

Review Report Che et al.: Aerosol hygroscopicity over the Sout-Easty Atlantic Ocean during the biomass burning season: Part II – influence of burning conditions on CCN hygroscopicity

The authors present the monthly averages of the particle hygroscopicity from Cloud Condensation Nuclei activity measurements at Ascension Island Station in the Marine Boundary Layer of the Southeastern Atlantic for two consecutive Biomass Burning (BB) seasons (2016 & 2017). They explain the observed differences in the monthly mean values with changes in the aerosol particle composition, namely the change in contribution of sulphate (SO₄) species. They claim that these composition changes are mainly stemming from changes in the BB conditions on the African continent.

The topic is suitable for this journal and of interest for the atmospheric science community. While I agree with the general direction of their conclusion (BB aerosol has a very important influence on the hygroscopicity in the SEA region), I am not convinced by their specific arguments and interpretation as I specify in my comments below. Some of the authors' claims appear quite bold to me and lack enough supporting evidence from the presented data. I recommend major revisions to present a more comprehensive interpretation of the data.

Major comments

- 1) Focussing on SO₄ contribution to explain the trends – while ignoring NaCl from sea salt for most of the discussion.

This is my biggest concern about this manuscript. The authors use the change in SO₄ contribution as the main argument to explain the observed trends within a year and between the two years. They do mention that NaCl from marine sources probably influences the hygroscopicity and even prove the presence of NaCl in Section 3.2. In the paragraph lines 299 – 304, they state that the main differences between flaming and smouldering burning conditions is indeed the amount of BB aerosol reaching the station. Thus, the burning condition determines the ratio between (more hygroscopic) marine and (very likely less hygroscopic) BB aerosol. For me, this is a key finding but the authors then completely omit the presence of NaCl from their arguments and continue to use the SO₄ ratio as the main argument.

NaCl will affect the observed hygroscopicity much more than SO₄ related compounds as it has by far the largest k value of all included species and thus even a small amount will strongly change k . Since the ACSM cannot quantify NaCl, it is impossible to judge how much it is contributing at different times.

In short, I do not believe that the small change in SO₄ contribution can explain the observed differences while ignoring the other constituents – especially NaCl which the ACSM cannot see. In Specific comment (1), I provide more details about my concerns using the approximation of k from the ACSM & SP2 composition to show my doubts about the SO₄ fraction argument. The authors need to revise their chain of arguments and broaden their discussion to include the sea salt/NaCl impact and not just focus on SO₄.

- 2) Separating data from clean periods and BB plumes before averaging.

The authors present most of the data as monthly averages which are, of course, of general interest and should be reported to better understand the average hygroscopicity of this region. (Dobracki et al., 2024) provide an in-depth analysis of composition and optical properties of the 2017 part of the data set. In their Fig 1, they show that there are distinct plumes in the burning season of 2017. From the data in their Table 2, I calculated that the clean air periods account for 5% (September 2017) to 15% (July 2017) of the data. I assume the 2016 data will also show significant differences between the months and potentially also between the years.

This aspect (the frequency of BB plumes) is not covered in the discussion. Especially for the Section 3.3 and 3.4 it would be beneficial to separate the data from clean periods from the plume ones. In Figs 4 and 5 the clean period data points are probably close to $BC/\Delta CO=0$ and are not distinguished from the smouldering data points with $BC/\Delta CO < 0.003$. I would hazard a guess that a lot of the spread of the data points with $BC/\Delta CO \sim 0$ comes from having both smouldering BB plume data and clean air.

Separating the clean and plume data may also improve the correlation (R^2 values are pretty low) and thus strengthen the conclusions drawn from these Figures.

3) I find the approach for the correction of the “counting error” problematic and need some more information and clarifications.

- The authors only show data for the BB seasons (June – October in both years), but their description sounds like that there were continuous measurements for 18 months at the location. How does the rest of the data look like? Was there a continuous drift from Type 1 to Type 2? I.e., was the issue getting gradually worse with time or was there a sudden change?

A gradual change would point towards drift in instruments and no connection to the aerosol characteristics. A sudden change could point to some event affecting the instruments. If the difference seems chaotic (no clear trends) it is more likely that the discrepancy is linked to some aerosol property that changes over the months (e.g., special features of the size distribution, aerosol type).

- According to Zuidema et al. (2018), there were two more CPCs (cutoff at 10nm and 2.5nm) and a UHSAS at the station. How does the total number concentration from these instruments compare to SMPS and CCNC? Do they also become more different from 2016 to 2017?
- How often were the instruments calibrated during the 18 months? (and which calibrations were performed?)
- I assume there were regular SS calibrations with ammonium sulphate (AS) using the SMPS setup with the same CPC as during the measurements? Was the same concentration mismatch observed in these calibration measurements? Did the mismatch change between 2016 and 2017? Was there a size dependency?

If the calibrations also showed the discrepancy, it is very likely that there is simply a discrepancy between the CPC and CCNC. TSI states that their CPC counting is +/- 20% directly after calibration. If the calibration data looked fine, there is potentially some other systematic reason for the “counting error” and that it is different in 2016 and 2017.

If there was a size dependence in the AS data, there was probably a more complex issue than a simple counting error which probably cannot be fixed by a simple correction factor.

- The authors modify the approach by using an activation diameter corresponding to $k=0.6$. From the data presented in Fig 2, this value is a good estimate for the 2017 data. But the 2016 values are lower probably more like 0.3. How much does that affect the D_{50} in your calculation and how much will that then change the NSMPS value.
- Other source for overcounting of a CCNC: sheath air filter lets particles pass. The artefact gets more severe with higher particle concentrations and cannot be corrected with a simple correction factor. Was the sheath air filter regularly checked? Or at least at the start and the end of the campaign?

Specific comments

- 1) Focusing on the data for 2017, where composition information is available, one can compare the k values from the CCNC (k_{CCN}) with the estimation from the composition data (k_{chem}). I used the simple ion pairing scheme (Gysel et al., 2007) and typical values for density and κ (see Table 1) assuming that there are only the “usual” compounds (i.e., ammonium sulphate (AS), ammonium bisulphate (ABS), ammonium nitrate (AN), sulfuric acid (SA), organics (Org), and black carbon (BC)). To account for the range of k_{org} I used 0.1 as a lower estimate and 0.2 as a reasonable upper value. Using the values I took “by eye” from Fig 2 in the manuscript for June 2017 (Case 1 in Table 2), I calculate a k_{chem} of 0.367 ($k_{org}=0.1$) or 0.41 ($k_{org}=0.2$). k_{chem} is of course only an estimation relying on several assumptions (e.g., the value for k_{org} and density of organic, and that the ACSM composition is representative for the particles size range that activates). But the calculated k_{chem} values are so much lower than the average k_{CCN} .

However, the monthly trends for 2017 are reflected in the ACSM composition. Changing only the contribution of SO₄ and BC in the range that I estimated for the August 2017 case (BC doubles from 0.12 to 0.24 and SO₄ decreases by the same amount), k_{chem} decreases to 0.251 (Case 2). The amount of change (decrease by ~0.11) is similar to the decrease in k_{CCN} from June to August 2017.

In Case 3 (Table 2), I created an example of how much the composition would have to change to get k_{chem} in the range of 0.6. This is still assuming that there is no other compound in the particles. In this artificial case, the inorganic mass fraction is 0.75 and BC+organic are only 0.25. The particles are also shifted to the acidic regime (ABS and/or SA instead of AS) as ABS and SA have higher k values than AS. While this Case 3 is an arbitrary combination of numbers to reach $k > 0.6$, it shows how much the SO₄ to org+BC ratio would have to change to be in the right range for the k_{CCN} values for August 2017. The Case 3 also doubles to illustrate how much the SO₄ contribution would have to change to explain the difference between the 2016 values (avg k_{CCN} 0.3 – 0.45) and the 2017 ones (avg k_{CCN} 0.5 – 0.6). To repeat: to achieve a 0.2-0.3 increase in k , the SO₄ contribution would have to change from 35% to 75%! I considered that an unlikely scenario for this location.

To summarise, I found it not possible to achieve the observed k_{CCN} values of ~0.6 from the ACSM composition while using reasonable values for the parameters. I.e., the observed k_{CCN} values cannot be explained by the species measured with ACSM (and BC). But adding a small fraction of NaCl (e.g., 20%) easily creates k_{chem} values in the observed range.

Table 1: density and k values for the aerosol species/compounds

	density	kappa
AS	1.77	0.61
ABS	1.78	0.91
AN	1.72	0.67
SA	1.83	0.9
Org	1.3	0.1 or 0.2
BC	1.7	0

Table 2: Mass fraction of ACSM species and volume fractions calculated using the ion pairing scheme and the values from Table 1.

	Case 1	Case 2	Case 3
	mass fraction	mass fraction	mass fraction
SO4	0.35	0.23	0.625
NO3	0.025	0.025	0.025
NH4	0.1	0.1	0.1
Org	0.4	0.4	0.15
BC	0.12	0.24	0.1
	volume fraction	volume fraction	volume fraction
AS	0.174	0.305	0
ABS	0.213	0	0.556
AN	0.029	0.028	0.031
SA	0	0	0.098
Org	0.475	0.459	0.193
BC	0.109	0.21	0.098
	k_{chem}	k_{chem}	k_{chem}
$\kappa_{org}=0.1$	0.367	0.251	0.66
$\kappa_{org}=0.2$	0.414	0.300	0.675

The filter sample discussed later in the text prove that there are sea salt compounds (probably mostly NaCl) as well as K₂SO₄ and KNO₃ (and potentially KCl) from BB. Potassium salts are also not quantifiable by ACSM. But due to the low number of available samples this data cannot prove or disprove their importance for the observed k_{CCN} . But the fact that there is a considerable amount of other inorganic species with very high hygroscopicity means that changes in their contribution need to be considered when interpreting the composition/hygroscopicity relationship.

- 2) Paragraph 44 – 55 and Line 362ff: “...changes in aerosol hygroscopicity become crucial in influencing cloud properties.”: hygroscopicity (described by k) is indeed very important for the CCN activity. But for the formation of cloud droplets, the particle size distribution also matters a lot. E.g. an aerosol population with a lower k can lead to more cloud droplets if the size of this population is shifted to have a larger number concentration at $D_p > D_{50}$. How does this size effect compare to the k changes in the current data set? Or in other words, how much does the size distribution vary at this location? Any process that increases mass probably increases the average particle size and thus the ratio of particles with $D_p > D_{50}$.

Dobracki et al. 2024 shows some average size spectra for clean and plume periods (Fig 11). Size distribution completely changes from being dominated by the smaller size mode at 30-40 nm to the second mode at 160 – 220nm. The effect of the size change on NCCN/CDNC will be much higher than the hygroscopicity change. Is this size change also linked to burning condition? How does the effect of the size change measure up vs the impact of a different k when estimating, e.g., Cloud droplet number concentration?

- 3) Methods section: More information about the used instrumentation is needed. The brand and models of the instruments should be named. This can go into a table in the supplement information.
- 4) Line 88: The SMPS size range is given in Zuidema et al. 2018 is 15-450nm. Which values are correct? This is relevant as later there is an extrapolation up to 1000nm
- 5) According to the report and some of the other publications there was also a UHSAS with a range of 50 – 1000nm. Why was that data not utilised?
- 6) Fig 2: The “error bars” in the box plot (10% and 90%) suggests that there were some results in 2017 with k almost =1. To my knowledge no atmospheric organic aerosol can reach such high values. Only inorganics like NaCl or H₂SO₄ have such high k . Looking at the corresponding size distributions in Dobracki 2024, this would mean almost all particles activated at SS=0.1% SS. I find that difficult to believe – could the authors please comment on this. Also combining this with the stronger “overcounting” of the CCNC in 2017 I get suspicious. The authors suggest that their correction method fixed the issue. But without knowing what was really causing the change from 2016 to 2017 I have some doubts about the robustness of the results.
- 7) Line 218ff: It is not clear which of the filters in (Dang et al., 2022) are utilised here. The description in Table 1 of Deng et al and in section 2.3 has some discrepancies. Deng et al lists 15 filters for 2017 not 17. I assume the 6 samples labelled “below cloud” are the MBL cases the authors used. There 4 were marine and 2 BB plumes – not evenly distributed. These two BB cases were the most aged emissions in the study (9 and 15 days from fire). All were collected between August 17th and September 7th. The ACSM data shows the lowest SO₄ contribution for August 2017 and k_{CCN} is lowest. I wonder how representative these measurements will be for the whole BB season. To reiterate: the interpretation is based on 2 filters collected on August 24th and Sept 2nd! From the observation that a significant portion of SO₄ is linked to BB sources during those two days, the authors extrapolate that the observed monthly and yearly differences in k_{CCN} are linked mainly to the changes in SO₄ from BB sources. I find that very bold. Variations in sea salt contribution, changes in BC ratios, contribution of potassium salts are ignored in this interpretation.
- 8) Fig 2 and Fig 8 in (Dobracki et al., 2024) seem to not have data for the first week of September 2017. One of the two BB plume filters was collected on September 2nd. I do not know how far away the aircraft was from the station, i.e., how much later the air mass sampled by the aircraft would have arrived at Ascension Island. But this makes me wonder even more how the authors can base so much

of their interpretation on a filter sample that may not be very representative for the majority of their dataset.

- 9) Line 242: Does this really show that SO₄ stems from BB? Or does it mean that SO₄ is produced along the path of the BB particles before they get over the ocean? I am wondering if there are other not BB related SO₄ sources on the African continent along the trajectories. I.e., for time periods with more BB influence, the air is coming from the region with these other sources and thus times with more BB contribution will also have more of these not directly BB related SO₄ sources.
- 10) The assumption that the extrapolation of the k_{CCN} vs OA mass fraction relationship yields k_{org} is only strictly correct if no important aerosol constituent was missed in the calculation of OA mass fraction. As described above, it is highly likely that there is a considerable amount of inorganic compounds that ACSM&SP2 do not detect. Thus, the OA fraction is probably too high.
- 11) Paragraph 332- 340: Beside the previous point, this is another case where I find the authors quite bold in their interpretation of the data. The fast majority of data points has OA mass fractions of <0.6. This means a very “far” extrapolation towards OA mass fraction =1. Also the R^2 values are very low 0.21-0.24. How reliable is such a extrapolation in this case?
- 12) Fig 7b, Line 390 ff: Is the difference in wind significant? Is a 4% change enough to change the burning condition? How does this compare to the effect of the increase in easterly wind direction? I.e., less transport from BB source region to the measurement station.

Language & minor things

Overall the language and presentation is very good.

Line 22 “and thus a lower κ ” verb is missing (reduced from the first part of the sentence does not work for the second part)

Line 44 the “where” in this sentence refers to SEA which is not the place where the aerosol is emitted.

Line 94 “which Δ denotes” “which” is the wrong word here

Line 98&138 both section are numbered as “2.2”

Eq 1: (Petters and Kreidenweis, 2007) clearly state that this specific equation is an approximation for $k > 0.2$. The use of it is probably ok as most k values are indeed > 0.2 in this study. But the authors should use wording that represents that this equation is an approximation.

Fig 1: What are the values on the x axis? NSMPS total or 31-1000nm?

Fig 2: why did the authors chose not to use the established AMS/ACSM colour scheme (with green for organic and dark blue for NO₃)?

Fig 5 y axis label has $\Delta BC/\Delta CO$ but text uses $BC/\Delta CO$.

Fig 5 caption. “monthly percentages”. That is not the best way to describe what this figure is showing.

Fig 5 b where do the total carbon values come from?

Fig 7a what is meant with mean wind/RH 2016? Mean over the observed months?

References

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