Atmos. Chem. Phys. Discuss., 9, C9556–C9566, 2010
www.atmos-chem-phys-discuss.net/9/C9556/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Size-resolved aerosol water-soluble ionic compositions in the summer of Beijing: implication of regional secondary formation" *by* S. Guo et al.

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Received and published: 11 January 2010

Thank you for your careful and critical review of our paper. The followings are our responses to your comments. General comments Comment: Although the authors have obtained 3 or 4 modes of the aerosol sources, which the discussion, I feel, in the later section of 3.3 does not well make use of. This may be due to some confusion of general terminologies of "coarse", "fine", etc. and those defined originally in the present study.

Response: We agree with the reviewer that the general terminologies of "coarse", "fine" etc. made some confusion. In fact, the discussion in the section 3.3 was based on PMF

resolved particle modes rather than measured "fine" and "coarse" particles, so the text in section 3.3 is revised to make this clear and also more discussion with PMF results was added in the text as following: 1)First paragraph of the section 3.3.1 was deleted as well as fig. 5 to make the discussion more concentrated on PMF model results (resolved particle modes) rather than description of measured data. 2)The terms "fine" and "coarse" in the text were all replaced by more accurate expression to make this point clear. See line 311 to 313 as following: "Moreover, both measured and model resolved mode concentrations of K+ and sulfate showed poor correlations at the two sites." 3)Necessary explanations of how to use PMF results to estimate the contributions of each formation pathway was added in the text. See Line334 to 339 and Line 350-351 as following: "In this study, by using PMF model, different modes of sulfate were resolved from total sulfate, and the concentrations of resolved condensation mode, droplet mode and coarse mode can be regarded as the sulfates that were formed by gas-to-particle condensation process, in-cloud or aerosol droplet process and SO2 on soil particles heterogeneous reaction process, respectively." "The PMF results showed that 59% and 16% of the nitrate were formed by in-cloud and gas-to-particle condensation process." 4)Ca(NO3)2 in PM1.8 was estimated by using PMF results rather than measured results. See Line 431-439 as following: "Assuming the resolved coarse mode nitrate was as the form of Ca(NO3)2 by the reaction of HNO3 with crustal particles. Thus, the model results showed that 13%, 30% and 7% of nitrate in PM1.8 was as the form of Ca(NO3)2 at PKU site in the morning, afternoon and night, respectively. The corresponding fractions at Yufa were 5%, 12% and 3%. As mentioned above, theses Ca(NO3)2 may the one reason for the peak "shift" at PKU. However, this was not an important reason, because an average of only 14% of the nitrate was formed as Ca(NO3)2 in fine particles, and the fraction was the lowest at night when the fine mode peak "shifted" to lager size."

Comment: In the section 3.2.2 the authors concluded that "these particles may from in-cloud process of long range transport". I am confused by the terminology of "in-cloud". I am sure that the authors consider "the bigger size droplet mode" aerosol

is produced by the cloud activity. However, where did the aerosol meet the cloud? Maybe not fog? Considering that the air mass was advected from Yufa to PKU over the ground surface (probably within a few hundred meter above the ground), it could not meet the cloud. Although I know that Beijing is located inland, I wonder if you often have afternoon/evening shower in summer time in Beijing?? A recent work by Chen et al. (J. Geophys. Res. 114 (2009) D08306) may give a hint for this question. They suggested the existence and explanation for the polluted layer a few km above Beijing during summer. The convection during daytime may bring aged? aerosol in the lower free troposphere back to the surface.

Response: We thank the reviewer to give us this very useful information so that we can explain the bigger size droplet mode more adequately. More explanations were added in the text after Line287-294 as following: “A recent work by Chen et al. (2009) gave a support for this explanation. They suggested the mountain-valley breeze dominated the wind flow of the Beijing region during summer. Air pollutants were injected from the planetary boundary layer into the free troposphere due to the convection during daytime, and then were long distance transported from south to north. At the night time the particulate pollutants were transported back to the city again, when they were aged by in-cloud process and grow up.”

Comment: Description for measurements by a steam jet aerosol collector should be incorporated to the experimental section, in order to give the understanding that the authors have carried out not only the MOUDI observation.

Response: We thank the reviewer to point out this. The description for measurements by a steam jet aerosol collector was added in the experimental section as following: “2.2 Online instrument Online instrument Wet Denuder-SJAC (Steam Jet Aerosol Collector) system (Slanina, et al., 2001) was also used in this study to measure particle compositions SO42-, NO3-, NH4+ and gaseous NH3 and HNO3. A wet denuder system is used to scavenge interfering gaseous nitrogen compounds, in this case ammonia and nitric and nitrous acid. The absorption solution is a 10-5 M carbonate solution which

effectively retains all gaseous interferences. Then particles can go through the wet denuder and are captured by steam which is generated by SJAC. The solution was finally analyzed by ion chromatogram. The sampling flow rate is 16.7 L/min and the time resolution was 30 min.”

Comment: Figure 1 maybe better redraw. I am confused with the "polluted episodes" and "clean episodes" at a first glance because the time series were not perfectly match with PKU and Yufa samples. Please identify the episodes evidently. The criteria may include some ambiguity. For instance, the authors states that "the SORs during the clean episodes were lower than 0.2", which is not always true. The aerosol concentration at Yufa on August 29th was very low. Also, why was not September 5th included as the clean episode 2? The aerosol concentration at Yufa on the day was low as well.

Response: We thank the reviewer to point out this. We checked the data again, corrected some mistakes and redrew Figure 1. August 29th was a special day. Although the concentrations were very low at both sites, the SORs were very high (>0.3). Thus, we decided August 29th was classified as neither “clean” nor “polluted” episode. On September 5th, Yufa met the “clean episode” criteria, however PKU did not. Also because there was no data of September 4th at PKU, clean episode 2 was only for Yufa, and the period was changed to be September 4th to 5th. Fig.1 was redrawn to keep consistent with the text. The text in Line 139-141 was revised as following: “Two “clean episodes” were observed during August 20th to 21st and September 4th to 5th (figure 1: C1-C2, samples were not collected on Sep. 4th at PKU for technical reason, so C2 is only for Yufa site), . . .”

Comment: Relating to this, please add the definition of the samples in the caption, for instance; the samples are given the id as yymmdd-X, where X denotes sampling core time of morning (A), afternoon (P) and night (N).

Response: Thanks for reviewer’s suggestion. Definitions of the samples were added in the figure 1 caption as following: “Figure 1 PM10 and size-segregated particle mass

concentrations for each sample during the campaign. (a) PKU, (b) Yufa. The samples are given the ID as yymmdd-X, where X denotes sampling core time of morning (A), afternoon (P) and night (N)"

Comment: I do not understand the final conclusion of the section 3.1 in page 23960 stating that "by scavenging and dispersions". No real information on the precipitation is given thus its role is unclear. This is a drawback of the present paper.

Response: We agree with the reviewer's comments that there was no information on the role of precipitation. For the scavenging and dispersion process are not the focus here, the statement in this paragraph was revised to describe the results of scavenging rather than its role. The text was revised as following: "The stagnant atmosphere favored secondary transformation and pollution accumulation. The precipitation or strong wind from north interrupted the pollution accumulation process. Thus the "polluted" and "clean" episodes occurred alternately."

Comment: In the PMF analysis you can obtain better fit by increasing the number of the factors. Therefore, it should be stated why the authors chosen 3 or 4 factors to resolve the present data.

Response: We agree with the reviewer's comments. The statement why 3 or 4 factors were chosen was added in the text. Please see Line 206-209 as following: "Three factors were chosen because two similar modes would be resolved if factor number was fixed at four. The reason is the same for PKU site. Moreover, numbers of factors were also decided according to the measured size distribution and scientific rationality."

Comment: English is fluent in general, but some ambiguity and lengthy expressions remained in the present text. I recommend having native speaker's check in case.

Response: We thank the reviewer for pointing out this. English was checked again throughout the whole text.

The following lists the technical suggestions. Comment: Many sentences omit 'that'.

This may be better to add. In page 23956 at 7th line: PMF model was -> PMF model analysis was. . .

Response: We really thank the reviewer for such careful and patient work. The text was revised as the comments.

Comment: In the same page at 11th line: indicating it must be taken into account in summer. ->that secondary components are important especially in summer.

Response: This sentence was revised as following: ". . ., indicating that the gas-to-particle condensation process was also important in summer."

Comment: In page 23957 at 2nd line: Beijing EPB -> Beijing Environmental Protection Bureau??(EPB)

Response: Yes. The full name of EPB was added in the text.

Comment: In the same page at 16th and 18th lines: It's-> It is In page 23958 at 3rd line: two more stages -> two more fine stages

Response: We thank the reviewer to point out this. The text is revised as suggested.

Comment: In the same page at 20th line: in a refrigerator -> Please add how much temperature was in a refrigerator.

Response: Thanks for pointing out this. The temperature was added in the text. Please see Line 88-89 as following: ". . ., and stored in a refrigerator at the temperature of -20 C"

Comment: In the same page at 24th line: formate, acetate, oxalate -> formate, acetate, and oxalate

Response: We thank the reviewer to point out this. The text was revised.

Comment: In the same page at 25th line: Please mention not only "the same as Hu et al. (2005b)." but about 'ion chromatographic methodology' in brief.

Response: We agree with the reviewer's comment, and the ion chromatographic methodology is added in the text as following (see Line 91-99): "The samples were extracted by 10 ml de-ionized water using an ultrasonic bath for 30 min at room temperature, and then the extracted liquid was analyzed by ion-chromatograph (DIONEX, ICS-2500). The IC analysis methods were the same as Hu et al. (2005b). An AS11 column (4 mm) with an AG11-HC (4*50mm) guard column and an Anion Trap column (ATC-3, 9*24mm, for 4 mm) were used for anion detection with an eluent of 0.4–6mM/L NaOH (1.2mL/min, gradient). Cations were analyzed by CS-12A Column, with a CG-12A(4*50mm) guard column, CSRS-I suppressor. The eluent was 20 mM/L MSA with a flow rate of 1.0 mL/min."

Comment: In the same page at 26th line: Please add the rough figure for the detection limits.

Response: We agree with the reviewer's comment, and added detection limits in the text in Line 100-104 as following: "Totally five kinds of cations (Na+, NH4+, K+, Mg2+ and Ca2+), four kinds of anions (F-, Cl-, NO3- and SO42-), and three kinds of low molecular weight water soluble organic compounds (formate, acetate and oxalate) were analyzed, with the detection limits of 0.03, 0.06, 0.1, 0.1, 0.05,0.03, 0.03, 0.01, 0.01, 0.06, 0.06 and 0.02 mg/L in liquid."

Comment: In page 23959 2nd paragraph starting from 14th line: The explanation for Fig. 1 seems to be needed here.

Response: We agree with the reviewer's comments, and more explanation was added in the text in Line 129-133 as following: "Figure 1 showed the size resolved PM10 concentrations and SORs (molar ratio of the particulate sulfate to the total sulfur SO42-+SO2) at two sites. Particles in stages of 0.56-1 um and 1-1.8 um consisted large fraction of total particles. PM10 as well as SORs exhibited similar trend at both sites with obvious cycles of pollution increase and decrease."

Comment: Equation 1 in page 23961: Definitions of gik and fkj should be given.

Response: Thanks the reviewer to point out this. Definitions of gik and fki were added in the text. See Line 183-185 as following: "where gik is the amount of mass contributed by each factor to each individual sample, fkj is the species profile of each source, eij is the residual for each sample/species."

Comment: In page 23961 at 25th line: showed -> shown In the same page at the next line: measured -> determined

Response: These two sentences have been revised. Thanks for pointing out this

Comment: In page 23963 at 26th and 27th lines: "due to more resuspended dust by traffic and more construction works before Olympics." sounds simply as a speculation.

Response: We agree with the reviewer's comment, and more explanations are added in the text. See Line 259-262 as following: "For road dust and construction work were major contributors to coarse mode particle in summer of Beijing (Song et al., 2006), more resuspended dust by traffic and more construction works before Olympics may be the reason why PKU site had a larger coarse mode."

Comment: In page 23965 between 6th and 8th lines: I cannot follow well "The absence of the nighttime correlation between sulfate and SO2 suggests the deposition of sulfate was of greater importance than aqueous-phase production during the nighttime."

Response: We thank the reviewer to point out this. This section is omitted together with Fig. 5.

Comment: In page 23965 at 23th and 24th lines: "mass concentrations of K+ to sulfate . . . biomass burning particles." This needs reference.

Response: We thank the reviewer to point out this. The reference is added in the text.

Comment: In page 23966 between 14th and 18th lines: "the contributions of different formation pathways have not been quantified yet due to lack of suitable analysis technique." I can not follow the logical flow of this sentence and the next conclusive

sentence.

Response: Thank for the comments, and the sentence was revised to make it more logical and easy to understand. See Line 330-334 as following: “Although the previous study has concluded the sulfate was attributed to in-cloud processes in the summertime of Beijing (Yao, et al., 2003), the contributions of different formation pathways have not been quantified yet due to lack of suitable analysis technique, because different particle modes cannot be quantificationally separated only by measured data.”

Comment: Table 1: Compare -> Comparison, reference -> Reference, 2001-7 -> 2001-Jul, and the present results should be at the top of the table. Table 2: condensation, droplet, etc. should be typed as Condensation, Droplet, etc. Some data accompany more than 4 digits, which seem less reliable as the effective figure.

Response: We thank the reviewer to point out this. The text was revised as suggested.

Comment: Table 3: The number of the samples should be given.

Response: Thanks the reviewer to point out this. The number of the samples is added.

Comment: Fig. 3: The line drawn by yellow cannot be seen clearly. Also, legends should be easily readable (make larger).

Response: We thank the reviewer to point out this. Fig. 3 is redrawn to make it more readable.

Comment: Fig. 5 may be omitted.

Response: We agree with the reviewer, and Fig.5 is omitted.

Comment: References should follow the format of the present journal. Please check them again.

Response: Thanks for pointing out this. The references were checked again.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 23955, 2009.

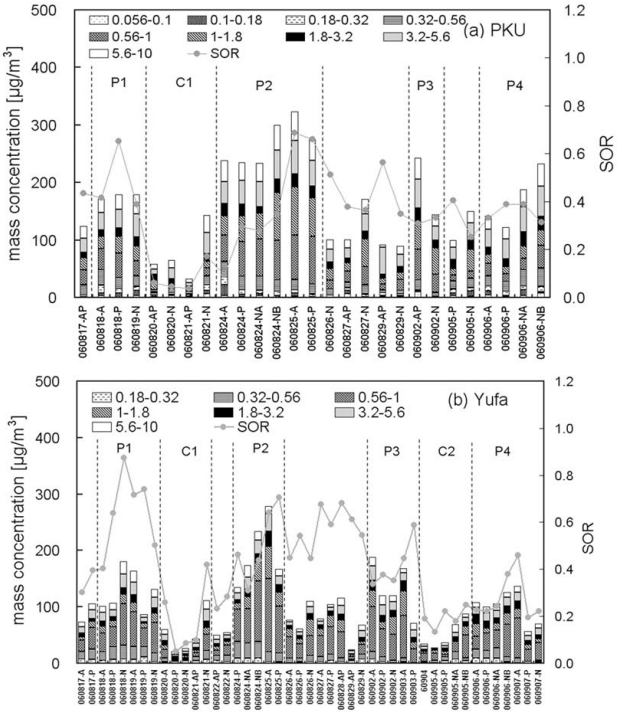

Fig. 1. Revised Figure 1

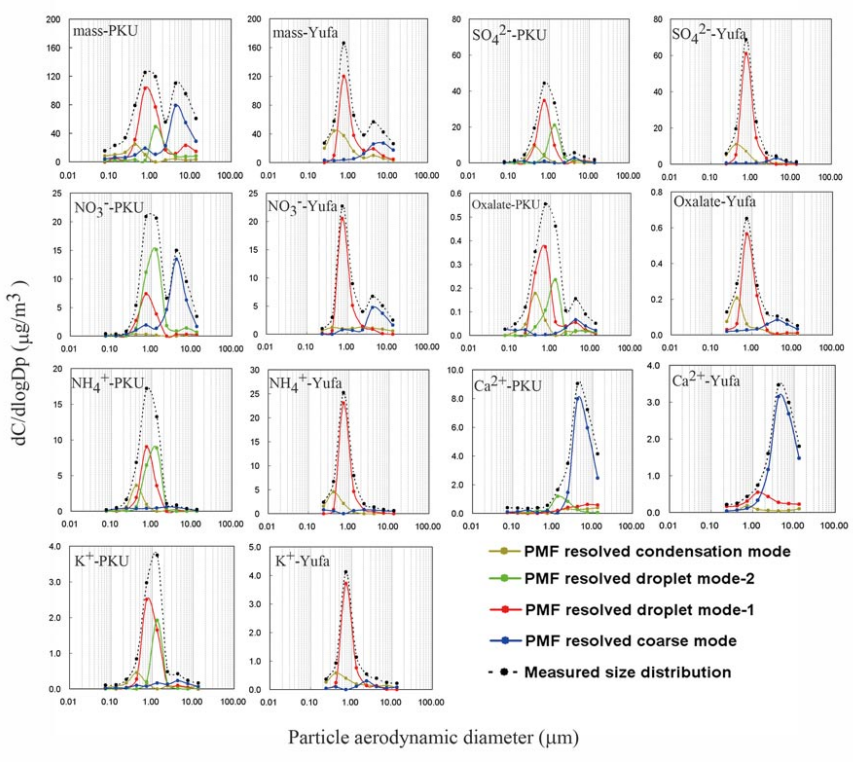

Fig. 2. Revised Figure 3