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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Individual particle analysis of aerosols collected under haze and non-haze conditions at a high-elevation mountain site in the North China plain" *by* W. J. Li et al.

W. J. Li et al.

liweijun@sdu.edu.cn

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We thank the two referees for their constructive comments. The manuscript was revised according to the comments, suggestions and questions. Here are the point-to-point replies.

Anonymous Referee#1

1) Page 22387, line 18, are "subjected" to.

Reply: Changed

2) Page 22388, line 2, ": : : to answer how aerosols are transported into : : :".

Reply: Changed

3) Page 22389, section 2.1, I suggest to give a map here, which would be helpful for readers to understand where the location is.

Reply: We added a map in the revision to show the location.

4) Page 22391 line 3-5, I suggest to change the sentence as "although this instrument has a range of 10 nm to 10 um, we set the upper limit as 1um because of low collection efficiency of larger particles".

Reply: Changed

5) Page 22392, line 4-8, how to recognize the haze event? Based on visibility or other meteorological parameters? It's better to give some explanation.

Reply: We added the explanation.

In the text: "The Chinese Meteorological Administration (CMA) defines clear and hazy days as follows: "clear": visibility $\geq$ 10 km and "hazy": visibility < 10 km and RH $\leq$ 80%. Haze layers with visibility < 5 km were observed in phase-I (except 21 April) and phase-II, but haze was not observed after 26 April."

6) Page 22393 line 11 different compositions

Reply: Changed

7) Page 22396 line 1-4. During the dust storm, the dust particles transported by cold front are well known. Thus, these sentences could be removed.

Reply: Changed

8) Page 22396, section 3.4 and Fig 6, I suggest to show the phase I, II and III on the figure, and mark the x-axis with hour intervals.

Reply: We modified Fig. 6.

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9) Page 22396, line 21-22, give more explanation why NPF was weak and particle growth events were robust in phase-III compared to phases I and II.

Reply: We gave the discussion in third paragraph of section 4.

10) Page 22397, line 23-25, how to obtain this result? Please give a brief explanation.

Reply: The question was also asked by the referee#2. We gave explanations in 42 from the referee#2.

11) Page 22400, line 21-23, the conclusion section. Since this study did not determine the radiation of aerosol particles with sulfates and soot particle, this conclusion should be deleted.

Reply: We deleted this sentence.

12) In Fig.1, relative humidity after noon increased quickly. However, the author didn't consider its effects during the particle growth process in section 3.4. It is difficult to quantitatively calculate the contribution, but a qualitative description of the role of humidity in the growth process should be indicated.

Reply: Yes, We fully agree with the referee's comments. The humidity increasing in the afternoon should have enhanced particle growth in size because of water vapor absorption. The following description was added in section 4.1 in the revision. Because the details on this point are beyond this study, we are unable to give more details with data on this point.

In the text: "The increasing RH after 16:00 on Mt. Tai (Fig. 2) might also influence particle's size because of particle hygroscopic growth."

Anonymous Referee#2

1) The claim that "ultrafine" soot and fly-ash particles played a role in particle nucle-

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ation appears to be unsubstantiated, since the TEM images show these anthropogenic particles to be much larger than the new particles as measured with the WPS and shown in Fig. 6.

Reply: We carefully considered your comment. Please see our reply in 42.

2) The criteria for the distinction of particle types are unclear (see below), please provide more detail.

Reply: We added detailed information in the section 3.2. In the classified criteria, we firstly considered the highest peaks in the EDS spectra. If one EDS spectrum shows the highest sulfur peak and the highest weight in the quantitative EDS data except the peaks of carbon and oxygen, the particle will be acted as S-rich (Figure 4a). Moreover, morphologies of individual aerosol particles also were referred, as described in section 3.2. Different particle types show different morphologies under the electron beam, such as shapes and beam sensitive. The observations will guarantee to distinguish some particles of similar compositions or morphologies. For example, fly ash and some crustal mineral particles both contain Si and Al, but they display spherical and irregular shapes; fly ash, metal and some organic particles have similar spherical shape but they contain different compositions.

Because our one previous paper (Li and Shao, 2009) described the classified criteria for the distinction of particles types, we only give very brief explanation in this paper. Also, the reference was added here.

In the text: “In the classified criteria, we firstly considered the highest peaks in the EDS spectra of individual aerosols and then determined their morphologies (Li and Shao, 2009b). Therefore, some particles of similar composition (e.g., fly ash and crustal mineral) or morphology (e.g., spherical fly ash, metal and organic particle) can be efficiently identified.”

3) Writing and editorial inconsistencies need to be fixed (such as labeling of Figure 3,

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incomplete or grammatically incorrect sentences); these are listed below.

Reply: Thank you for your help. We revised words and grammars and asked a native speaker to help to fix the text again.

4) Abstract: "Each fine refractory particle can enlarge the sulfate particles by 10–20 nm." Presumably, the fine refractory particles have a range of diameters that probably extends beyond 20 nm. I suggest to be less specific about the size change.

Reply: We deleted this sentence in abstract. In the text, we mentioned the size range according to the referee's suggestion.

5) Page 22388, line 1-2 ..around the top of the planetary boundary layer... ..what types of aerosols...

Reply: Changed

6) Line 4: Either "significant" or "important", but not both

Reply: Changed

7) Line 7: Delete "extremely" (if "absent", then it cannot be "slightly" or "extremely")

Reply: Changed

8) Line 8: Delete "of"

Reply: Changed

9) Line 18: Move "size-dependent" before "chemical and physical properties.." Paragraph starting at line 22: Please use either present or past tense consistently.

Reply: we changed the sentence and the tense in the last paragraph in section 1.

10) Page 22389, line 23: Used

Reply: Changed

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11) Page 22390, line 10: Please do not use the word "scanned" because readers may confuse the technique with SEM. "obtained" would do.

Reply: Changed

12) Page 22391, line 20: Replace "these" with "the"

Reply: Replaced

13) Page 22392, line 2: Which day?

Reply: added the date

14) Line 6: "..suggesting that the conditions on the summit of Mt. Tai adequately represent the results of the important air pollution advective patterns..."

Reply: Changed

15) Lines 11-12: Please provide exact criteria for the distinction of different particle types. For example, how did you distinguish S-rich from Na/K-S/N? Did you use threshold values from EDS results? (For example, if Na exceeds 5 at%, then it is a Na-S particle instead of S-rich?)

Reply: We added the criteria in the revision.

16) Line 11: "internally mixed with organic matter.."

Reply: Changed

17) Line 14: Delete "other"

Reply: Deleted

18) Line 20: "Minor K and Na occurs in most sulfates.." Does this statement refer to type-A or type-B S-rich particles? It seems to repeat the statement in lines 15-17.

Reply: Yes, the statement repeated. We deleted "the minor K and Na occurs in most sulfates", and moved the last part of this sentence forward.

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19) Fig. 3 Labeling is absolutely confusing. Many panels are marked a) and b), and the captions do not seem to correspond to the labeling. Please label each of the 14 panels in an unambiguous way and provide clear captions.

Reply: Labels and captions are fixed in the revision.

20) Line 25: "We noticed that externally mixed soot..”

Reply: Changed

21) Page 22393, line 3: Which Fig. 3b? There are 7 of them.

Reply: We modified the labels in Fig. 3

22) Line 5: Delete "physical” – coagulation is always a physical process

Reply: Deleted

23) Line 14: "were” instead of "have been frequently”

Reply: It is modified in the revision.

24) Lines 21-23. The sentence is incomplete, please rephrase.

Reply: We modified this sentence.

In the text: “In this study, three major mineral particle types are defined by their elemental composition (Fig. 4d and S1), including Ca-rich (calcite and dolomite, particle a), Si-Al (clay and feldspar, particle b), and Si-rich (quartz, particle c). Shi et al. (2005) indicated that those mineral types were the major crustal minerals in Asian dust storms over northern China.”

25) Lines 21-25: Hard to follow in the lack of proper labels on Figure 3. "A similar coating on Ca-rich particles reported” – similar to what? Please rephrase.

Reply: We modified this sentence.

In the text: “Particle a in Fig. 3d shows a visible coating on the surface of Ca-rich

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particles. The similar coatings found by Li and Shao (2009a) in the polluted NCP were considered to be Ca(NO3)2, formed by the heterogeneous chemical reaction of calcite (or dolomite) with NO2 or HNO3."

26) Lines 25 and 29: In the lack of quantitative compositional information (EDS analysis of O and N can be qualitative at best) how did you identify Ca(NO3)2? Did you do electron diffraction? Same for NaNO3 (line 5 on next page).

Reply: The quantitative O and N data in the EDS were not available and electron diffraction cannot determine their phases because they are amorphous. We didn't have direct evidence to identify Ca(NO3)2. It is a speculation because Ca(NO3)2 is the most possible state upon the composition of O, N and Ca. About calcium nitrate in the atmosphere, some studies have been done in the polluted North China. In the revision, this point is clearly addressed.

In the text: "EDS spectra of these particles suggest that they could be of two kinds,"

27) Page 22394, lines 6-10: "the products of heterogeneous chemical reactions of sea salt and halite from ground soil with acidic SO2 and HNO3 gases (Laskin et al., 2002)." "In this case, based on air mass back trajectories shown in Fig. 2 and on their rounded shape, the particles were likely from aged halite." Do you mean terrestrial halite? (Sea salt is also halite.)

Reply: Yes, we mean terrestrial halite. We modified this sentence.

28) Line 23: Replace "into" with "in"

Reply: Replaced

29) Line 24 Replace "through" with "according to" Where is Table S1?

Reply: Replaced. Table S1 includes the concentrations of PM2.5 and water-soluble ions in the supplement.

30) Page 22395, line 18 "both the PM2.5 and water-soluble ionic conãĂĄcentrations

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on Mt. Tai are higher than on other mountaintops of similar altitude elsewhere in the world."

Reply: Changed

31) Line 22 Delete "ground"

Reply: Deleted

32) Line 26 "..looked like on clear days.."

Reply: Changed

33) Page 22396, line 5: "New particle formation and growth events"

Reply: Changed

34) Lines 6-7: At what time of the day did new particle formation occur? It is not clear from the diagram in Figure 6.'

Reply: We modified the Figure 6 according to the referee#1's comments. The hour intervals in Figure 6 were shown. Particle number in nucleation mode can know the NPF period in Figure 6b. We added one new sentence in the paper.

In the text: "The peaks of particle number in the nucleation and Aitken modes in Fig. 7b represent the NPF and particle growth periods on each day, respectively."

35) Lines 12-13: "The result shows that aerosol particles through gaseous transformation greatly contributed into the top of PBL. The heights of air masses nearby the summit of Mt. Tai further display that most new particles were possible formed around 1000– 2000m in the regional scale (Fig. 2).." Meaning unclear, please rephrase these two sentences.

Reply: We deleted this sentence and modified second sentence as follow. We also adjusted the position of the second sentence after "...near the surface layer in the NCP".

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In the text: “Moreover, air mass back trajectories in Fig. 3 show that most of particles in the nucleation mode were possibly formed 1000-2000 m above ground on a regional scale.”

36) Page 22397, lines 9-10: "..in the elevated air masses enough maintained new particle growth for more than 4 h..”

Reply: Changed

37) Line 12: "in” instead of "into” and "It is interesting to note”

Reply: Changed

38) Line 13: "may have enlarged”

Reply: Changed

39) Line 18: "refractory” instead of "non-refractory”

Reply: Changed

40) Line 19: "whether” instead of "that”

Reply: Changed

41) Line 24: particles

Reply: Changed

42) Lines 25-29: "These mixing characteristics are direct evidence that the ultrafine aerosol particles from steel industries, coal-fired power plants, and vehicular emissions may participate in the initiation of particle nucleation through condensation and may contribute to their subsequent growth through coagulation in the upper atmosphere over the NCP.” While I agree with the second part of the sentence, the claim that soot and fly-ash particles "may participate in the initiation of particle nucleation” is not supported by the TEM images in Fig. 7. The soot, metal and fly-ash particles appear to be several tens of nm large, whereas the new particles in Fig. 6 have diameters less than

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10 nm.

Reply: Yes, the soot, metal and fly ash particles in Fig. 6 show diameter more than 10 nm. We deleted the diameter range in this sentence and added more explanations in the paper. TEM observations show that the fine refractory particles from anthropogenic sources were abundant in the haze layers in morning and afternoon. However, many field experiments have not considered the influences of these pre-existing particles for the new particle formation in the atmosphere (Zhang et al., 2004; Wu et al., 2007; Shen et al., 2011). In this study, we cannot determine whether the fine refractory particles participate in the initiation of the particle nucleation. However, once large amounts of fine refractory particles occurred in the atmosphere, they can influence new particle lifetimes. At this point, our investigation should raise this open question. As the referee's comments, we modified the paragraph and add more explanations.

In the text: "These mixing characteristics indicate direct evidence that the fine aerosol particles from steel industries, coal-fired power plants, and vehicular emissions might have contributed to their subsequent growth through condensation and coagulation in the upper atmosphere over the NCP. Moreover, the TEM observations suggest that fine refractory particles from anthropogenic sources were plentiful in the haze layers – numerous enough to suppress the initiation of particle nucleation via condensation and to subsequently weaken the NPF. Further attention to this issue should be paid in the North China plain with its diverse and numerous large emission sources such as coal-fired power plants, steel industries, populated cities, and deserts."

43) Page 22398, line 8: replace "acids" with liquids"

Reply: Changed

44) line 11 downwind

Reply: Changed

45) line 14: in which sulfur acids or sulfates

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Reply: Changed

46) line 17: delete "certain"

Reply: Deleted

47) Page 22400, lines 18-22 Again, the nm-sized new particles are unlikely to be refractory anthropogenic particles. It is also not convincing that these particles "enlarge sulfate particles by 10-20 nm" – how was this calculated?

Reply: We deleted particle size range and modified this sentence. The detailed explanations were provided in 42

Reference:

Li, W.J. and Shao, L.Y.: Observation of nitrate coatings on atmospheric mineral dust particles, Atmos. Chem. Phys., 9 (6), 1863-1871, 2009a.

Wu, Z., Hu, M., Liu, S., Wehner, B., Bauer, S., Ma βing, A., Wiedensohler, A., Petaja, T., Dal Maso, M., and Kulmala, M.: New particle formation in Beijing, China: Statistical analysis of a 1-year data set, J. Geophys. Res., 112 (D9), D09209, doi:10.1029/2006JD007406, 2007.

Zhang, Q., Stanier, C.O., Canagaratna, M.R., Jayne, J.T., Worsnop, D.R., Pandis, S.N., and Jimenez, J.L.: Insights into the Chemistry of New Particle Formation and Growth Events in Pittsburgh Based on Aerosol Mass Spectrometry, Environ. Sci. Technol., 38 (18), 4797-4809, 2004.

Shen, X.J., Sun, J.Y., Zhang, Y.M., Wehner, B., Nowak, A., Tuch, T., Zhang, X.C., Wang, T.T., Zhou, H.G., Zhang, X.L., Dong, F., Birmili, W., and Wiedensohler, A.: First long-term study of particle number size distributions and new particle formation events of regional aerosol in the North China Plain, Atmos. Chem. Phys., 11 (4), 1565-1580, 2011.

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C11065/2011/acpd-11-C11065-2011-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 22385, 2011.

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