Point-to-Point Response to Comments and Questions

on MS No.: acp-2010-965 (Elevated aerosol layer embedded in aged soot particles in a polluted urban atmosphere by G. Shi et al.)

Anonymous Referee #1 (7 March 2011)

General Comments

This paper presents the simultaneous collection of soot in conjunction with the measurement of several atmospheric state variables via tethered balloon. This approach is unique and yields interesting insight into how meteorology is coupled to aerosol aging dynamics. The authors should give more detailed description of the methods they used to obtain their results because some statements in the manuscript appear to be contradictory. Specifically, the authors should describe how they identify and count soot particles. They stated that 80-90% of the particles were soot at all levels of the atmosphere, which seems high. Perhaps with a more detailed description of their methods, readers can properly gauge any systematic or experimental uncertainties regarding any statistical analysis. Also, the soot particles were indirectly observed to be in the aqueous phase even though the relative humidity (RH) never exceed %30. After discussion of these points and the points detailed below in the "Specific Comments" section, the paper should be publishable in Atmospheric Chemistry and Physics.

***Response*:**

We show responses to these comments and suggestions in the following descriptions. The manuscript is modified concerning these points. Please refer to the following responses.

Specific Comments

Page 1643, Line 13: Suggest citing Molina et al.'s overview paper describing the campaign rather than an isolated result from that campaign[1]

***Response*:**

The reference is replaced according to this suggestion.

Page 1644, Line 24: Clarify what "speculated" conditions are.

***Response*:**

In the revision, "speculated conditions" is replaced with "an assumption that the vertical distribution of aerosols was proportional to specific humidity".

Page 1646, Line 4: Please specify what is meant by "The weather was fine".

***Response*:**

In the revision, “The weather was fine” is replaced with “It was clear”. For this, “it was clear” in the last paragraph of Introduction (line 17 page 1645 of the discussion version) was removed.

Page 1646, Line 21-end of paragraph: I find the description aerosol sampler lacking. It is also not adequately described in Matsuki et al. How was the sampler controlled? What was the nozzle to impaction plate distance?

***Response*:**

We designed and manufactured the samplers by ourselves. Each sampler is composed mainly of a control system, a low volume pump, and battery sets as power of the pump and the control system. All of these are packaged in a box (250mm×160mm×96mm) – we call it sampler. In each sampler, a two-stage cascade impactor is set to collect particles. The impactor is fixed in the box (totally about 2.2kg without battery) and outside air is introduced straight (without curve) to its inlet via a 6-mm-diameter silicon tube. The length of the tube is usually less than 15 cm with its inbox part always about 4cm. To avoid contamination of tube setting, the tip of the inlet tube is wrapped with parafilm. The film is removed and about 2cm of the tube tip is cut just before balloon ascending. To avoid contamination during the balloon ascending and descending, the sampler has an auto-controlled valve at the entrance of the inlet tube into the box. The sampling time for each sampler is preset by a timer of the control system. The sampling start is controlled by a pair of radio transceivers, one onboard the sampler. The particle collection was started by sending a radio signal to the onboard transceiver with the other one on the ground. After the onboard one gets the signal, the control system starts to work. The valve of the inlet is automatically opened and the pump automatically starts to pump air from the outlet of the impactor. After the time preset for particle collection, the pump automatically stops and the valve is automatically closed. During the particle collection, the paired transceivers exchange signals every 30 seconds (preset) in order to let us know the sampler is working or not, from which we know if the collection is started or finished.

A brief description of samplers is added into the fourth paragraph of Method section in the revised manuscript. For this, there is a minor modification (line 3 of next paragraph:’ switched on by a remote controller and’ is removed) in the revision. We feel the samplers are not technically difficult ones and adding all the above details will make the paper tedious.

About the question on the distance between nozzle and plate, please refer our response to the question on Page 1651 Line2.

Page 1650, Line 19: How were the number fractions “roughly” identified? Please give detailed descriptions on how particles were identified. What kind of uncertainty and systematic error are realized in these measurements?

***Response*:**

We use ‘roughly’ because we did not confirm the elemental composition of every particle by EDX analysis. Instead we used the shapes and morphologies in electron microscopic pictures first and then used EDS confirm part of the particles in each category. In the revised manuscript, the word “roughly” was removed.

The details of particle identification were described in section 3.2. We did not introduce them in the section of methods because we think it is easier to understand the identification with reference to Fig. 3, which showed the results of the analysis. In the statistical analysis of

particle shape and size, we analyzed every particle we could see in all photos. This is mentioned in the section of method. Since we have only one sample at each altitude, we could not check the uncertainty due to particle collection. Uncertainties are from the particle identification. At 280 m, 550 m, 740 m and 880 m, the identification should not result in large uncertainties because particles in the range applied for the statistical analysis (diameter larger than 0.2 μm) are easily identified according to the criteria shown in section 3.2. There are large uncertainties for particle at 1080 m because in the sample from this altitude there were a number of particles showing weak electron absorption but not electron-dense (for the size matter of particles at 1080 m, we described as "a state of opacity" in the Line 23-25 page 1651 in the discussion version) which were apparently different from those we considered as secondary particles. In case of characterizing such particles as soot particles, the number ratio of soot particles at 1080 m was 90, and if not, 67%. In the revision, a table (Table 2) showing the number ratios at each altitude is added into the last paragraph of section 3.2 and the uncertainties was showed and described there.

Page 1650, Last paragraph: That 80-95% of the particles contain soot seems high. Based on the images shown (Figure 3), I am not convinced of these numbers. What criteria did they use for soot detection? These sorts of measurements would be useful for modeling purposes, but it might be a mistake to undertake a model calculation using measurements having large uncertainties or systematic errors.

***Response*:**
The criteria used for soot detection were described between Line 20 of page 1649 and Line 3 of page 1650 of the discussion version.
Except the ratio in the upper layer (1080m) which had large uncertainties, the ratios in other altitudes are correct. Please note that the ratios are for particles in the size range of 0.2-1.3μm. In the analysis, we measured every particle which we could see in EM photos. The total counted number of particles from each altitude sample is actually 821 for 280m, 979 for 550m, 280 for 740m, 457 for 880 m, and 933 for 1080 m. But many particles were smaller than 0.2 μm, which is the effective lower size bound of the impactor. There was particle loss for particles smaller than this size in the sample. So we cannot include particles smaller than 0.2 μm in the statistical analysis and we excluded them according to size. We chose pictures for Fig. 3 to show the typical morphologies of particles at each altitude and did not choose pictures to show the ratios. If the figure is seen under a large amplification, the ratios of soot particle occupied in these pictures are actually close to 100% except the one of 1080 m.

Page 1651, Line 2: Wouldn't you need to have the distance between the nozzle exit and the impaction surface to estimate the cut point? Please discuss.

***Response*:**
No, this is because the estimation of 50% percentage cutoff diameters is based on theoretical calculation with an ideal condition that flow passing the nozzle exit could keep as a jet to splash onto the mesh films. Details of the theoretical calculation can be found in Marple et al. (2001: Interial, Gravitationla, Centrifugal, and Thermal Collection Techniques, in *Aerosol Measurement: Principles, Techniques, and Applications*, edited by P. A. Baron, and K. Willeke, Wiley press, 2001) The actual distance of the nozzle of the impactor we used is about 0.2 mm. The estimated results of course contained bias (they also depends on the density of particles), and are considered as reference size ranges. That is why we used the diameters we measured on mesh films other than the cutoff sizes. In the revision, the

theoretical calculation is mentioned by citing the book of Baron and Willeke. Citing the book other than the paper in it is because the book is also cited in another place in the manuscript.

Page 1651, Line 7, Page 1652, Line 7, Page 1653, Line 3: I am somewhat surprised that the particles were in the aqueous phase considering that the maximum RH was 30%. A detailed discussion of this is needed. Is it possible that the RH of the air mass was once much higher (>70%, the deliquescence point of many common aerosol salts)? If not, then how do the authors explain the phase of the particles?

***Response*:**
In fact, we do not know the exact reason. We noticed this fact and think that it could not be ignored in the manuscript although we cannot explain the reason confidently. A possible and acceptable reason is that the coating, as mentioned, was a mixture of salt (sulphate, nitrate, and secondary organic compounds which were produced on the surface of the particles (Hu and Guo, 2009)) and liquid water. Since the particles existed in the layer from the pervious day, the production of the salt should have been occurring since then. Secondarily-produced sulfate and nitrate have very strong ability to absorb water vapour. In particular, at night time, due to the decrease of temperature, relative humidity would have increased, which favours the condensation of water vapour onto the particles. Although RH was 30, previous studies (Laskin et al. 2005: Direct observation of completely processed calcium carbonate particles in polluted atmospheric environment. Faraday Discussion 130, 453–468. Gibson, et al.2006: Aerosol chemistry and climate: laboratory studies of the carbonate component of mineral dust and its reaction products, Geophys. Res. Lett., 33, L13811, doi:10.1029/2006GL026386. Shi et al. 2008: Influences of sulfate and nitrate on the hygroscopic behaviour of coarse dust particles Atmospheric Environment 42, 822–827) showed that nitrate in conjunction with calcium could make the particles in a liquid phase even at the relative humidity smaller than 20%. Thus it is possible for a particle containing nitrate on its surface to keep a liquid coating under the conditions of the present study.

"The soot particles in the EAL were emitted into the air in previous days. Their surface had gradually become a mixture of salt such as sulphate and nitrate. Night-time increase of relative humidity in elevated layers favoured the condensation of water vapour onto the particles. Although the RH was 30% at the moment when the particles were collected, previous studies showed that it was possible for particles containing nitrate to exist in aqueous phase when RH was smaller than 20% (Laskin et al., 2005; Gibson et al., 2006; Shi et al., 2008)." is added into the first paragraph of section 4.2. References are added into the reference list.

Page 1651, Line 8: Whether the particles assume a hemispherical shape or not will most likely depend on the physical properties of the particles – whether they are solid are liquid. If they are liquid, it would then depend on the contact angle of the aerosol material with the substrate. Is there any way that the authors could make a better estimation of the true geometry of the impacted particles?

***Response*:**
Yes, it is true that the shape of a liquid particle splashing onto a film depends on the contact angle. Unfortunately, there is not a way which can estimate the geometry much more accurate than the other way when using electron microscope photos to confirm the geometry of impacted particles. The major reason is that too many processes and factors influence the geometry, such as the splashing angle, dry or wet state of the particles, viscosity of the liquid

material coating or forming the particles, volatile or non-volatile properties of the aqueous components, and etc. A shading method was suggested by and has been applied in many studies. But it still had large bias for particles dominated by volatile components or in solid phase. So we chose the simplest way: using the on-film diameter. Actually we found the results using this way were not very different from that using shading method previously. This sizing method can be understood easily by readers and we think it will not mislead readers, when being cited to compare with sizes in other approaches.

Page 1651, Line 25: If the particles were too opaque to identify soot inclusions for the 1080 m layer, then how was it calculated that 90% of these particles contained soot (Page 1650, Line 23)? These are very inconsistent statements/results.

***Response*:**
We found some particles at 1080m had some ability of electron absorption (but not electron-dense) which was stronger than that of particles we identified as secondary particles. It is not suitable to characterize them as secondary particles in accumulation mode produced via coagulation of secondary particles and/or condensation. So we considered them as soot particles in the first submission, because of which the ratio was 90%. If we considered them as other particles, the ratio of soot particles was 66.7%, and the ratio of other particles was 24.3%. These data are added into the revisions as Table 2 to accurately show the ratios.

Page 1655, Line 20: Here the authors state that there are "a large number of secondary particles in the EAL besides soot particles". What number % was this?

***Response*:**
In the size range of 0.2-1.3μm, the number ratio of secondary particles was 16.8% at 740m (197 particles) and 24.6% at 880m (248 particles). In the total particles we analyzed (including particles smaller than 0.2μm: note there was loss for them), the ratios are 21.8% at 740m (280 particles) and 37.2% at 880m (457 particles). Both ratios are apparent larger than those at 280m and 550m. We add the data of size range 0.2-1.3 μm as Table 2 into the part of the mentioned paragraph.

Page 1656, Line 8: The authors conclude that a core shell model may be a good simple model for well aged particles. Adachi et al.2 showed that many soot particles are "embedded" and that they did not exhibit the core-shell morphology. Some discussion of these results with those obtained here is warranted.

***Response*:**
We do not think the suggestion of a core-shell model for well aged particles conflicts with that of Adachi et al.. The reason is that we suggest this model for "well-aged soot particles". The soot particles reported by Adachi et al. and also in many other papers were observed on the ground in urban atmosphere and they usually showed many different kinds of morphologies because there are fresh, young and aged ones in such samples. This is similar to the particles in the lower layers in our observation. Since the aging of soot particles in urban atmosphere is very fast (in a time scale less than a few hours), it is usually found a large number of aged but not well-aged soot particles (in shrunk or compact morphologies frequently with thin coating) in urban atmosphere. It is more proper to call such particles "embedded". They were in the stage prior to what we called "core-shell" stage. We mentioned,

in the discussion, that if soot particles in the mixing layer repeat the fate of those in the EAL, they would become core-shell particles. And we emphasize that our suggestion is on well-aged soot particles in the manuscript. In the revision, “aged” the mentioned part (in Page 1656, Line 12 of the discussion paper) is replaced with “well-aged” to make this clearer.

Page 1657, Line 29: Since soot itself does not deliquesce (it is insoluble in water), suggest "deliquescence of soot containing particles".

***Response*:**
It is corrected as the suggestion.

Technical Corrections

P1642, Line 23: after “and” insert “represent an important contribution to overall PM in the urban atmosphere.” To make the sentence sound better.

***Response*:**
It is modified as the suggestion.

Page 1642, Line 25: delete “as a carrier of black carbon” – this sounds awkward.

***Response*:**
It is replaced with “Because of the black carbon content” in the revision.

Page 1643, Line 1: Instead of a comma, use a dash

***Response*:**
It is modified as the suggestion.

Page 1643, Line 5: Instead of a comma, use a dash

***Response*:**
It is modified as the suggestion.

Page 1643, Line 7: Delete “remarkably” –sounds awkward.

***Response*:**
It is modified as the suggestion.

Page 1644, Line 27: Did the authors mean “sensitive” rather than “sensible”?

***Response*:**
Yes. It is corrected in the revision.

Page 1645, Line 8: “constraining” may work better than “restraining” because it is more common in scientific literature.

***Response*:**
It is modified as the suggestion.

Page 1646, Line 21-22: It sounds as if the impactor was used to coat the microscopy grids. I don’t think this was the case. Typically thin films are not applied using the sampler.

***Response*:**
The sentence is changed into “Aerosol particles were collected onto electron microscope meshes by using the samplers. The meshes were coated with carbon-sprayed Formvar film.”

Page 1647, Line 16: replace “atom” with “atomic”

***Response*:**
It is modified as the suggestion.

Page 1648, Line 2: “Barometric meter” is not a common term. Please precisely define what was used to obtain height.

***Response*:**
It is changed into “Here and also in the following descriptions, the altitudes in meter were calculated with the static equilibrium equation.”

Page 1650, Line 14: replace “submicron meters” with “sub micrometer”.

***Response*:**
It is modified as the suggestion.

Page 1650, Line 17: replace “flying ash” with “fly ash”.

***Response*:**
It is modified as the suggestion.

Page 1651, Line 11: Use of the term “more or less” is confusing here. Which is it? I think the authors meant that projected diameter of the particles is larger after impaction.

***Response*:**
“more or less” is removed in the revision.

Page 1651, Line 13-14: By “geometric size” I think the authors mean “original size of the ambient particle”.

***Response*:**
It is changed as the comment.

Page 1655, Line 24-25: Replace “size segregated distributions” with “size distributions”.

***Response*:**
It is changed as the suggestion in the revision.

Page 1656, Line 2: Replace “nocturnal” with “nocturnally”.

***Response*:**
It is changed as the suggestion in the revision.

Page 1657, Line 25, 27: Replace soot “parts” with “inclusions” or “cores”.

***Response*:**
They were replaced with “inclusions” in the revision.

References: (1) Molina, L. T. et al. Air quality in North America’s most populous city - overview of the MCMA-2003 campaign. Atmospheric Chemistry and Physics 2007, 7, 2447. (2) Adachi, K.; Chung, S. H.; Buseck, P. R. Shapes of soot aerosol particles and implications for their effects on climate. Journal of Geophysical Research-Atmospheres 2010, 115.

p.s. According to the request of Dr. Guangyu Shi, the order of the first two authors is exchanged in the revision.

Thank you very much for your helpful comments and questions.