

## Response to the Referee (RC) 1

Review to “Hygroscopicity of Size-Selective Aerosol Particles at Heavily Polluted Urban Atmosphere of Delhi: Impacts of Chloride Aerosol”

The authors present field measurements of size-resolved aerosol hygroscopic growth at 90% RH and bulk aerosol composition of non-refractory PM<sub>1</sub> during wintertime in Delhi, India, and investigate the impacts of chloride on aerosol hygroscopicity and its potential to enhance aerosol-bound liquid water. The paper provides observational evidence of Ammonium Chloride as the major contributor to aerosol hygroscopic growth and liquid water content in Delhi, which highlights the role of Ammonium Chloride in aerosol-water interaction and related haze development. I would recommend publication once the following concerns are addressed.

Major comments:

1) The manuscript is a bit long and wordy to me. The authors put too much effort on the overview of the 1.5-month field measurement, and enumerate the ranges of many aerosol properties, e.g., PM<sub>1</sub> mass concentration, chemical composition mass of different species. For example, “BBOA mass concentration varied between 0.0 to 134.7  $\mu\text{g}/\text{m}^3$ ”, I feel sentences like this are not as informative, and should be reduced as much as possible.

Response:

Authors thank the reviewer for highlighting this point. We have removed the sentences which were not much informative. Please see the changes in the revised manuscript (MS).

2) I strongly suggest the authors add a representative case study including major gaseous pollutants, aerosol size distribution, chemical composition, and GF-PDF of 1~2 sizes, to showcase the driving effect of NH<sub>4</sub>Cl on aerosol hygroscopicity and see if NH<sub>4</sub>Cl exists in all size ranges (i.e., 20~200, from GF-PDF).

Response:

Authors thank the reviewer for the constructive comments. Your suggestion looks very legitimate.

*However, we have specific limitations concerning aerosol chemical composition. ACSM gives only bulk chemical composition without size-resolved composition. Therefore, we chose only the most suitable 200 nm aerosol particle to look at the driving effect of NH<sub>4</sub>Cl on aerosol hygroscopicity. We have already discussed all sizes of GF-PDF and hygroscopicity in case studies like H-BB, H-Cl, H-HOA, and Clean periods. However, we think making additional case studies to incorporate your suggestion seems too repetitive here. Therefore, instead, we described major gaseous pollutants and aerosol size distribution in addition to H-BB, H-Cl,*

*H-HOA, and Clean periods in the revised manuscript in such a way that you described in your comment.*

3) As shown in Fig. 3a, the  $\kappa$  of 20 nm particles look quite scattered to me. For the GF-PDF of 20 nm, I am curious about how many counts of 20 nm particles were sampled for each cycle. As the counting statistics may affect the inversion of GF-PDF. According to a recent study, a total of at least 100 particle counts might be a requirement for reliable GF-PDF inversions (<https://doi.org/10.5194/amt-15-2579-2022>).

Response:

Authors thank the reviewer for mentioning the importance of counting statistics requirement for reliable GF-PDF inversions.

*We have gone through the above-mentioned article and checked the counting statistics and GF-PDF of 20 nm. We found that the 20 nm particle counts are less than the recommended statistics from recent article for low aerosol loading times. Authors already followed various recommended filtering processes for good scans, as mentioned in the section, and discarded significant scans. However, authors think that for region like Delhi using HTDMA instruments it will be well justified to have a slightly lesser count.*

4) As shown in Fig. 4, the diurnal variation of  $\kappa$  is overshadowed by the hydrophobic mode (e.g.,  $HGF < 1.2$  for 100 nm). I would suggest the authors to isolate the hygroscopic mode and calculate the corresponding  $\kappa$ . To do so, you could either set a fixed threshold of HGF or fit the bi-modal GF-PDFs and calculate  $\kappa$  using the more hygroscopic mode. By doing this, the authors could probably compare the  $\kappa$  of the hygroscopic mode to pure  $NH_4Cl$ .

Response:

Thank you for your constructive comments. Your suggestion looks very legitimate.

*We calculated the  $\kappa$  for  $HGF > 1.2$  per the reviewer's suggestion. However,  $\kappa$  ( $0.26 \pm 0.03$ :  $HGF > 1.2$ ) was not comparable to the 0.93 hygroscopicity of pure  $NH_4Cl$ . In addition, assuming only inorganic salts contribute to  $HGF > 1.2$ , the calculated hygroscopicity was found to be  $0.52 \pm 0.10$ , higher than the observed value of  $0.26 \pm 0.03$ . It could be due to the secondary organic aerosol significantly contributing to the  $HGF > 1.2$ . As we mentioned earlier, we could not calculate hygroscopicity for  $HGF > 1.2$  due to the instrument limitation.*

5) Line 351-352: The authors attribute the two-peaked pattern in the GF-PDF to daytime photochemical reactions. If that is the case, why does the HGF decrease at noontime when photochemical activities are supposed to be even stronger.

Response:

Thanks for the comment.

*We agree with the reviewer. Therefore, the primary peak ( $HGF < 1.2$ ) shifted towards the higher due to the intense daytime photooxidation, as shown in Fig. 5. However, at the same time, lower inorganic contribution, especially  $NH_4Cl$ , and the secondary peak ( $HGF > 1.2$ ) shifted towards the lower HGF side, potentially responsible for the lower daytime HGF.*

6) Regarding the minor difference in  $\kappa_{200nm,90\%}$  for H-BB and H-HOA events, I doubt if that because the two events are not well separated from each other. Do the authors have a general criterion for separating the three different events, or at least show how much overlapping there is between the two events.

Response:

Thank you for your comment.

*H-BB and H-HOA were separated according to significant BBOA and HOA concentration peaks, respectively. We feel that there is no overlapping of the events as these events do not subsequently happened, as mentioned in Fig. 2. Previous studies (Chakraborty et al., 2014 and Mandariya et al., 2019) in the IGP have shown that BBOA and HOA are difficult to distinguish as they both have significant mixed signatures ( $m/z$  43, 55, 57, and 60) in their mass spectra. ACSM has limitations concerning OA mass spectra as it proved only bulk  $m/z$  without high-resolution  $m/z$  fragmentation mass spectra. It could be the reason for the possible mixing of H-HOA and H-BB events. However, as mentioned in the supplementary, we followed standard protocol to separate the HOA and BBOA sources. Therefore, there is a non-significant ( $p > 0.05$ ) difference in hygroscopicity, possibly due to the relative changes in primary, secondary OA, and inorganic species. In the H-HOA events, the negative effect of a significantly higher fractional (41%) contribution of HOA to OA possibly balances with a positive impact of a 7% increment in secondary OA relative to H-BB.*

Chakraborty, A., Bhattu, D., Gupta, T., Tripathi, S. N. and Canagaratna, M. R.: Real-time measurements of ambient aerosols in a polluted Indian city: Sources, characteristics, and processing of organic aerosols during foggy and nonfoggy periods, *J. Geophys. Res.*, 120(17), 9006–9019, doi:10.1002/2015JD023419, 2015.

Mandariya, A. K., Gupta, T. and Tripathi, S. N.: Effect of aqueous-phase processing on the formation and evolution of organic aerosol (OA) under different stages of fog life cycles, *Atmos. Environ.*, 206(November 2018), 60–71, doi:10.1016/j.atmosenv.2019.02.047, 2019.

Minor comments:

1) Line 101: Use subscript in “ $(NH_4)_2SO_4$ ”.

Response:

Thanks for pointing it out. As suggested, this comment has been addressed in the revised manuscript.

*(Line 99-101) “The humidity sensors positioned in the second DMA were calibrated automatically with 100 nm ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) particles every 30 min at 90% RH to analyze the stability at high RH.”*

2) Line 159: Wrong expression in equation (1).

Response: Thanks for pointing it out. The equation has been corrected in the revised manuscript.

*(Line 152)*

$$\kappa_{H-TDMA_{90\%}} = (HGF_{90\%}^3 - 1) \left[ \frac{1}{RH} \exp\left(\frac{4\sigma M_w}{RT\rho_w D_o HGF_{90\%}}\right) - 1 \right] \quad (1)$$

3) Line 236: Full spell “MPSS” where it is mentioned for the first time.

Response:

Thanks. As suggested, this comment has been addressed in the revised manuscript.

*(Line 83-88 and 119-121) “Real-time atmospheric aerosol measurements were conducted simultaneously using Hygroscopic-Tandem Differential Mobility Analyzer (H-TDMA), Mobility Particle Size Spectrometer (MPSS), and Aerodyne Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research, Billerica MA) during winter (1<sup>st</sup> February 2020 to 16<sup>th</sup> March 2020) at the Indian Institute of Technology (IIT) Delhi in Block 5, at the height of nearly 15 m as shown in Fig. 1. The lab-2 is situated at the height of 15 m above the ground level and lab-1 is 50 m apart from lab-1.”*

4) Line 239-241: The value of OA mass concentrations does not seem to be consistent with that reported in Gani et al., (2019).

Response:

Thank you for your constructive comments. As suggested, we modified the statement for better explanation and this comment has incorporated in the revised manuscript.

*(Line 261-265) “The OA ranged between 1 and 293 (46.5 ± 39.6) µg/m<sup>3</sup> with the predominant fraction of PM<sub>1</sub>, consistent with the range of 53.3 to 166 (112) µg/m<sup>3</sup> observed during winter (December-February) at the present site (Gani et al., 2019). However, lower average OA*

*concentration could be explained by the measuring period of February-March, as aerosol loading starts decreasing in February after reaching its peak in December-January (Gupta and Mandariya, 2013)."*

5) Line 300: HGF<sub>90%</sub><sub>200nm</sub> of "1.12-1.179", but average to  $1.41 \pm 0.09$ ?

Response:

Thanks for pointing it out. We realize that it is typo mistake. This sentence has now been corrected in the revised manuscript.

*(Line 318-322) "The hygroscopic growth factors of 20 (HGF<sub>90%</sub><sub>20nm</sub>), 50 (HGF<sub>90%</sub><sub>50nm</sub>), 100 (HGF<sub>90%</sub><sub>100nm</sub>), 150 (HGF<sub>90%</sub><sub>150nm</sub>), and 200 nm (HGF<sub>90%</sub><sub>200nm</sub>) size particles varied between 1.00-1.41, 1.05-1.39, 1.11-1.49, 1.12-1.63, and 1.12-1.79 with an average of  $1.14 \pm 0.09$  (average  $\pm$  standard deviation),  $1.16 \pm 0.06$ ,  $1.27 \pm 0.07$ ,  $1.35 \pm 0.09$ , and  $1.41 \pm 0.09$ , respectively."*

6) Line 405: Full spell "ALWC" where it is mentioned for the first time.

Response:

Thanks for pointing it out. This sentence has now been modified accordingly in the revised manuscript.

*(Line 425-427) "Further, ammonium chloride has a more significant water uptake potential (Chen et al., 2022; Zhao et al., 2020), which can be justified by the solid correlation of aerosol liquid water content (ALWC) with a mass fraction of ACI in PM<sub>1</sub> as shown in Fig. 6(b)."*

Comments for figures:

1) Figure 1a and 1b: The lines are overlapped with the shaded boxes, looks like in-continuous data. Describe the shaded boxes of different colors in the caption.

Response:

Authors thank the reviewer for pointing it out. The Fig. 2 now has been corrected in the revised manuscript.

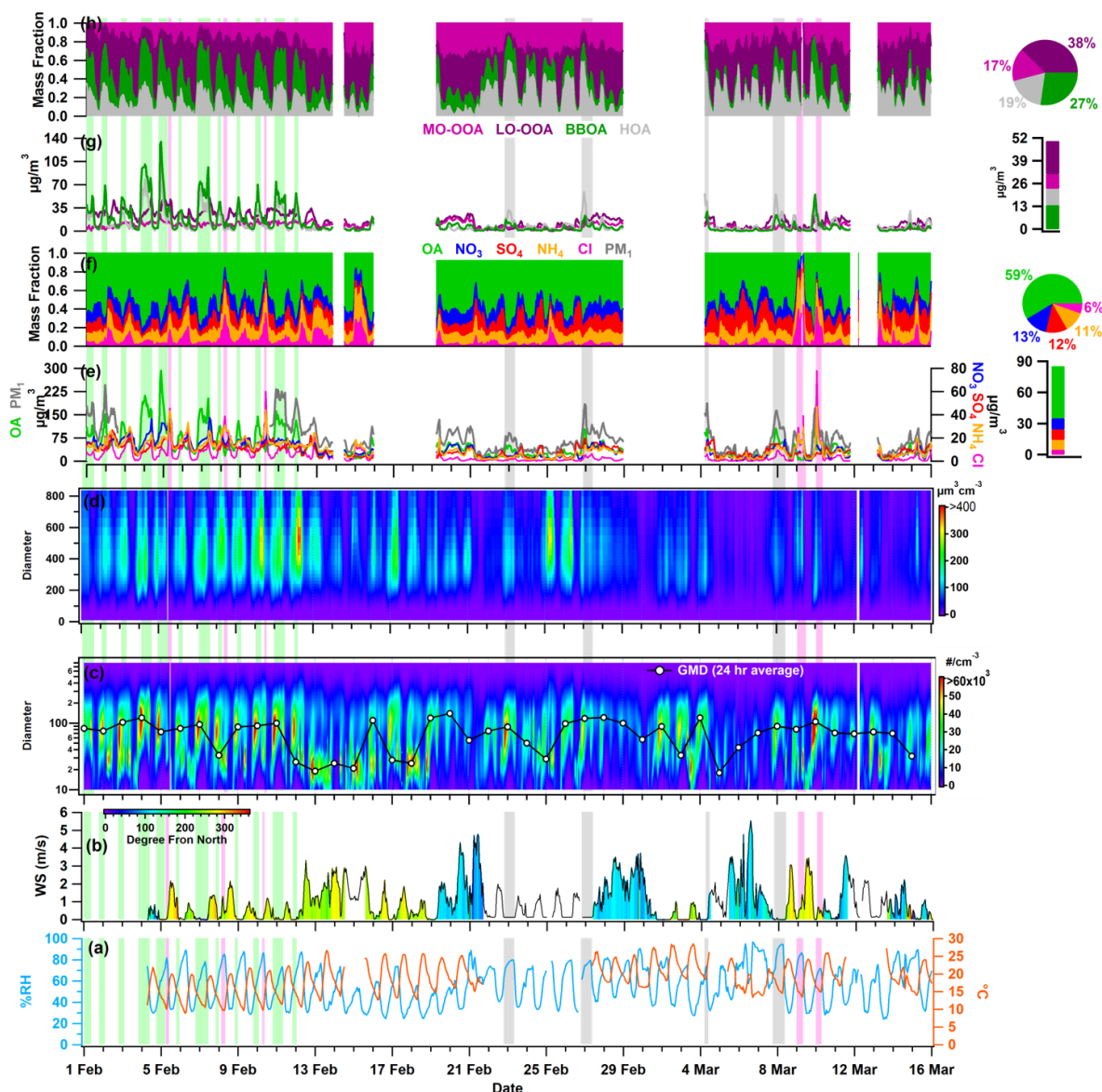


Figure 2: Temporal variability of ambient (a) relative humidity (RH), temperature (T), (b) wind speed (WS), wind direction (WD), (c) particle number-size distribution (PNSD), 24-average geometric mean diameter (GMD), (d) particle volume-size distribution (PVSD), (e) particulate matter ( $PM_{10}$ ), organic aerosol (OA), nitrate ( $NO_3$ ), sulfate ( $SO_4$ ), ammonium ( $NH_4$ ), chloride (Cl), (f) fractional contribution of OA,  $NO_3$ ,  $SO_4$ ,  $NH_4$ , and Cl in  $PM_{10}$ , (g) more oxidized-oxygenated OA (MO-OOA), less oxidized-oxygenated OA (LO-OOA), biomass burning OA (BBOA), hydrocarbon like-OA (HOA), and (h) fractional contribution of MO-OOA, LO-OOA, BBOA, and HOA in OA. The pie chart sub-plot represents the overall average contribution of species, and the bar sub-plot represents the overall campaign average value of different species. All other species are represented with specific color coding mentioned in legends. The light green, pink, and grey color shaded vertical line indicates the high-BBOA (H-BB), high-HOA (H-HOA), and high-Cl (H-Cl) events, respectively. The discontinuity in the data points marks the missing data or non-sampling time.

2) Figure 2o: The y-axis label is blocked.

We sincerely thank the reviewer for pointing it out. The plot has been corrected in the revised manuscript.

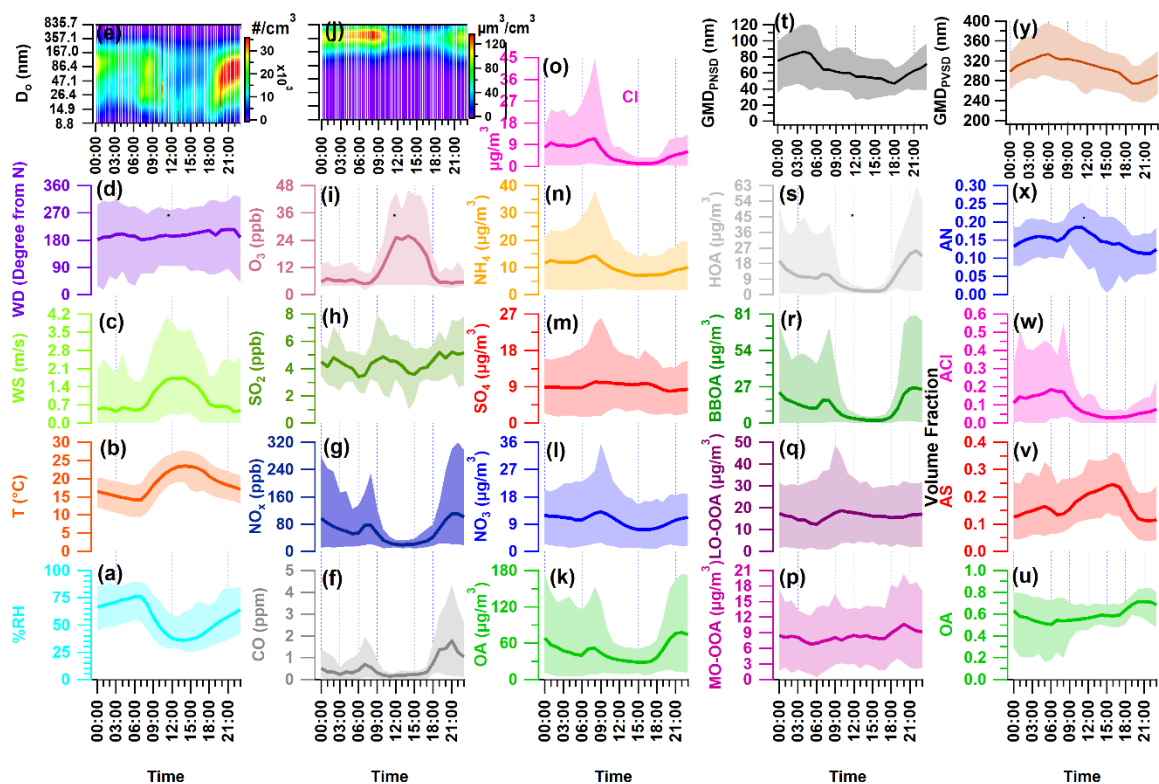


Figure 3: Diurnal variation of ambient meteorological parameters (a) % ambient relative humidity (RH), (b) temperature (T), (c) wind speed (WS), (d) wind direction (WD), and (e) particle number size distribution (PNSD), mass concentration of ambient trace gases (f) carbon mono-oxide (CO), (g) nitrogen oxides (NO<sub>x</sub>), (h) sulfur dioxide (SO<sub>2</sub>), and (i) ozone (O<sub>3</sub>), (j) particle volume size distribution (PVSD), mass concentration of aerosol constituents (k) organic aerosol (OA), (l) nitrate (NO<sub>3</sub>), (m) sulfate (SO<sub>4</sub>), (n) ammonia (NH<sub>4</sub>), and (o) chloride (Cl), mass concentration of organic aerosol species (p) more oxidized-oxygenated OA (MO-OOA), (q) less oxidized-oxygenated OA (LO-OOA), (r) biomass burning OA (BBOA), and (s) hydrocarbon like-OA (HOA), (t) geometric mean diameter of particle number size distribution (GMD<sub>PNSD</sub>) and volume fractional contribution of (u) organic aerosol (OA), (v) ammonium sulfate (AS), (w) ammonium chloride (ACI), and (x) ammonium nitrate (AN) in PM<sub>1</sub>, and (y) geometric mean diameter of particle volume size distribution (GMD<sub>PVSD</sub>). Upper and lower boundary of shaded area represents the 95<sup>th</sup> and 5<sup>th</sup> percentile values of respective species.

3) Figure 2d: The diurnal WD pattern looks quite different from the wind rose plot (i.e., Figure S6). The latter suggested a negligible fraction of southerly wind.

Response:

The authors thank the reviewer for the comment. The wind directions predominantly varied from 20 to 330 degrees from the north; therefore, Fig. 2d shows the statistically average WD of nearly 180 degrees. However, in a real scenario, southerly WD has a negligible fraction.

4) Figure 3: line 332, is Fig. 3d for 150 nm?

Response:

Thanks for pointing it out. As suggested, this suggestion has been incorporated in the revised highlights.



(Figure 4d: Line 352-353) “(d) 150 nm ( $\kappa_{150nm\_90\%}$ ), and (e) 200 nm ( $\kappa_{200nm\_90\%}$ ).”

5) Figure S5: Use a consistent unit, ppb or  $\mu\text{g m}^{-3}$ .

Response:

The authors thank the reviewer for the comment. Fig. S5 has been revised in the revised supplementary.

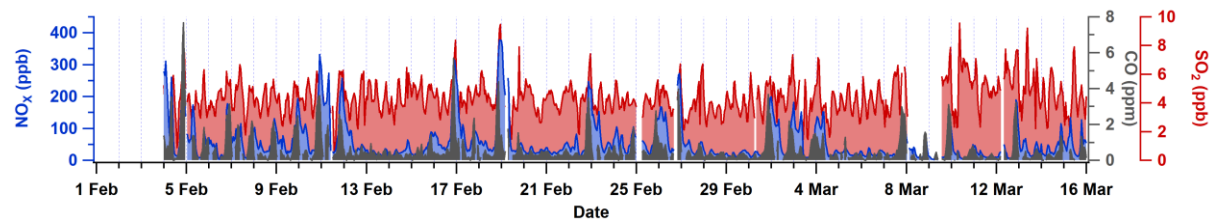


Figure S5: Temporal variability in atmospheric  $\text{NO}_x$ ,  $\text{CO}$ , and  $\text{SO}_2$  gases concentrations.

6) Figure 8: Add a legend for the pie chart here.

Response:

Thanks. We modified the plot and add color legends in the plot to accommodate your comment.

(Line 603-609)



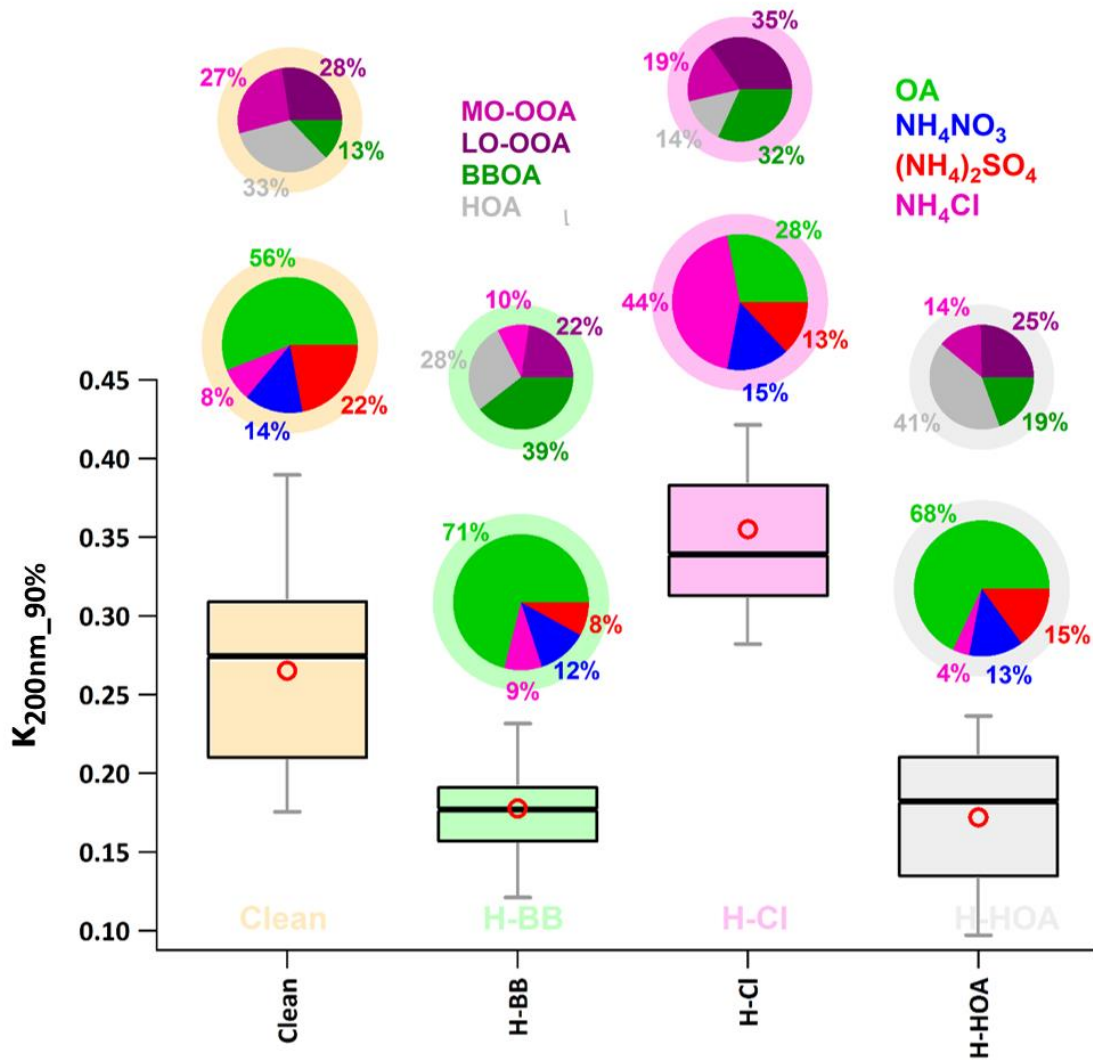


Figure 9: Box plot showing variation in H-TDMA measured hygroscopic parameter of 200 nm size particles ( $\kappa_{H-TDMA}$  ( $\kappa_{200nm\_90\%}$ )) in high biomass burning (H-BB), high-chloride (H-Cl), and high-hydrocarbon like organic aerosol (H-HOA) events. Different colors represent respective events in the plot. A bigger pie chart represents the overall average volume fractional contribution of various aerosol species indicated by color-coding. In addition, minor pie charts described the event average mass fractional contribution of different OA species in OA. Diffused ring color of the pie chart displays the respective event.