

Interactive comment on “Optical properties of atmospheric fine particles near Beijing during the HOPE-J³A Campaign” by X. Xu et al.

Anonymous Referee #1

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Review of “Optical properties of atmospheric fine particles near Beijing during the HOPE-J3A Campaign” by Xu et al.

Xu et al. present results from a study carried out around Beijing, China. The report on measurements of optical properties (extinction, scattering and absorption) and composition of PM₁, contributing to the rapidly growing literature on the characteristics of the severe air pollution in this region. I find that the measurements seem to be of good quality and that the results will be of interest to the community of scholars working in this area. However, I have concerns regarding some of the analyses presented, which are discussed further below. I also think that this work is much longer than it needs to be and suggest that it could easily be cut by 30% with no loss in content and an improvement in readability simply through a reduction in redundant discussion points.

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I find that substantial revisions will be necessary before this work will be publishable in ACP, although believe that with effort it should ultimately be.

Specific concerns:

P33680/L4: I find the meaning of “chemical extinctions” to be ambiguous here as it is not a commonly used term.

Equation S2: Although two references are given where this equation was used, has it been validated? It assumes additivity of MEE values on a diameter-by-diameter basis. A more common “mixing rule” is that associated with refractive indices. Is the MEE linearly related to the refractive index, thus justifying this equation, for example? Some additional discussion should be provided.

P33681: Was the SMPS really “calibrated” or was it simply “validated.” Calibration assumes some adjustment in the operating conditions or processing method based on the obtained results.

P33681: The authors provide no information as to the sensitivity, detection limits or uncertainties in the IBBCEAS measurements of light scattering and extinction. This information is critical to the assessment of this work and the reader should not have to look up the Zhao et al. paper. Also, the instrument performance should be reported based on the time between filter periods, not the averaging time, as this will determine the actual measurement uncertainty.

P33684 and general: Everywhere that the authors use the term “CRI” for “complex refractive index” I suggest they should instead substitute “effective CRI” since they are using an effective parameter, not a true physical parameter. This is necessary since they are using what amounts to a volume mixing assumption even though it is known that black carbon, in particular, does not conform to volume mixing relationships and can have a non-spherical particle morphology. Where the authors state “The CRI is one of the intensive optical properties of atmospheric aerosols, and determined by the

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aerosols' size, shape, mixing state and chemical composition" they should clarify that this is an effective property that averages over variations in the properties listed. The CRI is a fundamental property of a material, not of particles. They should also state that they are implicitly assuming that BC can be treated in a volume mixing approach and spherical particle assumption, which is not fundamentally correct but commonly done.

P33686 and IMPROVE: The authors should note that the IMPROVE algorithm was developed based on analysis of data collected in mostly remote environments (specifically, US national parks) and thus may not be appropriate for application to urban measurements due to potential differences in typical size distributions within a mode (which affects the MEE and $f(\text{RH})$ terms) and the split between "small" and "large" modes. Also, the authors never define what the $f(\text{RH})$ terms mean (presumably the awkwardly stated "the hygroscopic increase of inorganic component.")

P33687: The authors state "The dry mass extinction efficiencies for ammonium sulfate, ammonium nitrate and OM at $\lambda = 470\text{nm}$ were calculated by using the Mie theory and were compared with that values at $\lambda = 550\text{nm}$." These are not directly comparable due to the wavelength differences. I think that this is accounted for by the "scale factors" given on L9, but it is not clear as written what is being done or where these scale factors come from or why they differ so strongly between the different components. Maybe this is what is meant by "find out more in the Supplemental Section"?

Equation 5: It is not clear how the sea salt is being accounted for here. It is also not clear how the authors are treating ammonium.

Section 3.3: The authors calculate the MAE from the total absorption divided by the total PM1 mass. It is much more common to see this parameter defined relative to the amount of BC (or EC), rather than the total PM1 as it is the BC that contributes the absorption. I suggest that the authors use the terminology MAE_{PM1} (and where the _{PM1} indicates subscript PM1) throughout to make clear that these are not BC-specific

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MAE values and avoid confusion.

P33689 and Fig. 3: It is evident in looking at the figure that the measurements at 3 min are insufficient for accurate retrieval of the effective CRI when the signal levels are "low" (e.g. period 1, 2). The authors should strongly consider a longer averaging time (perhaps 1 h).

Fig. 3: It appears that the size cuts off at 661.2 nm, presumably reflecting the limits of the SMPS and the PM1 size cut. Does the calculated scattering fall to zero at this size, indicating that the authors have captured all of the actual scattering in their calculations? If not, is there any particular dependence on time or conditions that could influence the retrieval of the effective CRI values? Could this explain some of the differences between "periods?"

Fig 3/4: I would find it more useful if Fig. 3 and Fig. 4 upper panel were combined. This would help the reader to see the relationships between the met conditions and the optical property measurements more clearly.

Fig. 4: Why have the authors considered 10 clusters of trajectories but only 6 periods? I would think these should be equal. It would be much, much more helpful if the clusters were aligned with the periods (i.e. cluster 1 = period 1). Also, it is not clear how the "clusters" were determined. Or are these just individual trajectories?

P33691, L4: It is not clear how the authors arrive at this conclusion.

P33692, L8: The authors state "However, the real part of the CRI (1.40 ± 0.03) was larger than that of the earlier traffic-dominated pollution period." This conclusion is not justified, as the value reported for the "traffic-dominated" period was 1.38 ± 0.06 . These are identical within any reasonable uncertainties (and certainly within the stated uncertainties) and no difference can be inferred. Similarly, on P33692, L20 the authors conclude that 1.44 ± 0.03 is "larger than" 1.40 ± 0.03 . This difference is closer to being real, but the authors here need to add "but within uncertainties."

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P33693, L13: It would seem that a new sub-section heading is appropriate here.

P33693, L18: I find this to be confusing as the authors seem to be mixing changes in fractional contributions with changes in absolute concentrations (although it is not entirely clear). I actually find that the distinction between fractional and absolute concentrations is often unclear in this manuscript. And these numbers should be reconciled with those shown in Fig. 5b.

P33693, L20: The authors state that previous results indicate that inorganic species become more important during haze. They should relate their measurements here directly and explicitly to this, rather than leaving it to the reader to infer a connection. Their measurements can speak to this.

P33693, L24: The word “dramatic” should be removed.

Fig. 5b: Should state what this is a percentage of. Presumably mass concentration, but it is not stated in the caption.

I find “SNA” to be an awkward acronym and suggest it is removed, especially as it is only used a few times.

P33694: The authors are again a bit loose in terms of specificity when discussing absolute versus relative concentrations. I suggest that they revise to generally be clearer in this regard throughout the manuscript. They should state “relative” or “fractional” anytime that they are talking about relative or fractional concentrations or abundances, and reserve the term “concentration” for when they are talking about absolute values. I find much of the discussion on the bottom of this page (which is discussing results from another study, not this one) to be unclear due to confusion between absolute and relative abundance.

P33695 and Table 3: The authors compare their observations to a seemingly randomly selected set of other measurements from around the world. The authors should provide some actual discussion here, and not just repeat the information in the table in the text.

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Is there a specific reason for comparing these sites? What is the point here?

P33695, L21: The authors state “Higher SSA values suggest a more mixed origin for particles, including industrial emissions, domestic coal combustion, and agricultural emissions.” I do not believe that this is correct. One could have a binary source just as easily as one could have a single source that could lead to a given SSA value. Or three sources. It is not clear why higher SSA values equal “more mixed” sources. Perhaps they just need to be more precise as to what they mean by this statement. And the authors appear to ignore the role of secondary formation in this discussion. This statement should be justified further if it is to be kept. Also, in the sentences that follow the authors are a bit loose in providing references, giving them for some of the studies but not others.

Fig. 5a: I suggest that the authors also show the scattering weighted size distributions.

P33697: The authors should report standard deviations associated with the PM1 PM fractional contributions.

Section 4.2: I find that there is a great deal of redundancy in this section, with discussion of the particle components provided no less than 3 separate times in varying levels of detail. I strongly encourage that this section could be greatly streamlined. Also, there seems to be a lot of summarizing of other results with limited direct linking to the current study. As already noted, such connections should be made more explicit.

Section 4.2.3: The authors conclude that the extensive property distributions were not normal distributions. There is no reason to think that they should be since there is a lower limit (zero). Since values cannot be <0 , it is not possible for them to be normally distributed. This statement should be removed or revised.

Section 4.2.4: The authors should be more explicit as to how the lower boundary layer heights would lead to a shift in the timing of the morning rush hour peaks. In the amplitude, sure. But it is not clear from what is stated how this would influence timing. Also,

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the conclusions regarding the “striking” consistency of the increase in the absorption coefficients between the different periods seems to go against the conclusion regarding different boundary layer heights. If emissions do not depend on meteorology, then the increase in concentration should be larger when the boundary layer is lower. These disparate thoughts should be reconciled.

P33700, L10: The use of a negative sign for an underestimate would be helpful.

Fig. 8: The authors should indicate whether they have performed a 1-sided or 2-sided fit.

P33700, L20: It is not clear how the 16% value was calculated here. This should be stated.

Figure 8 and P33700: I find the “reconstructed mass” to be very confusing. How was this determined? This is not clear. It appears that it might just be the “summation of the concentrations all 5 groups.” (P33703). But how is this different than just the PM1 mass? In other words, how does “reconstructed” mass differ from “measured” mass concentration? I feel like the authors are just saying here that $A = A$. I strongly suggest that this section needs to be clearer, both the methodology and the point.

Section 4.3: Personally, I find little value in this section over what has already been presented. I say this because the “chemical apportionment” is just a linear transformation of the chemical measurements that were already discussed. This section is therefore highly redundant with section 4.2. I strongly suggest that the authors merge section 4.2 and 4.3. Or, if they prefer to keep these separate, to greatly reduce section 4.3 to focus on information that isn't effectively already stated in section 4.2 in the discussion of the concentration variations.

Fig. 10: I find it odd that the slope for absorption and scattering is greater for the entire campaign than it is for any of the subset periods. How is this the case and what does this mean? Is this just an artifact of some of the periods having large non-zero

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intercepts?

P33702, L15: The term “well-correlated” does not seem appropriate for the absorption measurements on polluted days ($R^2 = 0.43$).

P33702: The authors should note the substantial non-zero intercepts. Or modify their fitting to fix the intercept to zero. And they should state whether they have performed 1-sided or 2-sided fits. 2-sided fits are actually appropriate in this case, and if not performed the authors should justify this choice. They should also note that the uncertainties reported are fit errors, which are completely unrealistic and unrepresentative of the actual uncertainty on this value.

P33702: The authors report at the bottom of the page a MEE that is smaller than the MSE (4.35 vs. 4.66). This is impossible and obviously the result of fit error and limitations. That the $MEE < MSE$ should give the authors pause. They must revisit this issue and explain it sufficiently, as it is a physical impossibility. The entire section should be revised accordingly, as it is clear that the derived values are not robust.

P33703: I find all the discussion regarding the MSE values and how they depend on concentration to be a bit lacking. Specifically, it is well known that the primary factor that influence the MSE is particle size. The authors mention particle size variations, but almost as an afterthought. Particle size variations are the driver of the variations. It just so happens that particle size in this region correlates with mass concentration. I strongly suggest that the authors revise this to focus more on the fundamental relationship (size) and less on the secondary relationship (mass concentration).

P33703: The authors should report explicitly the EC/PM1 fraction, not just allude to it.

P33703, L21: I find the conclusion regarding “brown carbon” formation to be highly speculative and not sufficiently justified/demonstrated. It is also severely lacking in discussion. For example, why would there be more “brown carbon” during the slightly polluted period than the polluted period? What would cause this? Is it reasonable?

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Discussion is necessary if this is to be retained. Also, some uncertainty assessment is required. How precise are the EC/PM1 estimates? What are the MAE values with respect to EC only? Are they reasonable? Do they differ between periods in the same way?

P33703: It is not clear how the comparison between the observed and reconstructed MEE and MSE values in this section relates to the reconstruction in the previous section. I feel as if these should be directly relatable.

P33703, L25 and Fig. 11: As with the linear fitting above, there is something incongruous about the MSE's for each of the individual cases being smaller than the reconstructed method while the campaign average matches well and is larger than any of the cases. How is this possible? I would think that the campaign average should be in between the different cases. Also, unless I am missing something it is entirely unclear how the reconstructed MSE's were calculated. Equations are only given for the MEE (in the supplemental). Same is true for the MAE values. I also find it difficult to understand the large calculated (i.e. reconstructed) values shown in Fig. 11. The individual component MEE values given in Eqn. 2 only range from 2.88 to 3.64 for inorganics and organics (not counting the "large" component, which the authors stated were ignored). The fractional contribution to EC is too small for it to substantially increase the MSE. And the composition does not change substantially between periods in terms of the inorganic/organic difference and thus one would not expect the reconstructed MSE to change very much either. I find this bit to be lacking in key methodological details. (Note: I also don't understand why Eqn. 5 has "large" components when the authors seem to indicate that these are ignored. If they are ignored, they should just be removed from the equation. If they are not ignored, then much more detail is needed in section 3.2.)

P33706: I find the last two sentences of the conclusions to be particularly awkward in terms of writing in a way that makes them difficult to understand. I suggest these need revising, as do all of the conclusions in relation to the issues raised above.

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Technical corrections:

Fig. 2: The axes labels should be changed to avoid the use of abbreviations (e.g. coeff = coefficient and concen = concentration)

There are numerous typos throughout the manuscript, too many to take the time to document here. The authors should have this read over by a native English speaker.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 33675, 2015.

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