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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Size-resolved measurement of the mixing state of soot in the megacity Beijing, China: diurnal cycle, aging and parameterization" *by* Y. F. Cheng et al.

Anonymous Referee #2

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This paper presents VTDMA measurements of the size and mixing state of soot-containing particles during the CAREBeijing campaign. They use the data to derive a time constant for the conversion of externally mixed soot to internally mixed soot in Beijing. In addition they use observed correlations between the internally mixed soot fraction and other photochemical age indicators (such as the NOz/NOy ratio) to parameterize a calculation of the internally mixed fraction of soot particles using more commonly measured chemical tracers in the absence of VTDMA measurements.

The results presented here are an interesting addition to the current literature on the aging of soot particles and it should be published in ACP after the authors address the

following concerns.

1. This is a very equation-heavy paper and I don't think that all of the equations presented increase the clarity of the manuscript. For example, it seems to me that equations 2-7 could be combined into 1 or 2 equations. Equations 3 and 7 are already the same. For example you could have Eq 1 as d(nex)/dt = (condensation term ex → in) + (coagulation term ex → in) + emissions + transport + deposition and highlight that that includes both population transfer from ex → in as well as total particle number changes due to physical processes. Then state that, to first order, you are going to ignore everything other than condensation such that the total particle number is assumed to be constant and go right to a combination of 6 and 7 (- dnex/dt = dnin/dt = kex→in*nex for example). Similarly combine 9+10 and, in general, I recommend including only those equations that will help the reader follow the logic rather than converting into equations assumptions that can easily be stated in the text.

2. It is hard for me to visualize how the particles might be transitioning between non-BC, internally-mixed BC and externally mixed BC.I wonder, for example if, instead of calling 45%-82% Dp300/Dp internally mixed you called Dp300/Dp of 30-70% internally mixed, would that change the absolute values of Fin but leave the trends (diurnal and as a function of particle size) unchanged? It might be helpful to include a figure of histograms of observed Dp300/Dp for at least a subset of the particle sizes/times you are talking about. Maybe 100nm and 200nm at 6:00 and 13:00.

3. The discussion of the hygroscopicity is rather disconnected from the rest of the discussion. As it now reads the only utilization of the CCNC data is to look at the variation of the width of the kappa distributions as a function of the internally mixed soot fraction measured with the VTDMA and that information is presented simply as a confirmation of measurement reliability. It seems that more could be said about this data. While I realize that, since soot particles likely contribute a very small fraction of the total aerosol mass, it is difficult to relate kappa to soot particle properties but it would be interesting to know if there is any trend in kappa as a function of Fin.

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Even if there isn't, it would be reasonable to mention that fact and to explain why it's not surprising to see the effect of soot particles manifesting solely in sigma and not in kappa itself. Also, this discussion should probably at least be referenced in the conclusions.

4. I have significant difficulties with your discussion of the estimation of the soot emission rate and its incorporation into the calculation of the actual turnover rate of soot. Mainly, even after multiple readings, I don't totally understand what you did or how sensitive your reported turnover rates are to uncertainties in this calculation. To break my questions down into manageable chunks: a.) If I understand your discussion of figure 5 correctly, the "emission rate" trace is simply a plot of normalized CO. If that's the case, just call it that and say that you assume BC emissions have a similar pattern. If not, you should better describe how you got that trace. b.) While I see why it is important to minimize the impacts of vertical and horizontal transport to calculate emissions, it seems that your choice of acceptable time window entirely determines your calculated rate. You say that you wound up doing the calculation at 20:00 because that was when Emis/m was highest but that's not when it reached its peak. It had peaked earlier in the day and that was merely when it was at a maximum for the times you selected (somewhat arbitrarily it seems). If, instead, you had chosen to look at 19:00-7:00 your "maximum" would have been at 19:00 and you would calculate a different emission rate, wouldn't you? c.) Once you have this 13%/hr emission rate, I don't see how you can assume that that stays constant over the whole day. If that were true (that concentrations continue to go up by 13% /hr over the day) it would be impossible to replicate the observed diurnal profile of EC unless there is significant lateral transport. If lateral transport is that important at certain times of day shouldn't you exclude them from the overall analysis? Later you say that you calculate Emis tot by multiplying a "generic diurnal cycle of emissions" by the 13%/hr so perhaps I have entirely misunderstood what number you are trying to extract but I don't understand what you did or why it makes sense. I would recommend starting this calculation with Eq 16 to illustrate how emissions can impact Fin and to justify the need to calculate Emistot as a function of

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time. Then you need to clarify your discussion of the calculation of Emistot and how you get from an observation-based calculation of emissions at a particular time of day to an inferred diurnal profile of emissions.

5. Similar to the above, I am unclear on what you are doing in Section 3.5. It would help if you gave units for Kshift. The units given in the figure are nmˆ-2 but there must also be a tˆ-1? Also, the equations from Seinfeld and Pandis gave you changes in size distributions as a function of time but I don't see how you can talk about only internally or externally mixed BC using the same equations because you are looking at not only growth for the whole population but also a conversion from externally mixed to internally mixed particles. You probably even have some particles that are falling off into the non-BC categorization at the same time. (a 30nm particle that has a 15nm soot fraction, once it grew to the 50nm size range would no longer be classified as soot containing). Are you trying to quantify the rate at which internally mixed particles in the aitkin mode transition to the accumulation mode? If all you are trying to say is that condensational growth will tend to move particles from the smaller size bins into the accumulation mode, you could do that using equations 18-20 and figure 7. It is much more complicated to try to tease out the combined effects of morphology changes, conversions between externally mixed to internally mixed and the overall condensational growth of the whole population. If you want to do that, I think this treatment is poorly explained and probably overly simplistic. Also, I don't think it adds substantially to the conclusions of the paper. The final paragraph of the section is the only place where you relate the equations presented to the observed behavior and it is both qualitative and confusing. I don't understand how condensational growth could ever lead to an increase in externally mixed particles for example. Also, I don't understand how emissions "overwhelm condensation" to increase Fin for 30nm particles late in the day when the coated fraction of the emissions should be lower than the observed Fin. In summary, I would recommend omitting the second half of this section. If the discussion must be kept it needs a substantial rewrite.

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6. In section 3.6 I think you need to make very clear up front that this parameterization is specific to Beijing. That point should already be apparent to the reader and it is mentioned in the conclusions but it needs to be highlighted in the discussion as the emission ratios of the different observed components could be wildly different in other locations with different sources (and with different OH concentrations). I don't understand where equation 27 comes from and I therefore can't assess how specific this parameterization is to Beijing but the authors should comment on potential sources of variation for these numbers.

Minor comments:

1.What is the lower limit for the size of particles detected by the VTDMA?

2.You should have some references to previous work using the NOx/NOy and (IM+OM)/EC ratios as indicators of photochemical age.

3.In the conclusions "time courses" → "behavior"

4.Figure 9 - It would be interesting to see this figure color coded by the size of the particles.

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