Response to interactive comment on "Size-resolved measurement of the mixing state of soot in the megacity Beijing, China: diurnal cycle, aging and parameterization" by Referee #1

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Major Comment 1:

The paper uses measurements taken during the CARE-Beijing experiment to develop an empirically based model of the conversion of externally mixed soot particles to internally mixed particles. In addition, parameterizations of the fraction of internal mixed particles based on air mass aging indicators are proposed. The results presented in the paper should add to the basic understanding of the processes and time scales involved in the conversion of externally to internally mixed soot particles. The paper should be published in ACP after the following issues are adequately addressed.

<u>Response:</u>

We gratefully appreciate the referee's comments and suggestions. Please find our point-by-point responses in the following text. The comments from the reviewers are in italic, our responses are in plain text, and the revised texts in the manuscript are marked in blue.

Major Comment 2:

The analysis presented relies heavily on VTDMA measurements of particle volatility as a function of particle size. Section 2.2 provides a good description of how the VTDMA measurements are made and used in the analysis. In contrast, Section 2.4 describing the treatment of the CCN counter data and how they were adapted to this analysis is lacking detail.

<u>Response:</u>

Please see the detailed response to specific comment #15.

Specific Comment 1:

Abstract line 1: omit "regarded"

<u>Response:</u>

The "regarded as" has been deleted from the sentence.

Text:

"Soot particles are ~~regarded as~~ the most efficient light absorbing aerosol species…"

Specific Comment 2:

Abstract, line 28: Need to describe the "size shift". Does it refer to the growth of smaller Aitken mode sized-particles to larger sizes?

Response:

The sentence has been revised.

Text:

"Diurnal cycles of F_{in} were different between Aitken and accumulation mode particles, which could be explained by the faster growth of smaller Aitken mode particles into larger size bins."

Specific Comment 3:

p. 32164, lines 7 – 8: Yields a more realistic description of F_{in} relative to what?

Response:

The parameterization of F_{in} by air mass indicators, such as $[NO_z]/[NO_y]$, $[E]/[X]$, and $([IM]+[OM])/[EC]$, yields a more realistic description of F_{in} relative to the simple treatment of soot mixing state (internal or external mixture) in regional/global models. There are also models that specifically deal with the evolution of soot mixing state, however, their computational costs are mostly extremely high.

The sentence in the abstract has been revised.

Text:

"Such a parameterization consumes little additional computing time, but yields a more realistic description of F_{in} compared with the simple treatment of soot mixing state in regional/global models."

Specific Comment 4:

p. 32164, line 21: Change to "Soot particles, after emission, undergo aging processes…"

Response:

The sentence has been modified accordingly.

Text:

"Soot particles, after emission, generally undergo aging processes by…"

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Specific Comment 5:

    p. 32164, lines 25 – 26: Why does internally mixed necessarily mean coated and externally mixed means uncoated? Other mixing configurations are possible and have been observed.

Response:

    We agree that various mixing configurations are possible and have been observed in the real atmosphere. In this study, we consider the coated particles (method-defined) as internally mixed ones, which was in line with previous VTDMA studies (e.g., Wehner et al., 2009). But it shouldn't be interpreted the other way round, i.e. internally mixed don't necessarily mean coated.

Specific Comment 6:

    p. 32164, line 27: change to "related to its direct radiative..."

Response:

    The sentence has been revised accordingly.

    Text:

    "…(related to ~~their~~ its direct radiative effects)…"

Specific Comment 7:

    p. 32165, line 6: change to "and hence influence cloud formation processes..."

Response:

    The sentence has been revised accordingly.

    Text:

    "…and hence influence ~~the~~ cloud formation processes…"

Specific Comment 8:

    p. 32165, lines 7 – 10: This sentence needs to be re-written for clarity.

Response:

    The sentence has been re-written.

    Text:

    "For these reasons, the mixing state is a crucial parameter for soot particles, uncertainty about which has made it difficult to accurately assess its climatic impact of soot (Jacobson, 2001)."

Specific Comment 9:

p. 32165, line 11: Why is "turnover rate" being used to describe what is really a conversion rate? Even the text says that "the turnover rate is used to describe the conversion rate..."

Response:

In our understanding, "conversion rate" is a more general term than "turnover rate". The conversion rate of soot from externally to internally mixed can be described in different ways. The "turnover rate" specifically means in a given time (e.g., 1 hour) how many percentage of externally mixed soot would have been converted into internally mixed, similar to the concept of "decay rate". The conversion process can be also described by other parameters, such as the increase rate of F_{in}. For example, in field studies of Moteki et al., 2007 and Shiraiwa et al. (2007), they use the later one to describe the soot conversion rate as 1.0-2.3 %h^{-1}, which corresponding to a turn over rate of 1.3-5.8 %h^{-1}. The "turnover rate" is used thought the manuscript following the convention in air quality modeling studies (Cooke and Wilson, 1996; Cooke et al., 1999, 2002; Lohmann et al., 2000; Jacobson, 2001; Koch, 2001).

Specific Comment 10:

p. 32165, line 13: use "assumed" instead of "taken"

Response:

The sentence has been revised accordingly.
Text:
"…a constant $k_{ex->in}$ was ~~taken~~ assumed in most studies…"

Specific Comment 11:

p. 32165, line29: change "determine" to "detect"

Response:

The sentence has been modified.
Text:
"Among these methods, only the VTDMA is able to ~~determine~~ detect the mixing state of particles smaller than 0.1 μm."

Specific Comment 12:

p. 32166, line 6: change to "and OC to EC"

Response:

The sentence has been revised accordingly.

Text:

"…ratio of… and OC to EC (organic carbon/elemental carbon)…"

Specific Comment 13:

p. 32166, line 18: change to "and the influence of emissions on it"

Response:

The sentence has been revised accordingly.

Text:

"…(3) calculation of $k_{ex\text{->}in}$ and the influence of emissions on it…"

Specific Comment 14:

p. 32168, lines 16 – 18: Sentence starting with "For large particles..." needs to be re-written for clarity.

Response:

The sentence has been re-written.

Text:

"During daytime, the condensation dominates the aging processes, especially for relatively large particles (Jacobson, 1997; Riemer et al., 2004). "

Specific Comment 15:

Section 2.4.: More detail should be added to help the reader understand exactly how the cumulative distribution function of particle hygroscopicity was derived from sizeresolved CCN efficiency. A first step in the description would be explaining how the CCN counter and the DMA were operated to produce size-resolved CCN activation curves. The sentence on lines 16 – 19 on p. 32170 needs to be re-written and elaborated on for clarity.

Response:

We have added the following text to clarify the CCN measurement and the calculation of $H(\kappa, D_p)$.

Text:

Page 32170 line 14-21:

"… calibrated with ammonium sulfate aerosol as described by Rose et al. (2008).

For each CCN measurement cycle, ΔT was set to 5 different levels (2.0–11.9 K) corresponding to S values in the range of 0.07–0.86 %. For each ΔT and the respective S, the diameter of the dry aerosol particles selected by the DMA (D_p) was set to 9 different values in the range of 20–290 nm depending on the supersaturation selected. At each D, the number concentration of total aerosol particles (condensation nuclei, CN), N_{CN} was measured with the CPC, and the number concentration of CCN, N_{CCN}, was measured

with the CCNC. The integration time for each measurement data point was 30 s, the recording of a CCN efficiency spectrum took ~16 min (including a 50 s adjustment time for each new particle size and 4 min for adjustment to the next supersaturation level), and the completion of a full measurement cycle comprising CCN efficiency spectra at 5 different supersaturation levels took ~85 min (including 5 min of settling time for the changeover from highest to lowest S). For a detailed description of CCN measurements in the campaign, see Gunthe et al. (2011).

Size-resolved CCN efficiency spectra can be used to derive the cumulative distribution function of particle hygroscopicity, $H(\kappa, D_p)$, which is defined as the number fraction of particles with a given dry diameter, D_p, and with an effective hygroscopicity parameter smaller than the parameter κ (Petters and Kreidenweis, 2007; Su et al., 2010). The data pair of D_p and N_{CCN}/N_{CN} in a CCN spectrum can be converted to a corresponding data pair of κ and $H(\kappa, D_p)$ by solving the Köhler-κ model equation (refer to Eq. (21) and (22) in Su et al., 2010)."

Specific Comment 16:
p. 32171, line12: perhaps you mean "...this does not mean that the age of an air mass can become infinitely large as injection of fresh emission..."

Response:

Yes, you are right. The sentence has been revised accordingly.
Text:
"However, this does not mean that the age of an air mass can become infinitely large as injection of fresh emissions into the air mass would reduce its age."

Specific Comment 17:
p. 32171, lines13 – 15: Fix sentence for clarity.

Response:

The sentence has been rewritten for clarity.
Text:
"They are based on the fact that the aging will change the chemical compositions of air masses. So parameters reflecting such changes can indicate the aging stage."

Specific Comment 18:
p. 32172, line 6: change to "which reduces"

Response:

The sentence has been revised accordingly.
Text:
"As an air mass ages, more secondary aerosol is produced, which reduces the

mass fraction of soot particles.”

Specific Comment 19:

p. 32173, lines 21 – 22: Are there single scattering albedo data that can be reported from this campaign? SSA needs to be defined the first time it is discussed and any relevance to the aging process should be described.

Response:

Yes, there are single scattering albedo (SSA) data that can be reported from this campaign. Total aerosol scattering coefficients and hemispheric backscattering coefficients at three different wavelengths (450 nm, 550 nm, and 700 nm) were measured with an integrating nephelometer (Model 3563, TSI). The aerosol absorption coefficient at 532nm was determined simultaneously with a photoacoustic spectrometer (PAS; Desert Research Institute). The single scattering albedo was therefore calculated as the ratio of scattering and extinction (scattering plus absorption) coefficients at wavelength of 532 nm. For more details about instrumentation and data processing, please refer to section 2 in Garland et al. (2009). We have updated the reference lists with this paper. Since aerosol aging/mixing and its influence on aerosol optical properties during the same campaign had been discussed intensively in Cheng et al. (2009) and Wiedensohler et al. (2009), we preferred not to repeat similar discussions in this paper.

Specific Comment 20:

Figure 5. The caption needs to clearly state what each parameter shown is normalized by.

Response:

We have added the following text into the figure caption.
Text:
“All parameters are normalized by their diurnal means, respectively.”

Specific Comment 21:

p. 32174, last paragraph: Clarify what the starred parameters represent.

Response:

The star stands for the normalized parameters. We have revised the text in Sect.3.3 to clarify it.
Text:
“The emission rate can be divided into a diurnal profile describing its relative variation and the absolute value of any point on this profile. In this study, we adopt the diurnal profile of CO (carbon monoxide) emissions from traffic systems in Beijing

areas (Zhou et al., 2010) and assume that soot emissions have a similar diurnal pattern. Then measurement data of EC are used to estimate the absolute emission rate at certain period during night-time. With these two kinds of information, the whole emission profile can be quantified.

Note that the emission rate is often expressed as a flux in mass per area per time while its impact on EC concentrations, $(\partial[EC]/\partial t)_{Emis}$, has a unit of mass per volume per time. From the aspect of Eulerian grid models, the diurnal profile (relative variation) of the emission flux and $(\partial[EC]/\partial t)_{Emis}$ is the same while their absolute values differ by a factor of the grid height.

Figure 5 shows the diurnal profile of the emission rate $(\partial[EC]/\partial t)_{Emis}$ used in this study. To estimate its absolute values, we tried to find a time period when the concentration variation is dominated by emissions, i.e., $\partial[EC]/\partial t \approx (\partial[EC]/\partial t)_{Emis}$. The EC concentration is also shown in Fig. 5. It is clear that [EC] is not always increasing though $(\partial[EC]/\partial t)_{Emis}$ is always positive. This is because transport plays an important role on the diurnal variation of [EC].

To minimize the impact of transport and obtain an optimal estimate on absolute values of $(\partial[EC]/\partial t)_{Emis}$, we adopted the following criteria, eliminating days with average wind speed >2m s^{-1} (20, 22 August, 3, 4, 5, 6 and 8 September), excluding the time periods with strong vertical mixing (from 8:00 to 19:00 LT), and choosing periods with largest ratio of normalized $(\partial[EC]/\partial t)_{Emis}$ to [EC] (at 20:00 LT). The reason of choosing low wind speeds and night-time periods is to minimize the impact of horizontal and vertical transport processes on [EC]. Large ratios of $(\partial[EC]/\partial t)_{Emis}/[EC]$ ensures that the emission term could dominate the variation of [EC].

Finally, $\Delta[EC]/\Delta t$ at 20:00 (~0.89 μg m^{-3} h^{-1}) was taken as an optimal estimation of $(\partial[EC]/\partial t)_{Emis}$ at 20:00. It was then used to calculate $(\partial[EC]/\partial t)_{Emis}$ for the rest time of a day by applying the diurnal profile in Fig. 5. Table 3 summarized the diurnal variation of the measured [EC] and the calculated $(\partial[EC]/\partial t)_{Emis}$. The mean emission rate is ~13% of the mean soot concentration per hour (13% h^{-1})."

Specific Comment 22:
p. 32176, line 19: change to "...and low $k_{ex->in}$ resulting from both slower..."

Response:
The sentence has been revised accordingly.
Text:
"…and low $k_{ex->in}$ <u>resulting from</u> both slower condensation and coagulation processes…"

Specific Comment 23:
p. 32176, lines 20 - 24: These sentences are confusing. Attention should be paid to what values? Daytime? Night-time? And why? The last sentence of this paragraph

needs to be edited for clarity.

Response:

In the present study, we made an assumption in the calculation of the turnover rate, that the condensational growth dominates the growth/aging aging process. However, during nighttime, the coagulation-induced aging could become more important than the condensation (Riemer et al., 2004), which violates our assumption. Therefore, the turnover rate ($k_{ex->in}$) calculated for nighttime periods required caveats.

The sentences have been re-written.

Text:

"Although $k_{ex->in}$ for night-time periods are also presented in Fig. 6, these night-time values require caveats because the coagulation-induced aging could become more important than the condensation during night-time (Riemer et al., 2004; Riemer et al., 2010), which violates our assumption of $k_{ex->in}$ calculations."

Specific Comment 24:

p. 32182, line 16: change to "...by the time they leave..."

Response:

The sentence has been revised accordingly.

Text:

"…by the time ~~the~~ they leave…"

References

Cheng, Y. F., Berghof, M., Garland, R. M., Wiedensohler, A., Wehner, B., Müller, T., Su, H., Zhang, Y. H., Achtert, P., Nowak, A., Pöschl, U., Zhu, T., Hu, M., and Zeng, L. M.: Influence of soot mixing state on aerosol light absorption and single scattering albedo during air mass aging at a polluted regional site in northeastern China, J. Geophys. Res., 114, 10.1029/2008jd010883, 2009.

Garland, R. M., Schmid, O., Nowak, A., Achtert, P., Wiedensohler, A., Gunthe, S. S., Takegawa, N., Kita, K., Kondo, Y., Hu, M., Shao, M., Zeng, L. M., Zhu, T., Andreae, M. O., and Pöschl, U.: Aerosol optical properties observed during Campaign of Air Quality Research in Beijing 2006 (CAREBeijing-2006): Characteristic differences between the inflow and outflow of Beijing city air, J. Geophys. Res., 114, 10.1029/2008jd010780, 2009.

Riemer, N., Vogel, H., and Vogel, B.: Soot aging time scales in polluted regions during day and night, Atmos. Chem. Phys., 4, 1885-1893, 2004.

Riemer, N., West, M., Zaveri, R., and Easter, R.: Estimating black carbon aging time-scales with a particle-resolved aerosol model, Journal of Aerosol Science, 41, 143-158, DOI: 10.1016/j.jaerosci.2009.08.009, 2010.

Wehner, B., Berghof, M., Cheng, Y. F., Achtert, P., Birmili, W., Nowak, A., Wiedensohler, A.,

Garland, R. M., Pöschl, U., Hu, M., and Zhu, T.: Mixing state of nonvolatile aerosol particle fractions and comparison with light absorption in the polluted Beijing region, J. Geophys. Res., 114, 10.1029/2008jd010923, 2009.

Wiedensohler, A., Cheng, Y. F., Nowak, A., Wehner, B., Achtert, P., Berghof, M., Birmili, W., Wu, Z. J., Hu, M., Zhu, T., Takegawa, N., Kita, K., Kondo, Y., Lou, S. R., Hofzumahaus, A., Holland, F., Wahner, A., Gunthe, S. S., Rose, D., Su, H., and Pöschl, U.: Rapid aerosol particle growth and increase of cloud condensation nucleus activity by secondary aerosol formation and condensation: A case study for regional air pollution in northeastern China, J. Geophys. Res., 114, 10.1029/2008jd010884, 2009.

Zhou, Y., Wu, Y., Yang, L., Fu, L., He, K., Wang, S., Hao, J., Chen, J., and Li, C.: The impact of transportation control measures on emission reductions during the 2008 Olympic Games in Beijing, China, ATMOSPHERIC ENVIRONMENT, 44, 285-293, DOI: 10.1016/j.atmosenv.2009.10.040, 2010.