence of particle size on nucleation efficiency) seen as exponential increase in concentration towards lower temperatures (Bigg, 1961). If a strong marine source of biological origin exists it can be expected to be detectable as an inflection in IN-concentration at temperatures above -16 °C where the ice nucleating fraction of dust particles is small.

The concentration of potential IN measured at a certain location and temperature ~~undergoes rapid changes (Bigg, 1961; Bigg and Hopwoo~~ undergo large changes on timescales of days (Bigg, 1958) or hours (Bigg, 1961). This can be seen as indication that in terms

of IN the atmosphere is poorly mixed. Pockets of high concentration can be followed by an almost IN free period as air moves by the location of measurement.

The two main factors influencing IN-concentration and variability at a certain location are:

1. the characteristics of the present population of aerosol particles (e.g. size-distribution, composition)
2. transport processes (initial concentration of the IN at its source, location of the source relative to the sampling location, modification and dilution during transport (Anderson et al., 2003)).

Membrane filter samples have been used to detect ice nuclei at low supercooling since the beginning of ambient IN-concentration measurements (Bigg, 1961; Bigg et al., 1963). ~~Long sampling times are necessary to collect enough air volume to be sensitive to~~ To measure the low concentration of ~~rare IN~~IN, able to initiate immersion freezing ~~at low supercooling (~~above -20 °C~~).~~ , it is necessary to collect particles from a large enough air volume. The time required to collect this volume depends on the sample flow through the filter, which is influenced by its type (fiber or membrane), fiber or pore size, and the capacity of the pump. Long sampling times may be necessary. Some problems of long sample exposures were identified by ~~(Mossop and Thorndike, 1966)~~Mossop and Thorndike (1966). The collected particles are subject to gas condensation, aging or can be covered by aggregating smaller particles during sampling which could reduce the concentration of active IN. Daily integrated samples not only average out minor erratic fluctuations but also potential high count periods (e.g. due to the dissipation of the nocturnal inversion) within the ~~sample~~ sampling time. Higher IN-concentrations (up to three orders of magnitude, cf. Sec. 8) than the reported background concentration can be expected on timescales smaller than what is resolved by the used filter collection.

2 Sampling site

Samples are taken at the Cape Verde Atmospheric Observatory (CVAO; 16,848 °N, 24.871 °W) strategically placed ~~at~~ on the northeastern shore of São Vincente (one of the northern islands of the Cape Verde archipelago). Cape Verde islands are located 16 °N, 570 km off the coast of West Africa. Situated in the trade wind zone, the northeasterly winds prevail throughout the year, bringing in air masses from the open ocean. São Vincente is downwind of the coastal upwelling region on the west coast of Africa with high marine biological productivity and the outflow of the Saharan desert. Characteristic aerosol particles are of marine origin (e.g. sea-spray) mixed with a continental background (mineral dust and smoke from biomass-burning), (Fomba et al., 2014). From ~~Dec-Feb~~ Dec.-Feb. an usually strong Saharan desert dust period is typical. Filter samples are collected on a tower 30 m above the sea surface, 70 m from the coastline. The 30 m tower reaches out of the high sea salt loaded ground layer (Blanchard and Woodcock, 1980) into the mixed, maritime boundary layer.

3 Experimental method

150 mm quartz fiber filter, sampled using a Digitel filter sampler (DHA-80) with a PM_{10} inlet are used to obtain a time series of ice nuclei concentration with 1-3 day resolution. The PM_{10} inlet excludes particles $\geq 10\,\mu m$ from being sampled. To determine

the IN-concentration, 103 random sub-samples, each containing aerosol from an air volume of 37-114 L are punched out of each filter, immersed in 100 µl droplets inside 0.5 ml safe-lock tubes and subject to temperatures down to -25 °C, allowing ice formation by immersion freezing. Freezing by impurities in the water typically sets in below -20 °C. Blank sub-samples taken from filter through which no air was drawn, start to cause freezing below -16 °C. It is not before -20 °C that the filter material initiates ice formation in 50% of the samples. The drop freezing assay is set up following the description in Conen et al. (2012), with the difference that the circular sub-samples used for the present measurements are only 1 mm in diameter. According to Vali (1971), the cumulative concentration of IN per air volume as a function of temperature ($K(\theta)$) can be calculated by

$$K(\theta) = (\ln N_0 - \ln N(\theta))/V, \tag{1}$$

with N_0 denoting the number of sub-samples, $N(\theta)$ the number of unfrozen sub-samples at temperature θ and V the volume of air passed through each 1 mm sub-sample. With the given number of sub-samples, their diameter and sampled air volume the method is sensitive to concentrations from approx. 0.08-130 $\mathrm{IN/m^3}$. Following Conen et al. (2012) the uncertainty (one standard deviation) in measuring $K(\theta)$ is given by

$$dK(\theta) = \pm\sqrt{K(\theta)}/(N_0 \cdot \sqrt{V}). \tag{2}$$

For clarity of presentation, data in the figures below are shown without the range of uncertainty given in Eq. (2).

During a field campaign in Jan.-Feb. 2016 concentration measurements of IN active at low temperatures, were conducted using the SPectrometer for Ice Nuclei (SPIN). SPIN is a parallel plate continuous flow diffusion chamber designed based on the chamber discussed in Stetzer et al. (2008). Aerosol was sampled at a flow of 1 L/min through an inlet up on the same 30 m high tower where the PM_{10} filter sampler was located. An impactor (TSI, 0.071 cm orifice) was used to limit the particle size sampled with SPIN. For details on the SPIN instrument we refer to the description in Garimella et al. (2016)

4 Temperature spectra of cumulative nuclei concentration

The temperature spectra (Fig. 1) summarizes data from 500 analyzed filter samples which were collected from 2009 - 2013 at the CVAO. Data in red, green and blue represent measurements at -8 °C, -12 °C and -16 °C. These data are shown in the same colors in following Figs. 2, 3, 4, 5, B1, C1. 30 min average concentrations measured with SPIN during the intense campaign in 2016 complement the data set in the temperature range from -24 °C to the onset of homogeneous freezing below -38 °C. The range of measured IN-concentration at constant temperature is large. Measurements vary up to three orders of magnitude for the 24 to 72-h filter samples and cover up to four orders of magnitude in the 30 min SPIN data. For the filter data, the temperature dependent change in concentration is similar to the slope of the approximation proposed in Fletcher (1962), indicated in Fig. 1. Concentrations measured with SPIN at lower temperatures show a weaker temperature dependence, vary in a larger range and diverge from the Fletcher approximation (cf. Fig. 1).

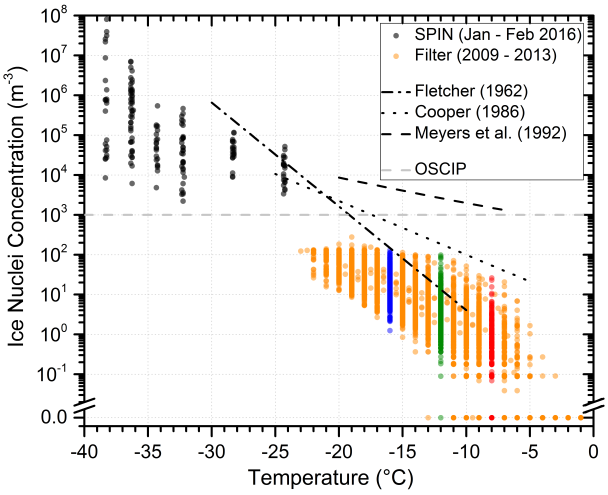

Figure 1. Cumulative ice nuclei concentration as function of temperature. Date and method of measurement are indicated in the figure. Filter data at -8 °C, -12 °C and -16 °C are color coded red, green and blue. This data are shown in the same colors in subsequent figures. ~~The~~ Parametrizations from Fletcher (1962)~~approximation is~~ , Cooper (1986) and Meyers et al. (1992) are given for comparison~~and the~~ . All parametrizations are shown in their valid temperature range. The OSCIP (Onset of Significant Concentrations of Ice Particles, Rangno and Hobbs, 1988) indicates a guideline concentration for effecting cloud properties by primary ice nucleation.

It seems indistinguishable if few particles with a high probability to act as IN or many less active aerosol particles represent the concentration of IN at a certain temperature. From the cumulative temperature spectra, it can be argued that the former is the case. A low activated fraction of an abundant IN at one temperature would generate a steep increase in concentration with decreasing temperature in a narrow range (~~ev~~cf. Appendix A for an extended discussion on the interpretation of IN temperature spectra). Concentrations measured at CVAO are observed to increase exponentially ~~with supercooling~~from -5 °C to -38 °C, indicating a broad variety of particle properties (e.g. size, composition, ice active surface sites) responsible for ice formation at different temperatures.

The temperature dependent increase in concentration (slope of the temperature spectrum) is not constant for different filters, indicating active IN of varying nature and abundance that contribute to the temperature spectra at different occasions. For additional discussion of the variability in slopes we refer to Bigg (1961) and Appendix A. ~~The scatter in~~ Assuming that particles make a significant contribution to the temperature spectrum only in the temperature range where their ice nucleation activity is high (Appendix A), scattering in the IN-concentration at a temperature ~~of interest is caused by~~ T can be explained by the variation in concentration of ~~IN~~ particles with a certain property~~in the sampled air mass~~. If properties of IN, active at a certain temperature, and therefore measured IN-concentration can be correlated to bulk chemical aerosol composition or air mass origin is analyzed in Sec. 6 and 7.

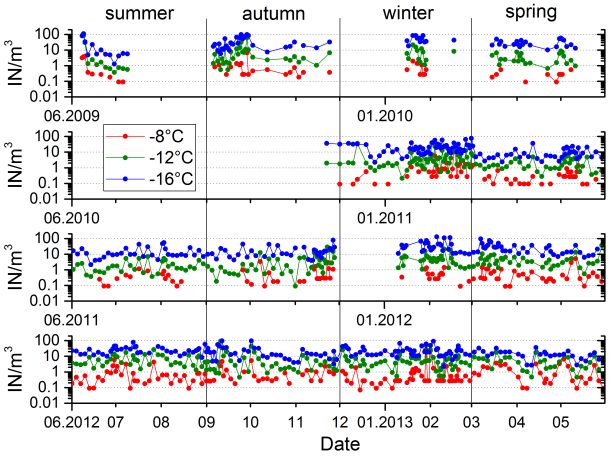

Figure 2. Four-year time series of ice nuclei concentration at three temperatures indicated in the figure.

5 Time series

The variation of ice nuclei concentration with time is ~~exemplary shown for~~ exemplified by data at -8 °C, -12 °C and -16 °C in Fig. 2. The four ~~year~~ years during which filter samples were collected, represent a cross section of the different atmospheric conditions (dust events, rain, dry-tropical) encountered ~~on~~ in Cape Verde. Neglecting extreme values, IN-concentration is changing within two orders of magnitude, without obvious cycles in the series. The measurement in the time series are positively first-order autocorrelated for all temperatures between -6 °C to -16 °C, i.e. persistence in above/below average IN-concentration on consecutive filter samples. Concentrations measured on samples further apart are not autocorrelated. Variations in IN-concentration are non-synchronous at different temperatures (cf. Fig. 2), indicating differences in origin of the ice nuclei populations active at different temperatures. This observation is analog to the change in slope of the temperature spectra for different filter samples discussed in Sec. 4. With increasing difference in temperature, the variation in IN-concentration at two temperatures become less correlated (R^2=0.30, R^2=0.37, R^2=0.09 for -8 °C to -12 °C, -12 °C to -16 °C, -8 °C to -16 °C). The time series shows no distinct seasonal or inter-annual trends during the four years of measurements (see Appendix B for an inter-annual comparison of season separated IN-concentrations).

6 Bulk chemical composition

The 24 to 72-h filter samples were used to analyze the bulk chemical composition of the collected aerosol. Methods and details of the chemical analysis can be found in Fomba et al. (2014) where the results of the chemical analysis from samples collected between 2007 - 2011 at CAVO are presented. Besides the derivation of the PM_{10} aerosol mass the chemical analysis included ion mass concentrations of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, organic (OC) and elemental carbon

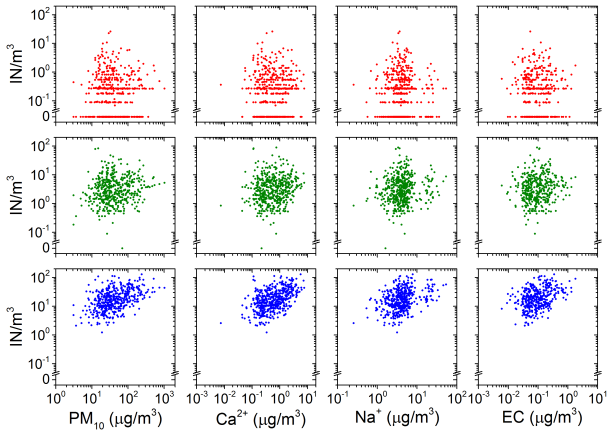

Figure 3. Relation between the concentration of IN at -8 °C (red), -12 °C (green), -16 °C (blue) and total particle mass concentration, mass concentrations of calcium (Ca^{2+}), mass concentration of sodium (Na^{+}) and mass concentration of elemental carbon (EC). Ca^{2+}, Na^{+}, EC are tracers of continental, marine and combustion sources, respectively.

(EC).

The sampling time allows to resolve aerosol mass concentration and composition on a synoptic scale (on the order of 1000 km). It is assumed in this sampling strategy, that aerosol composition mainly changes with horizontal changes in air masses (e.g. frontal systems) that occur on this scale. Additionally, variation in bulk aerosol mass concentration and composition on the synoptic scale can often be related to sources via back trajectories (Anderson et al., 2003). If IN sources were related to the sources of bulk chemical components, they could be used as tracer to identify source region or aerosol constituents contributing to the IN population. Fig. 3 shows scatter-plots of IN-concentration at -8 °C, -12 °C and -16 °C versus PM_{10} as tracer for desert dust and concentrations of Ca^{2+}, Na^{+}, EC as indicators of continental, maritime and combustion sources. Except an insignificant tendency (R^2=0.11, R^2=0.17) of higher IN-concentrations at -16 °C towards higher PM_{10} and Ca^{2+} mass concentration, the scattering is uncorrelated. Using Spearman statistics, monotonic association (more is more or more is less) between the IN-concentration at temperatures from -5 °C to -16 °C and mass concentration of all chemical components is tested. No significant correlation exists. While the IN-concentration at temperatures above -16 °C is not correlated to the amount of continental aerosol, evidence for the importance of the Sahara desert as source of IN at lower temperatures is found in the analysis of air mass origin (Sec. 7). This apparent contradiction can be explained as a non-constant ice active fraction of Saharan dust aerosol transported to the Cape Verde. A variable ratio of dust to IN-concentration has previously been observed by Bertrand et al. (1973) who measured in West Africa. A comparison of IN-concentration to the abundance of aerosol particles larger than a certain size can be found in Appendix C.

7 Effect of air mass origin

The origin of ~~air mass sampled from 2009-2013 on the filter~~ the air mass collected on the filters from 2009-2013 is determined using the NAME dispersion model (Jones et al., 2007) and classified into 7 categories (as shown in Carpenter et al., 2010). NAME dispersion footprints are calculated for the air arriving at the site, showing where the air masses had been in the surface layer (0-100m) in the previous 10 days. For each footprint, the proportional residence time in each geographical region (Atlantic, North America, Europe, coastal Africa and North Africa) is used to classify each period into one of the 7 air mass categories as shown in Fig. 4. Concentrations measured under the different categories at -8 °C,-12 °C and -16 °C are shown as box plots in Fig. 4. Slightly elevated concentrations are found for dust (from the Saharan and Sahel region) and Europe influenced air mass. The influence of dust on IN-concentration increases towards lower temperatures, where more dust minerals become ice active. Although air mass origin is correlated to season (dust storm season from ~~Dec-Feb~~Dec.-Feb.), no seasonal trend in IN-concentration is found. Which ice active aerosol Europe contributes is unclear. It could be of industrial or agricultural origin. From the comparison of the 7 situations categorized in Fig. 4 it is seen that continental ~~effected~~ affected air masses contain higher IN-concentrations than pure maritime air mass. Vice versa, even though the location of measurement is in vicinity to high primary oceanic productivity no correlation of high IN-concentration with coastal and marine air mass have been found in the temperature range accessible by the drop freezing method.

8 Frequency distribution

The IN-concentration and variability measured ~~in~~ at one location depends on the nature of the IN sources (strength and ice nucleation efficiency) and modification during transport (aging and dilution). While the cumulative temperature spectra (discussed in Sec. 4) can provide information on the efficiency and abundance of IN, the frequency distribution can be used to investigate the effect of transport.

It is found that log-normal frequency distributions best approximate the measured variability in concentrations at each individual temperature (cf. Fig. 5). The suitability of a log-normal distribution to approximate IN-concentrations frequency distributions has been recognized previously by Maruyama (1961); Isaac and Douglas (1971); Radke et al. (1976). Isaac and Douglas (1971) demonstrated that the frequency distribution of IN-concentration does not follow a Poisson distribution, thereby proving that IN are not randomly distributed in the atmosphere.

An explanation for the log-normal frequency distribution in concentration (such is also often found in concentrations of ambient pollutions) has been given by the theory of successive random dilutions (Ott, 1990). A log-normal distribution indicates that the initial IN-concentration at the source has undergone a series of random dilutions while being transported. In the case of IN-concentration where ice nucleating particles are lofted from the surface and transported in the free atmosphere to the measurement site, turbulent mixing randomly dilutes the initial concentration. Variation in source strength (e.g. particle concentration) does not change the log-normal standard deviation of the distribution, but causes a shift in concentrations. Only proximity of the measurement location to the IN source, and thus the maximum concentration possible (no dilution) would

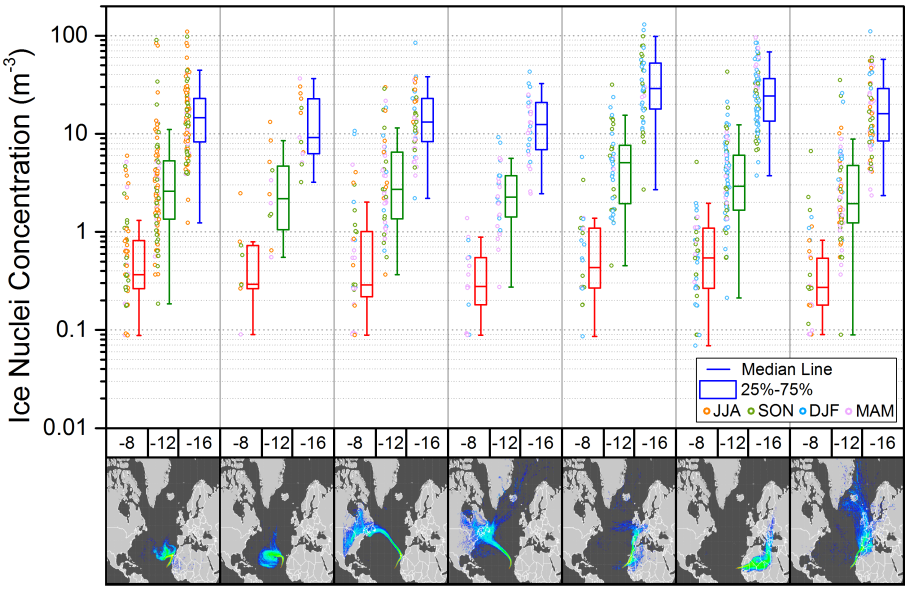

Figure 4. Variation of ice nuclei concentration classified into 7 situations of air mass origin at three temperatures. Data shown right of each box plot is color-coded by season (JJA=~~Jun-Aug~~Jun.-Aug., SON=~~Sep-Nov~~Sep.-Nov., DJF=~~Dec-Feb~~Dec.-Feb., MAM=~~Mar-May~~Mar.-May). Air mass classification from left to right: 1. African coastal, 2. Atlantic marine, 3. North American, marine and coastal, 4. North American and marine, 5. dust and Europe, 6. dust (e.g. Saharan and Sahel region), 7. coastal and Europe.

cause an even more skewed frequency distribution with a stronger downward bend at high concentrations (Ott, 1990). Neither the frequency distribution obtained from filter measurements nor the measurements with SPIN show this feature. The uni-modal, regular bell shape of the frequency distribution on the log-scale indicates the absence of a strong local source. Measured concentrations can therefore be assumed to represent the background concentration in a subtropic, maritime environment defined by long-range transport.

9 Discussion

The comparison of IN-concentrations from filter samples to chemical bulk aerosol composition did not allow to identify the nature or source of IN active at low supercooling. Potentially important particle classes are mineral dusts and biological particles advected with dust or from marine ~~source~~sources. Based on laboratory measurements of the ice nucleation efficiency of Saharan dust from the Hoggar region, Pinti et al. (2012) suggested that during dust events sufficient dust IN active between -13 °C and - 23 °C could be present at Cape Verde to initiate cloud glaciation. Classification of source regions into 7 prevalent situations support the importance of continental IN by slightly elevated median IN-concentration during continental air mass situations.

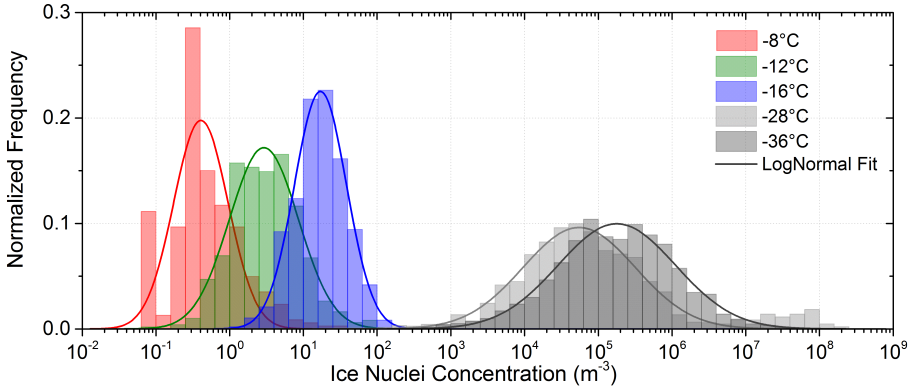

Figure 5. Frequency distribution of measured IN-concentration with log-normal fit curves.

From Lidar observations discussed in Ansmann et al. (2009) it is known that generally temperatures need to drop below -20 °C for glaciation to ~~start~~ be detected in altocumulus clouds (altitude 7 km) over the Cape Verde. Cases when clouds glaciated at higher temperatures between -5 °C to -20 °C could often be attributed to seeding of the supercooled cloud with ice crystals from clouds at higher altitude. The present measurements of potential IN-concentrations at ground level indicate that glaciation can start at higher temperatures, but OSCIP (indicated in Fig. 1) would typically be reached at -20 °C.

The main problem to identify the composition or source of IN by correlating concentration measurements with information on bulk chemical composition must be the small fraction of IN in all particles. Only when an IN source contributes ~~a~~ an unusual large fraction to the aerosol e.g. during a dust storm (Boose et al., 2016) or downwind of a forest fire (McCluskey et al., 2014), bulk chemical composition can corroborate the IN source. Efforts to pinpoint the ~~contribution to IN-concentration~~ contributions from specific sources should focus on measuring close to the source or investigating collected samples under laboratory conditions.

No evidence was found that the ocean is a general source for high IN-concentration in the subtropics. This confirms observations by e.g. Isono et al. (1959); Carte and Mossop (1960); Hobbs and Locatelli (1970) that IN-concentration in air masses with a purely maritime trajectory tend to be low. Ice nucleating particles that can originate from sea water and are active at low supercooling (Schnell and Vali, 1975; DeMott et al., 2016) might be airborne in too low concentrations and in general only contribute as a minor source to the background concentration. However, low IN-concentrations must not indicate low ice crystal numbers in developed clouds if conditions favor secondary ice multiplication mechanisms. Also in particular circumstances (e.g. algae bloom) the purely marine IN could be of regional importance. Burrows et al. (2013) and Vergara-Temprado et al. (2017) suggest strong regional differences in the importance of marine biogenic and dust IN, with the highest impact of marine IN on cloud properties in the remote Southern Ocean far from strong dust sources.

Filter samples are collected on timescales of 1 to 3 day sampling time, resolving variations on a synoptic scale (order of 1000 km, typical for frontal systems). The sampling strategy is chosen based on the assumption that concentration and compo-

sition of aerosol are constant within the horizontal scale of the air mass passing the sampling spot in this time (Anderson et al., 2003). Using filter samples aiming for aerosol composition monitoring therefore provide insight into variation and concentration of IN on a synoptic scale. The sampled air volume and the drop freezing method confine the sensitivity of the measurement to the rare IN active at low supercooling. Consequently the present time series obtained from filter samples gives information on the variation and concentration of highly active IN on a synoptic scale. From SPIN measurements (cf. Fig. 5) using a sampling time of 10 s (corresponding to a scale on the order of 100 m), high variability within the synoptic scale is observed. Although SPIN measurements are at lower temperatures where different particle types contribute to the IN population, the variability of rare IN counts, if it could be observed at high temporal resolution, could be of the same order as the variation in low temperature IN-concentration. Only due to the extend of the filter time series, the range of variability at the sample location ~~partly covers a range of variability that~~ approaches the range observed in the much shorter time domain. This highlights the need to collect large enough (long time-serie or high frequency) data sets to characterize variability and correlation to aerosol properties.

10 Conclusions

Typical IN-concentrations in the subtropic, marine environment are obtained from 500 particle filter samples collected over ~~4-year~~ 4 years and from a 2-month field campaign with the SPIN instrument. ~~Besides establishing typical concentrations in a broad temperature range, fluctuations in the continuous filter data set are compared to aerosol chemical information and airmass origin to investigate possible sources and probable chemical composition of IN. The subtropic, marine ice nuclei concentration is highly variable~~ Concentrations increase exponentially from $10^{-1}\,\mathrm{m}^{-3}$ to $10^{6}\,\mathrm{m}^{-3}$ between -5 °C to -38 °C. Over time, the concentration varies up to three orders of magnitude on a synoptic scale ~~and even more~~ (filter samples) and up to four orders of magnitude on a higher resolution (SPIN measurements). The frequency ~~of measured concentration is approximately log-normally distributed, pointing to a major influence of turbulent~~ with which certain concentrations are measured at a temperature T follows a log-normal distribution, characteristic for successive random dilution during long-range transport~~from the source on IN-concentration. Dilution during transport can effect the~~. The log-normal frequency distribution is found at all investigated temperatures. Parametrizations in numerical models should reproduce this feature.

For the long-term series of filter measurements, we find that random dilution during transport could account for larger fluctuations in IN-concentration ~~more than season, air-mass source region or bulk chemical~~ than seasonal changes, changes in air mass origin and changes in the bulk aerosol composition. ~~Continental~~ At Cape Verde, the later do not reveal a clear correlation to the measured IN-concentration. The only observable tendency is that continental air mass contain higher ~~IN-concentration~~ IN-concentrations than maritime air mass~~. The more marine air-masses are mixed with continental air the lower the IN-concentration. Consequently, mainly long-range transport of randomly diluted continental sources of IN account for the concentration in the cumulative temperature spectra. However, low concentrations of probable biogenic IN, active at T > -10 that could originate from the ocean are found~~, in agreement to previous measurements (e.g. Bertrand et al., 1973) and model predictions (e.g. Burrows et al., 2013). The absence of an annual trend despite a dust and a biological active season is surprising and

highlights the lack of knowledge about the nature of ice nucleating particles.

~~Diversity~~ The diversity of the ice nuclei population manifests in ~~an exponential increase in concentration towards lower temperatures~~ the shape of the cumulative temperature spectra. ~~By comparing the IN-concentration at low supercooling to the aerosol bulk chemical composition it is demonstrated that neither air masses rich in biogenic nor desert dust aerosol generate a strong increase in the measured ice nuclei concentration. Consequently the small subset of aerosol active as IN from these sources is either not constant or different sources account for the fraction of ice nucleating particles in the maritime environment.~~ The contribution of each source to the ~~cumulative~~ temperature spectra depends on the source strength, ~~fractional mixing (according to the successive, random dilution theory) with IN free air~~ dilution during transport and the temperature range to which the source contributes ~~ice nucleating particles~~efficient IN. Multiple sources~~of temperature specific activity~~ , together with random dilution~~create~~ , could produce the appearance of an ubiquitous, almost constant background concentration of IN.

~~Irrespective of season and air mass origin, the frequency distribution of ice nuclei concentrations at a certain temperature can be described by a log-normal distribution. Parametrizations in numerical models should reproduce this feature.No fixed ration between the concentration of dust, marine or any other particle type and IN-concentration was found. This is in agreement with Bertrand et al. (1973) who observed a varying ration between the concentration of dust and IN at -20 in West Africa.Assuming 1000 IN/m^3~~ Assuming $10^3\,\mathrm{m}^{-3}$ to be a threshold ~~concentration (Rangno and Hobbs, 1988)~~ IN-concentration to have a significant, primary effect on properties of supercooled clouds, temperatures below the range covered by the drop freezing ~~experiments~~ experiment used in this study, need to be reached to have an effect. If the temperature dependent IN-concentration exponentially increases with the slope of the Fletcher (1962) approximation, a primary effect of ice nucleation by immersion freezing on cloud glaciation and precipitation formation can be expected at $-20\,^{\circ}\mathrm{C} \pm 5\,^{\circ}\mathrm{C}$, matching the -20 °C alto cumulus cloud glaciation temperature over Cape Verde reported by Ansmann et al. (2009). The SPIN data measured at temperatures below -24 °C support the temperature trend. Given that measurements of IN-concentrations at ground are representative for higher altitudes, the observation of cloud glaciation at $-20\,^{\circ}\mathrm{C}$ where IN-concentrations reach OSCIP support the importance of immersion freezing on cloud properties in a subtropical, marine environment.

Acknowledgements. We acknowledge financial support from the European Union's Seventh Framework Programme (FP7/2007-2013) project BACCHUS under grant agreement n°603445. We would like to thank the UK Met Office for use of the NAME dispersion model and the STFC JASMIN supercomputer for hosting the model. Collection of filter at CVAO was made possible thanks to support by the German BMBF within the SOPRAN I and II projects (FKZ: 03F0462J and 03F0611J). *É*lise Beaudin, Nadja Samtleben, Lisanne H*ö*lting, Mareike L*ö*ffler and Pit Strehl were principally responsible for preparation and conducting the filter sample experiments. Thomas M*ü*ller provided particle size distribution measurements from CVAO.

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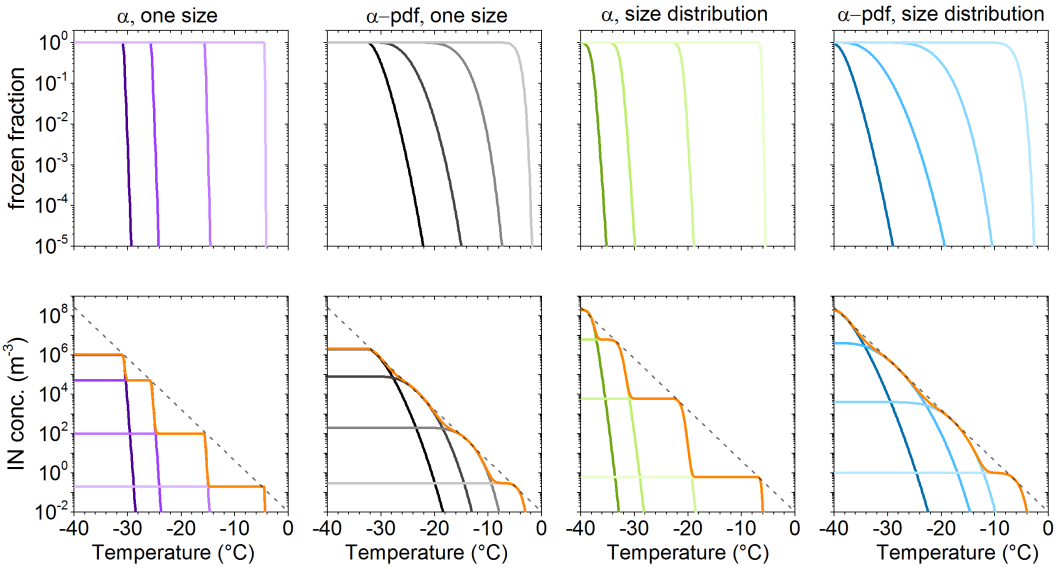

Figure A1. Illustration of the framework of the cumulative temperature spectrum. Each sub-figure in the upper row shows frozen fraction curves of four IN-groups with mean contact angles (α) of 120°, 90°, 60°, 30°. Above the sub-figures, variation in contact angle and particle size distribution within the IN-groups are indicated. A normal-distribution of contact angles (with $\mu = \alpha$, $\sigma = 6°$) and a log-normal particle size distribution are used to visualize the effect of variability within the four IN-groups. The second row shows scaling of frozen fraction with IN-concentrations per group chosen so curves touch the exponential parametrization of Fletcher (1962).

Appendix A: Temperature spectra of cumulative IN-concentration

Four exemplary temperature spectra, produced using classical nucleation theory to describe immersion freezing are shown in Fig A1. A contact angle distribution (α-pdf, e.g. Welti et al., 2012) emulates the variation of ice nucleation efficiencies within a macroscopic homogeneous (size, composition) population of particles. Including particle size-distribution describes the effect of different surface area within a particle population of the same material. Comparing the four sub-figures in the top row of Fig. A1, it can be seen that the effect of a contact angle distribution on flattening the slope of the frozen fraction (FF) is stronger than particle size variation.

In the following we explore typical features found in temperature spectra. We refer to IN species with the same frozen fraction curve as IN-group. The number of IN in an IN-group scaled with its temperature dependent FF determines the IN-concentration a group contributes to the temperature spectra. The number of IN as a function of temperature, i.e. the cumulative temperature spectra of an ambient measurement, consists of the IN-concentration from several IN-groups with partly overlapping activation temperatures (temperature where 0<FF>1).

Several IN-groups can sum up to an almost smooth exponential temperature spectra with no inflections (bumps). In this case the points of inflection in the frozen fraction of individual IN-groups (FF=0.5) construct the slope of the spectra (cf. Fig. A1

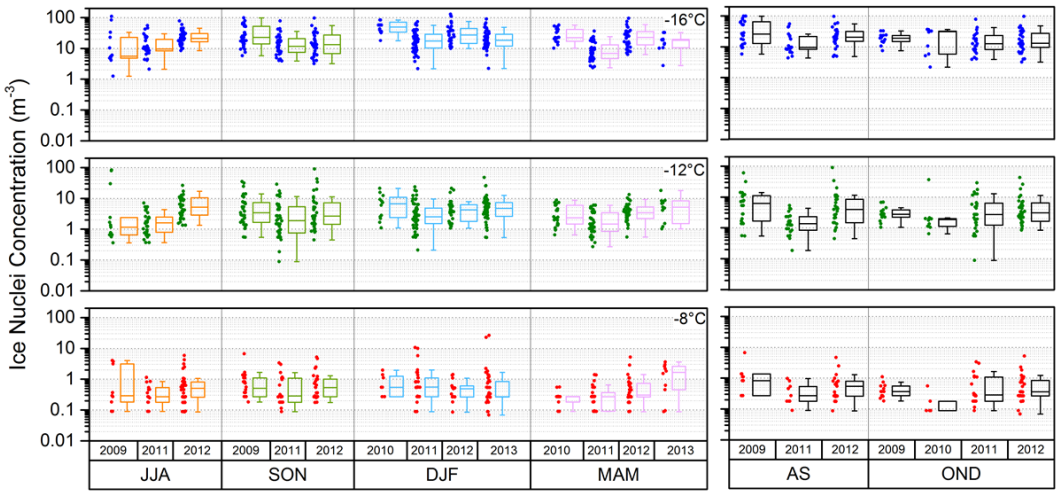

Figure B1. Seasonal variation in ice nuclei concentration separated for each year of measurement. (JJA=~~Jun.-Aug~~Jun.-Aug., SON=~~Sep.-Nov~~Sep.-Nov., DJF=~~Dec.-Feb~~Dec.-Feb., MAM=~~Mar.-May~~Mar.-May). Boxplots of the rainy season (AS=Aug.-Sep.) and the season of high biological productivity (OND=Oct.-Dec.)

second row). Reporting average freezing temperatures (T_{50}) of FF=0.5 from laboratory studies are therefore a well suited measure to transfer these results to ambient ice nucleation.

Fluctuations in the number of IN in different IN-groups (e.g. due to advection of incompletely mixed air parcels with different IN content, Bigg and Hopwood, 1963) lead to a variation in the slope of the temperature spectra or cause a bump (see below). A multitude of temperature spectra make the spread in observed IN-concentration seen in Fig. 1 with the frequency distribution shown in Fig. 5.

Temperature spectra with bumps, from the combination of 4 IN-groups are shown as orange lines in the bottom row of Fig. A1. The more narrow the IN properties of an IN-group, the steeper the increase in FF and the more step like it appears in a temperature spectra. A broader distribution of IN properties decreases the slope. High concentration of a single IN-group would emerge as step like peak over the other contributions. Note that a combination of 4 IN-groups with broad distribution of IN properties suffice to approximate an exponential temperature spectra.

Additional discussion of temperature spectra can be found in ~~Bigg (1961); Bigg and Hopwood (1963)~~ Bigg (1961); Bigg and Hopwood (19 Vali (1971).

Appendix B: Seasonal variation of IN-concentration

Fig. B1 shows the range of seasonal and inter-annual variation in IN-concentration during the measurement period. Although air mass origin is correlated to season (dust storm season from Dec-Feb, cf. Fig. 4), no seasonal trends are found. Inter-

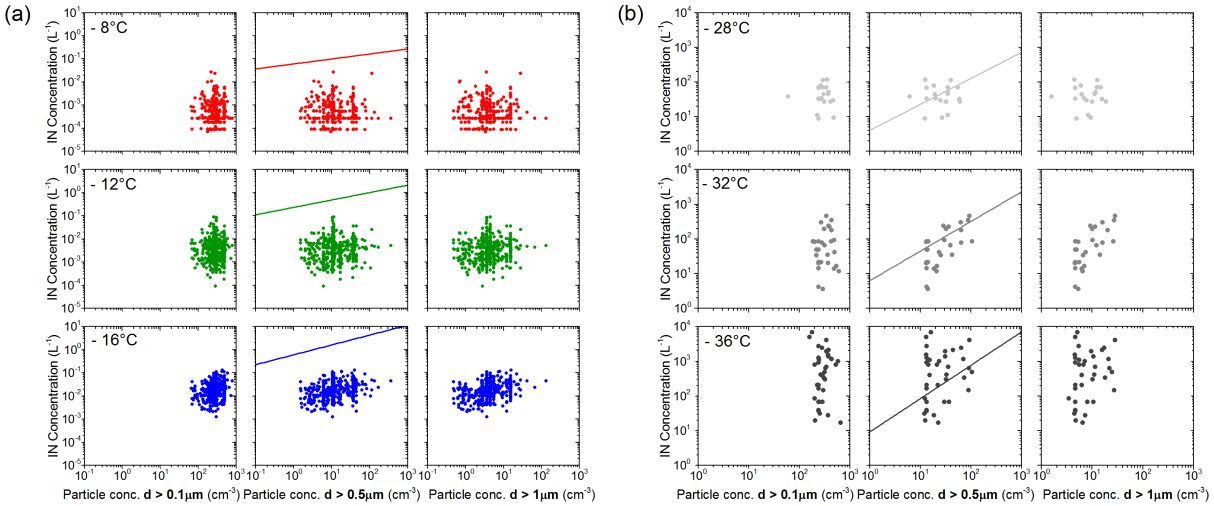

Figure C1. (a) 24 to 72-h average IN-concentration from filter experiments on the y-axis against total concentration of particle with diameter larger than 0.1µm, 0.5µm, 1µm on the x-axis, (b) 30min average IN-concentration from SPIN experiments versus total concentration of particles larger than 0.1µm, 0.5µm, 1µm. IN-concentration predicted by the DeMott et al. (2010) parametrization are given in the center row of (a) and (b).

annual variability within seasons are small during the four year of measurements. Rainy season and season of high biological productivity do not affect the measured range of IN-concentration.

Appendix C: Comparison of IN-concentration to number concentration of aerosol particle with diameter larger than 0.1µm, 0.5µm, 1µm

IN-data in Fig. C1(a) at -8 °C, -12 °C, -16 °C are from filter measurements. IN-concentrations shown in Fig. C1(b) at -28 °C, -32 °C, -36 °C are measured using SPIN. The comparison is made for concentration of particles with diameter larger than 0.1 µm, 0.5 µm, 1 µm. IN- concentrations calculated according to the DeMott et al. (2010) parametrization which connects the concentration of aerosol particles above a threshold size to IN-concentration, roughly match the range of SPIN data in Fig. C1(b) within one order of magnitude. Discrepancy is largest for low particle concentrations. IN-concentrations from filter measurements are systematically lower than predicted by the parametrization. Note that the predicted concentration lies above the range of sensitivity of the filter method used in this study. Correlation of IN-concentration to the concentration of particles larger than a certain size is higher for 0.5µm and 1µm than 0.1µm. Non of the correlations is significant.

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