Properties of cloud condensation nuclei (CCN) in the trade wind marine boundary layer of the Eastern Carribean Sea - response to reviewers

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Dear Editor

We would like to thank you for handling this manuscript - and we would like to thank the two anonymous reviewers for their thorough review of the manuscript. We find that their suggestions have improved the paper. Below we present our response to the referee comments (I), and a revised version of the manuscript (II).

I. The referee comments are listed and addressed below in a point-by-point fashion. Our comments/changes are written in *italics*. A couple of minor changes have been included in this version of response to referees - relative to the comments posted online on ACPD as part of the discussion - and those are indicated in **bold**. Below the response to referees - a few minor changes suggested by the authors are listed. All page- and line-numbers below refer to the published ACPD paper.

II. After the response to reviewers a version of the revised manuscript is included - with changes indicated in **bold**. A few changes are not indicated in bold - such as the modified title, the modified running title, the added references, and the minor graphical changes made to figures 1, 2, 3, and 6.

Anonymous Referee #1

The manuscript "Properties of cloud condensation nuclei (CCN) in the trade wind marine boundary layer of the Eastern Caribbean Sea" by Kristensen et al. presents the results of a month-long campaign in Barbados focusing on the CCN properties of the ambient aerosol. The paper discusses on-line particle measurements, including CCN number concentrations and aerosol particle size distributions, as well as the CCN parameters derived from these measurements. The presented work is further supplemented by an off-line particle analysis utilising transmission electron microscopy and energy-dispersive X-ray spectroscopy techniques. In general, the paper is a wellrounded overview of the CCN properties in the marine environment in question; it is well-written and contains new and

exciting information in the field of ambient CCN studies. I recommend this paper for the publication in the Atmospheric Chemistry and Physics journal after the following general comments and technical corrections have been considered.

General comments

1. At the moment the main concern of the manuscript is exactly why there is not as much sea salt aerosol (and hence, low kappa values) as one would expect from a marine environment location. The authors say that the wind direction was from the ocean sector for > 95% of the time, and the top panel in Fig. 1 shows that the wind speed was predominantly above 6 m/s throughout the campaign. All begging the question: where was the sea salt? CCN in marine environments have been investigated in detail in published literature, and authors do compare their results to other campaigns in the region. However, at the moment, the discussion as to why exactly sea salt concentrations were so low and such low kappa values were observed is insufficient. An unsuspecting reader would be very surprised to see kappa values of 0.3 across the whole size range for a location dominated by marine air masses. I recommend to expand sections 5.2 and/or 6 to include the discussion about the abovementioned apparent discrepancy. What was so different about the meteorological conditions (besides the wind speed) during the first day of measurements? Do the references of (Monahan and Muircheartaigh, 1980; O'Dowd and de Leeuw, 2007) provide any numerical estimates of the fluxes of sea salt particles as a function of wind speed, and how do the presented data compare to those numbers? Was anything different about the instrumental setup during the first day of measurements? Has anybody previously reported such low hygroscopicity in the marine environment? Was the Köhler equation used correctly (see minor comment #7 below)? Since the presented results are that different from the published literature (both experimental and modelling), it is important to provide enough detail as to why that is the case.

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Referee 1 finds that in comparison to the literature the reported κ_{CCN} values are unexpectedly low, and the influence from sea salt is surprisingly low. The CCN activity results presented in the manuscript provide information related to the mobility particle diameter size range from ⌣50 to ⌣200 nm. Based on hygroscopicity measurements for that size range available in the literature from the marine boundary layer (MBL), it appears that the hygroscopicity typically is dominated by inorganic sulphate species with a potential significant influence from organic species and occasionally a moderate influence from sea salt (Swietlicki et al., 2008) with the most pronounced hygroscopicity mode being represented by a κ value of ⌣0.45 (Wex et al., 2010). Pringle et al. (2010) modelled the CCN activity in the MBL in the region where our measurements were carried out. They predicted a κ value of 0.6-0.7 in winter and a κ value of ⌣0.4 in summer, which fits very well with our reported results from the summer period and the previous measurements in the region carried out during winter (Allan et al., 2008; Hudson, 2007; Pringle et al., 2010). Hence, our reported CCN activities are very much in line with what could be expected from various previous measurements and model studies. Furthermore, our results agree with the reported chemical composition of particulate matter in the relevant size range in the region being dominated by inorganic sulphate and organic species (Novakov et al., 1997).

Answers to specific questions raised by the Referee:
During the first day of measurements - nothing but the maximum in wind speed stands out when it comes to the local meteorology. Hence, it may be that the indication of an enhanced fraction of sea salt was to a larger extent produced up-wind on this particular day.
O'Dowd and de Leeuw (2007) mention that sea salt can reach a maximum number concentration in the MBL of 50-150 cm^{-3} under high wind conditions. Of course much higher wind speeds than the observed ⌣14 m/s can be encountered in the MBL, so it is likely that the number concentration of sea salt in general is much lower in our case - as also indicated by our findings.
The instrumental set-up was identical for the entire time period covered in the manuscript.

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The Köhler equation was used correctly - as shown below ('Minor and technical comments': #7)).

To sum up: Our findings of a negligible influence from sea salt in the diameter range from ⌣50 to ⌣200 nm agrees very well with most previous findings in the MBL. It is likely that relatively higher wind speeds are needed for a significant fraction of sea salt particles in that size range.

The text has been modified accordingly to make this agreement with previous findings more clear. A comparison to the modelled κ is included (see below under 'General comments': #2) (Pringle et al., 2010). The following has been added after P30770L22: "Wex et al. (2010) reviewed measurements of particle hygroscopicity for sub-saturated conditions in the MBL and found that the dominant κ value was around 0.45, but also several observations with lower κ values and fewer with higher κ values have been made. Hence, our inferred κ values are slightly lower than what most frequently can be expected in the remote MBL."

2. While the authors do compare their results to several other published studies, it might improve the paper to put the results in the global perspective using any of the many overview papers discussing CCN properties at a multitude of locations around the world (including marine). CCN concentrations can be compared to e.g. Andreae (2009), while CCN concentrations and hygroscopicity can be compared to e g. Paramonov et al. (2015).

The CCN number concentration has been compared to results reviewed by Andreae (2009), and the inferred κ values have been compared to the model results presented by Pringle et al. (2010).

The following sentence has been added after P30769L14: "Andreae (2009) reviewed measurements of CCN number concentrations at an SS=0.4% in the 'clean' MBL and reported an average concentration of 107 ± 56 cm^{-3}, with slightly higher values for the

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Atlantic. Hence, the median CCN number concentration of 205 cm^{-3} we observed for an SS=0.4% is in the higher range for the remote marine MBL."

The following sentence has been added after P30770L22: "Pringle et al. (2010) modelled the κ values in the region to have a maximum of $\backsim$0.7 in winter with a κ value of $\backsim$0.4 in summer, which agrees very well with our findings."

Minor and technical comments

1. While the paper is well-written, its quality and clarity can be greatly improved with the proper use of punctuation. This refers to the use of connector words, the word "respectively" and sentences consisting of two or more clauses.

Commas have been added in the following lines: P30759L05, P30770L21. [**We have consulted a native British speaking person who does not agree that the specific proposed punctuation will improve the language in the manuscript. We also do find that the scientific messages do not suffer from the chosen punctuation. However, the punctuation details are not crucial to us - and if wished for by ACP - the suggested punctuation changes can be carried out easily.**]

2. Similarly, please, be consistent with the use of British English or American English (e.g. sulphate vs. sulfate).

"Sulfate" has been changed to "sulphate" in P30759L09 and P30766L23

3. Make sure that all instances of the noun "data" in the text reflect its plurality.

The plurality of data is now reflected in the following lines: In P30771L19: 'data was' -> 'data were'. In P30772L08: 'data provides' -> 'data provide'. In P30787 Fig. 2 caption line

2+3: 'data covers' -> 'data cover'.

4. Please, consider the use of past tense when talking about the experiments you conducted. Section 4.2 is one instance where the present tense is used in several sentences.

Past tense has been introduced in the following lines:
P30766L14: "is" -> "was". P30766L24: "remain" -> "remained". P30766L25: "can conclude" -> "concluded". P30767L01: "is" -> "was".

5. page 30759, line 1 – change the (IPCC, 2013) reference to (Boucher et al., 2013)

The reference has been changed from (IPCC, 2013) to (Boucher et al., 2013) as suggested.

6. When discussing the marine organic compounds and their effect on CCN hygroscopicity (as, for example, on page 30760, 2nd paragraph and on page 30776, 2nd paragraph), a useful reference could be Ovadnevaite et al. (2011).

Ovadnevaite et al. (2011) do not report the CCN activity of the studied aerosol particles, and their qualitative arguments related to the CCN acitivity does not account for differences in particle number size distributions. The focus of their study is primary marine organic compounds. The organic compounds present in the current study are likely to be of secondary origin (Mayol-Bracero et al., 2001; Novakov et al., 1997). Thus, we do not find that there is a firm basis for comparing our findings to what is reported in the suggested study.

7. page 30761, equation 1 – what exactly is SS in the equation? If SS is supersaturation in %, it should be possible to enter e.g. 0.7%; this, however, is incorrect as it will lead to an

error. Please, refer to Equation A(30) in Rose et al. (2008) for the correct equation.

SS in the equation is the supersaturation in %. It is indeed possible to use Eq. (1) with e.g. an SS=0.7%, so It is not quite clear which error in Eq. 1 the Referee refers to? If eq. A2 and eq. 30 from Rose et al. (2008) are combined, then Eq. (1) is obtained as presented in the manuscript.
From Rose et al. (2008):

$$S = (s - 1) \cdot 100\% \quad (A2)$$

$$s = \frac{D_{wet}^3 - D_s^3}{D_{wet}^3 - D_s^3(1 - \kappa)} exp\left(\frac{4\sigma M_w}{RT\rho_w D_{wet}} \right) \quad (A30)$$

where S is the supersaturation in percent and s is the saturation ratio in their notation. The remaining parameters are as defined in the Kristensen et al. manuscript - with a few differences in notation. By combining the equations (A2) and (A30) from Rose et al. (2008) the following equation is obtained - which is identical to Eq. (1) presented in the manuscript:

$$\frac{SS}{[100\%]} = \frac{D_d^3 - D_p^3}{D_d^3 - D_p^3(1 - \kappa)} exp\left(\frac{4\sigma M_w}{RT\rho_w D_d} \right) - 1 \tag{1}$$

8. page 30763, line 12 – the units of the flow rate should be volume per time. Please, correct

In P30763L12: The flow rate unit has been corrected to $\sim 40 \, m^3/hr$.

9. page 30764, lines 7-10 – "a critical diameter (D_c) above which all particles activate into cloud droplets for a given supersaturation". This is true only if the aerosol is internally

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mixed. Please, modify

The sentence in P30764L07-10 has been modified to: "For an estimation of the CCN activity, the average CCN number concentration was compared to the simultaneously measured particle number size distribution. Thus, a critical diameter (D_c) above which all particles activate into cloud droplets for a given supersaturation was estimated assuming internally mixed aerosol particles in a sufficient neighborhood around the inferred D_c."

10. page 30766, lines 16-19 – the sentence is not very clear; please modify

The sentence in P30766L16-19 has been rephrased from: "As during particle analysis, the volatile material of the particle evaporates and the refractory fraction remains, images were recorded at the beginning of the electron bombardment and after no more visible change in particle structure occurred." to: "During the electron beam analysis, the particles absorbed energy and heated up. Hence, the volatile particulate material evaporated and only the refractory fraction remained on the substrate. To determine the original state, one image was recorded right at the beginning of the electron bombardment. When no more change of the remaining particle fraction was observed, a second image was recorded. Changes to the particles were derived from image comparison."

11. page 30767, lines 12-17 – the wind direction that is used to delineate the northern/ northwestern boundary between the open ocean and the local sources is used inconsistently throughout the text (335° vs. 360°). In text on page 30767 it says that Fig. 1 uses the 360° boundary, the caption of Fig. 1, however, mentions the 335° boundary. Please, fix. Also, lines 15-17 on this page can be removed from the text as they should be in the figure caption (see comment 1 for the Figures).

The 360° has been changed to 335° in P30767L16. P30767L15-17 have been removed.

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12. page 30768, lines 3-6 – this sentence belongs in the figure caption, not in the text.

The P30768L03-06 have been deleted - similar information is available in the figure caption.

13. page 30768, lines 24-25 – the end of the sentence after the comma should read ", and, thus, has not been carried out".

The text has been modified as suggested.

14. page 30770, lines 20-22 – chemical composition and potentially particle sources change with the seasons? It's probably likely that both chemical composition and particle sources vary throughout the year. Please, consider this and check the reference.

The sentence in P30770L20-22 has been modified to: "It is worth noting that the previous measurements were carried out in December and January respectively, and it is likely that the PM sources and chemical composition change with the seasons".

15. page 30771, lines 22-24 – this statement is only true for the time when the experiments were conducted (June and July). It is not possible to say whether this would be true at all other times of the year, since coarse particles may have different chemical composition throughout the year (see page 30770, lines 20-22 and the comment above). Please, modify

Yes, we agree. The following expression was added to P30771L22-24: 'during this campaign, where mineral dust mass concentrations were significant.'

16. page 30773, lines 18-19 – "where the last category contains all refractory substances not belonging to any of the first mentioned groups". Such as?

An example of a refractory particle not classified as 'soot', 'soot-mixture', 'dust', nor 'sea-salt' is shown in Fig. 5 V.b. As can be seen from Fig. 6.c+d: unidentified refractory particles did not comprise a significant volume fraction. The following sentence has been added after P30773L19: 'An example of a refractory particle classified as "other" is shown in Fig. 5V.b'.

17. On two different instances (page 30774, lines 15-18 and page 30776, lines 19-20) the paper mentions that the investigated aerosol can be considered to be representative of the (Eastern) Caribbean Sea. This is technically not true for two reasons. First, the geographical eastern boundary of the Caribbean Sea goes along the line of Lesser Antilles, of which Barbados is already the easternmost island. Second, it is mentioned in the text that during > 95% of the measurement time the wind direction was from the 0° to 130° sector (the ocean), meaning that the aerosol did not, in principle, spend any time at all above the Caribbean Sea. The investigated aerosol is, therefore, more likely representative of the Atlantic Ocean (or the westernmost tropical Atlantic, to be completely precise), with influence from long-range transport, as mentioned in the text. Please, modify.

The expression in P30774L17 has been changed from: "representative for the Eastern Caribbean Sea" to: "representative for the trade wind MBL of the Western North Atlantic.". As a consequence of this referee-comment/modification several other corrections have been carried out:
The title has been changed from: "Properties of cloud condensation nuclei (CCN) in the trade wind marine boundary layer of the Eastern Caribbean Sea" to "Properties of cloud condensation nuclei (CCN) in the trade wind marine boundary layer of the Western North Atlantic"
The running title has been changed from: "CCN Caribbean" to: "CCN in the trade wind

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*In the abstract, P30758L05: "Eastern Caribbean" -> "**tropical** Western North Atlantic".
P30759L27-28: "Eastern Caribbean" -> "**tropical** Western North Atlantic". P30777L14: "in
the trade wind marine boundary layer in the Eastern Caribbean Sea" -> "in the trade wind
marine boundary layer in the Western North Atlantic".*

*In P30776L the statement about the location does not only refer to our presented data
but also to the LIDAR measurements carried out by Groß et al. (2015) on the west coast
of Barbados. So "Mineral dust was observed over the Caribbean Sea" has been changed
to: "Mineral dust was observed over the Eastern Caribbean Sea/**tropical** Western North
Atlantic".*

18. page 30774, line 26 – "was" should be changed to "were"

P30774L26: "was" -> "were" as suggested.

19. page 30774, lines 26-27 continuing to the next page 30775, lines 1-7 – the authors
first state that during most of the campaign the mass concentrations of mineral dust were
significant. The authors then go further and say that the bulk of the particles was dominated
by non-refractory species and that the concentration of refractory PM was minor. This is
confusing and somewhat contradictory. The authors should either clarify what they mean by
"significant" when talking about mass concentrations of mineral dust or replace "significant"
with a more appropriate adjective.

*The fact that very small mineral dust concentrations are observed in the accumulation
mode by use of TEM is not necessarily contradictory to significant dust mass concen-
trations being present simultaneously - since the mineral dust appears to dominate the
supermicron size range during the campaign. To make that more clear - the following
sentence:*

"The majority of the investigated particles were found in the accumulation mode, and in general the bulk of the particles were largely dominated by non-refractory substances." *has been extended to: "The majority of the investigated particles were found in the accumulation mode, and in general the bulk of the investigated particles were largely dominated by non-refractory substances. Those findings indicate that the mineral dust primarily was present in the larger particle size ranges in the MBL during the campaign."*

20. page 30776, lines 2–4 – while the chemical composition can be comparable, the kappa values are most certainly not. Reconsider.

Novakov et al. (1997) and companion studies related to the properties of organic species in aerosol particles on/near Puerto Rico did not report any direct measurement of the CCN activity since the applied method/approach is indirect and associated with significant potential errors (Novakov and Penner, 1993; Novakov et al., 1994). So it is not quite clear if the κ value of the organic species in the previous studies indeed would be substantially higher than e.g. 0.08. Since our comment only is related to the organic fraction - we do not find that it is misleading.

21. page 30776, line 29 – please, fix the reference parentheses

The reference parenthesis has been modified as suggested.

22. page 30777, line 1 – should read ". . .emissions are the main source. . ."

The text has been modified as suggested.

Figures and Tables

1. Fig. 1 – for the mid panel (wind direction), please, extend the y-axis to 360°. The figure caption does not say what the horizontal dashed line is. If the boundary of 335° is correct (see minor comment #11 above), also include the horizontal line for this wind direction. Shading instead of the grey vertical dashed lines may also improve the figure.

The y-axis of the mid-panel has been extended to 360° as suggested, and the boundary of 335° has also been indicated by a horizontal dashed red line. The vertical dashed lines have been replaced by shading with a more light gray colour. The figure caption has been modified accordingly as suggested.

2. Fig. 2 – the first sentence of the figure caption should read "Size distributions corrected neither for particle losses in the tubing nor for detection efficiency". OR "Size distributions not corrected for particle losses in the tubing or for detection efficiency". Also, to improve the detail, the upper panel of Fig. 2 can be wider, if possible. The label of the colour bar must include (cm^{-3}).

The first sentence of the caption has been modified as suggested.

3. Fig. 3 – is there a reason that the data at SS of 0.3% are missing in the upper panel?

The reason for excluding the data at SS=0.3% was graphical and not due to any scientific reasoning. The data at SS=0.3% are now included in the figure for completeness.

4. Fig. 6 – in the caption for panels (a) and (b), there is no need to describe the refractory classes and the associated colours. This information is easily visible in the legend. Defining rf here is sufficient.

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The figure caption for Fig. 6 has been shortened as suggested.

5. Table 1 – in the caption, are presented kappa values averages or medians? Also, please, mention in the text (section 3) that the CCNC measured at the SS of 0.3% only during the last 15 days of the campaign.

The presented κ values are medians. The caption has been modified as suggested.
In P30763L03 the following has been added: "Supersaturation settings of 0.1%, 0.2%, 0.4%, and 0.7% were applied throughout the campaign, and an SS=0.3% was included during the last 2 weeks of the campaign."

Anonymous Referee #2

The paper presents cloud condensation nuclei concentrations together with aerosol particle number size distributions and off-line particle analysis as observed in the marine boundary layer (MBL) in the Eastern Caribbean (Barbados) in June/July 2013. With this set of instrumentation the authors wanted to assess how organic species from marine biological activity, long-range transported mineral dust, and sea salt particles affect the particles' ability to act as CCN since in the past several contradicting observations have been made for MBL aerosol. Better knowledge of aerosol-cloud interaction, however, is necessary for the correct incorporation of clouds in climate models, especially those in the MBL. Interestingly no significant number or volume fractions of sea salt or dust could be observed in the sub-micron range, which is the relevant size for CCN activation. Thus the inferred hygroscopicity parameter, kappa, can be only explained by a mixture of sulfate and organics. The paper is well structured and discusses the results nicely. The information given in this manuscript is relevant for the readers of ACP and of interest for the community in general. I recommend the paper for publication in ACP after the following comments and

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corrections have been considered by the authors.

General comments:

1. The authors mention that all the in-situ measurements were carried out through a PM10 inlet located at the top of a 17 m high tower. In contrast, the dust mass was obtained from a high-volume sampler collecting total PM and the TEM samples were taken with a cascade impactor with nominal cut-sizes of 530 nm to 90 nm or 330 nm to 90 nm, respectively. There are two things, which should be considered. Firstly, all instruments cover different size ranges. This should be emphasized a bit more in the paper by adding the size ranges at several places in the text (see following specific comments). Secondly, different line losses are probably involved in the measurements. Samples for off-line analysis were collected directly at the top of the tower, whereas the inlet for the online instruments was located on the top of the tower with the instruments placed on the ground level. It is written that no correction for coarse particles in the sampling lines was made because it is "uncertain". I do not understand what the authors mean with "uncertain". If they know all the tube lengths, bends and flow rates they should be able to calculate the losses (von der Weiden et al., 2009). I think that this correction is very important since one expects to have relatively high numbers of coarse particles for the air masses involving mineral dust and sea salt and since there was a quite long way from the inlet to the instruments. Indeed, the gravitational settling in a (hopefully mostly) vertical line are small, but already for short horizontal lines losses of particles larger than $1 \mu m$ are quite substantial. If the correction for line losses were included, it would affect the estimated PM but maybe also the derived kappa. In contrast, the offline samples should be, I guess, not affected by substantial losses. I do not know in which way the sampling lines were installed during the campaign, so maybe the effect is only little, but I think the authors should discuss in more detail in their paper what the effect of losses can be and how that translates in the comparability of the individual measurements.

The sampling line from the top of the tower down to the ground level was kept as close to vertical as possible, but it was put together by several different pieces and possible minor bends were not characterised in the field. That is the reason for not including any (uncertain) correction for losses of coarse particles in sampling lines. In Fig. 4 the dust mass measured from filter samples is compared to the PM mass estimated from the measured particle number size distributions in the size range above 0.5 μm. There is a high significant linear correlation between the two data series, and the total dust mass concentration is approximately a factor of 2 higher than the estimate obtained from the size distributions. It is likely to be due to losses in the sampling line of particles larger than $\smile$2 μm as indicated by the lower panels of Fig. 2. Hence, the actual coarse mode particle number concentration is likely to be a factor $\leq$2 higher than the measured one. As can be seen from Fig. 2 (lower panel to the left), the number concentration in the coarse mode is still an order of magnitude lower than the number concentration in the accumulation mode if a scaling factor of 2 is applied to the coarse mode number concentration. As argued below in P30764L07-10, the particle number concentration in the size range >0.8 μm did not contribute significantly to the total number concentration of CCN.

2. On page 30763, the authors write that "to minimize impacts from local sources sampling was controlled by a wind sensor and only carried out when the local wind direction was in the range 335° . . . to 130°, and the wind speed exceeded 1 m s^{-1}". This refers to the high-volume sampling, but does this also apply to the impactor sampling and to the size distribution and kappa averaging? It does not say so in the paper. If not, what would be the expected difference of data points within this wind pattern compared to the rest of the data points? Would not the influence of local sources be more significant for Aitken and accumulation particles (the main size range of TEM samples, CCN and size distribution measurements). Would it make sense to exclude times with local influence for the size distributions, CCN properties and TEM analysis?

The time periods where the wind direction indicates that local land based sources cannot be ruled out are indicated by gray shadings in the figures 1 and 3. In Fig. 4 only time periods when local land based sources can be ruled out are included in the figure. During the sampling of the TEM samples included in the present study, the wind direction was in the range from 84° to 110°, which is well within the boundaries for sampling the marine air masses (335° through North to 130°). The sentence: "Sampling was carried out while local wind directions were in the range from 84° to 110°" has been included in P30772L04. For all results presented in Table 1, time periods when local land based sources cannot be ruled out (based on local wind direction/speed) have not been included in the calculations. The following has been added to the beginning of the caption of Table 1: "For time periods where local land-based sources can be ruled out:"

3. The authors motivate their study with the need for better understanding of aerosol-cloud interaction in order to incorporate MBL cloud development into climate models. My question is whether it can be expected that the observed CCN properties also prevail at higher altitudes in the atmosphere, i.e., at levels where clouds form? What if there is a dense long-range transported dust layer at higher altitude including large numbers of coarse particles? They would all be activated into cloud droplets no matter what their hygroscopicity is. Please compare the study by Jung et al. (2013), who report significantly increased CCN concentrations in a Saharan dust layer at ∽2.2 km altitude compared to ground levels. It would be nice if the authors could discuss the effect of strongly changing aerosol load with height on cloud formation.

We expect that our measurements carried out ∽50 m asl are representative of the conditions in the well mixed marine boundary layer (MBL). Hence, our reported CCN properties are relevant to low level clouds. Werner et al. (2014) reported cloud bases down to 500 m asl and reported evidence for the Twomey effect in shallow trade wind cumuli near Barbados. During the SALTRACE campaign, shallow cumulus clouds were frequently observed at altitudes up to 2 km. At higher altitudes the mineral dust was present and typical

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relative humidities too low for cloud formation (Groß et al., 2015). Aircraft measurements of CCN properties were carried out during the SALTRACE campaign and the vertical profiles of CCN properties are subjects of publications in preparation.

To make it more clear that our study only is relevant for the MBL and low level clouds, the following change has been carried out: P30761L03-04: "...may influence the CCN properties in that region" -> "...may influence the CCN properties in the MBL in that region"

Specific comments/ Technical corrections:

TEM samples: On p. 30763 is written that there were two time periods of sampling for which different size ranges were analyzed. The different size range is an important point and should be mentioned not only in Sect. 3 but also in Tab. 2, Fig. 6, and/or Sect. 5.4. How much can the projected area equivalent diameter (PAED) differ from the aerodynamic diameter? I thought that in general they should be more or less equal. I am wondering because for period 2 the TEM samples have quite high number fractions for PAED > 0.3 μm (higher than for period 1) although the samples were only analyzed for impactor stages up to 330 nm.

TEM size range: The ambient aerodynamic diameter should actually be larger than the PAED for the observed particles, in the range of 1.2-1.5 (driven by density and unknown water uptake at the time of collection). However, we also made a mistake in the procedure description, as the 530 nm cut-off also was used for the second period, but the size range was additionally split by a 330 nm threshold. We have corrected this in the manuscript. The relatively larger fraction of relatively larger accumulation mode particles during the second period corresponds well with the measured particle number size distributions of the accumulation mode during the sampling periods.

Discussion on measured kappa (starting on p. 30775, l. 24): This paragraph tells a lot of estimation on how the measured kappa values could be explained. What I am missing is a bit more detailed explanation on the calculations. For example, it is written that assuming internally mixed species of organics and sulfate kappa is explained assuming 50% organic volume fraction with kappa = 0.08 and 50% sulfate with kappa = 0.6. I understand that this can be calculated from Eq. 2. But in another sentence is written that if an external mixture of sulfate and organics is assumed, an organic volume fraction of 25% would explain the observed kappa. Please make clear how this can be calculated.

P30776L05-07: More details about the calculation of κ assuming an external mixture are provided by replacing: ",but if an external mixture of sulphate and organic species is assumed, then an organic volume fraction at the order of 25% could also explain the observed κ values." by: "However, the measured CCN number concentrations can also be reasonably well modelled by integrations of the particle number size distributions by assuming an external mixture of inorganic sulphate (κ=0.6) and organic species (κ=0.08) and an organic number fraction of $\sim$ 25 % in the diameter range $\sim$ 50–300 nm."

p. 30762, l. 22-25: Please add the respective size ranges that are covered by the individual instruments.

Size ranges covered by the APS and the MPSS have been included.

p. 30764, l. 7-10: Which number size distribution was integrated – the one obtained by MPSS or by MPSS and APS? From the text following it sounds like only the MPSS size distribution was integrated. Please clarify. Since the CCN counter was attached to the PM10 inlet, it would also activate particles larger than 0.8 μm. There might be not many particles > 0.8 μm but still I guess it would make more sense to calculate the critical diameter from integrating the full (MPSS + APS) size distribution. This should lead also to a smaller kappa.

The κ values presented in the paper have been inferred with the measured APS number concentration with diameters >0.8 μm included. A sensitivity study of the inferred κ values was carried out applying factors of 0 and 2 respectively to the particle number concentration in the range >0.8 μm - and the variations in inferred κ values turned out to be insignificant compared to the random errors of the κ values.

p. 30763, l. 12: "flow rate of $1m^3$" per which time?

The flow rate in P30763L12 has been corrected to $\sim 40\,\mathrm{m}^3/\mathrm{hr}$.

p. 30765, 28: I do not understand what the "(SS = 0.074%)" tells.

The SS=0.074% is the actual supersaturation for the nominal SS=0.1%, when the temperature setting in the lower part of the CCN column was lower than the set-point. Change made: "(SS=0.074%)" -> "(with an actual SS=0.074%)"

p. 30773, l. 9: add "of" before "the super-micron"

"of" has been added before "super-micron"

p. 30774, l. 26: change "was" to "were"

P30774L26: "was" -> "were"

p. 30775, l. 9: ammonium sulphate in two words

P30775L09: "ammoniumsulphate" -> "ammonium sulphate"

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p. 30776, l. 1: "if it is. . ." change "it" to "is"

P30776L01: "if it it" has been changed to: "if it is".

p. 30776, l. 29: put the reference in brackets

P30776L29: Brackets have been added to the reference.

p. 30777, l. 10: add "of" before "organic species"

P30777L10: "of" added before "organic species".

Fig. 2: It would be more convenient to display the color bar as real concentration values and not as the logarithm of the concentration. Also, it would be better to distinguish between individual days, if the grid lines were on top of the colored surface plot.

The scale on the figure color bar has been modified and grid lines have been included.

Fig. 3: Please add the CCN concentration at SS = 0.3% to Fig. 3a. Would it make sense to plot the concentration and Dc on a logarithmic scale?

The CCN number concentrations for SS=0.3% have been included in the top panel. We find that a linear scale is appropriate for depicting the CCN number concentrations and the D_c in the relevant range.

Fig. 4: Please add the particle size range that is included in the dust mass and PM_{est}, respectively.

Information about the size ranges have been included in the figure caption: the mineral dust concentration was inferred from the sampled total suspended particulate matter, and the PM_{est} is based on the integration of the particle number size distribution (not corrected for losses in sampling lines) in the range 0.5-10 μm.

Fig. 5 a and b: What happened to the blue sea salt bar? It appears several times in one PAED group and is always behind the other colored bars. Should it not appear as a separate bar next to the others?

The blue color indicates the number fraction of the refractory PM in the given range of refractory fraction and particle size. To emphasize that only a fraction of the total refractory matter is comprised of sea salt - the blue coloring has been moved from the top of the bar to the lower part of the bar.

Corrections suggested by the authors

P30758L05-06: "to assess the respective roles of organic species, long-range transported mineral dust, and sea salt particles." has been changed to: "to assess the respective roles of **inorganic sulphate,** *organic species, long-range transported mineral dust, and sea salt particles."*

P30760L20: The reference Novakov et al. (1997) has been included to support the indication of a biogenic oceanic source of the organic species in the submicron size range.

P30775L01: "mass concentration of dust was" -> "mass concentrations of dust were"

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Properties of cloud condensation nuclei (CCN) in the trade wind marine boundary layer of the Western North Atlantic

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Abstract

Cloud optical properties in the trade winds over the Eastern Caribbean Sea have been shown to be sensitive to cloud condensation nuclei (CCN) concentrations. The objective of the current study was to investigate the CCN properties in the marine boundary layer (MBL)

5   in the **tropical Western North Atlantic**, in order to assess the respective roles of **inorganic sulphate,** organic species, long-range transported mineral dust, and sea salt particles.

Measurements were carried out in June–July 2013, on the East Coast of Barbados and included CCN number concentrations, particle number size distributions, as well as off-line analysis of sampled particulate matter (PM) and sampled accumulation mode particles

10   for an investigation of composition and mixing state with transmission electron microscopy (TEM) in combination with energy-dispersive X-ray spectroscopy (EDX).

During most of the campaign, significant mass concentrations of long-range transported mineral dust was present in the PM, and influence from local island sources can be ruled out. The CCN and particle number concentrations were similar to what can be expected

15   in pristine marine environments. The hygroscopicity parameter κ was inferred, and values in the range 0.2–0.5 were found during most of the campaign, with similar values for the Aitken and the accumulation mode. The accumulation mode particles studied with TEM were dominated by non-refractory material, and concentrations of mineral dust, sea salt, and soot were too small to influence the CCN properties. It is highly likely that the CCN

20   were dominated by a mixture of sulphate species and organic compounds.

1   Introduction

Clouds play an important role with respect to the radiation budget and thus climate on Earth. The concentration of cloud condensation nuclei (CCN) in the atmosphere influences the optical and physical properties of clouds (Andreae and Rosenfeld, 2008). Significant

25   uncertainties are related to the radiative forcing of aerosol–cloud interactions in the climate system (Boucher et al., 2013). Global climate is in particular sensitive to aerosol–cloud

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interactions over the oceans due to the large surface of the oceans and the significant difference in albedo between clouds and the open ocean. There are significant climate-relevant uncertainties related to the CCN budget in the marine environment (Pierce and Adams, 2006), and in general it is very challenging to incorporate marine boundary layer
5 (MBL) clouds correctly in climate models (Bony and Dufresne, 2005).

Submicrometer aerosol particles in the pristine North Atlantic marine environment are comprised of sea salt as well as **sulphate** and organic species dominating during periods with high marine biological activity (O'Dowd et al., 2004). With typically relatively low background aerosol particle number concentrations in the pristine MBL the CCN number
10 concentrations may be perturbed significantly e.g. due to long range transport. Mineral dust particles from Northern Africa are transported by the trade winds across the Atlantic Ocean particularly during the summer season in the Northern Hemisphere (Prospero and Lamb, 2003). Twohy et al. (2009) reported that a large fraction (79 %) of cloud droplet residual particles were comprised of crustal material in the Eastern Northern Atlantic. Jung et al. (2013)
15 reported a hygroscopicity parameter, κ value of 0.02–0.03 for the accumulation mode particles at different altitudes including the MBL, east of Barbados during a pronounced mineral dust episode. Such low κ values close to 0.01 as for pure dust (Garimella et al., 2014; Petters and Kreidenweis, 2007) are indicative of an accumulation mode dominated by dust with only minor amounts of hygroscopic particulate matter (PM) present. Hence, mineral
20 dust particles may play an important role as CCN under certain conditions over the North Atlantic.

Continuous measurements related to aerosol particle properties have been carried out on the east coast of Barbados since the mid 1960s (Prospero and Lamb, 2003). Upwind from the east coast of Barbados there is typically ~ 4000 km of Atlantic Ocean due to the
25 dominating easterly trade winds. Hence, aerosol particles **over** the **tropical Western North Atlantic** are typically of marine origin or are transported over long distances across the Atlantic Ocean. Savoie et al. (1989, 2002) investigated the composition of bulk PM sampled on the East coast of Barbados from the periods 1984–1987 and 1988–1991 respectively. Savoie et al. (1989) reported high correlations between the concentrations of non-sea-salt

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(nss) NO_3^-, nss SO_4^{2-}, and mineral dust which they ascribed to similar transport pathways of the mineral dust and the investigated water soluble nss inorganic species. Furthermore, they reported a minimum in the NO_3^- to SO_4^{2-} ratio in summer and suggested that Europe was likely to be the source region of those species during the summer season. Savoie et al. (2002) reported that biogenic marine nss SO_4^{2-} reaches maximum concentrations around May–June and comprises about 50 % of total nss SO_4^{2-} on a yearly average. Li-Jones and Prospero (1998) sampled size segregated PM at the same site during April, 1994, and they found that nss SO_4^{2-} dominated the PM with aerodynamic diameters smaller than 0.6 µm, while the supermicron PM primarily was comprised of mineral dust, sea salt, nss NO_3^-, and smaller amounts of nss SO_4^{2-}.

In addition to dust and water soluble salts, aerosol particles relevant as CCN over the Caribbean Sea may also contain organic compounds. A number of studies with focus on organic PM have been conducted primarily on or in the vicinity of Puerto Rico, and they are reviewed and summarised by Allan et al. (2008). In short, past studies indicate that there is a significant fraction of organic matter in PM with diameters < 0.6 µm (Novakov et al., 1997), the organic species are hygroscopic (Maria et al., 2002) and efficient as CCN (Novakov and Penner, 1993; Novakov et al., 1997). Mayol-Bracero et al. (2001) **and Novakov et al. (1997)** attributed significant amounts of the organic matter to natural oceanic sources. In contrast to most previous studies Allan et al. (2008) reported low concentrations of organic matter mostly attributed to local anthropogenic emissions. The optical properties of trade wind cumuli clouds over the Eastern Caribbean Sea are susceptible to increased levels of CCN and direct evidence for the Twomey effect has clearly been observed (Werner et al., 2014). The strong insolation at low latitudes and the remote location makes Barbados an ideal location for studying climate effects of long range transported CCN in the marine environment.

Only few studies of CCN properties have previously been carried out over the Caribbean Sea, and based on the limited and very different results reported, it is not evident what the dominant CCN properties are in that region. The objective of the current study is to investigate to what extent organic species, nss inorganic species, sea salt, and long-range trans-

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ported Saharan mineral dust may influence the CCN properties **in the MBL** in that region. The CCN activity was inferred from CCN concentrations in conjunction with particle number size distribution measurements. Particles in the dominant CCN size range were also investigated with transmission electron microscopy (TEM) combined with energy-dispersive X-ray spectroscopy (EDX), in order to identify refractory PM such as sea salt and mineral dust, and for estimation of the volume fractions of different types of PM. The present study was carried out on Barbados as part of the Saharan Aerosol Long-range Transport and Aerosol-Cloud-Interaction Experiment (SALTRACE) campaign during June–July, 2013.

2 Theory

The equilibrium saturation ratio of water vapour over an aqueous solution droplet can be described by the the Köhler equation. Petters and Kreidenweis (2007) introduced the hygroscopicity parameter κ and formulated the Köhler equation as:

$$\frac{\text{SS}}{[100\,\%]} = \frac{D_{\text{d}}^3 - D_{\text{p}}^3}{D_{\text{d}}^3 - D_{\text{p}}^3(1-\kappa)} \exp\left(\frac{4\sigma M_{\text{w}}}{R T \rho_{\text{w}} D_{\text{d}}}\right) - 1 \tag{1}$$

where SS is the supersaturation in %, M_{w} is the molar mass of water, ρ_{w} is the density of water, σ is the surface tension, $R = 8.314\,\text{J}\,(\text{K mol})^{-1}$ is the universal gas constant, T is the absolute temperature, D_{p} and D_{d} are the dry particle and droplet diameters respectively. The hygroscopicity parameter κ ranges from about 0 for nonhygroscopic components to ~ 1.4 for very hygroscopic species (Petters and Kreidenweis, 2007).

Based on the Zdanovskii, Stokes, and Robinson (ZSR) assumption (Petters and Kreidenweis, 2007) the κ value of mixed particles can be estimated by a volume weighted addition of the κ values of the pure compounds:

$$\kappa_{\text{add}} = \sum \varepsilon_i \kappa_i \tag{2}$$

where κ_i is the κ value of the species i and ε_i is the volume fraction of species i in the dry particles.

3 Experimental

The main part of the SALTRACE campaign was carried out from mid-June to mid-July, 2013 and involved a number of different atmospheric measurements mostly based on Barbados. The aim of the campaign was to investigate properties of Saharan mineral dust transported
across the North Atlantic to the Caribbean Sea. The campaign included airborne measurements west of Africa as well as in the vicinity of Barbados. A pronounced Saharan mineral dust layer was present at altitudes of 2-4 km over Barbados almost during the entire campaign (Groß et al., 2015). The ground based aerosol measurements included in the present study were carried out at Ragged Point ($13°09'54''$ N, $59°25'56''$ W) on the East Coast of
Barbados. Studies of long range transported aerosol particles have been carried out on the east coast of Barbados since the mid-1960s and at Ragged Point since the early 1970s (Prospero and Lamb, 2003).

For the in-situ measurements, the ambient aerosol was sampled through a PM_{10} inlet located ~ 50 m a.s.l. at the top of a 17 m high tower located on the edge of a 30 m high rocky
promontory adjacent to the ocean. The flow rate was 16 L min^{-1} inside a 3/4 inch stainless steel tube leading down to the ground level where different instruments were connected. Among the instruments were an Aerodynamic Particle Sizer (APS-3321, TSI) **covering the size range 0.5-10 µm**, a mobility particle size spectrometer (MPSS, TROPOS-REF-3) (Wiedensohler et al., 2012) measuring the particle number size distributions **in the size**
range 0.01-0.8 µm in parallel with a condensation particle counter (CPC-3010, TSI) determining the total particle number concentration, and a CCN counter (CCNC) from Droplet Measurement Technologies, USA (Roberts and Nenes, 2005), measuring the total number concentration of CCN at different supersaturations in the range from 0.1 to 0.7 %. **Supersaturation settings of 0.1%, 0.2%, 0.4%, and 0.7% were used throughout the campaign,**
and an SS=0.3% was included during the last 2 weeks of the campaign. These instruments (except for the APS) were all located inside an air conditioned container with the temperature kept constant at ~ 25 °C. The sample aerosol was dried to $\lesssim 40$ % with a Nafion dryer inside the container before being investigated. Particle number size distribu-

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tions were obtained for every ~ 14 min. The supersaturation settings of the CCNC changed every 10–15 min – in order to allow for the supersaturations to stabilise and still ensure a significant overlap in time with a measured particle number size distribution.

Samples for off-line analysis were collected at the top of the tower. A high volume sampler
5 was used to sample total PM on $20\,cm \times 25\,cm$ Whatman 41 filters with a flow rate of $\sim 40\,m^3/hr$ for analysis of the mineral dust concentration. A daily resolution was obtained and sampling typically started around 10:00 UTC. In order to minimize impacts from local sources sampling was controlled by a wind sensor and only carried out when the local wind direction was in the range $335°$ through North to $130°$, and the wind speed exceeded
10 $1\,m\,s^{-1}$. A quarter of each filter was rinsed with pure water and placed in a muffle furnace for 14 h at 500 °C. The mass of mineral dust was estimated from multiplying the mass of the remaining ash by 1.3. More details about the sampling sector and the procedure for inferring the mineral dust concentration are available in the literature (Prospero et al., 2005; Trapp et al., 2010).

15 Samples for TEM analysis were also collected at the top of the tower with a miniature cascade impactor (Kandler et al., 2007) on TEM Ni-grids coated with a formvar carbon film (FCF200F1-Ni, Science Services, Munich, Germany). **The nominal cut-off aerodynamic diameters for the stages analysed in the present work were 530 nm (upper) and 90 nm (lower). During the period from 22 June to 15 July, an additional stage in between with**
20 **a 330 nm cut-off was used.** Sampling was performed under ambient conditions with the impactor inlet oriented pseudo-isoaxially. While the flow conditions were considerably sub-isokinetic, for the regarded particles diameter range from 50 to 300 nm an aspiration bias is negligible. The samples were stored in a drying cabinet (silica gel) at ambient temperature.

Meteorological measurements were carried out at the top of the tower and included mea-
25 surements of wind speed, wind direction, precipitation, temperature and humidity.

4   Data analysis

4.1   Cloud condensation nuclei and particle number size distributions

For an estimation of the CCN activity, the average CCN number concentration was compared to the simultaneously measured particle number size distribution (MPSS
5 **data in the size range 0.01-0.8 µm merged with the APS data for sizes >0.8 µm). Thus, a critical diameter (D_c) above which all particles activate into cloud droplets for a given supersaturation was estimated assuming internally mixed aerosol particles in a sufficient neighbourhood around the inferred D_c.** The critical mobility diameter is inferred by integrating the particle number size distribution from the largest particle diam-
10 eter and downwards until a particle number concentration equal to the CCN concentration is obtained (e.g. Jurányi et al., 2010). This approach relies on the fact that the dry particle size is a very important parameter for whether a particle will activate into a cloud droplet (as given in Eq. 1).

In order to obtain a best estimate of and the error on the critical diameter, the integrations
15 were carried out for 10 000 Monte Carlo simulations, for which the errors on the CCN number concentration and the MPSS number concentrations in different size channels were taken into account. The relative random error on the CCN number concentration corresponding to one standard deviation was assumed to be represented by the inverse of the square root of the total CCN counts during a given time interval. The relative random error
20 on the MPSS derived particle number concentration in a given size channel corresponding to one standard deviation was assumed to be represented by 5 %. It was found to be a reasonable estimate of the random error from intercomparisons of neighbouring MPSS particle number size distributions during time periods where the total number concentration changed negligibly. The calibration of the CCNC in the laboratory prior to and after the cam-
25 paign clearly showed some systematic losses of ultrafine particles increasing linearly with decreasing particle diameters below ~ 80 nm. This effect is likely to be due to diffusional losses inside the CCNC (Rose et al., 2008). These losses were assumed to be the same

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in the field as in the laboratory, and this effect was accounted for in the data analysis when inferring the critical diameter.

The inferred probability density functions of the critical diameters were generally found to be well represented by Gaussian distributions.

Based on the supersaturation and the inferred critical diameter the hygroscopicity parameter κ was calculated (Petters and Kreidenweis, 2007). The error on the CCNC supersaturation is estimated based on the variation among numerous calibrations carried out in the laboratories at the Leibniz Institute for Tropospheric Research (Tropos). For SS $\geq 0.2\,\%$ the variation in the supersaturation appeared to be represented very well by a Gaussian distribution with a standard deviation of $0.037\,\%$ in relative terms. For SS $< 0.2\,\%$ an absolute value of $0.03\,\%$ SS represented one standard deviation. Rose et al. (2008) reported lower variations in the SS under controlled laboratory conditions ($\sim 1\,\%$) and larger relative errors while operating in the field ($\sim 5\,\%$) mainly due to temperature variations.

The probability density functions of the critical diameter and the supersaturation as described above were used as independent input for the calculation of the probability density functions of κ. The temperature at activation was estimated to be $0.5 \cdot (T_1 + T_2)$ where T_1 and T_2 are the temperatures at the top and at the midpoint of the CCNC column wall respectively. The temperature enters directly in Eq. (1) and it also enters indirectly through an influence on σ and ρ_w in Eq. (1). A surface tension of pure water was assumed in the κ calculations and a parameterisation of $\sigma(T)$ was obtained from results reported in the literature (Cini et al., 1972).

There were some systematic problems with the temperature setting at the bottom of the CCNC column wall (T_3) being too low (**with an actual** SS $= 0.074\,\%$) for the SS $= 0.1\,\%$ setting during the last weeks of the campaign. It was possible to correct for this error on the SS in combination with the size distributions due to a systematic alternation between correct and off-set T_3 settings, and it has been taken into account in all the results shown in the present study.

A very good agreement was found between the used MPSS and a reference MPSS before and after the campaign (Wiedensohler et al., 2012). The MPSS sizing was validated

in the field at the beginning and at the end of the campaign with mono-disperse polystyrene latex spheres (PSL) with a diameter of 203 nm.

4.2 Transmission electron microscopy (TEM)

The TEM analysis was carried out in order to provide information about the chemical com-
position of the aerosol particles. TEM grid samples were analysed with a Philips CM 20
(FEI, Eindhoven, the Netherlands) operated at 200 kV accelerating voltage and a LaB_6
gun. The images were recorded with a CCD camera (KeenView G2, Olympus Soft Imaging
Solutions GmbH, Münster, Germany) mounted at the bottom of the electron microscope.
The Transmission electron microscope **was** equipped with an energy-dispersive X-ray mi-
croanalysis with a Silicon Drift detector (X-Max 80 mm^2, Oxford, Oxfordshire, UK). Images
were acquired with a resolution of 1.32 pixels per nm. **During the electron beam anal-
ysis, the particles absorbed energy and heated up. Hence, the volatile particulate
material evaporated and only the refractory fraction remained on the substrate. To
determine the original state, one image was recorded right at the beginning of the
electron bombardment. When no more change of the remaining particle fraction was
observed, a second image was recorded. Changes to the particles were derived from
image comparison.** An exact temperature under this electron bombardment can not be
determined. However, the temperature conditions can be considered to be similar for all
measurements, as identical instrument settings were used. From a chemical analysis it
becomes obvious that nitrate and **sulphate** evaporated, while sodium chloride, all mineral
dust components and soot **remained** stable (Kandler et al., 2011). From the decomposition
behavior and the absence of sodium chloride melting, we **concluded** that the tempera-
ture is between 200 and 800 °C, most likely higher than 300 °C (Kiyoura and Urano, 1970;
Lide, 2009). Semi-automatic image analysis (determination of the particle projected area
and the projected-area-equivalent diameter (PAED)) was performed with the ImageJ soft-
ware 1.47c (Rasband, 2015). As the brightness of the images **was** uneven, instead of an
automatic brightness-based segmentation procedure a manual thresholding combined with
additional manual particle outlining was required. The volume fraction of refractory material

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inside each particle was estimated as the ratio of the projected area after evaporation to the projected area before evaporation, raised to the power of 1.5.

5 Results

5.1 Local airmass characteristics

Locally measured wind speed, wind direction, relative humidity (RH) and precipitation are shown in Fig. 1 for the time period from 14 June to 15 July, 2013, corresponding to the day of year (DOY) range from 165 to 196. All times presented in this section are in UTC (corresponding to LT+4 h). The wind speed shown in the top-panel of Fig. 1 ranged from ~ 2 to $\sim 15\,\text{m s}^{-1}$ with an average value of $8.8\,\text{m s}^{-1}$. The wind direction was dominated by easterly winds (Fig. 1-mid-panel). With wind directions in the range from $335°$ through North to $130°$ only the open ocean is upwind from the field station. For $> 95\,\%$ of the time the wind direction was in the range from 0 to $130°$. Only one time during the campaign a small vessel was noticed within eyesight of the measurement station. This indicates that local and land-based emissions are unlikely to influence our observations during most of the campaign. The local ambient temperature was on average $26.0\,°\text{C}$ with diurnal variations typically being $< 1\,°\text{C}$. The ambient RH ranged from ~ 65 to $\sim 85\,\%$ during most of the campaign (Fig. 1 – lower panel). Elevated levels of RH were typically associated with time periods with precipitation – which are indicated with blue in the lower panel in Fig. 1. Intense showers lasting for short time periods (often $< 1\,\text{h}$) occurred frequently during the campaign.

5.2 Particle number size distributions, CCN concentrations and CCN activity

The measured particle number size distributions (not corrected for losses in sampling lines and detection efficiency) are shown in Fig. 2. The size range of mobility particle diameters from 0.01 to $0.8\,\mu\text{m}$ is covered by MPSS data merged with APS measurements for volume equivalent diameters above $0.8\,\mu\text{m}$. The gaps in the data in the top panel are due to lack of measurements.

During most of the campaign the typical marine particle number size distribution with two submicrometer modes can be observed: an Aitken mode with a maximum close to 50 nm and an accumulation mode with a maximum close to 180 nm (Heintzenberg et al., 2004). A Hoppel minimum is typically observed around a mobility diameter of 80 nm. The average

5 critical diameters (more details given below) are also indicated in the figure and it is evident that for the lowest supersaturations (0.1–0.3 %) information about the accumulation mode is typically provided, while information the Aitken mode is provided for higher supersaturations. It is also clear from the median particle number size distribution that very low number concentrations are present in the super-micrometer range. The median parti-

10 cle volume size distribution inferred from assuming spherical particles is shown in the lower panel to the right in Fig. 2. The volume size distribution is dominated by particles larger than $\sim 0.5\,\mu$m, with a maximum generally reached at 2 μm followed by an abrupt decrease for larger particle diameters. The abrupt decrease is most likely due to losses of coarse mode particles in the sampling lines. The correction for losses of coarse particles in the sampling

15 lines is uncertain, **and, thus, has not been carried out.** The total particle number concentration is typically in the range from 200–400 cm^{-3}, with a few exceptions often associated with time periods, where influence from local land-based particle sources cannot be ruled out. Hence, the total marine background particle number concentration observed is in the lower end of the typical concentrations of 300–600 cm^{-3} found in the MBL (O'Dowd and de

20 Leeuw, 2007).

The measured number concentrations of CCN vs. time are shown in the upper panel of Fig. 3. The CCN number concentrations stay rather constant throughout the campaign with a few exceptions with remarkably reduced concentrations and one episode with elevated concentrations around the DOY = 185.5 (4 July). The time periods with low CCN concentra-

25 tions are associated with higher RH than average and also more precipitation than average as can be seen from the lower panel of Fig. 1. The median CCN number concentrations are included in Table 1 and range from ~ 80 cm^{-3} for an SS = 0.1 % to ~ 240 cm^{-3} for an SS = 0.7 %. Those CCN number concentrations are comparable to what has been observed over the western North Pacific (Mochida et al., 2011), and over the North Atlantic for

clean marine conditions (Reade et al., 2006), but often higher concentrations of CCN are observed in the MBL (Good et al., 2010; Jefferson, 2010; Sorooshian et al., 2009). **Andreae (2009) reviewed measurements of CCN number concentrations at an SS=0.4% in the 'clean' MBL and reported an average concentration of 107$\pm$56 cm^{-3}, with slightly higher values for the Atlantic. Hence, the median CCN number concentration of 205 cm^{-3} we observed for an SS=0.4% is in the higher range for the remote marine MBL.**

The critical diameters inferred as described above in Sect. 4.1 are shown in the mid-panel of Fig. 3. The calculated random errors are not shown in the figure. For the SS = 0.1 % the random errors corresponding to one standard deviation are in the range from ~ 2 to ~ 10 nm, while for higher SS the similar errors are in the range from ~ 1 to ~ 5 nm with decreasing average values with increasing SS. The average random errors on the critical diameter (δD_c) are included in Table 1. The critical diameters are slightly lower during the first days of measurements, but they appear to stay fairly constant throughout most of the campaign. For an SS = 0.1 % the D_c stays above 100 nm, and for an SS = 0.2 % the D_c is typically slightly above the Hoppel minimum so those data provide information about the accumulation mode CCN activity, while for higher SS information about the Aitken mode CCN activity is obtained.

The calculated κ values vs. time are shown in the lower panel of Fig. 3. The κ values are quite similar for the different supersaturations and thus also similar for the accumulation mode and the Aitken mode during the entire campaign. The probability density functions of the inferred κ values were found to be very well approximated by a Gaussian distribution in the range of ± 1 standard deviation relative to the median κ value. The random errors on κ representing one standard deviation ($\delta\kappa$) were on average 0.05 and increasing slightly with the supersaturation. The average $\delta\kappa$ values are included in Table 1. During the first day of measurements (DOY = 165, 14 June), the κ values are typically around or above ~ 0.6. In the time period from 168.0–173.0 DOY (17–21 June) most of the κ values are typically in the range from 0.3 to 0.5. During the last 22 days of measurements (22 June to 14 July) most of the κ values are found in the range from 0.2 to 0.4.

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The higher κ values above 0.6 during the first day is likely to be at least partly due to sea salt since most other species present in ambient aerosol have κ values close to or below 0.6 (Petters and Kreidenweis, 2007; Petters et al., 2009). The observations of elevated κ values coincide with the highest local wind speeds ($\sim 14\,\mathrm{m\,s^{-1}}$) observed during the campaign. It
5 fits with the expectation of the flux of sea spray particles depending highly on the wind speed (Monahan and Muircheartaigh, 1980; O'Dowd and de Leeuw, 2007).

The κ values inferred here are lower than the values of 0.6 ± 0.2 for Puerto Rico and 0.87 ± 0.24 for Antigua reported by Pringle et al. (2010) based on the measurements presented by Allan et al. (2008) and Hudson (2007) respectively. The κ values from the first
10 day of our measurements is comparable to the other literature values for the Carribean. It is worth noting that the previous measurements were carried out in December and January **respectively, and it is likely that the PM sources and chemical composition change** with the seasons (Savoie et al., 1989). **Pringle et al. (2010) modelled the κ values in the region to have a maximum of $\backsim$0.7 in winter with a κ value of $\backsim$0.4 in summer,**
15 **which agrees very well with our findings. Wex et al. (2010) reviewed measurements of particle hygroscopicity for sub-saturated conditions in the MBL and found that the dominant κ value was around 0.45, but also several observations with lower κ values and fewer with higher κ values have been made. Hence, our inferred κ values are slightly lower than what most frequently can be expected in the remote MBL.**

5.3 Mineral dust concentration

The daily total mass concentrations of mineral dust during the campaign are depicted as bars in Fig. 4 together with the estimated total mass concentration (PM$_{est}$) based on the integrated particle volume size distributions for diameters larger than 0.5 μm. Both of the depicted time series only represent time periods when the local wind direction indicated no
25 influence from local land based sources as described above. Most of the dust concentrations are based on sampling for ~ 24 h, and all the shown dust concentrations are based on > 12 h of sampling – depending on the local wind direction. The average mineral dust concentration during the campaign is $\sim 19\,\mathrm{\mu g\,m^{-3}}$, with noticeable variations on a daily

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scale. The maximum of the daily mineral dust concentration of $\sim 80\,\mu g\,m^{-3}$ was observed for 11–12 July (DOY = 192.4–193.4), which is a high concentration for this site. Only occasionally the daily average mineral dust mass concentration exceeds $100\,\mu g\,m^{-3}$ (Savoie and Prospero, 1977; Savoie et al., 1987; Jung et al., 2013). A strong yearly cycle of the
5 mineral dust concentration is present in this region with maximum concentrations in June–July (Prospero and Lamb, 2003), and significant (occasionally high) concentrations of dust were indeed present in the MBL during almost the entire campaign.

The mass concentrations estimated from the integrated volume size distributions shown in Fig. 4 are based on the assumptions of spherical particles and a particle density of
10 $2.6\,g\,cm^{-3}$ as for mineral dust (Bergametti and Forêt, 2014). The estimated total mass concentrations are likely to be biased low due to losses in the sampling tube and inlet, but it may also result in higher concentrations than for pure dust due to non-dust particles such as e.g. sea salt. However, there is a very significant linear correlation between the two data series depicted in Fig. 4 with a correlation coefficient of $r = 0.85$ for the 30 days where
15 data was available. From Fig. 4 it can also be seen that the magnitude of the two mass concentrations are comparable typically within a factor of 2. These observations indicate that the coarse particles dominating the volume size distribution (Fig. 2) primarily are comprised of mineral dust. Hence, the estimated total mass concentrations inferred from the measured particle number size distributions can be used as a proxy of the mineral dust
20 concentration with a higher time resolution **during this campaign, where mineral dust mass concentrations were significant**. Thus, it can be determined whether high or low dust concentrations could be expected e.g. during the relatively short time periods used for collecting samples for investigation with transmission electron microscopy.

5.4 Transmission electron microscopy (TEM)

25 Samples were collected on eight different days, where the mineral mass dust concentration was close to or above the average for seven out of the eight samples, based on the data presented in Fig. 4. **Sampling was carried out while local wind directions were in the range from 84° to 110°**. Details about the sampling times of the samples are provided in

Table 2. By use of TEM in combination with EDX information about the respective volume fractions of non-refractory and refractory particulate matter and information about the chemical composition of the latter was obtained. Thus, the TEM data provides a strong basis for interpretation of the CCN properties presented above. Some examples of images of the
5 studied particles are shown in Fig. 5. The particle shown in Fig. 5I.a is non-refractory and on timescales of seconds it evaporates. As can be observed in Fig. 5I.b, only an indication of a thin layer remains on the spot were the particle used to be. Similar types of particles have also been observed on Cape Verde with the same technique, and the remaining thin layer was suggested to be comprised of refractory organic compounds (Kandler et al., 2011).
10 The remaining thin layer is often observed in the present study. In general, this type of dominantly non-refractory particle with no well-defined refractory substance included were the most abundant type of particle in the investigated samples.

In Fig. 5II, an example of a sea salt particle is shown, and there were no significant amounts of non-refractory material associated with that particle. That was the case for
15 several sea-salt particles, but there are also some examples of sea-salt mixed with non-refractory substances. In Fig. 5III.a, an example of a mostly non-refractory particle with a small amount of soot adhering to it (Fig. 5III.b) is shown. These types of particles were typically dominated by the non-refractory material and with only small volume fractions of soot – either adhering to the surface – or covered completely or partly by non-refractory
20 material.

In Fig. 5IV, a soot particle not associated with non-refractory material is shown. Soot particles were by number the most abundant type of refractory substances in the samples studied, however almost all the observed soot particles were internally mixed with non-refractory matter. In Fig. 5V.a a partly non-refractory particle is shown – as can be seen
25 when comparing to the image in Fig. 5V.b. The refractory part of the particle shown in Fig. 5V.b contained significant amounts of sodium and potassium, and it may originate from biomass burning. In Fig. 5VI a dust particle is shown. In total 4 out of 871 particles were classified as dust in the investigated size range, and they were not or only very slightly associated with non-refractory PM. TEM was also used to study samples in the super-micron

range from the same site and aircraft samples collected at different altitudes in the vicinity of Barbados. Mineral dust typically comprised a significant fraction **of** the super-micron particulate matter, and at higher altitudes mineral dust also comprised a significant fraction in the sub-micron size range, which will be described in more detail in future publications.

5   Five samples from 17–21 June, and three samples from 27 June, and 4 and 11 July were studied (Table 2). The data obtained from the first five samples (period 1) and the last three samples (period 2) respectively, were grouped separately and binned according to the their initial PAED and the volume fraction of any refractory material in the range from 0 to 0.3, from 0.3 to 0.9 and > 0.9 as shown in Fig. 6a and b respectively. The refractory matter was classified as soot, soot mixtures, mineral dust, sea salt and "other", where the last category contains all refractory substances not belonging to any of the first mentioned groups. **An example of a refractory particle classified as "other" is shown in Fig. 5V.b**. In Fig. 6a and b, sea-salt is shown separately, while all the other refractory substances are grouped together. In Fig. 6c and d the volume fractions of non-refractory substances and all the different refractory particle groups are shown for period 1 and 2 respectively in different size ranges. It is worth noting that all the volume fractions of refractory PM presented here can be considered upper limits since more volatile species may have evaporated from the studied particles before closer inspection, and in many cases the evaporation of non-refractory PM has already started when the first particle image is produced.

20   As can be seen from Fig. 6 the majority of the investigated particles belonged to the accumulation mode in the PAED range from 100 to 300 nm. For the first period about 20 % of the 440 studied particles contained well defined refractory material, while it was about 30 % for the 431 particles in the second group. Out of the particles comprising refractory material – the majority of those were dominated by non-refractory material with a small volume fraction of refractory material. By number the majority of the small refractory particles were classified as soot. Only about 3 and 2 % respectively of all the investigated particles are comprised of a refractory volume fraction larger than 90 % for the two groups of samples. In the PAED range from 100–200 nm, it is only a small fraction (< 10 % by number) of the studied particles that contain any well-defined refractory matter, and in most of those cases

the refractory matter comprises a small volume fraction of the particles. For the particles larger than ~ 300 nm, the refractory matter is relatively more abundant both by number fraction and by volume. In the following section, it will be discussed how the information presented in this section can be combined with results presented in previous sections in

5 order to infer information about the chemical composition of the studied cloud condensation nuclei.

6 Summary and discussion

It has been shown in the sections above that during most of the campaign influences from local land-based particle sources can be expected to be very limited and thus, the investi-
10 gated aerosol can be considered as representative for **the trade wind MBL of the Western North Atlantic**. The CCN number concentrations and total particle number concentration are relatively low – and similar to pristine marine conditions. The particle number size distributions were typically dominated by an accumulation mode with a maximum near ~ 180 nm. Based on CCN number concentrations and size distributions measured in parallel the criti-
15 cal diameters were inferred and they ranged from ~ 50 nm for an SS = 0.7 % to ~ 150 nm for an SS = 0.1 %. The corresponding κ values were typically found in the range 0.2–0.5 for all supersaturations (0.1–0.7 %) with the exception of the first day of measurements, where it is likely that the influence of sea salt was relatively higher. Significant mass concentrations of mineral dust **were** present during most of the campaign, with occasional high mineral
20 dust mass concentrations. Impactor samples collected on eight different days, where significant mass **concentrations of dust were** observed, were analysed with TEM. The majority of the investigated particles were found in the accumulation mode, and in general the bulk of the **investigated** particles were largely dominated by non-refractory substances. **Those findings indicate that the mineral dust primarily was present in the larger particle**
25 **size ranges in the MBL during the campaign.**

Based on the presented results and some basic assumptions it is possible to estimate to what extent the minor concentration of refractory particulate matter is likely to influence the

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inferred CCN activity. It can be expected that significant amounts of the non-refractory PM in the studied size range is sulphate species (Li-Jones and Prospero, 1998). Pure **ammonium sulphate** and other inorganic sulphate species of atmospheric relevance have κ values of 0.6 or slightly higher when it comes to cloud droplet activation (κ_{CCN}). The κ_{CCN} values
5 inferred in the present study are typically below ~ 0.4. Some basic modeling using Eq. (2) and the information about the refractory PM volume fractions (Fig. 6) in combination with the particle number size distributions (Fig. 2) clearly indicates that the inferred κ values cannot be explained solely by mixtures of sulphate species and the refractory PM even when $\kappa = 0$ is assumed for all the refractory PM. The influence from the refractory PM is negligible since
10 the estimated volume fraction only exceeds 10 % for particles larger then 300 nm, and (i) as can be observed from Fig. 2 only a small number fraction of the CCN are present in that size range, and (ii) most particles (even with low CCN activity) with diameters larger 300 nm will activate into cloud droplets at supersaturations of 0.1 % or higher. Hence, the observed κ values are very likely to reflect a significant organic volume fraction, which is corroborated
15 by the skin-like remainder frequently observed in the TEM evaporation studies.

Most organic species of atmospheric relevance typically have κ_{CCN} values ranging from about ~ 0 up to ~ 0.3 (Petters and Kreidenweis, 2007; Petters et al., 2009). Kristensen et al. (2012) reported average κ_{CCN} values of ~ 0.08 for large fractions of ambient water soluble organic particulate matter in different environments. If such a κ_{CCN} value is assumed for
20 the organic species in the present study, then an internally mixed volume fraction of organic matter at the order of ~ 50 % in the diameter range ~ 50–200 nm could explain the observations, if it **is** assumed that the remainder of the PM in that size range is dominated by sulphate species. Such a composition is comparable to what has been reported for particulate matter with diameters below 0.6 μm on Puerto Rico (Novakov et al., 1997). From the
25 TEM studies it seems highly likely that the aerosol particles (at least in the accumulation mode) are internally mixed. **However, the measured CCN number concentrations can also be reasonably well modelled by integrations of the particle number size distributions by assuming an external mixture of inorganic sulphate (κ=0.6) and organic**

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species (κ=0.08) and an organic number fraction of ~ 25 % in the diameter range ~ 50–300 nm.

For the present study, it should be kept in mind that the TEM samples studied are limited with respect to the number or particles investigated and they also represent a limited period

5 of the entire campaign. Nevertheless, (i) a large fraction of the particles investigated with TEM had indications of organic matter as mentioned above, (ii) it is hard to explain ambient κ_{CCN} values in the range from 0.2–0.4 without organic species being present – if refractory matter such as soot and dust is likely to comprise a very minor volume fraction, (iii) significant organic fractions have previously been reported for the size range relevant as CCN

10 in the same region (Novakov et al., 1997; Mayol-Bracero et al., 2001; Maria et al., 2002). So there are several independent observations supporting that organic species are likely to play a role for the CCN activity observed in the present study.

Mineral dust was observed over the **Eastern** Caribbean Sea/**tropical Western North Atlantic** almost during the entire measurement period and the airmasses generally originated

15 from Northern Africa (Groß et al., 2015), so it cannot be ruled out that organic species in the gas phase or the particle phase also are transported across the North Atlantic. During the summer season significant amounts of biogenic precursers of secondary organic aerosol are emitted in North Western Africa (Capes et al., 2009), which may contribute to secondary organic aerosol in the trade winds. Biomass burning is also a source of organic

20 PM (and soot), but the studied PM was not dominated by biomass burning particles, and biomass burning typically occurs in the dry season in winter in Northern Africa. A study of the organic PM from Puerto Rico in the Eastern Caribbean indicated that oceanic emissions was the dominant source of organic PM (Mayol-Bracero et al., 2001). If oceanic emissions **are** the main source of the organic PM in the present study, then it can explain the generally

25 low κ values observed, also when the airmasses occasionally may not be influenced from continental sources.

The significant differences in CCN properties observed in the present and previous studies (ranging from very low κ_{CCN} values and dominance by mineral dust to higher κ_{CCN} and dominance of inorganic soluble species) may in part be due to different meteorological

conditions and seasonal variations in aerosol particle properties e.g. resulting in high/low biological activity and different vertical atmospheric mixing. It is clear that more and longer term studies will be needed in order to fully assess the CCN properties in the region and to identify the respective roles **of** organic species, nss inorganic species, sea salt and mineral
5 dust.

7 Conclusions

Aerosol particles (with a focus on cloud condensation nuclei properties) were investigated in the trade wind marine boundary layer in the **Western North Atlantic** during the SALTRACE campaign, June–July 2013. Local land-based particle sources could be ruled out for almost
10 the entire campaign, and particle number size distributions and concentrations were representative of pristine marine environments. Significant mass concentrations of mineral dust was present during most of the campaign. The inferred CCN activity could be represented by κ values typically in the range from 0.2–0.5 for both the Aitken and the accumulation mode. Investigations of particle compositions with TEM in combination with EDX showed
15 negligible concentrations of mineral dust ($< 0.5\%$ by number), and very minor concentrations of sea salt particles (1–2 % by volume) and soot ($\sim 2\%$ by volume) in the size range of the accumulation mode dominating the CCN number concentrations. The CCN population was almost entirely comprised by non-refractory particulate matter, and based on previous studies in the region and the inferred κ values, it is highly likely that the CCN largely were
20 comprised of a mixture of sulphate and organic species. An estimate of the organic volume fraction of the CCN would depend on the κ value of the organic species – but an organic volume fraction at the order of 50 % is likely.

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Table 1. For time periods where local land-based sources can be ruled out: The median CCN number concentrations, the median critical diameters (D_c), the average random error on D_c (δD_c), **median** κ values, standard deviations of the κ values (σ_κ), and average random errors on the κ values ($\delta\kappa$) for the different supersaturations.

SS [%]	CCN [cm^{-3}]	D_c [nm]	δD_c [nm]	κ	σ_κ	$\delta\kappa$
0.1	112	159	5	0.32	0.14	0.04
0.2	173	103	4	0.30	0.18	0.05
0.3	195[a]	79[a]	4	0.29[a]	0.13[a]	0.05
0.4	205	64	3	0.31	0.19	0.05
0.7	236	45	2	0.30	0.21	0.06

[a] The CCN counter was only operated with a supersaturation of 0.3 % during the last 15 days of the campaign.

Table 2. Information about the samples investigated with transmission electron microscopy. Date and UTC time represent the beginning of the sampling, while time in DOY is the midpoint of the sampling time. Duration gives the sampling time in minutes. N_p is the number of particles investigated.

| date	UTC time [h:min]	time [DOY]	duration [min]	N_p
17.06	15:00	168.63	20	160
18.06	14:03	169.59	12	46
19.06	13:20	170.56	20	29
20.06	13:50	171.58	20	57
21.06	18:20	172.77	20	148
period 1 in total			92	440
27.06	02:45	178.13	30	169
04.07	13:50	185.59	30	148
11.07	13:07	192.55	18	114
period 2 in total			78	431
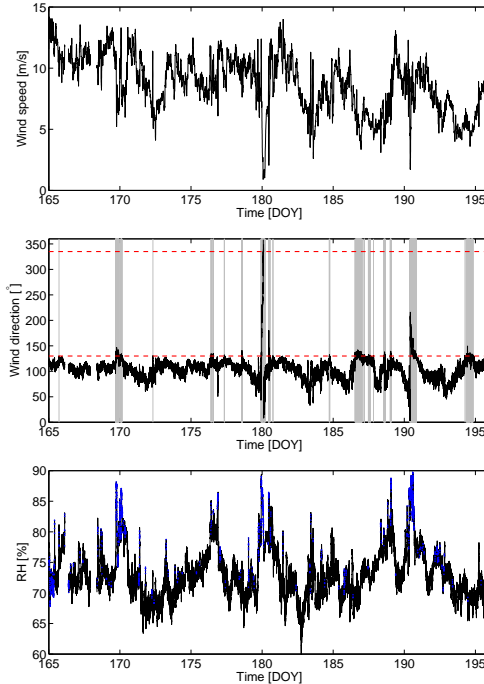
Figure 1. Local meteorological parameters measured at the top of the 17 m high tower. Top panel: the wind speed. Mid panel: the wind direction. **The grey shades indicate time periods where influence from local sources cannot be ruled out (wind directions in the range from 130° to 335°). Wind directions of 130° and 335° are indicated by horizontal dashed red lines**. Lower panel: the measured relative humidity with blue points indicating time periods with rain.

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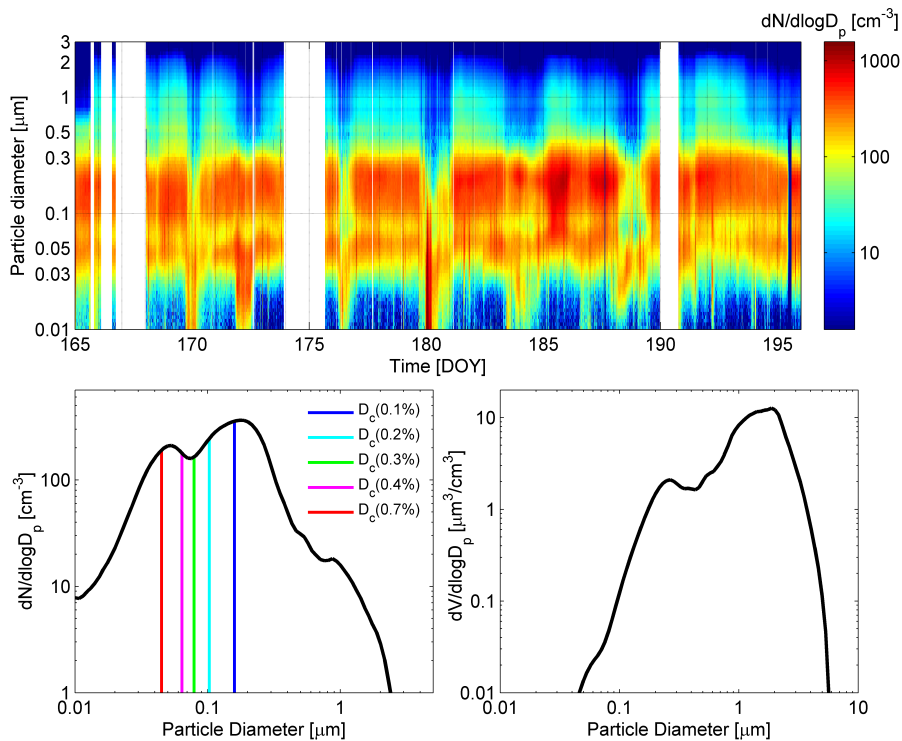
Figure 2. Size distributions **corrected neither** for particle losses in the tubing nor corrected for detection efficiency. MPSS data covers the mobility diameter range 0.01–0.8 μm, and APS data covers the range for volume equivalent diameters above 0.8 μm. Top panel: the measured aerosol particle number size distributions vs. time in days of year. The colour scale indicates the 10-based logarithm of $\mathrm{d}N/\mathrm{dlog}(D_\mathrm{p})$ in cm^{-3}. Lower panel: the median particle number size distribution, and the inferred median particle volume size distribution assuming spherical particles. The inferred median critical mobility diameters (D_c) are indicated with vertical lines for the different supersaturations together with the particle number size distribution.
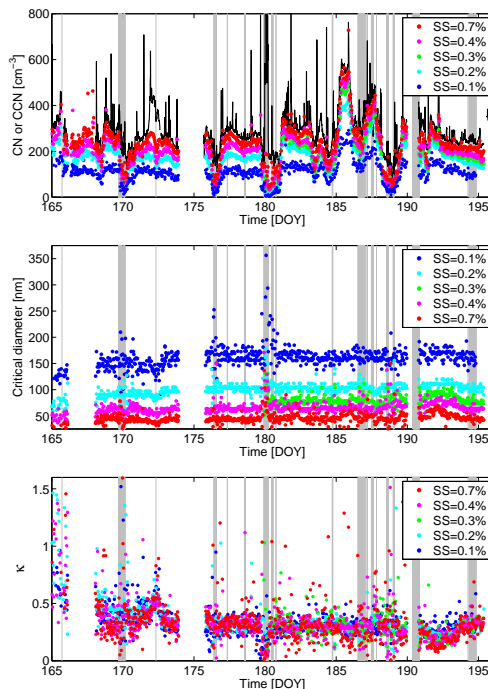
Figure 3. The measured CCN concentrations and associated properties. The grey shaded areas indicate time periods where local land based contamination cannot be ruled out as determined from the local wind direction. Top panel: the measured CCN number concentrations for the different supersaturations. The total particle number concentration (CN) inferred from the MPSS measurements is indicated with the full black line. Mid panel: the inferred critical diameter. Lower panel: the inferred κ values.

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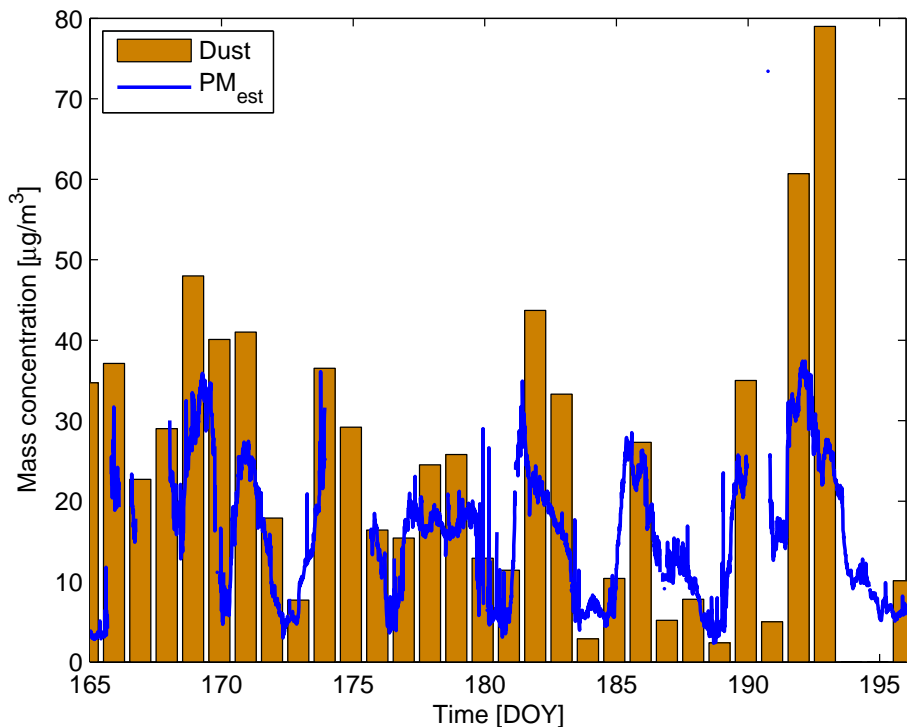
Figure 4. The mineral dust mass concentration (bars) **in the total suspended particulate matter** and the particulate matter concentration (PM$_{est}$, blue line) estimated from the integrated particle volume size distribution for diameters **in the range 0.5-10 µm** assuming spherical particles and a particle density of $2.6\,\mathrm{g\,cm^{-3}}$. The gap in the dust concentration around DOY = 194–195 is due to lack of data for those two days.
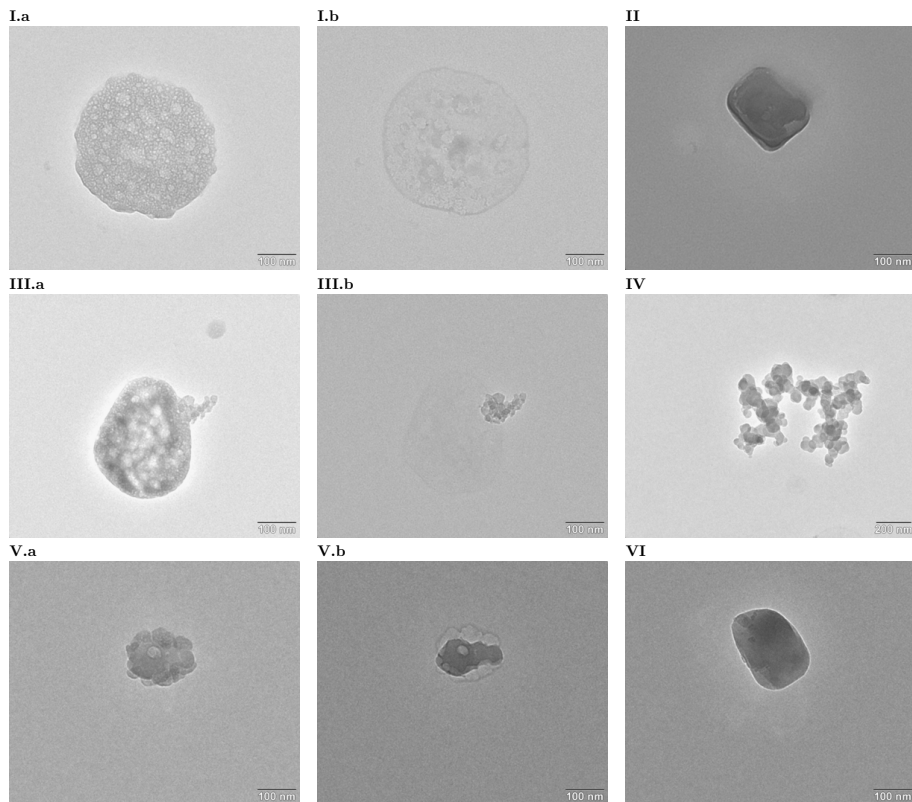
Figure 5. Transmission electron microscope bright field images of collected aerosol particles. Images I.a+b, III.a+b, and V.a+b are before and after evaporation of non-refractory material respectively. For II, IV, and VI no significant evaporation was observed. I: an example of a non-refractory particle. II: sea salt particle. III: A non-refractory particle with a small soot particle adhering to the surface. IV: A soot particle. V: Refractory particle with significant amounts of sodium and potassium. VI: A dust particle. The bar in the lower right corner of each image represents 100 nm, with the exception of IV, where it represents 200 nm.

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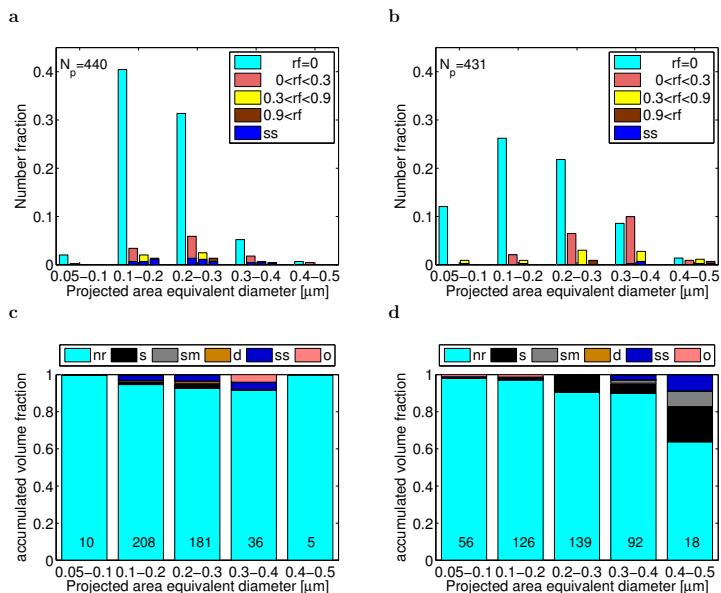
Figure 6. The classification of particles analysed with transmission electron microscopy. In **(a)** and **(b)** representing two different periods of the campaign: the fraction of the total number of particles studied (N_p) grouped according to the initial projected-area-equivalent diameter and the estimated refractory volume fraction (rf). Sea-salt is shown separately in blue in all the volume fraction ranges. In **(c)** and **(d)**, the volume fractions of the different groups of substances are shown: non-refractory (nr), soot (s), soot-mixtures (sm), dust (d), sea-salt (ss) and the refractory substances not falling into any of these classes are classified as "other" (o) for the same time periods as in **(a)** and **(b)** respectively. The numbers included in the lower part of each bar are the total number of particles with an initial PAED in that size range. More details about the individual samples are given in Table 2.

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