Author's response to reviewers' comments

We are thankful to both the reviewers for their comments, suggestions and corrections that have helped improve this work. All corrections have been included in the manuscript. The reviewers' comments are written in blue and bold. The corresponding responses are written in black. The additional references have been given in the end and included in the main manuscript. Two new figures and one table have been added.

Anonymous referee # 1

General comment (1)

1. **It would be easier for the reader if all figures representing the same regions were all placed in the same order, e.g. as seen in Fig. 2 and keep the same regions in all other figures. For example, in Fig.2 SA branches (L, R1, R2, R3) are in the far right panels, while in Fig. 3 they are in far left panels and in Fig.4 they are in the middle. It may be a detail, but it would help uniformity and help the reader.**

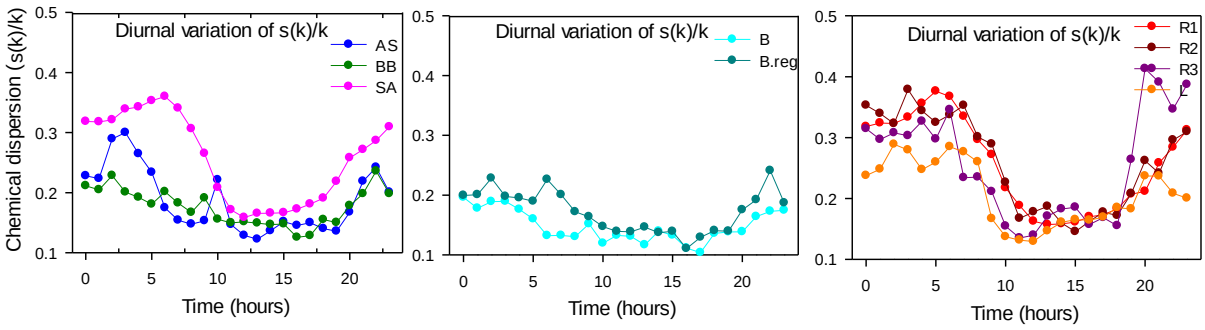
Response: The order of figures has been corrected and kept the same throughout the manuscript.

Specific comments (2-8)

2. **The standard deviation of κ (σ(κ)) around κ is often used as an estimate of the degree of heterogeneity (chemical dispersion) of particles (Psichoudaki et al., 2018; Lance et al., 2013). This could further be associated with the diurnal variability in the observed activation fractions as well as the chemical composition.**

Response: We appreciate that this analysis was pointed out. The chemical dispersion for all air masses and their sub-branches have been shown in the figure below. The chemical dispersion for SA air mass during the early hours (6:00-8:00) coincided with chloride emissions and during the late night after 20:00 with POA and OOA emissions. During the time of high chloride emissions, κ also peaked since inorganics are associated with high hygroscopicity, while during the late hours, κ dropped due to an increase in organics associated with low hygroscopcity. The diurnal patterns of activated fraction, GMD and chemical dispersion were also similar. This implies that higher heterogeneity shifts GMD to a high value, thereby increasing the available regime for activation and vice-versa. There was no discernable pattern noted for the other air masses. This explanation has been included in Section 3.5. Figure 1(a) has been included in the manuscript; 1(b) and 1(c) have been included in the supplement.

Figure1: Diurnal variation of chemical dispersion for the various air masses (a) AS, BB and SA, (b) B and B.reg, and (c) L, R1, R2 and, R3.



3. Since an AE33 aethalometer was used, the contribution of BCwb can be estimated (e.g. Sandradewi et al. 2008) in order to further verify the presence of biomass burning aerosol in the SA branches (P11,L7-8 and elsewhere (e.g. P11,L20-21)). The second component (BCff) could also verify traffic emissions (e.g. P13, L8-11).

Response: Thank you for pointing out this analysis. The contribution of BCwb and BCff for all air masses was carried out (Sandradewi et al. 2008), and the following table has been included in the supplement. Since fossil fuel sources are active the year-round, there is a strong presence of BCff ranging from 70% to 86%. However, biomass burning is only active during certain specific times for short durations and is very prominent in the north-west direction for the SA air masses. It was observed that the more distant air masses exhibited a higher BCwb contribution compared to those originating within close proximity. Hence, while L was associated with 13.9% BCwb, R3 exhibited 29.2%BCwb. The BCwb contribution for A and BB air masses was 21%. It can thus be concluded that both biomass burning and traffic emissions are important sources contributing to the chemical composition of the various air masses. This analysis has been included in the manuscript.

Table1: Contribution of BCwb and BCff for the various air masses

Cluster	BCwb	BCff
A	21%	79%
BB	21.60%	78.40%
SA	24.70%	75.30%
B	26.80%	73.20%
B.reg	21.60%	78.40%
L	13.90%	86.10%
R1	25.20%	74.80%
R2	29%	71%
R3	29.20%	70.80%

3. **P2,L1-3: High activation fractions as high as 0.8% at 0.38% SS have been observed at the eastern Mediterranean for air masses originating from the South (Bougiatioti et al., 2009)**

Response: P2, L1-3 has been edited as "The a_f was governed mainly by the Geometric Mean Diameter (GMD), and such a high a_f (0.71±0.14 for the most dominant sub-branch of SA air mass (R1) at 0.4% SS) has not been seen anywhere in the world for a continental site." This statement was made with reference to continental locations.

4. **Fig.3 BB (middle panels) for BC: it seems that many points are missing in the diurnal variability for B region, which is not commented in the text (P11,L20-28, P12,L21-28). Why is that?**

Response: Unfortunately, the aethalometer was not working during that time period and hence BC data could not be collected. The unavailability of data for BC for B region has now been pointed at P12, L 22-23.

5. **P14, L14-15: Also for the city of Athens, Greece, during wintertime when biomass burning is an important source of organic aerosol, overall hygroscopicity parameter ranged from 0.15 to 0.25 with lower values (around 0.16) being observed during night when biomass burning particles prevailed (Psichoudaki et al., 2018).**

Response: The above detail has been added after P14, L14-15.

6. **P3,L7 Detailed CCN and _ measurements have been carried out (delete "in India") .**

Response: The term "in India" has been deleted.

7. **Fig.2 (c) should read PM1 species, as now it is identical to (a)**

Response: Fig.2(c) has been corrected to read PM1 species.

Anonymous referee # 2

General comments (1-2)

1. **At the moment there is no evaluation of the quality of the data since there was no independent PM1measurement or CCN counter. But something can be done. A straightforward way would be to make a closure study of mass calculated from the number size distributions measured with the SMPS and as the sum of the chemical constituents of the ACSM + BC. Doing that remember the SMPS shows size distributions using mobility diameters whereas the ACSM size range is with aerodynamic diameters. I would like to see scatter plots for the major air masses and some discussion on them.**

Response: This analysis is indeed important. However, it has already been covered in a parallel manuscript Gani et al. 2019 that addresses the DAS (Delhi Aerosol Supersite) campaign. This detail has been added to the manuscript. The relevant scatter plot for mass closure has also been shown in the supplement (Figure S1). The following excerpt taken from Gani et al. 2019 addresses the above comment:

"*Using speciated mass concentrations and the PSD, we observed that C-PM_1 was highly correlated with SMPS-PM_1 (R^2=0.83), and we achieved almost complete mass closure (Fig. S1). That most of the PM_1 was composed of nonrefractory material and BC was consistent with past literature from Delhi which observed that metals and other nonrefractory crustal materials, which we did not measure in this study, constituted less than 5 % of PM_1 (Jaiprakash et al., 2017). We estimated that the C-PM_1 concentrations observed at our site were generally ~85 % of the $PM_{2.5}$ concentrations (R^2=0.54 and slope=0.85 for linear fit of hourly C-PM_1 and $PM_{2.5}$ concentrations over entire campaign) measured at the nearest monitoring station that is operated by the Delhi Pollution Control Committee (DPCC), R.K. Puram (3 km away), where the annual average $PM_{2.5}$ concentration for 2017 was 140 µg m^{-3}*."

2. **Another thing that I noticed is that the hygroscopicity parameter was calculated using only ACSM data. There was a lot of BC in air and that definitely as also an effect on κ. Find κ (BC) from the literature and repeat the calculations taking also BC into account.**

Response: κ (BC) has been taken as zero in several studies in the past (Hong et al. 2014, Leng et al. 2014, Wu et al. 2013). However, even on including BC in κ calculations, the difference in κ that was introduced was on an average 10%, shifting the mean κ of 0.32 to 0.29. The BC mass fraction and volume fraction was 10% and 9% respectively. The change in κ is not significant. The impact of BC on κ has been included in Section 3.4.

Detailed comments (3-27)

3. **P1,L12-13 The first sentence of the abstract "This work presents for the first time long term and time-resolved estimates of hygroscopicity parameter (κ) and CCN for Delhi" emphasizes that the measurements were long term. That is not really true since in generally long-term measurements are such that also trends of various properties can be estimated. A bit more than one year of data cannot be considered long term. Another thing is that the paper mainly presents variations of chemical composition, only a small part is about CCN. So it is somewhat misleading to start the abstract with the κ and CCN.**

Response: The first sentence of the abstract has been modified as "Delhi is a megacity that is subjected to high local anthropogenic emissions and long-range transport of pollutants. This work presents for the first time time-resolved estimates of hygroscopicty parameter (κ) and CCN spanning for more than a year derived from chemical composition and size distribution data."

With reference to CCN and κ estimates, such studies are usually short term and span over a month. This data is hence huge as it spans for more than a year. The term "long term" has been replaced by "spanning for more than a year". In addition to it, the paper presents variations of chemical properties but it has been tried best to capture their effects

on both κ and CCN. The aim of starting the abstract with this idea is because this is the most valuable contribution of the work and is extremely relevant for the Indian sub-continent that faces a dearth of such data.

4. **P3,L31-32 "... relatively lesser traffic compared to the city in general ..." "lesser" is wrong here. The comparative of little is "less", not "lesser". -> ... relatively less traffic than the city in general.**

Response: The word "lesser" has been replaced by "less".

5. **P3, Section 2.1 This is the section showing the ACSM instrument. Write the particle size range it measures.**

Response: It has been mentioned in Section 2.1 that ACSM is equipped with a PM1 cyclone.

6. **P4,L13 in the title 2.2, is the acronym OOA right or should it be POA?**

Response: It should be OOA as the speciation of organics has been discussed.

7. **P4,L31 What are the residuals here? Explain.**

Response: Residuals represent the deviation of the cluster means from the reference profiles. The mathematical definitions have been given in Equations 1 and 2in the manuscript.

8. **P5,L6-17 This text looks like it is taken from a computer program. Explain in a short text the contents of it and move this text to the supplement.**

Response: The referred text has been replaced with the following text:

"The residuals of the cluster means were then compared with the reference residuals as per six conditions described in detail in Text S1 and classified as HOA, BBOA, OOA or mixed."

9. **P5,L24-26. Present the hygroscopicity parameters of the different compounds clearly in a table and add there the references of the papers where you got them from. A compilation like that helps the readers.P5,L32 Bhattu et al. (2015) calculated Dc using ammonium sulfate, ammonium nitrate, insoluble organics and soluble organics and gives the respective constants. You have different constituents so you should show all constants you have used either in a table or in the text like Bhattu et al. (2015) did.**

Response: This has been addressed by the addition of the following text:

"κ_i values were taken as 0.61 for $(NH_4)_2SO_4$, 1.02 for NH_4Cl and 0.67 for NH_4NO_3 (Sullivan et al., 2009; Petters and Kredenweis 2007). The density values to estimate the volume fraction of the inorganic constituents were taken as 1770kgm^{-3} for $(NH_4)_2SO_4$, 1519 kgm^{-3} for NH_4Cl and 1720 kgm^{-3} for NH_4NO_3 (CRC Handbook of Physics and Chemistry, 95th Edition). The density of organics was taken as 1.5 gcm^{-3} (Bougiatioti et al., 2009)."

The hygroscopicity parameter for organics has already been reported in the manuscript.

10. P6,L1, "...CCN.." -> NCCN

Response: CCN has been replaced by 'NCCN'.

11. P6, Eq (4) correct toulene -> toluene

Response: *The word 'toulene' has been corrected to 'toluene'.*

12. P7,L1 [OH] is definitely not constant, it varies a lot. Discuss this a bit.

Response: The value for OH has been taken as $1.5X10^6$ molecules cm^{-3} for aging calculations similar to Nault et al. 2018 for aging calculations**.** We agree that [OH] is not constant, however, assuming it to be constant for aging calculations is standard practice (Nault et al. 2018). As per the authors' knowledge, the detailed diurnal variation of [OH] for Delhi is not known and hence has not been commented upon. The following detail has been added to the manuscript "The [OH] concentration is not constant and varies considerably temporally and spatially, but due to unavailability of data pertaining to its variation for Delhi, it has been assumed constant for aging calculation."

13. P8,L19 Define aerosol neutralization ratio. Explain and give formulas.

Response: Aerosol Neutralization Ratio (ANR) is defined as per Zhang et al. 2007 as the normalized ratio of the measured NH_4^+ concentration to the NH_4^+ concentration needed for full neutralization of the anions. The formula for the same is given below:

$$ANR=\frac{NH_4^+ meas}{NH_4^+ neut}=\frac{(NH_4^+/18)}{(2XSO_4^{2-}/96)+(NO_3^-/62)+(Cl^-/35.5)}$$

This detail has been added to the manuscript.

14. P8,L28, 1 < R > 2 is never possible. Correct.

Response: This has been corrected to 1<R<2.

15. P9,L12 "...AS was associated with BBOA...". What does this mean?

Response: It implies that the organic aerosols for the AS (Arabian Sea) air mass are of biomass burning type.

16. P10,L15, "... ammonium nitrate is relatively more stable than ammonium chloride..." Give a reference.

Response: This has been explained in Kaneyasu et al., 1999.

17. P10,L20 "chloride depletion". Give formula or explain clearly what you mean here. I have calculated chloride depletion when comparing Cl-to-Na ratios in filter samples with the same ratios in pure sea salt. Now it is not possible, ACSM gives no Na concentrations.

Response: "Chloride depletion" refers to the decrease in chloride concentrations for SA air mass beginning close to mid-day. This is not with reference to Cl-to-Na ratios. To avoid ambiguity, it has been replaced with the term "reduction in chloride concentrations."

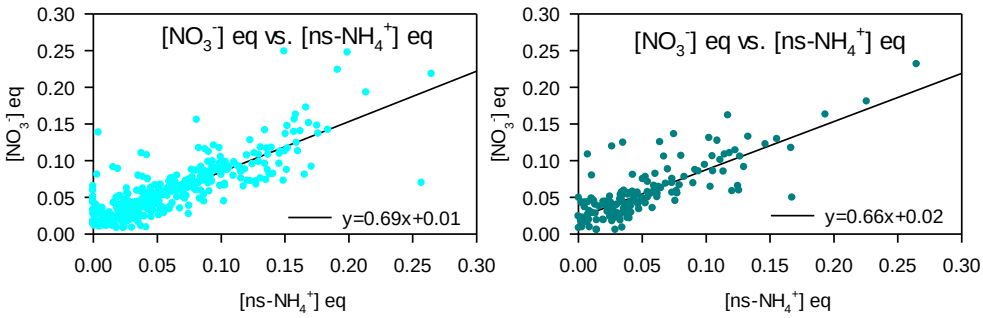
18. **P11,L4 "Hike in sulphate concentration...". What does hike mean here? Explain or rewrite clearly.**

Response: "Hike in sulphate concentration..." implies a peak or increase in sulphate concentration and the word 'hike' has been replaced by the word 'peak' for clarity.

19. **P12,L14 "The correlation of NO3 with ns-NH4 was found to be very poor..." Show some scatter plots, eithier in the main text or the supplement.**

Response: Thank you for pointing this out.The noise in the data for correlation calculation was not removed for B.reg. For both B and B.reg, ns-NH_4^+ correlated well with NO_3^-, the correlation values being 0.63 and 0.70 respectively. The scatter plots for the same have been included in the supplement and are shown below.

Figure2: Scatter plots between ns-NH_4^+ vs. NO_3^- for B (left) and B.reg (right) branches.



This also resulted in a change in the dominant salt assumption for B.reg, which was earlier only $(NH_4)_2SO_4$. It has been changed to $(NH_4)_2SO_4$ and NH_4NO_3. Following changes have specifically been made.

1. P12, L14-L18 have been edited as under:

"The correlation of [NO_3^-] with [ns-NH_4^+] was found to be appreciably high for both B and B.reg. For both of these branches, the fossil fuel combustion resulting in NO_3^- emissions in combination with NH_4^+ (Rajput et al., 2015; Pan et al., 2019) can lead to NH_4NO_3 formation."

2. P9, L7 has been edited as under:

"Coupling of ns-NH_4^+ with NO_3^- revealed a good correlation for B (0.70) and B.reg (0.63)."

3. P9, L10-11 has been edited as under:

"Thus, the dominating salts are $(NH_4)_2SO_4$ for AS, $(NH_4)_2SO_4$ and NH_4NO_3 for BB air-mass and NH_4Cl for SA and its sub-branches."

20. **P12,L21 " The BC concentration in BB air masses was considerably lower than SA." Here is a grammatical error. The sentence means that BC concentration is smaller than South Asia! It should be " The BC concentration in BB air masses was considerably lower than in the SA air masses." There are similar errors in several sentences in the paper. Check and correct.**

Response: P12, L21 has been corrected to “The BC concentration in BB air masses was considerably lower than in SA air mass”. All such errors have been likewise corrected.

21. **P13,L5 "lesser" is a wrong word. Rewrite the sentence**

Response: The word “lesser” has been replaced by “less”.

22. **P13,L13 " Both BC and POA are quite less compared to SA." I don't understand, rewrite.**

Response: P13, L13 implies that the BC and POA concentrations for the AS air mass are substantially low relative to their concentrations for the SA air mass. It has been replaced with the text: “Both BC and POA for AS air mass are less than in the SA air mass.”

23. **P13,L17-24 This text is clearly conclusions so why don't you have it there in the "Conclusions" section?**

Response: P13, L17-24 has been moved to the “Conclusions” section.

24. **P13, L26 A bit more than a year is not "long term".**

Response: This has been discussed in response to 3.

25. **How do the κ values look like when you take BC into account?**

Response: This has been discussed in response to 2.

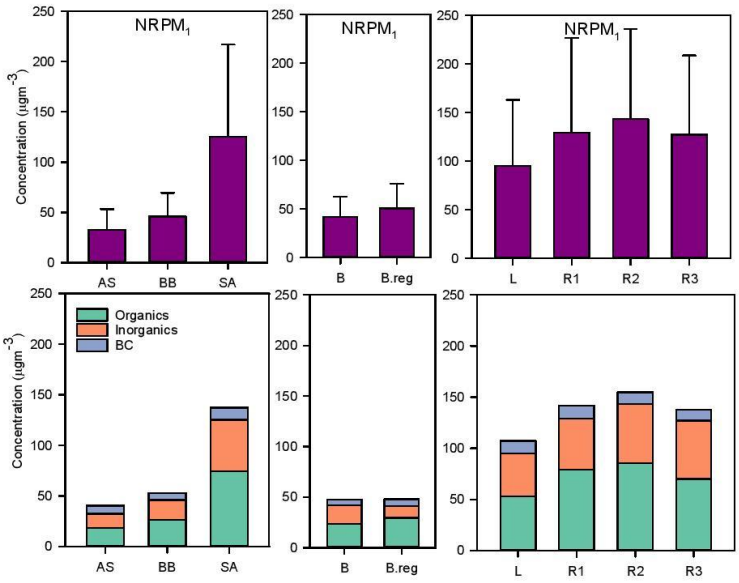
26. **P15,L19- Note that NCCN was measured with a CCN counter in the other studies and the activated fraction was actually measured. So I would be careful in making very strong conclusions.**

Response: The values of activated fraction for this study were found to be very high and N_{CCN} values were consistent with other polluted sites in the world based on size distribution data and chemical speciation data. It is the best that could be done with the data available at hand. However, I do believe that with the actual measurements, there can be new developments and any work of science is open to criticism based on scientific evidence, and so is this work.

27. **P31,Fig 1. In the uppermost subfigures the bars should be the mean values of NRPM. In the middle subfigs the sum of the constituents should be the same as in the upper subfigures. But they are not. What is wrong?**

Response: Thank you for pointing this out. The figure has been corrected and is shown below.

Figure 3: Mean values of (a) $NRPM_1$ (b) Organics, inorganics and BC



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