A point-by-point response to reviewers

Dear Editor,

We are very pleased to submit a revised manuscript entitled with “The density of ambient black carbon retrieved by a new method: implications to CCN prediction” for possible publication in journal of ACP.

I'd like to thank you for your efforts and time on handling the paper. I also would like to thank the reviewers for their valuable comments and suggestions, all of which have been considered carefully during the revision (a point-by-point response to reviewers as follows). We believe all the comments from the reviewers have been addressed, and the paper have been greatly improved after the revision.

Yours sincerely,

Fang Zhang

On behalf of all authors

A point-by-point response to reviewer

Reviewer #2

This study attempts to derive the "density" of BC from the hygroscopic growth factor measured by the HTDMA and total BC mass by the aethalometer. I appreciate the authors' effect to derive the density of BC from measurements not directly linking with BC. This is indeed challenging from a bulk HTDMA measurement to derive BC information, as the BC only constitutes of a small fraction of ambient atmospheric particles. However, the current method is still not convincing. The crucial points are:

1)The total hydrophobic particle number was measured, and a fixed fraction of 70% of hydrophobic OA is used to obtain the hydrophobic BC from the total. This fixed "70%" is obviously not correct. Additionally, how have you got the number concentration of OA.

Re: Thanks a lot for the comments.

(1) It is true that, the POA particles would be mixed with the secondary inorganic or organic particles during the aging process. The number fraction of the nearly-hydrophobic POA would change with the emission and aging processes. As the reviewer commented, instead of using a fixed fraction of 70%, we just have applied different values for fractions of hydrophobic POA under clean, moderately polluted, and heavily polluted conditions by referring the literature (Liu et al., 2021a). Updated results have been given in the revised manuscript. However, a real-time variation of the fractions of hydrophobic POA is not yet available due to the lack of such measurements data. Using the variable fractions of hydrophobic POA only under three different atmospheric conditions could still cause uncertainties. An uncertainty analysis has also been conducted (**Section 2.3**), showing that the assumption on $NF_{\text{NH-POA}}$ can lead to relative deviations (uncertainty) of -17 %–+27 % for the retrieved BC density (Fig. R1 or Fig. 2a).

Some discussions about this issue have been included in the revised paper, see section **2.3** or **Lines 298-319**, as follows:

"… The figures show that the In-BC density gradually decreases with the increment of the $NF_{\text{NH-POA}}$, implying the higher fraction of bare POA particles correspond to the early aging stage of aerosol particles. With increase of κ_{SOA}, the In-BC density is generally reduced, but with small fluctuations (Fig.1a, Fig. 2b). This suggests a complex impact of assumptions of κ_{SOA} on the retrieved BC density. In

addition, the In-BC density decreases very slightly as $\rho_{Ex\text{-}BC}$ increases (Fig. 2e), suggesting applying a larger $\rho_{Ex\text{-}BC}$ would derive smaller values for In-BC density. The In-BC density is insensitive to the changes of the density of POA and SOA, showing an almost negligible effect on the retrieved results (Fig. 2c and d).

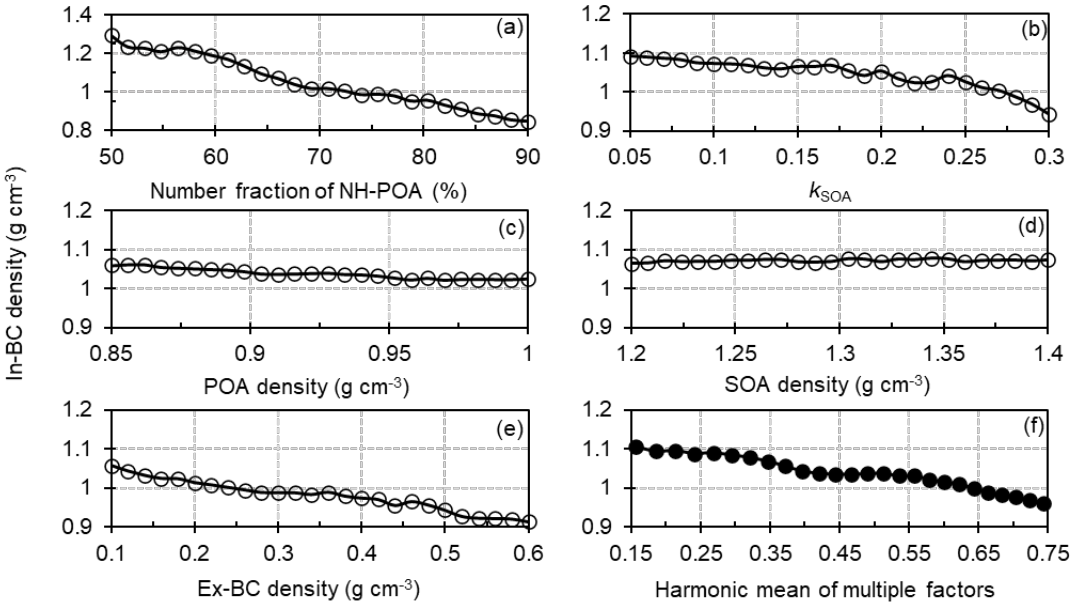

Fig. R1 Sensitivity of the In-BC density to variations in the number fraction of nearly hydrophobic (NH) POA (a), the hygroscopic parameter of SOA (b), the POA density (c), the SOA density (d), the externally mixed BC density (e) and the harmonic mean of multiple factors (f).

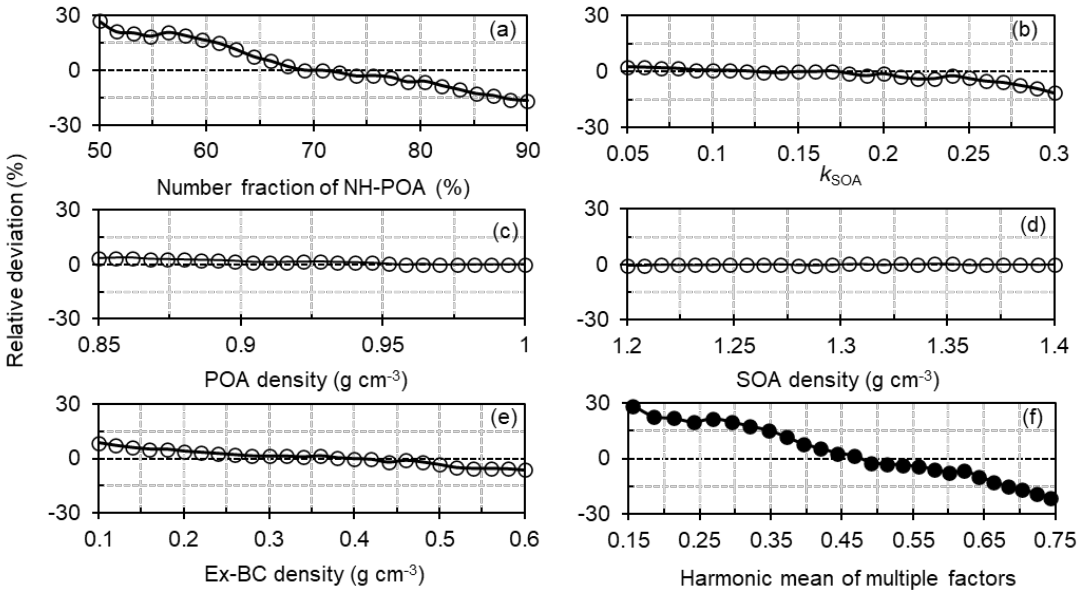

Fig. R2 Relative deviations of the number fraction of nearly hydrophobic (NH) POA to the In-BC density (a), the hygroscopic parameter of OA to the In-BC density (b), the

POA density to the In-BC density (c), the SOA density to the In-BC density (d), the externally mixed BC density to In-BC density (e) and the combined deviations based on multiple factors mentioned above (f).

The uncertainty analysis shows that, by comparing the results based on the mean fractions of the $NF_{NH\text{-}POA}$ with a typical atmospheric observed range of 50-90 % for the $NF_{NH\text{-}POA}$ (Liu et al., 2021a), we show that the assumption on $NF_{NH\text{-}POA}$ can lead to relative deviations (uncertainty) of -17 %–+27 % for the retrieved BC density (Fig.3a)."

(2) method to obtain the number fraction of POA

Some description about the method to calculating the number of POA has been given in the revised text, see **Lines 162-176** or as follows:

"… The nearly hydrophobi**c** mode consists of both externally mixed POA (Ex-POA or bare POA) and externally mixed BC (Ex-BC). Since the number fraction of the nearly-hydrophobic POA would change with the emission and aging processes, in this study, we have applied different values for the number fractions of hydrophobic POA (NH-POA) under clean (91 %), moderately polluted (70 %), and heavily polluted conditions (31 %) by referring the literature (Liu et al., 2021a), as shown in Fig. S2. The number concentration of Ex-BC was then calculated using the total number fraction of NH mode minus the number of NH-POA.

$$N_{POA-containing} = N_{total} \times NF_{POA-containing}$$

$$N_{bare-POA} = N_{POA-containing} \times NF_{bare-POA}$$

$$N_{Ex-BC} = N_{NH} - N_{bare-POA} \quad (3)$$

where $N_{POA\text{-}containing}$ and $NF_{POA\text{-}containing}$ are the number concentration and fraction of POA-containing particles, N_{total} is the total number concentration, $N_{bare\text{-}POA}$ and $NF_{bare\text{-}POA}$ are the number concentration and fraction of bare POA particles, and N_{NH} is the number of nearly- hydrophobic group …"

2) A fixed effective density of 0.4 g cm-3 is assumed for hydrophobic BC to derive its mass, which is not correct. The effective density of BC obviously depends on the particle shape and it can't be fixed.

Re: Thanks for the comments. It's true that there is some bias in deriving the mass concentration by assuming a fixed value for $\rho_{Ex\text{-}BC}$. Generally, the $\rho_{Ex\text{-}BC}$ would change as a function of the mobility diameter and its morphology (Park et al., 2003; Rissler et

al., 2014; Wu et al., 2019). By reviewing and summarizing the existing results about, we found that typical values of density for the freshly emitted or externally mixed BC observed in the winter of urban Beijing or North China Plain spans over 0.14-0.50 g cm^{-3}, with mean of ~0.40±0.10 g cm^{-3} (Fig.R3 or Fig. S3), in the size range of 100 to 300 nm, where the mass concentration of externally mixed BC accounted for a large proportion in urban Beijing (Peng et al., 2016, 2017; Wu et al., 2019; Liu et al., 2020; Zhao et al., 2022). Therefore, an average $\rho_{Ex\text{-}BC}$ of 0.4 g cm^{-3} was used for calculating the mass concentration of externally-mixed BC in our study. The uncertainty analysis exhibits that the variations of the $\rho_{Ex\text{-}BC}$ could lead to an average deviation of ±10 % in the calculating In-BC density (Fig. 3e) by increasing the $\rho_{Ex\text{-}BC}$ from 0.1 to 0.6 g cm^{-3}, showing a relatively small impact on the retrieved result. A summarized figure of the existing results about $\rho_{Ex\text{-}BC}$.and sensitivity test has been included in the revised paper.

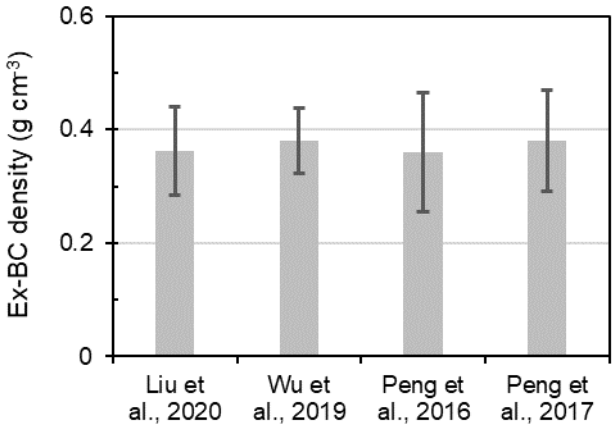

Fig. R3 Summary of the ambient externally mixed BC density particles in North China Plain from literatures.

3) By the following very complicated calculations, are you attempting to derive the BC density only for the hydrophilic mode? It is very confusing here as you have just used a fixed density of 0.4 but now why performing such calculation again.

Re: In this study, only when retrieving the density of internally-mixed BC, we assumed the density of the externally mixed BC is 0.4 g cm^{-3}; when retrieving the bulk BC density, however, we didn't apply such assumption.

Since the Gf-PDF measured by the HTDMA can reflect the mixing state of aerosol particles (Tan et al., 2013; Hong et al., 2018; Chen et al., 2022), and the hydrophobic mode generally refers to components like freshly emitted BC or POA, which are externally-mixed with the aerosol particles populations; while the hydrophilic mode is those secondary inorganic or organic salts and aged BC. In this study, we think the aged

BC is hydrophilic and should be internally mixed with the secondary inorganic or organic salts, so defined as internally mixed BC. To retrieve the density of internally-mixed BC density, we assumed the density of the externally-mixed BC, $\rho_{Ex\text{-}BC}$, is 0.4 g cm^{-3}; As described in Section **2.2.1**, we first retrieved the mixing state of BC based on the Gf-PDF. After obtaining the number fraction of the externally mixed BC from measured Gf-PDF, the $\rho_{Ex\text{-}BC}$ was used to calculate the mass concentration of the externally mixed BC ($m_{Ex\text{-}BC}$). Then, the mass concentration of the internally mixed BC ($m_{In\text{-}BC}$) was calculated by subtracting $m_{Ex\text{-}BC}$ from the bulk BC mass concentration measured by AE33, and finally, the $m_{In\text{-}BC}$ was used for retrieving the density of internally-mixed BC as described in Section 2.2.2.

Scientific significance to retrieve the density of internally-mixed BC: since the BC particles experience rapid aging once they were emitted to the atmosphere, particularly, in the polluted urban regions, the BC could undergo more rapidly aging to internally mixed with other components compared to that in relative clean atmosphere (Peng et al., 2016). It has been observed that more than 80 % BC are internally-mixed with other components in the atmosphere (Chen et al., 2020). During aging, the physiochemical properties (morphology, density, hygroscopisity and CCN activity, etc.) of BC could be very different depending on its aging degree (Zhang R et al., 2008; Zhang F et al., 2022). however, in the current models, the internally-mixed BC density was treated as a void-free sphere throughout its atmospheric lifetime, which caused biases in the calculation of the BC absorption enhancement and CCN activity of In-BC particles. Therefore, it is with great scientific significance of understanding the density of the internally-mixed BC particles.

The effective density of BC can be obtained through combing the SMPS and mass measurement as many people did (as the authors are aware), I can't really understand why the authors have spent such efforts using an HTDMA measurement to perform such analysis (but this instrument is not intrinsically designed for such application).

Re: Yes, although various techniques have been developed to quantify the mixing state and density of BC in recent years, as we addressed in the Introduction section. However, such techniques or measurements are not available in many previously conducted filed campaigns. To obtain insights on the real-time variations of BC density in the polluted urban atmosphere, and to further study the effects of BC density variations on CCN activity and prediction, in this study, we attempt to retrieve the mixing state and effective density of ambient BC particles by combining field measured hygroscopic

growth factor and aerosol chemical composition and Köhler theory (Petters and Kreidenweis, 2007). We think that the current work is with scientific significance for that the effective density of BC is a crucial factor relevant to its aging degree that would add uncertainty in evaluating its climate effect. As the reviewer #1 commented, "… Since the BC density is difficult to measure, it is worth trying to develop new methods for retrieving accurate BC density from available measured data. It is quite interesting …"

Actually, the reviewer #2 also commented that "… This is indeed challenging from a bulk HTDMA measurement to derive BC information, as the BC only constitutes of a small fraction of ambient atmospheric particles. However, the current method is still not convincing…". We are greatly appreciated for these insightful comments, which has let us think this work more deeply and revise it more carefully. Especially, for the methods, we have conducted more analyses and evaluations of the assumed parameters which may lead to uncertainties in the retrieved results in the Section 2.3. The overall uncertainty of the retrieval method was evaluated within ±25 %. Regarding to the small fraction of ambient BC particles as the reviewer #2 commented, we have noted that, this method fails to retrieve the BC density when organics account for a large fraction (>60 %). This is because that a higher fraction of OA usually corresponds to lower total volume of all the other species like BC, yielding negative values for $v_{\text{In-BC}}$ introduced in equation 11. As a result, 39 % of the data observed during the campaign were excluded when calculating the BC density.

In addition, according to the reviewer's comments, in the revise version, instead of using a fixed fraction of 70%, we just have applied different values for fractions of hydrophobic POA under clean, moderately polluted, and heavily polluted conditions by referring the literature (Liu et al., 2021a). Updated results have been given in the revised manuscript. Also, we compared our results with the laboratory and field measurements reported in the literature. It shows generally good agreement with the previously reported values, indicating that the method is feasible.

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