Responses to anonymous referee #1

General Comment:

Ye Kuang et al. presented a field campaign results to characterize aerosol hygroscopicity with high time resolution at 80 % RH using humidified nephelometer. A high-resolution time-of-flight mass spectrometer was used to determine size-resolved aerosol chemical composition. Additionally, NOx and O3 concentrations were measured, which allowed tracing diurnal variations of organic constituents. Using measurements results of particle size distribution as inputs of Mie theory and -Köhler model the hygroscopicity κf,80% was obtained. Based on ZSR rule the organic hygroscopicity parameter, κOA was retrieved and analyzed. It was documented that κOA weakly correlate with oxidation level parameter O/C of the total organic. More detailed analysis shown that κOA negatively correlate with hydrophobic and night time formed OA fractions, while it positively correlate with aged biomass burning aerosol (aBBOA) (r = 0.35; O/C = 0.39) and more oxidized organic (MOOA) (r =0.64; O/C ~ 1). In contrast κOA negatively correlate with low oxidized organic (LOOA) (r = -0.25) having O/C ratio of ~0.79. It is suggested that the contrasting effect of LOOA and aBBOA on κOA is the result of a complex processes leading to SOA formation with different chemical composition, functional properties and microphysical structure, which are not captured by a single O/C parameter. The science in this paper is relevant to ACP's audience. The reviewer thinks that further clarification would be required prior to publication in ACP.

Response: We thank the reviewer for raising important questions that need to be clarified, which helped improve the quality and readability of this manuscript. Based on the suggestion of the reviewer, we have performed several simulation experiments to quantify the accuracy of using $\kappa_{f(\mathrm{RH}),PM_{10}}$ represent κ_{chem,PM_1} and quantify the uncertainties associated with κ_{OA} derivation, estimate potential impacts of aerosol mass concentrations perturbations on the relationships between κ_{OA} and organic aerosol factors. We believe that the revised manuscript is now more convincing than before.

Major comments:

Comment: What is the aerosol resident time at 30 % and 80 % RH? Have you performed test measurements to make sure that the humidified residence time is sufficient to allow PM1 particles to grow to equilibrium? This is important, given that particles in the range of 200-800 nm make the main contribution to the scattering coefficient.

Response: Thanks for your comment. The controlling factor that determines the aerosol equilibrium with the fixed RH environment is the sensing volume of nephelometer and the sample flow rate, and sensing volume of the nephelometer is about 0.4 L (from the brochure for Aurora 3000 nephelometer), and sample flow is 3 L/min, thus the estimated residence time of aerosol in the fixed RH environment is about 8 s. In addition, the residence time of aerosols in the humidifier tube and downstream tube is about 6 s. We did not perform the test measurements to make sure that the humidified residence time is sufficient to allow PM_1 particles to grow to equilibrium before the start of this field campaign, but previous experiences with the same instrument have shown that the residence time is enough for equilibrium. This humidified nephelometer system is used for RH scan aerosol light scattering enhancement factor measurements with a flow rate of 4 L/min (larger than 3L/min of this campaign) (Zhao et al., 2019), the observed Ksca (RH=80%) show similar ranges with this field campaign. The results shown in Zhao et al. (2019) demonstrate that the equilibrium is always reached with RH>80%.

Comment: What is the accuracy in κOA calculation? Besides environmental factors that are a mainly source of random errors, inaccuracy associated with the calculation of κ_{fRH} volume fractions and aerosol composition measurements can lead to serious systematic error. Have you estimated their input to κOA when using Eq.(3)? If yes, please show it.

Response: Thanks for your valuable suggestion. We agree with reviewer that we didn't perform comprehensive uncertainty analysis in the original manuscript, and we should show these results to boost readers' confidence about this method. In Eq.3, other than aerosol composition measurements, what's the accuracy of using $\kappa_{f(\mathrm{RH}),PM_{10}}$ to represent κ_{chem,PM_1} need to be carefully quantified, although simulation results using different PNSDs coupled with different size-resolved κ distribution scenarios are discussed in Sect 3.2 of the original manuscript. As discussed in Kuang et al. (2020a), the difference between κ_{chem,PM_1} and $\kappa_{f(\mathrm{RH}),PM_{10}}$ are both influenced by aerosol PNSD and size-resolved κ distribution. To cover as many cases as possible, we have performed a simulation to investigate the relative differences between κ_{chem,PM_1} and $\kappa_{f(\mathrm{RH}),PM_{10}}$ under different conditions of aerosol chemical compositions through varying size distributions of ammonium nitrate, ammonium sulfate, organic aerosol, dust and BC, and their mass fractions randomly, and the mass size distributions follow lognormal distributions, that is:

$$\mathrm{dM/dlogDp} = \frac{\mathrm{Mtot}*\mathrm{fx}}{\sqrt{2\pi}\log(\sigma_{g,x})}\exp\left[-\frac{(\log(D_p)-\log(D_{g,x}))^2}{2\log^2\sigma_{g,x}}\right], \qquad \text{Eq. 1}$$

where x corresponding different aerosol compositions, and fx corresponding to its mass fractions. The parameters used in simulations are listed in Table 1, the number of randomly produced datasets for simulating κ_{chem,PM_1} and $\kappa_{f(\mathrm{RH}),PM_{10}}$ is 10000.

Table 1. used parameters for simulating differences between κ_{chem,PM_1} and $\kappa_{f(\mathrm{RH}),PM_{10}}$, m and σ corresponds to average and standard deviation respectively.

	fx range (%)	D_g (nm)		σ_g		ρ		κ	
		m	σ	m	σ	m	σ	m	σ
Ammonium Nitrate	0-50	450	100	2.2	0.25	1.72		0.56	
Ammonium sulfate	0-50	550	100	2.2	0.25	1.78		0.56	
Organic Aerosol	10-60	450	150	2.2	0.25	1.2	0.05	0.15	0.05
Dust	5-50	2500	500	2.2	0.25	2		0.05	0.015
BC	0-12	250	100	2.2	0.25	1.7		0	

Based on the simulation result, the first paragraph of the Sect3.2 is revised as the following:

“The aerosol hygroscopicity parameter κ can be calculated from aerosol chemical composition measurements (κ_{chem}) on the basis of volume mixing rule, thus the organic aerosol hygroscopicity parameter κ_{OA} were usually estimated through closure between measured κ and estimated κ using aerosol chemical measurements. In this study, the size-resolved aerosol chemical compositions of PM_1 were measured using the SP-AMS, however, the overall aerosol hygroscopicity was only derived based on aerosol light scattering measurements of PM_{10} bulk aerosols. Results of Kuang et al. (2020a) demonstrated that κ_{chem} calculated based on bulk chemical compositions of PM_1 are quite consistent with $\kappa_{f(\mathrm{RH})}$ of PM_1 (κ_{chem,PM_1}) therefore also consistent with $\kappa_{f(\mathrm{RH})}$ of PM_{10} ($\kappa_{f(\mathrm{RH}),PM_{10}}$). However, simulation results in Kuang et al. (2020a) demonstrated that the ratio between κ_{chem,PM_1} and $\kappa_{f(\mathrm{RH}),PM_1}$ varies with PNSD and size-resolved κ distributions, and the applicability of this conclusion under varying aerosol chemical compositions and size distributions need further clarification. Thus, we have designed a simulation experiments, to simulate the ratio between κ_{chem,PM_1} and $\kappa_{f(\mathrm{RH}),PM_{10}}$ considered wide ranges of aerosol chemical compositions and size distributions, details of the simulation are introduced in Part 2 of the supplement. The simulated results are shown in Fig.1. The results shows that the average relative difference ($\frac{\kappa_{f(\mathrm{RH}),PM_{10}}-\kappa_{chem,PM_1}}{\kappa_{chem,PM_1}}\times 100\%$) was 2.1±5.3%, which demonstrates that in general $\kappa_{f(\mathrm{RH}),PM_{10}}$ can be used to represent κ_{chem,PM_1} under varying atmospheric conditions. The results also show that the ratio=$\kappa_{f(\mathrm{RH}),PM_{10}}/\kappa_{chem,PM_1}$ is positively correlated with the effective radius of the aerosol population, which means that different levels of bias may exist under different PNSD conditions, and for effective radius range of this field campaign, the average relative difference is 0.7±4.9%. Given this, we have further simulated the $\kappa_{f(\mathrm{RH})}$ of PM_{10} and κ_{chem} of PM_1 under different PNSDs of this campaign

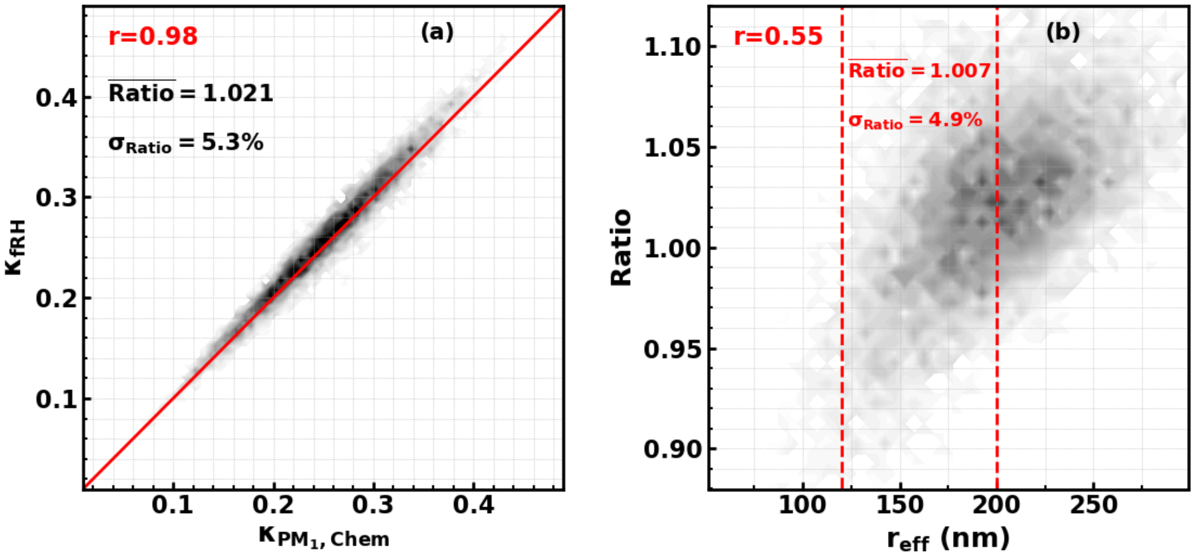

Figure 1. Simulated κ_{chem,PM_1} and $\kappa_{f(\mathrm{RH}),PM_{10}}$, red texts give correlation coefficients, ratio=$\kappa_{f(\mathrm{RH}),PM_{10}}/\kappa_{chem,PM_1}$, r_{eff} is the effective radius of the aerosol populations, dashed red lines show the r_{eff} range during the field campaign of this study.

coupled with different size-resolved κ distribution scenarios (as shown in Fig.S2a). As shown in the results in Fig.S2b, κ_{chem,PM_1} and $\kappa_{f(\mathrm{RH}),PM_{10}}$ are quite close to each other and the simulated average relative difference was -0.4±3%. Thus, $\kappa_{f(\mathrm{RH}),PM_{10}}$ was used as the measured κ_{chem,PM_1} in the following discussions."

Based on above analysis, 9% (3 standard deviations and based on results shown in Fig.S2b) can be used as the uncertainty of κ_{chem,PM_1} to estimate the overall effects of parameter perturbations on κ_{OA} derivations using Eq.3 during this field campaign. And the following part is added in Sect3.2 of the revised manuscript, after Eq.3 is introduced.

"Table 2. Effects of parameter perturbations on κ_{OA} derivations using Eq.3

Parameter	Uncertainty (3 standard deviations)	κ_{OA} variations (1 standard deviation)
SO_4 mass concentration	20%	0.01
NO_3 mass concentration	20%	0.006
NH_4 mass concentration	20%	0.002
OA mass concentration	20%	0.003
$\boldsymbol{\kappa_{chem}}$	9%	0.014
$V_{tot,PM1}$	25%	0.003
κ_X	0.03	0.003

The effects of κ_{chem} perturbations, aerosol mass concentrations, $V_{tot,PM1}$ as well as κ_X perturbations on κ_{OA} derivations are simulated using Monte-Carlo method for each data point of the κ_{OA} time series (1000 cases are randomly produced for each data point κ_{OA}) and average effects are summarized in Table 2. The perturbation parameter of κ_{chem} is based on the simulation results using PNSDs of this field campaign shown in Fig.S2. The perturbation parameters of aerosol mass concentrations are consistent with Hong et al. (2018), and that of $V_{tot,PM1}$ is from Ma et al. (2011).

The perturbation parameter of κ_X is specified based on that κ of dust in general ranges from 0.01 to 0.08. The results show that the accuracy of using $\kappa_{f(\mathrm{RH}),PM_{10}}$ to represent κ_{chem,PM_1} affects most on κ_{OA} derivations."

To test if effects of parameter perturbations on κ_{OA} derivations have significant effects on the relationships between κ_{OA} and organic aerosol PMF factors, we impose random perturbations on parameters listed in Table 2 in each κ_{OA} derivation. The comparison between originally derived κ_{OA} and perturbed derivation of κ_{OA} results is shown in Fig.4. The average difference between derived κ_{OA} with and without random errors is 0, the standard deviation is 0.03. However, the relationships between κ_{OA} derived with random errors and organic aerosol PMF factors changed only a little bit, and the results are shown in Fig.3. And these discussions are added in the revised manuscript as the following

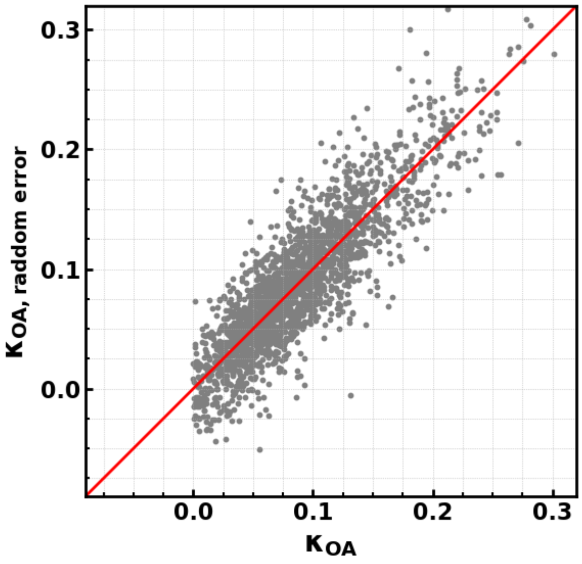

Figure 2. Comparison between κ_{OA} derived with and without random errors

"To test if effects of parameter perturbations on $\boldsymbol{\kappa_{OA}}$ derivations have significant effects on the relationships between $\boldsymbol{\kappa_{OA}}$ and organic aerosol PMF factors, we impose random perturbations on parameters listed in Table 2 in each κ_{OA} derivation. The comparison between originally derived κ_{OA} and perturbed derivation of κ_{OA} results is shown in Fig.S5. The average difference between derived κ_{OA} with and without random errors is 0, and the standard deviation is 0.03. However, the relationships between κ_{OA} derived with random errors and organic aerosol PMF factors changed only a little bit, and the results are shown in Fig.S6."

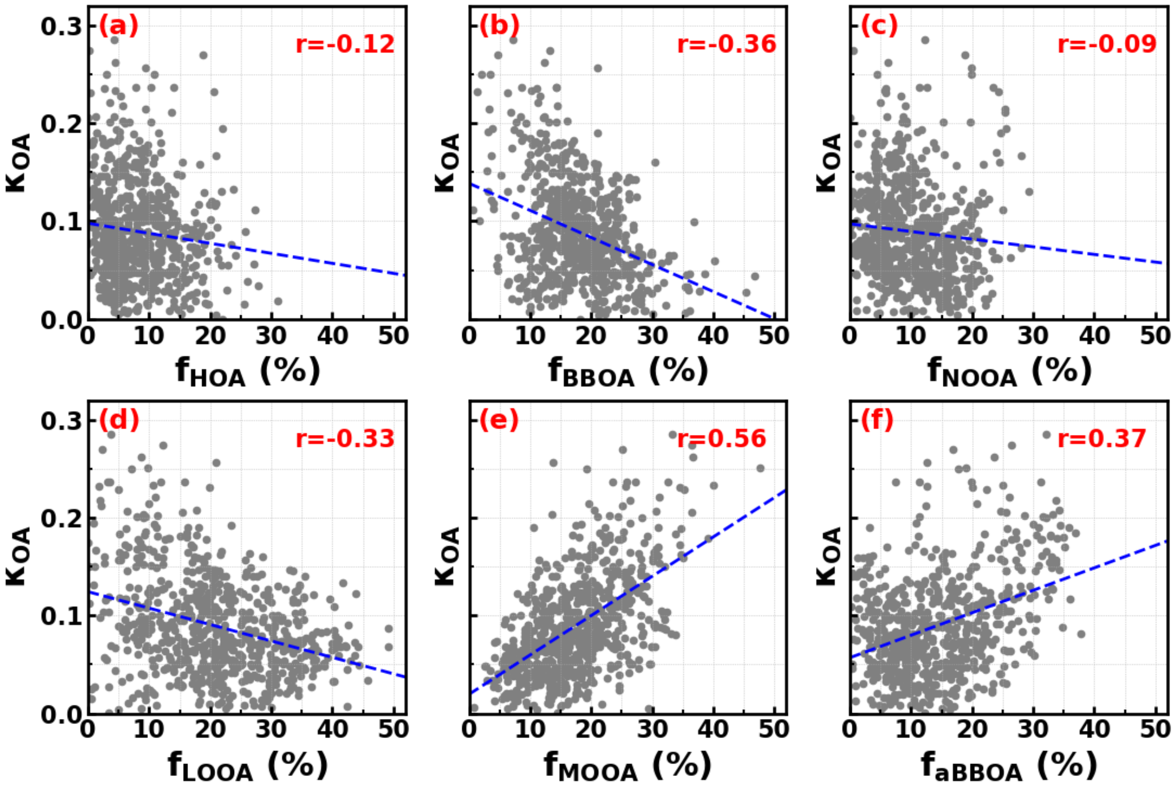

Figure 3. Correlations between κ_{OA} derived with random errors and mass fractions of OA factors in total OA mass

Comment: By default, it is assumed that at 80% humidity, the $\kappa f, RH$, follows the ZSR rule and can be used to calculate κOA. Numerous studies have shown that at low RH, like 80% used in this study, the hygroscopic properties of multicomponent particles are not additive. Core-shell particle morphology, complex interaction between the components, limited solubility of sparingly soluble compounds, kinetic limitation caused by semi-solid state are the main factors, which lead to nonadditive water uptake. These factors may provide significant uncertainty in κOA . The CCN retrieved κCCN and κOA may help to estimate the effect of low humidity on the uncertainty in scattering-derived κOA. Are the results of CCN measurements available for this field campaign?

Response: Thanks for your suggestion. We agree with the reviewer that uncertainties embedded in the ZSR assumption might have significant impacts on κ_{OA} derivation. But we might not have a better choice to investigate atmospheric κ_{OA} evolutions based on field measurements. We thought that the derived κ_{OA} might not be the real value of entire OA populations if only the OA populations are measured, however, the derived κ_{OA} can be treated as ZSR-equivalent organic aerosol hygroscopicity, and how much κ_{OA} derived with ZSR rule and the real one in atmospheric conditions needs further investigation, and we do not have a clue on this. Actually, at the very beginning, we also have similar worries with the reviewer because of the reasons the reviewer has mentioned. But we are curious about what can we get if the ZSR rule is used, just like what have been done by previous researches using field measurements HTDMA or CCN. We already got one successful try using the same method but aerosol chemical and light scattering enhancement factor (at RH of 85%) measurements are conducted in the North

China Plain (Kuang et al., 2020a). The final results have convinced us that derived κ_{OA} values is meaningful for readers and the summarized conclusion should be convincing and new to the community: (1) The derived κ_{OA} ranges are consistent with current literature values; (2)Most importantly, the κ_{OA} derivations are completely independent of the PMF results, but we can get that derived κ_{OA} of hourly time resolution is highly and positively correlated with that of MOOA; (3) The correlation coefficient between κ_{OA} and $f_{MOOA+aBBOA}$ even reaches beyond 0.8 during certain period as shown in Fig.7. **Both experiences in the North China Plain and this campaign demonstrate that meaningful results can be obtained using ZSR rule under relatively lower RH conditions (80%-90%), thus we really want these results can promote more examinations about the applicability of ZSR rule in different RH and atmospheric relevant conditions**.

The reviewer mentioned that the CCN measurements might be helpful in constraining the κ_{OA} uncertainty which is a good choice according to the physical understanding if the hygroscopicity of a particle is measured both with CCN instrument and the aerosol light scattering instrument. However, after careful thinking, we think the κ_{CCN} can not be used to estimate influences of possible non-additive effects on κOA derivations. Size-resolved CCN measurements reflect overall hygroscopicity of aerosol population of diameter less than 200 nm that can be activated thus derived κ_{OA} represents overall κ of sub-200 nm organic aerosols, however, the κ_{OA} derived using the method in this study represents the overall hygroscopicity of the entire organic aerosol population mainly ranges from 200-760 nm of PM_1 (Kuang et al., 2020a). Many previous studies have demonstrated that chemical compositions of organic aerosol under different diameter ranges differ much, and are not the same at all (Kuang et al., 2020b), thus hinders the direct comparison between κ_{OA} derived from light scattering enhancement measurements and CCN measurements.

Comment: In my opinion, the κOA and its uncertainty are poorly defined and additional efforts are needed to specify them. Otherwise, the conclusion about a weak relationship between kappa and O/C ratio and reasoning about the contrasting effects look unconvincing.

Response: We really appreciate your comments. The comments about the uncertainty of κ_{OA} inspired us to perform a comprehensive evaluation about how much κ_{chem,PM_1} and $\kappa_{f(\mathrm{RH}),PM_{10}}$ differ under varying conditions of aerosol chemical compositions and size-distributions. And further quantified impacts of aerosol mass concentration perturbations and other key parameters on κ_{OA} derivations.

Technical points.

Comment: Line 232. Figure S2 have no panels 2a and 2b

Response: Many thanks, we have added (a) and (b) in Fig.S2

Comment: Lines 257, 266 hydrophilic ?

Response: Thanks, changed to “hydrophobic”

Comment: Line 263. Fig.S4?Line 282. NR-PM1 this abbreviation is not determined.

Response: The average ε_X is added in Fig.S4. And the NR-PM1 abbreviation is added

Comment: Line 335. 0.053± 0.006 ? may be 0.53 ± 0.06

Response: Thanks, should be 0.53 ± 0.06

Comment: Line 346. There are no references to Fig. 4a-4f in the text, although all panels are labeled as (a)-(f).

Response: Thank you, we have removed labels on these panels.

Comment: Figure 5. Blue line – NOOA. This abbreviation is not determined. Why do need both panels?

Response: The NOOA abbreviation is changed to Night-OA, and legend is changed on one panel.

Comment: Line 356. Fig. 3c? May be Fig.5c.

Response: Changed to Fig.5c

Comment: Line 364. Figure S4. Please check this figure. There is no nitrate concentration.

Response: Sorry for the typo of figure number which misled the reviewer. The sentence has been revised: "κ_{OA} was also negatively correlated with Night-OA fraction, which increased during nighttime (Fig. 6b). The Night-OA factor was highly correlated with nitrate concentrations (Figure S6), likely associated with the NO_3 nighttime chemistry as discussed in Sect. 4.1."

Comment: Figure 7. Red line –NOOA. This abbreviation is not determined.

Supplement Fig.S4 . I did not find a text where this figure was discussed.

Response: The NOOA abbreviation is changed to Night-OA. The discussion about Fig.S4 is added in Sect3.2

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