Reply to Reviewer#1

Direct observations of organic aerosols in common wintertime hazes in North China: insights into direct emissions from Chinese residential stoves

Chen et al.,

We appreciated the reviewers' comments which significantly improve quality of the manuscript. We carefully answer them one by one as below.

1. Selection of sampling sites needs to be introduced in more details, especially the importance and significance of the three sites. I understand that the Jinan city is regarded as the representative of uncontrolled coal combustion site, but in fact the urban area of this megacity might not rely on coal for domestic energy anymore and instead, the petrol and gas might be its major energy sources. This manuscript is designed to explain domestic coal combustion in the vast area of countryside, but no this type of sampling sites were selected.

   Answer: We added more information about sampling sites. We admit that air pollutants in Jinan city represented complicated sources such as industrial, vehicular, and residential emissions. If the reviewer noticed the finding of the whole paper, you can find aerosol particles collected in weak photochemical environment in winter. In other words, most of aerosols were primary particles instead of less secondary particles transformed from SO_2, NOx, and VOCs. Although the industrial and vehicular emission could be dominant, they mostly emitted trace gases (e.g., SO_2, NOx, and VOCs). Among these major sources in Jinan city, coal combustion in residential stoves only emitted large amounts of primary particles, in particular, they emitted abundant primary organic particles.

2. "1 Introduction" part: the introduction needs to be succinct and should be more concentrated on the organic aerosol particles and related hazes. The current text in the introduction part is too complicated and not well focused on the main aims.

   Answer: We revised introduction. Please notice that we deleted large part in second paragraph.

3. The classification of the six types of organic particles needs to be careful. For example, the type 4 particle (domelike) looks more like a mixture of possible organic and other materials such as ammonia or nitrates, and the type 5 particle (dispersed) may be the results of the shrinkage of organic-coated particle.

   Answer: In this study, we used EDX to examine chemical composition of individual particles. If the type 4 particle contain ammonia or nitrates (except organic nitrate), these particles should not be stable under the electron beam. We found that these particles were stable in the TEM. The type 5 particle is other important particle types which is different from organic-coated particles. The particle types have been well described in our latest paper in JGR-Atmos. which is under review.

   About the type 4 particle, we collect similar particles from coal combustion in stoves in laboratory. Based on our observations in previous studies and laboratory experiments, we can surely that the classification is no problem.

4. Line 30: “(Tai, S2)” might be “(Mt. Tai, S2),”
   Answer: We revised this to Mt. Tai

5. Line 33: I suggest to change “OM-coating” into “coating OM” for the type 6 particle.
   Answer: To make consistent with our previous study, we want keep the OM-coating particles. We used the particle name in one new paper under review in JGR.

6. Line 71: “the various air pollution levels” may be changed into “the various air quality levels”
   Answer: We changed the “pollution” to “quality”.

7. Line 74: the definition of “Haze as a weather phenomenon is defined by visibility ≤ 10 km and RH ≤ 95%” requires references.
   Answer: We revised this sentence and added reference for this definition. Please see Line 75.

8. Line 117 and also throughout the whole manuscript, acronyms and abbreviations must be explained at first occurrence. For example, the first appeared “BrC” should have a full word phrase.
   Answer: We added the full name of BrC: “brown carbon (BrC)”.

9. Line 129-133: the methods mentioned here are repetitive of the “2 Experimental Methods” part.
   Answer: We deleted the repetitive sentence and revised this part. Please see Line 120.

10. “2.1 Sampling sites and particle collection”: In Line 145, the authors mentioned that “aerosol particles collected at S1 mainly reflect local, ground-based urban and industrial emissions”. This means the S1 site can’t represent the potential uncontrolled coal combustion source?
    Answer: Please see our first reply (1).

11. Line 151: “During the winter monsoon season, S3 is the downwind of the Jing-Jin-Ji area … and Shandong province.” This looks not correct. From the map, S3 is located in the east of the JJJ area, and how can we regard it is the downwind of S1 and S2? Furthermore, S3 is not located upwind area, it may not appropriate to serve as a background (clean) site.
    Answer: Maybe the reviewer misunderstood our meaning. We change words to make more clearly here. We didn't address that S3 site is downwind S1 and S2. Here, three different sampling sites represent different environmental functions. In this study, S3 is treated as a polluted background site instead of the normal background site.

12. “2.3 NanoSIMS analysis” part: It is good to see that the NanoSIMS gives the ions $12C^-$ and $12C14N^-$ which could represent the organic matter in individual particles. However, to the study of this manuscript, how many of the individual particles were analyzed? Were all particles measured by NanoSIMS?
    Answer: The NanoSIMS is very complex and expensive instrument. It is not necessary to examine all the organic particles. The NanoSIMS only confirmed the organic findings from TEM. The routine procedures for this study will be shown as below.

Firstly, we used the TEM to observe organic particles.

Secondly, we selected some typical samples which contain large amounts of organic particles for NanoSIMS experiments.

13. Line 198: "with 20, 25, and 13 individual particles analyzed by this method for each of the three sampling sites." Which sites exactly these numbers correspond to?
    Answer: We added sites here. Please see Line 199.

14. Line 229-230: Soot may also be the C-dominated particles?
    Answer: We agreed and changed "C-dominated" to "OM-like" particles.

15. Line 254: Please check if it is "…ratio of width and height…" or ""…ratio of height and width…".
    Answer: We revised this sentence to "ratio of length and width…" in Line 267.

16. Line 275-276: The category of "soot, mineral, metal, fly ash, and sulfate particles" is not same as that of the line 229-230?
    Answer: We corrected them and added the metal in Line 230.

17. Line 278: The OM-fly ash might be the overlapped particles during sampling and not necessarily the mixed particle in the air?
    Answer: The sampling duration was controlled to avoid overlap among different particles on the substrate. If the reviewer carefully looks at Figure 5c, you will find the connection between OM and fly ash which could not form during sampling process.

18. Line 314, "For example, Moffet et al. (2013) suggested : : :: : :Based on these comparisons, we conclude that those type 1-3 OM particles were not emitted by vehicular emissions in the NCP". However, all these data for comparisons were from North America and Japan, which I don't think can exclude the type 1-3 OM particles present from vehicular emissions in urban areas of Chinese Cities.
    Answer: Thank you very much. We added more explanation here including our previous studies in urban air and remote mountain air. Please see Line 351.

19. Line 325, the authors didn't analyze the emissions from heavy industries or coal fired power plants, so I don't think they can obtain the conclusion that "the type 1-3 OM particles were not emitted from heavy industries or coal-fired power plants" and that "they were from coal combustion or biomass burning for household heating and cooking in wintertime". More evidence needs to be provided.
    Answer: Same to the above reply. We added more explanation here.

20. Line 413: Please check if the 1-3 OM occupy 70% of aerosol particles or 70% of the organic particles?
    Answer: We revised this to "70% OM-containing aerosol particles". Please see Line 453.

21. “5. Conclusions and atmospheric implications” needs to be simplified, and what are major conclusions?
    Answer: We revised and shortened the “conclusions and atmospheric implications” section.

22. “Acknowledgments”: There are some repetitive words between line 424 and line 425.
    Answer: We removed the extra words here.

23. Table 1: The decimal number should keep consistent.
    Answer: We unified the data format in Tables.

24. English of the text needs to be polished by a native English speaker.
    Answer: We invited a native English speaker (Dr. Peter Hyde) to polish the English writing.

Reply to Reviewer#2

Direct observations of organic aerosols in common wintertime hazes in North China: insights into direct emissions from Chinese residential stoves

Chen et al.,

We appreciated the reviewers' comments which significantly improve quality of the manuscript. We carefully answer them one by one as below.

1. Although the observations of individual particles probed by TEM can provide certain information to relate to the sources, the conclusions regarding the exact sources should be carefully evaluated. It could be expected that the sources during such haze events are complicate. To exclude the other sources and limit it to residential stove emission, additional information is needed to support such conclusion. For example, as discussed in the manuscript, there are two particle types, OM-fly ash and OM sulfate(K)-fly ash as shown in Figure 5, what are the possible sources of these fly ash containing particles, what are the composition of these fly ash? Is it possible that these are from coal-fired plants or industrial emissions? In Line 142, as indicated by the authors that S1 can be influenced by the industrial emissions. The statements regarding the sources in Abstract and Conclusion section should be reworded if no further supporting evidences is provided to constrain the sources.

   Answer: We really appreciated your comments. Spherical fly ash typically contains Si and O which indicates coal-fired power plant. In the revised manuscript, we largely revised section 4.1 (Sources of OM-containing particles) and added more references. We also slightly revised abstract and conclusion.

2. The Introduction and Conclusion sections should be revised. In the Introduction section, there is a long discussion between the severe haze and L&M haze events and their differences, but later there is no comparison or further discussion in the main text. This part should be shortened. It may be beneficial to reader or to the context to focus more on single particle analysis or source characterization. The Conclusion and Atmospheric Implication section can be more concise and focus more on the findings from these observations. For example, the discussion of BrC and the implications, for such discussion should be limited to a certain extend unless data are provided showing the OM particles are BrC.

   Answer: We revised and shortened the discussion between the severe haze and L&M haze events. We deleted most parts suggested by the reviewer.

3. The classification of the particle types is not very clear and straightforward in the current form. It is suggested to add a figure or table to describe how the particles are grouped.

   Answer: The classification of particle types were based on their chemical composition and morphology in the TEM/EDX, and then calculated their shapes in the computer algorithm. We added Figure 2 to describe the flow chart of particle classifications.

4. Some definitions are not consistent. For example, the "OM-coating (type 6)" in L33, "C-dominated" in L230, "OM-containing particles" in L237, "OM coating" in L269, these terms are confusing and not consistent throughout the text.

   Answer: We revised the name of "C-dominated" to "OM-like". TEM could not exactly determine

OM particles, so called OM-like particles before we showed the NanoSIMS result in the context. Because OM particles were internally mixed particles, we used OM-containing particles to represent all the OM-related particles. OM-coating represents one OM mixing structure in the internally mixed particles. The individual aerosol particles classifications were shown in Figure 2.

5. In Figure 3 (e), the type 5 dispersed-OM is very similar to the particle in Figure5 (d) which was bleached by the beam, why it is classified as OM particle which seems to have S and K?
   Answer: We revised Figure 2 to show the classification here. Figure 5d shows the OM-mixed containing S and K belong to the classifying rules in this study.

6. In Figure 3, for the type 6, what is the chemical composition of cores?
   Answer: The cores in type 6 are secondary inorganic components such as sulfate and nitrate. Please see the Figure 5f, the core is sulfate.

7. Should type 6 belong to OM internally mixed particles as showing in Figure 5?
   Answer: Yes, It belongs to OM internally mixed particles as shown in Figure 5. We revised the Figure 2 to show how we classified the particles.

8. L31, use “morphologies”?
   Answer: We revised this word.

9. L37, what does “cooling, polluted plumes” mean?
   Answer: We revised this sentence to: “formed in cooling process after polluted plumes emitted from…”. Please see Line 38.

10. L38, what kind of detector is used for EDX analysis? Please justify the use of “Si-O-C ratio” to estimate to contribution of coal combustion.
    Answer: The EDX is from oxford instruments. TEM/EDX only can obtain semi-quantitive data for elements. Therefore, we could not make any significant conclusion from the each element in individual particles. However, it is significant to make comparisons of Si-O-C in many OM particles detected under the same TEM/EDX, which can avoid some impacts from the substrate or instrument. The same method has been used in Li et al., JGR, 2012 and Posfai et al., JGR, 2004 in the reference list.

11. L44, “aerosols” means “particles and gases”
    Answer: We revised “aerosols” to “particles”.

12. L46, use “to” instead of “into”?
    Answer: We revised this word.

13. L58, the sentence should be revised.
    Answer: We revised this sentence. Please see Line 59.

14. L61 , “Poschl” should be “PÖschl”

Answer: We revised this name.

15. L70-71, It is suggested to use “Ministry of Environmental Protection of People’s Republic of China”. I guess the Ministry of environmental protection is not monitoring the PM2.5 by itself. Please revise the statement.
Answer: We revised this to “Ministry of Environmental Protection of People’s Republic of China”.

16. L73, please use the right document citation, what is “HJ 663-2012”?
Answer: We revised this citation.

17. L75-76, use “associated with different levels of PM2.5 concentrations and RH”?
Answer: We revised this sentence to “haze levels normally are associated with different levels of PM2.5 concentrations and RH” in Line 77.

18. L93, delete “been”
Answer: We revised this sentence to “physicochemical properties…have been well understood”. Please see Line 83.

19. L94 delete “their”
Answer: Please see the answer for comment 18. We revised this sentence.

20. L98 delete “different”
Answer: We deleted this “different” in line 90.

21. section 2.1, more details should be provided regarding the sampling procedure and sample sites. What was the sample height at each site, what about the sampling time and duration?
Answer: Thanks, we provide it in supplement as Table S2.

22. L155, use “represent” instead of “display”
Answer: We revised “display” to “represent ”.

23. L163, the impactors are used to collect particles not aerosols
Answer: We changed “aerosols” to “particles” here.

24. L168, one sample for each day was analyzed? What is the sampling duration for each grid?
Answer: Yes, We added the information about analyzed samples in Table S2.

25. L174, use “acquired”?
Answer: We revised the word to “acquired”.

26. L183, what is brand and model for NanoSIMS?
Answer: We added the brand and model “NanoSIMS 50L, CAMECA Instruments, Geneviers, France”. Please see Line 185.

27. L218-221, it is not clear what the authors try to discuss. Please revise.
Answer: Here, we deleted descriptions about back trajectories in this manuscript.

28. L253, please revise how the reference is cited.
Answer: We revised it in line 262.

29. L301-302, The sentence is not clear.
Answer: We revised this sentence like this: "This result suggests that the type 1-3 OM sources were similar in the same haze layer over the NCP". Please see Line 333.

30. L318, there is no sufficient evidence to support this conclusion.
Answer: We added more explanation here including our previous studies in urban air and remote mountain air. Please see Line 351.

31. L326-331, this section should be carefully revised as discussed in the General Comments.
Answer: We revised this section and added other references for this conclusion.

32. L333, what is the EDX detector; detector background may contribute to Si signal?
Answer: No, the background from EDX detector has been calibrated to remove the possible influence. As we used EDX to detect the background film, we could not detect the Si signal. It should not be worried about that.

33. L339, as it is shown in Figure 8, the ratios are not following the lines, the data points are sort of deviating from the lines. Please discuss in more details.
Answer: Thank you for your comments. As you know, we obtained the data from internally mixed particles. Elements from OM in the EDX data should not be like pure OM or influenced by other aerosol components mixed in individual particles. Therefore, it should have one range like in Figure 8.

34. L363-365, This is not very clear. Considering the scatting of the data points, is it significantly different among these three cases? It would be more straightforward if coating thickness is calculated and compared among these sites with statistical test.
Answer: As our result, it is not significantly different among these three sites. We added average coating thickness in Figure 9.

35. L368, the statement is not convincing if only consider the number fractions of type 6 OM particles.
Answer: Yes, we revised this sentence. Please see Line 414.

36. L393, "in other words"?
Answer: We deleted this sentence here.

37. Figure 1, are the two black lines for each site indicating the range of the backward trajectories?

Answer: As other reviewer requests, we deleted backward trajectories in the Figure 1.

38. Figure 6, it is not easy to distinguish the green colors for the OM-soot and OM-soot sulfate.
Answer: We revised the color in Figure 6.

39. Figure 9, “OM coating”, do you mean “OM-coating particles”?
Answer: Yes, We revised this. Please see the description for this Figure in Line 419.

Reply to Reviewer#3

Direct observations of organic aerosols in common wintertime hazes in North China: insights into direct emissions from Chinese residential stoves

Chen et al.,

We appreciated the reviewers' comments which significantly improve quality of the manuscript. We carefully answer them one by one as below.

1. Comments Line 22: Qualify this statement with "North China" after "haze episodes" because this statement is generally not true- many studies have focused on many different levels of hazes.
   Answer: We added "North China" after "haze episodes".

2. Line 22 : "freqent" is a typo.
   Answer: We revised this word to "frequent".

3. Line 72: Define "$PM_{2.5}$" at first usage.
   Answer: We added the definition of $PM_{2.5}$ (aerodynamic equivalent diameter $\leq$ 2.5 μm). Please see Line 71.

4. Line 80: Add "in China" after "episodes"
   Answer: We added them.

5. Line 99: How is a haze day defined with respect to time? How long do high concentrations or poor visibility have to last to be considered an episode? How different are the timescales for moderate versus heavy haze days?
   Answer: We added one statistic data for an example to show occurrence of haze episodes and the timescales (Figure S2).
   We statistically analyzed frequency of haze episodes in winter for nine cities. If one heavy haze episode persists more three days, the government will have the highest alert (red). Figure S2 shows that only two severe haze days occurred in wintertime. However, the light and moderate haze episodes are common and persistent longer (Figure S2).

6. Line 117: Define "BrC" at first usage.
   Answer: We added the full name of BrC. Please see Line 108.

7. Line 122: "inidividual" is a typo
   Answer: We revised this word.

8. Line 131: Were the same TEM grids used for all three analyses?
   Answer: 33 TEM grids were analyzed for TEM/EDX analysis. Three typical samples (one grid for each site) were chosen for AFM and NanoSIMS analysis because of the consistency of samples.

9. Line 142: Please provide elevations of S1 and S3.
   Answer: We added the elevations of S1 and S3.

10. Line 152: Remove “the” from between “is” and “downwind”
    Answer: Deleted

11. Line 157: Please provide more detail regarding the choice of 9-11.5 hour sampling period. Was this sampling repeated continuously? Or was it repeated daily only at the same time each day?
    Answer: We added the details about sampling periods (daytime: 7:30-19:00 and nighttime: 19:30-7:00 (next day)) and revised this sentence. Please see Line 156.

12. Line 164: Did the TEM grid sampling occur on the same sampling schedule as the bulk sampling?
    Answer: Yes. It should be noticed that different samples have different sampling duration. Individual particle samples must be collected in a short time. We added more information to explain it. Please see Table S2 which includes the details of samples.

13. Line 168: How were the 11 aerosol samples chosen? What time periods did the samples correspond to?
    Answer: We added the time periods and other information for samples at three sites in Table S2. The selected samples as much as possible represent the whole hazes.

14. Line 170: What was the order of the analysis for the three methods? How was destruction to particles from electron beams or vacuum minimized in the order of the analysis?
    Answer: The order of analysis is TEM, AFM, and NanoSIMS. Some particles (e.g., sulfate and nitrate) can be destroyed under the electron beams in TEM, but particles in other areas of the same sample still keep well. AFM doesn't destroy the samples. Finally, we used NanoSIMS to analyze the same samples. Because the TEM grids must install on the special plate in NanoSIMS, we cannot take them back anymore. We used the special TEM grids with letters which can help us to find locations. The method is the best way to integrate three different analyzed instruments for the same samples.

15. Line 202: Define EVD and ECD at first use.
    Answer: We added the definitions of EVD and ECD and added their formulas in supplementary material.

16. Line 211: What time periods to the MODIS images correspond to?
    Answer: We added the date. These two MODIS images were got on December 14 and 19, respectively.

17. Line 213-214: It is not clear what time periods averages correspond to? All periods above 75 μ g/m3?
    Answer: Yes, all the haze periods were above 75 $\mu g/m^3$ here. Please see Figure S4.

18. Line 226: Point out that although the concentrations increased between haze and clear days, the fraction of $PM_{2.5}$ that is organic did not change that much. It appeared that the fraction of organics and inorganics remained fairly stable regardless of higher haze events.

Answer: We revised this section and we added that "the fraction of OC to $PM_{2.5}$ remained fairly stable regardless of L&M haze and clear days". Please see Line 223.

19. Line 232: Was nanoSIMS performed on all TEM grids so that the carbon content of the particles could be confirmed this way? Obtaining carbon contribution from TEM grids using TEM/EDX is obviously very uncertain given the interference from the grids.
    Answer: No, we could not do all the TEM grids. We just chose typical OM particles to confirm their chemical ions. We admitted TEM/EDX obtained uncertain carbon contribution, but it doesn't influence our classification based on all the elemental compositions of individual particles. The method is quite normal for individual aerosol analysis in TEM and SEM (e.g., Li et al., JGR, 2012; Moffet et al., ACP, 2010)

20. Line 237: The interference of the grid makes determining OM content of particles from TEM qualitative at best. How is this avoided with this analysis?
    Answer: We used morphology and EDX data both to identify OM particles, and then we can account their number faction.

21. Line 240: Were the OM particle morphology characterized subjectively? Meaning, did a single user determine the type of each particle based on visual inspection, or was this somehow determined by a computer algorithm?
    Answer: We made such a classification firstly based on visual inspection and then made their shape by a computer algorithm. I think the potential user can to identify the OM particles as this way.

22. Line 242: Can the authors provide some additional description of the "domelike" particles? What does this "domelike" structure imply?
    Answer: Here we only define it based on their morphology. We suspect the domelike particles are organic gels. As we have known that organic gel is a type of material which is translucent. Indeed, we found similar particles from biomass burning and coal used in residential stoves in the laboratory experiments.

23. Line 243: Did any of these OM-type particles behave differently under the beam or vacuum?
    Answer: In the TEM, these analyzed OM particles behaved stable. Obviously, they were non-volatile OM.

24. Line 245: For which site?
    Answer: We made the three sampling sites together for analysis.

25. Line 261: It would be clearer if the equation for AR was moved up into the "Aspect Ratio" section.
    Answer: We moved up the equation into the AR section.

26. Line 286: This information would fit better in the previous paragraph.
    Answer: Yes, we moved it to previous paragraph and revised this sentence. Please see Line 301.

27. Line 283-292: According to line 166, the D50 for this sampler is 0.25 μ m. Was a collection efficiency applied to the data to account for this? If not the size information should be considered qualitative at best (especially since the maximum bin is 4.5 μ m). Some mention of this should be made in this section. Are the bin widths greater than the uncertainty in the size data? To assist with the interpretation of Figure 6, the data from all sites should have the same size bins and scale on the figures.

Answer: We didn't consider the sampling efficiency. We know that the sampler should have higher loss efficiency, so we used size bins to make possible comparisons. Otherwise, the particle number cannot be direct compared. We revised the size bins in figure 6.

28. Line 294: Parts (a) and (b) would be more easily compared if they had the same scale. Part (a) has a log-scale and (b) does not, so the size distributions are difficult to compare. Also, what is the significance of the OM-containing particle diagrams within part (a)? Does part (a) include all OM-containing particle types (1-6) while part (b) only include the subset 1-3? Which haze event does figure 7 correspond to? What does the bimodal peak around 0.8 um correspond to in part (b)?

Answer: Figure 7a represents the size distribution of individual particles in all L&M haze episodes during sampling period in NCP. Please noticed we covert the particle number N into dN/dlogDp in the y-axis, so the x-axis can be considered as log mode. Figure 7b only represents size of type 1-3 OM in one haze event. The y-axis is real number faction so x-axis should use the normal size. Figure 7b correspond to one haze event on December 14-15 (we added it in the Figure caption).

We checked all the data and found the peak is too low to give more strong information for particle sources.

29. Line 314: Change "coating" to "coated"

Answer: We deleted this sentence.

30. Line 316: Where in North America?

Answer: We deleted this description here.

31. Line 318-9: I am not sure how this conclusion follows from the previous comparisons?

Answer: We added some references (Li and Shao, 2010) and (Li et al., 2015) in this part. They found only a few type 1-3 OM particles in urban and remote mountain air in China. Based on the comparison, we conclude that the type 1-3 OM particles were not directly emitted by vehicular emissions in the NCP.

32. Line 327-328: State how OM 1-3 particles from coal-combustion from power plants and residential heating/cooking would differ that leads to this conclusion. What additional evidence?

Answer: In our previous studies, we studied aerosol particles associated with power plants, they didn't emit spherical OM. We revised the section and added other references for this conclusion.

33. Line 336: I have several questions/concerns from the data presentation and analysis in this

paragraph. First, including and comparing C and O from the TEM/EDX analysis here is concerning given the interference from the grids. I am not sure that carbon data are very meaningful in this context. I see the description of how Si-O-C line for haze determined from the supplemental, but some mention should also be included in the paper. Haze can correspond to very different particle composition and would not likely have a single Si-O-C ratio. Is corn combustion representative of biomass burning in the region during this time of year? Again, I am not convinced these data are meaningful given the C and O interference.

Answer: TEM/EDX only can obtain semi-quantitive data for elements. Therefore, we could not make any significant conclusion from the each element in individual particles. However, it is significant to make comparisons of Si-O-C in many OM particles detected under the same TEM/EDX, which can avoid some impacts from the substrate or instrument. The same method has been used in Li et al., JGR, 2012 and Posfai et al., JGR, 2004 in the reference list.

We added some description in the paper about the Si-O-C line for haze.

Thank you for your comments. As you know, we obtained the data from internally mixed particles. Elements from OM in the EDX data should not be like pure OM or influenced by other aerosol components mixed in individual particles. Therefore, the data points could not perfectly along with the lines. It should have one range like in Figure 8.

In the NCP, farmers harvest their corn in autumn and storage these corn stalks to burn in wintertime.

34. Line 345: The sphericity of OM 1-3 particles does not necessarily suggest that these emissions are from coal combustion. Many other studies have reported on spherical OM particles that originated from biomass burning. Shape alone does not necessarily correspond to emission type.

    Answer: We agreed your comments. We revised the discussion about type 1-3 OM sources in the revised manuscript and deleted the description here between their shapes and sources. Please see Line 370.

35. Line 347: I suggest restating that the vehicular emissions at S1 led to higher contributions of soot particles because no mention of vehicular emissions at S1 has been made up to now. Instead, one might infer that the high contribution of soot particles at S1 could likely be from vehicular emissions in an urban area.

    Answer: We deleted the descriptions about the sources of soot and fly ash particles here and focus on the OM particles in the revised manuscript.

36. Figure 6 shows fly-ash as part of two different types (OM-sulfate metal/fly ash and OM-fly ash) and how is that reconciled with the contributions shown in Figures S7?

    Answer: Fly ash is a tracer of coal-fired power plant and heavy industrial, so it is an important kind of particle. Figure 2 shows only 19% of OM-sulfate particles were mixed with fly ash/metal. In Figure 2, we made OM-fly ash particles into a class and OM-sulfate mixed with fly ash into OM-sulfate group.

37. If the presence of fly ash is the evidence used for large stationary sources, than this designation should be made earlier (see comment for line 327).

    Answer: Yes, we deleted the discussion about sources of fly ash and soot particles, but focus on

the main sources of OM particles.

38. Line 356: The back trajectories for all sites look similar during haze events, so I am not convinced that aging can be determined separately for sites based on Figure 1.
Answer: We deleted the back trajectories because they only represent the air masses above 1500 m. We added more description about possible sources or location of the sampling sites.

39. Line 365: Define "coarse"
Answer: We revised this sentence. Please see Line 410-411.

40. Line 376: How would a secondary organic particle appear in the TEM analysis? One might argue that the mixed OM-sulfate or the coated particles are secondary in nature. I also disagree with the statement that not many inorganic aerosols were observed given that Table S1 states the inorganic fraction of $PM_{2.5}$ was actually higher than $TC/PM_{2.5}$ at all sites.
Answer: Thank you for your comments. Please notice that many OM-mixed particles more or less contain secondary inorganic species, which can be reflected in the classified names. The OM-coating particles cannot represent all the OM-sulfate particles. From the TEM observation, the OM-coating particle is much less in the samples collected in L&M hazes in winter than our previous study in summer or severe hazes in winter.

41. Line 381: Many hygroscopicity studies have demonstrated water associated with particles at RH values less than 60%.
Answer: Maybe it is true in some locations. We used the RH value for haze in North China from the reference (Zheng et al., 2015).

42. Line 386: This statement seems inconsistent with line 377 that states that SOA are common in heavy haze but only 31% in winter hazes. What type of hazes?
Answer: They did two researches in different haze levels and we added the haze type. Please see Line 438.

43. Line 394: Recall from Figure 1 that back trajectories suggest different transport on haze days. Are the authors trying to state that cooking and heating only from other regions are influencing the hazes? Can the authors reconcile and clarify this argument?
Answer: Your suggestion is very good, and we revised the Figure 1.
We did back trajectories at 1500 m for all sites in Figure 1 which could not represent ground pollutants' transportations.

44. Line 402: Some comment here on the bulk OC and EC data and comparisons to the single particle results would be useful. Is the relative abundance of soot particles on haze days consistent with higher EC measurements? Is this also true for OM-containing particles?
Answer: As the other reviewer's comments, we deleted the paragraph. The comparison can be done but we didn't focus on the EC in this study. Also, we want to mention that the particle classification cannot reflect the all the aerosol components. In the aged particles, many soot particles were internally mixed with OM and sulfate.

45. Line 410: The influence of direct emissions on haze stability has not been established in this paper.
Answer: Thanks, we deleted this part.

46. Line 413: What does “70% aerosol particles” mean?
Answer: We revised this sentence to “OM-containing aerosol particles”. Please see Line 453.

47. Line 417: Transport must be taken into account when making the statements regarding differences in moderate and heavy hazes, as well as meteorological controls such as boundary layer depth, wind speed, etc. Heavier hazes could be associated with stagnant conditions when pollution builds up, but emissions could be the same.
Answer: We agreed with your comments. The different haze levels must associate with meteorological data. Here we only focused on OM particle morphology.

48. Figure 1: What dates do the MODIS images correspond to?
Answer: We added the specific date of the MODIS images.

49. Figure 6: As mentioned in the comments, the figure would be more easily compared if the bin widths and figure scales were the same.
Answer: We revised this Figure’s size bins.

50. Figure 7. Provide the significance of the OM-containing particle diagram within part (a); it can be interpreted a few different ways. Convert the x-scale in part (b) to log and use the same scale as part (a), same as with the y-axis.
Answer: Thank you for your advice. These two figures have different purpose. Figure 7a shows size distribution of the analyzed particle number. Please notice we also convert the y-axis using dN/dLogDp, so the log mode can make clear size distribution in the limited particle number. In contrast, Figure 7b only show number fraction with particle size. If we use log mode, the peaks will not clear anymore. Therefore, we do not change the x-scale in Figure 8b

51. Figure 9: Does size here refer to EVD? How was sulfate core size measured?
Answer: In Figure 9, particle size refers to EVD. We directly measure sulfate core size using the iTEM software (details in sections 2.2 and 2.4), and convert into EVD.

52. Table 1: It is not necessary to report so many digits for the average sphericity and AR values; only significant digits are necessary.
Answer: We revised Table 1.

Direct observations of organic aerosols in common wintertime hazes in North China: insights into direct emissions from Chinese residential stoves

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Abstract

Many studies have focused on the physicochemical properties of aerosol particles in unusually severe haze episodes in North China instead of the more frequent and less severe hazes. Consistent with this lack of attention, the morphology and mixing state of organic matter (OM) particles in the frequent light and moderate (L&M) hazes in winter in North China Plain (NCP) have not been examined, even though OM dominates these fine particles. In the present work, morphology, mixing state, and size of organic aerosols in the L&M hazes were systematically characterized using transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy, atomic force microscopy, and nanoscale secondary ion mass spectrometer, with the comparisons among an urban site (Jinan, S1), a mountain site (Mt. Tai, S2), and a background island site (Changdao, S3) in the same hazes. Based on their morphologies, the OM particles were divided into six different types: spherical (type 1), near-spherical (type 2), irregular (type 3), domelike (type 4), dispersed-OM (type 5), and OM-coating (type 6). In the three sampling sites, type 1-3 of OM particles were most abundant in the L&M hazes and most of them were internally mixed with non-OM particles. The abundant near-spherical OM particles with higher sphericity and lower aspect ratio indicate that these primary OM particles formed in cooling process after polluted plumes emitted from coal combustion and biomass burning. Based on the Si-O-C ratio in OM particles, we estimated that 71% of type 1-3 OM particles were associated with coal combustion. Our result suggests that coal combustion in residential stoves was a widespread source from urban to rural areas in NCP. Average OM thickness which correlates with the age of the air masses in type 6 particles only slightly increased from S1 to S2 to S3, suggesting that the L&M hazes were usually dry (relative humidity < 60%) with weak photochemistry and heterogeneous reactions between particles and gases. We conclude that the direct emissions from these coal stoves without any pollution controls in rural areas and in urban outskirts contribute large amounts of primary OM particles to the regional L&M hazes in North China.

1 Introduction

Atmospheric particulate matter is composed of diverse chemical compounds, both organic and inorganic matters. Organic aerosol particles are of two types: primary organic aerosol (POA), directly emitted from fossil fuel combustion, biomass burning, vehicular exhaust, and cooking; and secondary organic aerosol (SOA), formed from the oxidation of gaseous volatile organic compounds (Kanakidou et al., 2005). Organic aerosols account for 18-70% of the non-refractory submicron aerosol particles in the atmosphere (Zhang et al., 2007). It is well known that organic aerosols affect the atmosphere through the interaction with reactive trace gases, water vapor, clouds, precipitation, and radiation (Fuzzi et al., 2006). Organic aerosols also influence the physical and chemical properties (e.g., size, light-absorptivity, and hygroscopicity) of other particles; they directly affect visibility and climate by scattering and absorbing solar radiation (PÖschl, 2005;Kanakidou et al., 2005;Kulmala et al., 2004). Although most organic aerosol components are known to have a cooling effect on global climate, brown carbon in organic aerosols can absorb solar radiation at shorter wavelengths and lead to warming (Alexander et al., 2008). Moreover, many organic compounds (e.g., benzene, polycyclic aromatic hydrocarbons (PAHs), toluene), which are toxic to human and other biological species have been found in atmospheric particles (Mauderly and Chow, 2008).

In recent years, haze episodes have become one of the most serious environment problems in China, following the rapid urbanization and population growth in eastern China. Ministry of Environmental Protection of People's Republic of China on 1 January 2013, started to monitor daily $PM_{2.5}$ (aerodynamic equivalent diameter of particles $\leq$ 2.5 μm) concentrations and defined the daily average air quality levels as: excellent (0~35 μg m^{-3}), good (35~75 μg m^{-3}), light (75~115 μg m^{-3}), moderate (115~150 μg m^{-3}), heavy (150~250 μg m^{-3}), and severe (> 250 μg m^{-3}) (Chinese National Ambient Air Quality Standards). Haze as a weather phenomenon is defined by visibility $\leq$ 10 km and RH $\leq$ 80% (Chinese Meteorological Industry Standard).

77 Previous studies have shown that haze levels normally are associated with different
78 levels of $PM_{2.5}$ concentrations and RH (Shen et al., 2015;Wang et al., 2006;Chen et al.,
79 2014). Based on their results, we classify severe haze days (< 5 km) with $PM_{2.5}$
80 concentrations ≥ 250 μg m^{-3} and light (8-10 km) to moderate (5-8 km) haze days at
81 75-250 μg m^{-3}, both with RH < 80%.
82 Because of their unusually high $PM_{2.5}$ concentrations (> 250 μg m^{-3}) and low
83 visibility (< 5 km), the physicochemical properties of aerosol particles in severe
84 wintertime hazes in China have been well understood (Huang et al., 2014;Guo et al.,
85 2014;Zheng et al., 2015). Recently, Zheng et al. (2015) suggested that characteristics
86 of aerosol particles in severe hazes would not be the same in L&M hazes. Although
87 this knowledge is critical to understand severe haze formation and its impacts on
88 human health, the frequency of severe haze episodes is low and their duration is short.
89 For example, we statistically analyzed haze days during the winter (~ 92 days) of
90 2014-2015 in nine cities. Figure S1 shows that light and moderate (L&M) haze days
91 occurred 22-63% of the time and that severe haze days were less frequent at 4-32%,
92 with the variation dependent on location within the NCP. Jinan city was an example
93 showing the timescale of severe and L&M haze episodes (Fig. S2). Compared to
94 severe hazes, the L&M hazes were most frequent in winter and lasted longer in the
95 NCP. Therefore, understanding aerosol particles in the more common L&M hazes in
96 the NCP is important to further evaluate their impacts on human health and regional
97 climate.
98 Various ‘‘bulk’’ analytical instruments have been used to study organic aerosol
99 particles during haze episodes. High resolution time-of-flight aerosol mass
100 spectrometry (HR-AMS) was applied to determine the mass concentrations and bulk
101 composition of organic aerosols (Sun et al., 2010). Gas chromatography-mass
102 spectrometry (GC-MS) provided chemical composition and structures of organics in
103 aerosols (Fu et al., 2012;Wang et al., 2009). It should be noted that bulk analytical
104 techniques only provide average properties of $PM_{2.5}$ and the mixing state, phase, and
105 morphology of organic particles remain unknown. Detailed information about

individual organic particles, moreover, is critical to evaluate their formation, sources, and their hygroscopic and optical properties in the atmosphere. For example, copious tar balls containing homogeneous brown carbon (BrC) ocurr in the smoldering smoke from biofuels (Chakrabarty et al., 2010;Adachi and Buseck, 2011;Alexander et al., 2008;Chakrabarty et al., 2013;China et al., 2013;Hand et al., 2005;Posfai et al., 2004). Atmospheric particles undergo liquid-liquid phase separations and go on to form OM coatings on inorganic aerosol particles (You et al., 2012). The surface coating by OM on individual particles influences water uptake and evaporation of individual particles and their heterogeneous reactions in the atmosphere (Shiraiwa et al., 2011;Zawadowicz et al., 2015;Riipinen et al., 2011). Despite the importance of these phenomena, the morphology and mixing state of OM particles in wintertime L&M hazes in the NCP have not been examined, although OM is dominant in fine particles (Sun et al., 2013).

To characterize organic aerosols in greater detail in L&M hazes, individual particles in the NCP in winter were analyzed using different individual particle instruments. Morphology, mixing state, and size of organic aerosols were systematically characterized and compared at the three sampling sites (background island site, mountain site, and urban site) in the same haze. This information enables the discussion of source and ageing mechanisms of OM particles, which leads to insights about the formation of regional wintertime L&M hazes in the NCP.

2 Experimental Methods

2.1 Sampling sites and particle collection

$PM_{2.5}$ and individual particle samples were simultaneously collected during 13-23 December, 2014 at three sampling sites: an urban site (S1), a mountain site (S2), and a background site (S3) in the NCP (Fig. 1).

S1-urban site in Jinan (53.9 m a.s.l., 36.67 °N, 116.98 °E) is 50 km north of S2. S1 is a typical polluted city with high-density residential areas surrounded by large industrial zones (Li et al., 2011c). Central-heating in Jinan city used coals for

inhabitants in wintertime. People living in outskirts of Jinan (50 km away from Jinan urban center) used stoves to burn coals for cooking and heating in winter. Aerosol particles collected at S1 were mainly fresh particles and can reflect the emissions from local urban and industrial, residential stoves in winter.

S2-Mt. Tai (1534 m a.s.l., 36.251 ℕ, 117.101 𝔼) is the highest mountain in the middle of the NCP, ~230 km inland from the Bohai and Yellow Seas. S2 is the perfect location to observe air pollutants near the planetary atmospheric layer over the NCP. Aerosol particles collected at S2 were aged particles and represent regional transport in the NCP (Li et al., 2011a).

S3-Changdao Island, the National Station for Background Atmospheric Monitoring site (153 m a.s.l., 38.19 ℕ, 120.74 𝔼), is in the Bohai Sea. During the winter monsoon season, S3 is downwind of the Jing-jin-ji area (i.e., Beijing city, Tianjin city, and Hebei province) and Shandong province (Feng et al., 2012). Therefore, S3 serves as a polluted background site from the transport of continental air. Therefore, aerosol particles collected at the three sampling sites represent the different pollutant characteristics of polluted urban air, upper air layer, and background island air in the NCP.

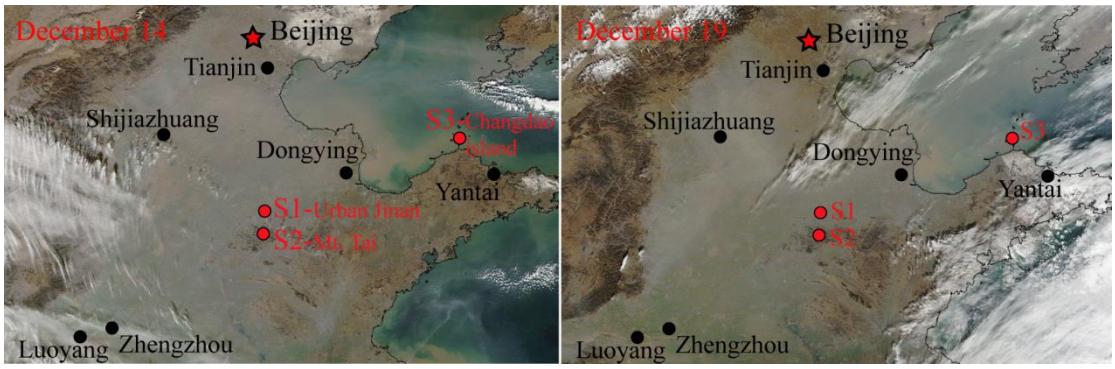

Figure 1. Regional haze layer covering the North China Plain: S1 (urban Jinan), S2 (Mt. Tai top), and S3 (Changdao island) sites. MODIS images on December 14 and 19 show grey haze layer during the light and moderate regional hazes over the NCP.

$PM_{2.5}$ was collected on 90 mm quartz filters for 11.5 h (daytime: 7:30-19:00 and nighttime: 19:30-7:00 (next day)) using three KB-120 samplers at a flow rate of 100

158 L/min. The quartz filters were stored in a refrigerator for OC, EC, and water soluble
159 ion analysis. In the study, OC and EC concentrations of 70 quartz filters were
160 analyzed by an OC/EC analyzer (Sunset Lab) and water-soluble ions (i.e., K^+, Na^+,
161 Ca^{2+}, Mg^{2+}, NH_4^+, F^-, SO_4^{2-}, NO_3^-, and Cl^-) by an ion chromatography system (Dionex
162 ICs-90). Three single-stage cascade impactors with a 0.5-mm diameter jet nozzle at a
163 flow rate of 1.0 L/min were used to collect particles onto copper TEM grids coated
164 with carbon film (carbon type-B, 300-mesh copper, Tianld Co., China). Individual
165 particle samples were collected at the same time in everyday at three sites. The
166 sampling duration were different based on the different levels of air quality (Table S2).
167 The collection efficiency of the impactor is 50% for particles with an aerodynamic
168 diameter of 0.25 μm and with a density of 2 g cm^{-3} (Li et al., 2011a). After sample
169 collection, the Cu grids were placed in a sealed, dry and clean environment until the
170 TEM analysis. Based on their distribution of samples, 11 aerosol samples (Table S2)
171 at each sampling site were selected and analyzed by the TEM.

172 **2.2 TEM analyses**

173 The JEOL JEM-2100 transmission electron microscopy operated at 200 kV with
174 energy-dispersive X-ray spectrometry (TEM/EDX) was used to analyze individual
175 particles. An energy-dispersive X-ray spectrometer (EDX) can detect elements
176 heavier than carbon. EDX spectra were acquired for 15 s to minimize the potential
177 beam damage. TEM grids are made of copper (Cu), so the Cu element will be
178 excluded in the analyses. The distribution of particles on the TEM grids was not
179 uniform: coarser particles were deposited near the center and finer particles dispersed
180 on the fringe. To make sure that the analyzed particles were representative of the
181 entire size range, three to four areas were chosen from the center and periphery of the
182 sampling spot on each sample.

183 **2.3 NanoSIMS analysis**

184 After the TEM analysis, three typical samples were chosen for nanoscale
185 secondary ion mass spectrometer analysis (NanoSIMS 50L, CAMECA Instruments,
186 Geneviers, France), an ultrahigh vacuum technique for surface and thin-film analysis

at the Institute of Geology and Geophysics, Chinese Academy of Sciences. In this study, $^{12}C^-$, $^{16}O^-$, $^{12}C^{14}N^-$, $^{14}N^{16}O_2^-$, and $^{32}S^-$ ions in individual particles were obtained when the Cs^+ primary ion beam caused the ionization of atoms within the particles. Furthermore, ion intensity mappings of individual particles with nanometer resolution can show the distribution of different ions. $^{12}C^-$ and $^{12}C^{14}N^-$ represent the organic matter in individual particles (Chi et al., 2015;Ghosal et al., 2014;Li et al., 2016a).

2.4 AFM analysis

Atomic force microscopy (AFM) with a tapping mode analyzed aerosol particles under ambient conditions. AFM, a digital NanoscopeIIIa Instrument, can determine the three dimensional morphology of particles. The AFM settings contain imaging forces between 1 and 1.5 nN, scanning rates between 0.5 and 0.8 Hz, and scanning range sizes at 10 μm with a resolution of 512 pixels per length. After the AFM analysis, composition of the same particles was confirmed by TEM, with 20 (S1), 25 (S2), and 13 (S3) individual particles analyzed by this method for each of the three sampling sites. The Nanoscope analysis software can automatically obtain bearing area (A) and bearing volume (V) of each analyzed particle according to the formulas described by Chi et al (2015).

The definition and relationship of equivalent circle diameter (ECD, x) and equivalent volume diameter (EVD, y) are shown in Figure S3 in supplementary material (EVD=0.8334ECD (S1), EVD=0.7286ECD (S2), and EVD=0.6601ECD (S3)). Therefore, the ECD (x) of individual aerosol particles measured from the iTEM software can be further converted into EVD (y) based on these relationships.

3. Results

3.1 Regional haze periods in North China Plain

Aerosol particles were collected in three regional L&M hazes during 13-23 December, 2014 (Fig. S4). Moderate Resolution Imaging Spectroradiometer (MODIS) images on December 14 and 19, 2014 clearly display a regional haze layer covering the three sampling sites in the NCP (Fig. 1). The average $PM_{2.5}$ concentrations were

96.6 μg m^{-3} (range: 79-171 μg m^{-3}) at S1, 88.6 μg m^{-3} (range: 76-110 μg m^{-3}) at S2, and 80.3 μg m^{-3} (range: 75-84 μg m^{-3}) at S3 on haze days, twice as high as on clear days (52, 48, and 32.3 μg m^{-3}) during the sampling period. The RH at all three sampling sites was lower than 60% during the sampling period (Fig. S5).

The average concentrations of OC, EC, OC/EC, water-soluble ions and their mass proportions in $PM_{2.5}$ were much higher on haze days than on clear days at three sampling sites (Table S1). OC on haze days was more than 1.7 times higher than that on clear days at three sites. We found that the fraction of OC to $PM_{2.5}$ remained fairly stable regardless of L&M haze and clear days. OM concentration was estimated at 20-33 μg m^{-3} and OM/$PM_{2.5}$ ratio was at the range of 23-34% during haze days in the NCP (Table S1).

3.2 Morphology of organic particles

Based on morphology and chemical composition of individual particles using TEM/EDX, we identified five types of particles: sulfates (including K-rich sulfate and ammonium sulfate), fly ash/metal, mineral soot, and OM-like particles (Fig. 2 and Fig. S6). These results are consistent with previous studies during the haze episodes in the NCP (Li et al., 2012;Li et al., 2011c). In order to remove the interference of the carbon substrate on TEM grids, a nanoSIMS was employed to verify OM-like particles through $^{12}C^{14}N^-$ and $^{12}C^-$ mappings (Fig. 3 and Fig. S7). Figure 3 clearly shows that one near-spherical particle, which contains C, O, and minor Si on TEM grids, displays strong CN^- and O^- signals but no clear NO_2^- and S^- signals. As a result, this type of particle can be confirmed as the OM particle (Li et al., 2016a;Ghosal et al., 2014). TEM analysis showed that OM-containing particles were most abundant in all the haze samples, accounting for 70% of the 5090 analyzed particles (Fig. 2).

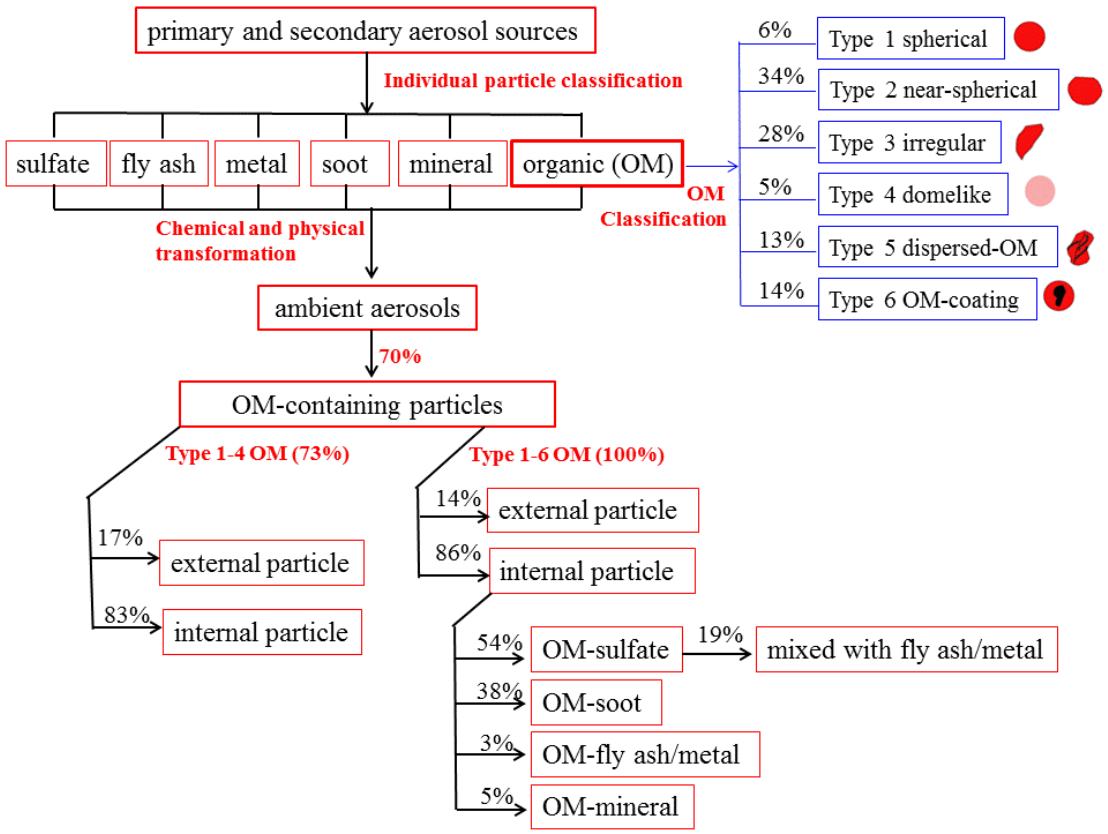

Figure 2. Flow chart of individual aerosol particles classification in L&M haze episodes in NCP based on TEM/EDX. 5090 individual particles were analyzed using TEM/EDX.

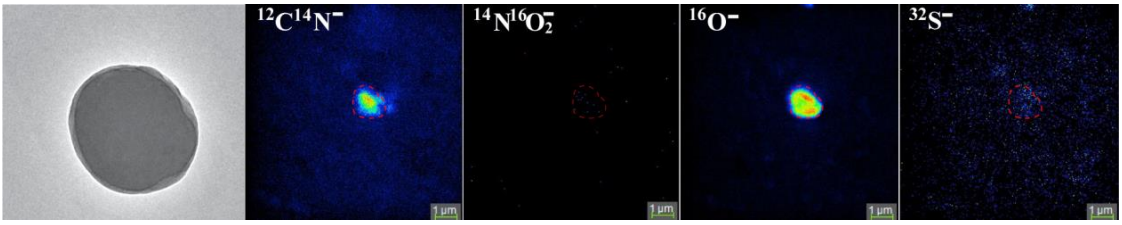

Figure 3. NanoSIMS-based ion intensity mappings of $^{12}C^{14}N^-$, $^{14}N^{16}O_2^-$, $^{16}O^-$, and $^{32}S^-$ from a near-spherical OM particle.

Based on the morphology of OM particles, they were divided into six different types: spherical (type 1, Fig. 4a), near-spherical (type 2, Fig. 4b), irregular (type 3, Fig. 4c), domelike (type 4, Fig. 4d), dispersed-OM (type 5, Fig. 4e), and OM-coating (type 6, Fig. 4f). Here, the domelike particles look like transparent droplet-like particles in TEM images.

Because the high-resolution TEM images of individual particles can clearly display particle interior mixing structures, it allows us to identify OM particles based

on their different shapes in OM-containing particles (Fig. S6). Figure 2 shows that the proportions of type 1-3 in OM particles was 73%, following type 4 at 5%, type 5 at 13%, and type 6 at 14% for the three sites as a whole. Further, we measured the projected area, the perimeter, the maximum projected length, and the maximum projected width of 967 selected OM particles. From these data, the sphericity (Sph) and aspect ratio (AR) of different types of OM particles were calculated, which characterize their shape and thereby imply their aging during transport and their emission sources (Li et al., 2016b). The Sph and AR were defined by the following formulas referred to by Li et al (2013).

Sphericity (Sph). Sphericity describes the sphericity or "roundness" of the measured object by using central moments. A sphericity of 1 (the highest value) indicates a particle is perfectly spherical.

$$Sph = \frac{\sqrt{4\pi S}}{P} = \frac{\sqrt{4\pi\pi R_1^{\,2}}}{2\pi R_2} = \frac{R_1}{R_2}$$

Aspect Ratio (AR). The maximum ratio of length and width of a bounding rectangle for the measured object is the aspect ratio. An aspect ratio of 1 (the lowest value) indicates a particle is not elongated in any direction.

$$AR = \frac{L_{max}}{W_{max}}$$

Where S is projected area, R_1 is equivalent area radius, P is perimeter, R_2 is equivalent perimeter radius, L_{max} is the maximum projected length, and W_{max} is the maximum projected width.

Table 1 displays the Sph and AR of individual OM particles measured by the iTEM software. At the three different sampling sites, OM particles were in the fine range with diameters < 1 μm. The statistics shows that spherical OM particles exhibited the highest Sph at 0.96-0.99 and the lowest AR at 1.01-1.03 at the three sites, followed by OM coating (Sph: 0.88-0.93, AR: 1.06-1.08), near-spherical OM (Sph: 0.82-0.83, AR: 1.12-1.13), domelike OM (Sph: 0.63-0.73, AR: 1.24-1.40),

irregular OM (Sph: 0.51-0.57, AR: 1.39-1.48) and dispersed-OM particles (Sph 0.50-0.58, AR: 1.35-1.49).

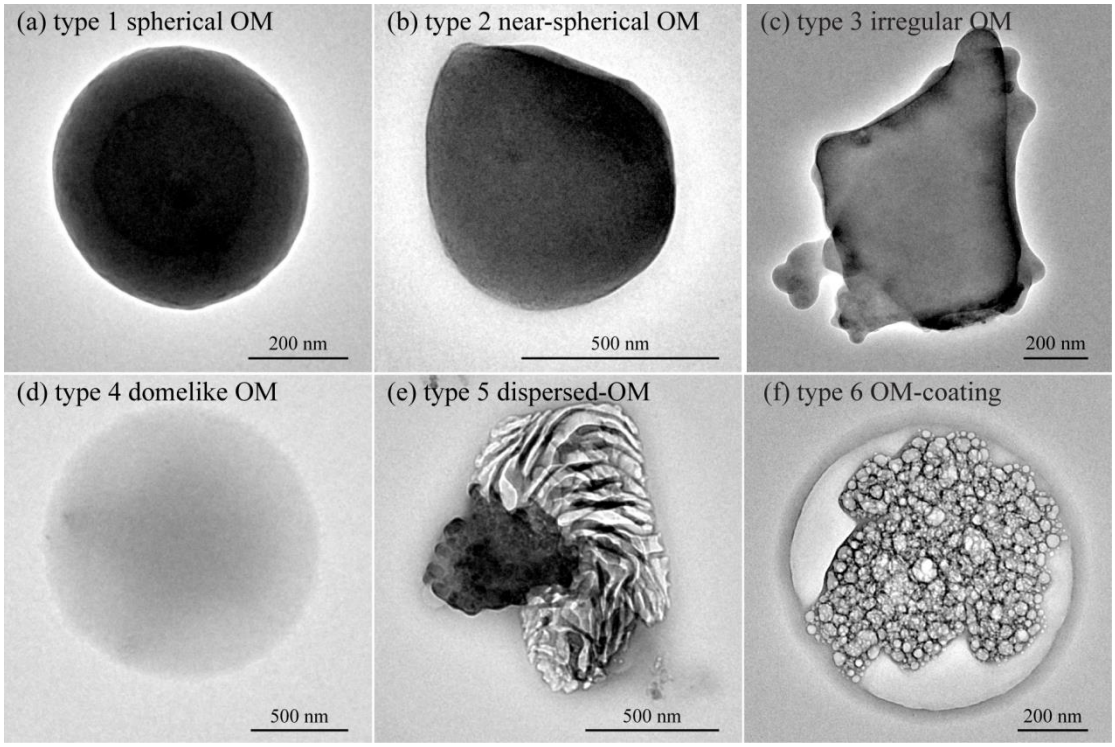

Figure 4. Typical TEM images of different types of OM particles. (a) Type 1: spherical shape; (b) type 2: near-spherical shape; (c) type 3: irregular shape; (d) type 4: domelike OM (droplet-like particle); (e) type 5: dispersed-OM; (f) type 6: OM-coating

288 **Table 1.** Average size, number, sphericity, and aspect ratio for different OM types at
289 the three sampling sites.

Sampling site	Type	Average Size（nm）	Number	Average Sph	Average AR
S1	Type1 spherical	408	18	0.97	1.02
	Type2 near-spherical	349	79	0.82	1.13
	Type3 irregular	539	151	0.51	1.48
	Type4 domelike	759	23	0.64	1.40
	Type5 dispersed-OM	751	64	0.50	1.49
	Type6 OM-coating	672	12	0.93	1.06
S2	Type1 spherical	282	22	0.96	1.03
	Type2 near-spherical	323	68	0.83	1.12
	Type3 irregular	399	62	0.57	1.41
	Type domelike	511	25	0.73	1.24
	Type5 dispersed-OM	847	34	0.58	1.42
	Type6 OM-coating	776	66	0.88	1.08
S3	Type1 spherical	392	27	0.99	1.01
	Type2 near-spherical	373	122	0.83	1.12
	Type3 irregular	375	117	0.57	1.39
	Type4 domelike	706	14	0.63	1.35
	Type5 dispersed-OM	575	35	0.55	1.35
	Type6 OM-coating	828	28	0.93	1.06

290

291 ### 3.3 Mixing state of OM particles

292 Although we identified different types of OM particles in individual particles, 86%
293 were internally mixed with non-OM particles, such as soot, mineral, fly ash, metal,
294 and sulfate particles (Fig. 2 and Fig. S6). Based on their morphological mixing state,
295 we discriminated four OM internally mixed particles: OM-soot (Fig. 5a and Fig. S8),
296 OM-mineral (Fig. 5b), OM-fly ash/metal (Fig. 5c), and OM-sulfate particles (Fig.
297 5d-e). Our results show that 83% of type 1-4 OM particles were attached to soot,

mineral, sulfate, and metal particles, only 17% of type 1-4 OM particles were externally mixed particles, and all the type 5-6 OM were internally mixed with sulfate particles (Fig. 2). In addition, the major OM internally mixed particles include 54% OM-sulfate particles and 38% OM-soot particles, followed by 5% OM-mineral particles and 3% OM-fly ash/metal particles (Fig. 2). Based on these analyses, the flow chart of classification of individual aerosol particles was summarized in Figure 2.

Figure 6 shows number fractions of OM internally mixed particles in different size bins from 0.04 to 4.5 μm at the three sampling sites. OM-soot particles commonly occurred at S1 but they were mixed with certain amounts of sulfates at S2 and S3 during the sampling period (Fig. S8). OM-soot containing particles dominated in the finer size range (< 300 nm) at the three sampling sites (Fig. 6). In addition, 19% of OM-sulfate particles were internally mixed with inclusions (i.e., fly ash and metal) at all the three sampling sites (Fig. 2).

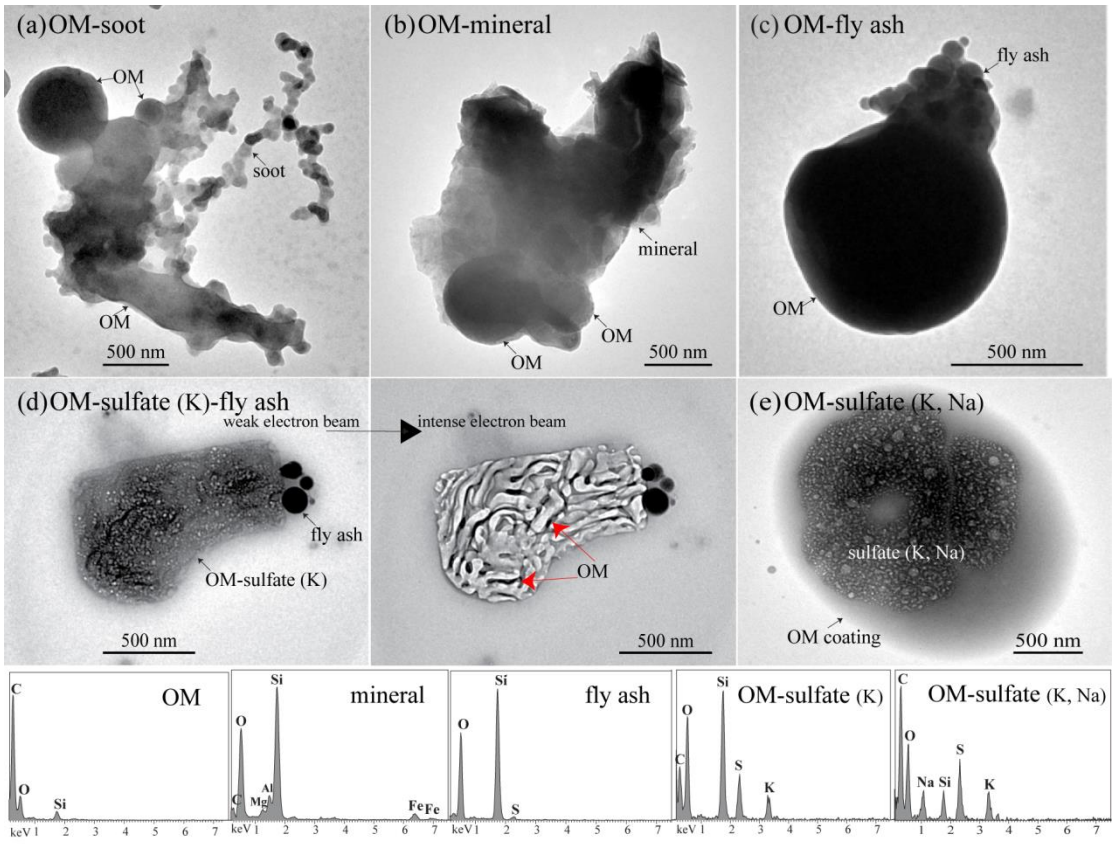

Figure 5. Typical TEM images of OM internally mixed particles (a) a spherical OM particle attached to a soot particle; (b) a near-spherical OM particle attached to a mineral particle; (c) fly ash particles attached to a near-spherical OM particle; (d) OM mixed with sulfate (K)-fly ash particle and its sublimed particle under strong electron beam; (e) OM as a coating mixed with a sulfate (K, Na) particle. The element compositions in OM, mineral, fly ash, and sulfate particles were measured by the TEM/EDX.

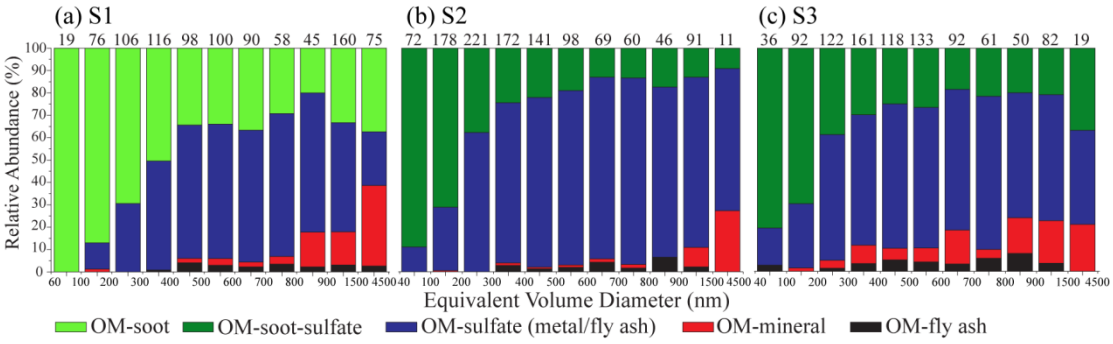

Figure 6. Number fractions of OM internally mixed particles at (a) S1 site (urban Jinan), (b) S2 site (Mt. Tai top), and (c) S3 site (polluted background). The number of analyzed particles in different size ranges is shown above each column.

3.4 Size distribution of OM-containing particles

Figure 7a shows size distributions of OM-containing particles at the three sampling sites. Aerosol particles collected at S2 and S3 display a similar peak at ~400 nm, much smaller than the peak at 600 nm at the S1 site (Fig. 7a). This result indicates that sizes of locally emitted OM-containing particles are much larger than the long-range transported OM-containing particles. We further obtain size distributions of type 1-3 OM particles at the three sampling sites during one haze episode. Interestingly, type 1-3 OM particles displayed similar peaks around 350 nm at all three sampling sites (Fig. 7b). This result suggests that the type 1-3 OM sources were similar in the same haze layer over the NCP.

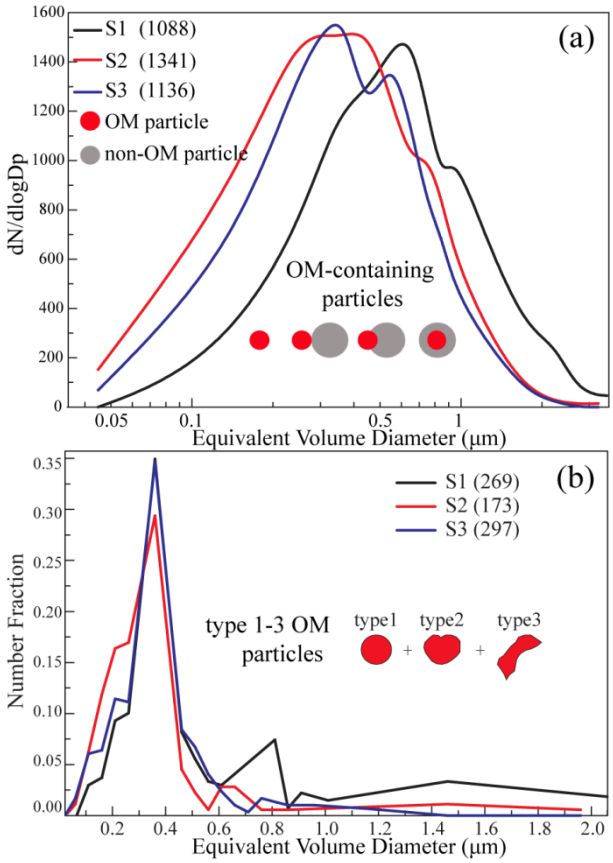

Figure 7. Size distributions of OM-containing particles and OM particles during L&M haze episodes. (a) Size distributions of 1088, 1341 and 1136 OM-containing particles collected at S1, S2, and S3 in all haze episodes during sampling period. (b) Size distributions of 269, 173, and 297 type 1-3 OM particles collected at S1, S2, and S3 in one haze episode during December 14-15.

4. Discussion

4.1 Sources of OM-containing particles

TEM adequately characterized the morphology and mixing state of OM-containing particles in wintertime L&M hazes. We found that the type 1-3 OM (Fig. 4a-c) particles were most abundant in the hazes and that most of them were internally mixed with non-OM particles (Fig. 2). This result is consistent with one previous study which found abundant amorphous spherical OM particles in the outflow of a haze plume in East Asia (Zhu et al., 2013). Moreover, Li et al. (2012)

found large amounts of type 1 OM particles in a coal-burning region in the China Loess Plateau in winter. However, some studies only found abundant type 5-6 OM particles in the atmosphere and only a few type 1-3 OM particles in urban and remote mountain air in China (Li and Shao, 2010;Li et al., 2015). Based on these comparisons, we conclude that those type 1-3 OM particles were not directly emitted by vehicular emissions in the NCP.

It should be noted that recent studies did not find abundant type 1-3 OM particles at three sampling sites in haze episodes caused by industries, coal-fired power plants and vehicular emissions in spring and summer (Li et al., 2011b;Yuan et al., 2015). However, these abundant type 1-3 OM particles occurred in haze episodes over a coal-burning haze caused by house-heating, heavy industries, and residential stoves in the China Loess Plateau in winter (Li et al., 2012). Based on the comparison, we may exclude that large amount of type 1-3 OM particles could be directly emitted from coal-fired power plants and heavy industries. Zhang et al. (2008) suggested that industrial boilers had cleaner combustion with much less by-product of particulate carbon and with much lower levels of OM, while residential stoves had significantly higher emissions of carbonaceous particulate matter with emission rates 100 times higher than that of industrial boilers. In addition, the latest studies found that uncontrolled solid fuels combustion in households had a major effect on haze episode in Beijing through aerosol modeling and satellite monitoring (Ru et al., 2015;Liu et al., 2016a). As a result, we believe that the type 1-3 OM particles can only be emitted by coal combustion and biomass burning in households while not emitted from vehicular, heavy industries, or coal-fired power plants in wintertime. In particular, the abundant near-spherical OM particles with higher Sph and lower AR indicate that these OM particles formed in cooling process after polluted plumes emitted from coal combustion and biomass burning.

Biomass burning and coal combustion both can produce types 1-3 OM particles and all contain a certain amount of Si beside C and O (Li et al., 2012;Posfai et al., 2004;Hand et al., 2005;Adachi and Buseck, 2011). Li et al. (2012) found that primary

OM particles contain much higher Si from coal combustion than biomass burning. Although EDX can only obtain semi-quantitative C, O, and Si from OM particles, the ratios of C-O-Si were comparable in different OM particles (Fig. 8). To evaluate OM sources in this study, we compared ratios of Si, O, and C in individual OM particles collected in haze and fresh OM particles (281 OM particles) from corn stalks (28 OM particles) and coal combustion (39 OM particles) conducted in the laboratory (supplementary material). Figure 8 shows that the haze OM particles were more associated with coal combustion compared with corn stalks from the point of coverage. The haze OM line is located between corn stalks and coal combustion (Fig. 8). This result revealed that the Si ratio in individual OM particles is ordered as coal combustion > haze particles > corn stalks; and that 71% of haze OM particles are associated with coal combustion. Based on the result, we can estimate that coal combustion contributes more type 1-3 OM particles than biomass burning in the wintertime L&M haze. This result is consistent with the source apportionment of OM particles based on their mass concentrations (Elser et al., 2016;Sun et al., 2013).

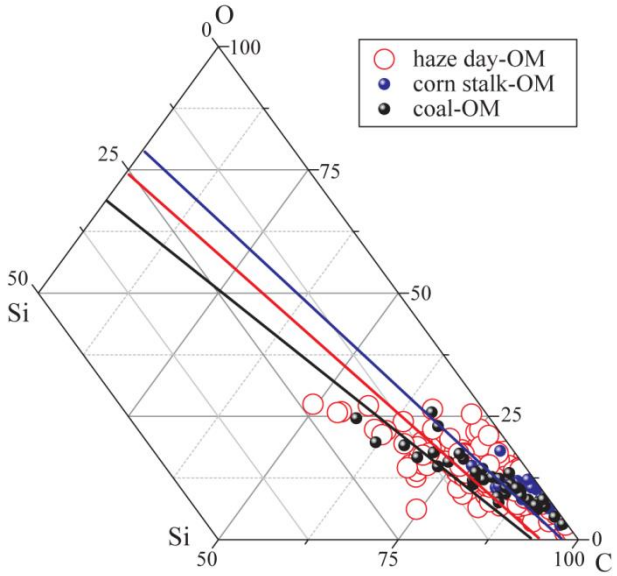

Figure 8. Triangular diagram of weight ratios of Si-O-C based on TEM/EDX data. 39 OM particles from coal combustion and 28 OM particles from corn stalks combustion, and 281 OM particles produced from the haze samples in this study. The three lines represent the connection of Si/O and Si/C for different OM particles.

4.2 Ageing of OM particles

The complicated mixing structures of individual particles can be used to evaluate particle ageing mechanisms (Li et al., 2016b). It is well known that S2 and S3 as the polluted background sites received aged particles after long-range transport and that the urban site of S1 received more fresh particles. Indeed, OM-soot particles at S2 and S3 sites were internally mixed with sulfates but not at S1 (Fig. 6 and Fig. S8). To evaluate particle ageing processes, we measured OM coating thickness in type 6 OM-coating particles (e.g., Fig. 5e) because coating thickness on secondary particles can be used to infer particle ageing during transport (Moffet et al., 2010;Moffet et al., 2013). In this study, OM coating thickness increased with particle size (i.e., 249.4 nm at S1, 274.5 nm at S2, and 305.6 nm at S3) and that their average values at the three sampling sites were ordered as S3 > S2 > S1 (Fig. 9). The results suggest that particles with larger sizes underwent more ageing than the fine particles and that the particles at S3 underwent the most ageing. However, number fractions of type 6 OM particles were small at three sampling sites (14.8% at S2 and 12% at S3, and 2.9% at S1) (Fig. 9). This phenomenon may be caused by the weak atmospheric reactions for SOA formation in the whole haze layer.

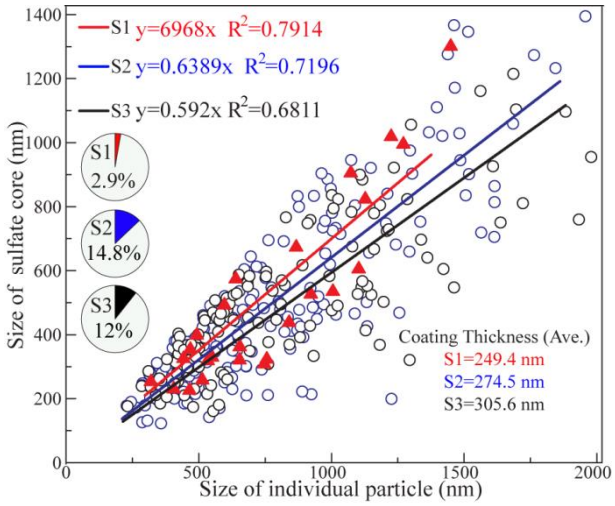

Figure 9. The relationship between the size of individual particles and their sulfate cores based on 366 OM-coating particles at S1, S3, and S3 sites. The smaller slope

represents the thicker OM coating. The number fractions of OM coating particles to OM-containing particles at three sampling sites are shown in the pie charts.

5. Conclusions and atmospheric implications

Abundant type 1-3 OM particles at S1, S2, and S3 suggested that coal combustion and biomass burning used for cooking and heating in residential sector in winter significantly contributed to the haze layer over the NCP. Although heavy industrial and coal-fired plants emitted large amount of gases such as SO_2, NO_x, and VOCs in the NCP (Wang et al., 2012;Zhang et al., 2015;Wang et al., 2013), we didn't observe an unusually large number of secondary organic and inorganic aerosols in wintertime L&M hazes; these aerosols are common particle types in heavy haze and fog episodes (Li et al., 2011c). The results indicated very weak photochemical reactions due to lower O_3 concentrations and weaker solar radiation, two constraints that reduce the conversion of the acidic gases into aerosol particles (Ma et al., 2012). Also, the L&M hazes were dry with RH < 60% (Fig. S5), which prohibits heterogeneous reactions between particles and gases (Zheng et al., 2015). These reasons can explain why we found higher number and mass fractions of abundant type 1-3 primary OM particles and lower type 6 secondary OM particles in the hazes. This result is consistent with a previous study using AMS (Sun et al., 2013), which showed 69% primary OM particles and only 31% SOA in winter L&M hazes.

Our microscopic observations of individual particles provide direct evidence on the regional L&M haze formation in NCP, which mainly caused by the residential coal stoves used for heating and cooking in winter. The result is consistent with the large scale modeling works and the field campaign in NCP from the recent studies (Liu et al., 2016b;Liu et al., 2016a;Ru et al., 2015). Therefore, we can conclude that these studies prove that these residential coal stoves in rural areas and in the urban outskirts have no pollution controls and directly emit particulate carbon and other pollutants. The emission control of residential coarse coal combustion is simply not regulated by the national environmental protection bureau, even though this bureau

has made much recent progress in controlling emissions from heavy industries and coal-fired power plants.

Our study indicated that measures should be taken to control the wide range of residential coal stoves in the NCP in wintertime. The type 1-3 OM particles from residential stoves mainly consist of PAHs (Zhang et al., 2008). In this study, we found that type 1-3 OM particles not only occurred in 68% OM-containing aerosol particles but also were concentrated on fine particles (< 1 μm) (Fig. 7a). Therefore, OM-containing particles in the frequent L&M hazes could pose a threat to human health for a long period throughout the winter. These microscopic observations results should be compared with models to evaluate our understanding of OM particles on human health, climate and acquired their hygroscopic and optical properties in L&M haze episodes.

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