

Reply to Referee#1:

General Comments:

In this study, an aging and optical change of organic tar particles in the regional haze was observed. Domestic coal and biomass burning are suggested to be the important reasons for haze formation in the NCP. It is found that with the evolution of haze, organic particles decreased, secondary inorganic aerosol increased, POT-SIA particles increased, and POT (primary organic tar) particles decreased, indicating that POT particles could provide surface for heterogeneous reactions of SO_2 and NO_x . It is also concluded that POT particles are coated with secondary inorganic aerosol, which leads to increased light absorption of particulate. Therefore, the “lensing effect” should be further considered on the POT particles in radiative forcing models. The results obtained in this study are interesting and worthy to be published in ACP.

Response: We appreciated referee#1's careful reading and positive feedback. All the comments and suggestions are valuable for improving the quality of our paper. Our point-to-point replies to the referee's comments are listed below and the changes are incorporated into the revised manuscript marked in red color.

Specific Comments:

1. The diagrams are too complex to understand, and some of the parameters in the diagrams have not been analyzed. For example, the mass concentrations of CO and NO_2 in Figure 2.

Response: According to the referee's suggestion, we redraw the figures. Because the variations of the gaseous pollutants were used in this manuscript only to help understand the evolution of haze episodes, they were not the main concerns of this manuscript, therefore we did not discuss them in detail and we moved the lines of gaseous pollutants in Figure 2 into the Supplementary Information (Figure S2) to make the figure more concise to read.

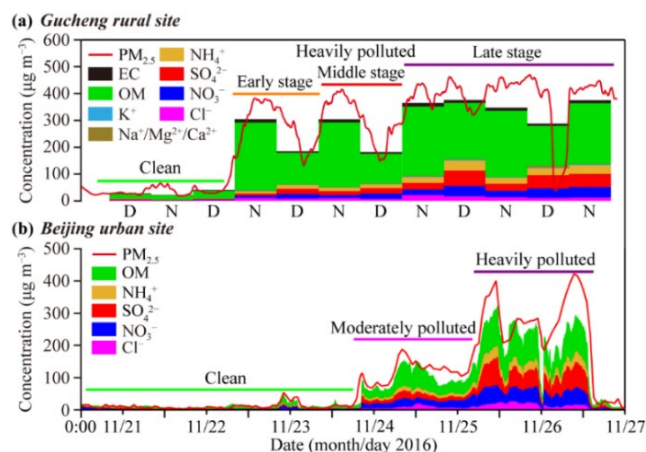


Figure 2

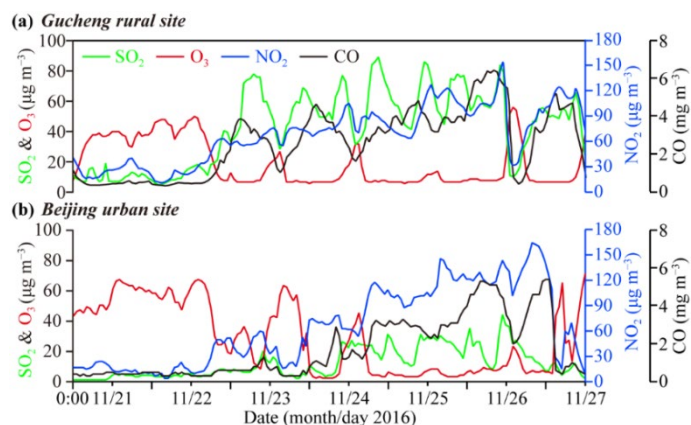


Figure S2

2. The offline bulk sample analysis is used for rural site while the online analysis is used for urban site. Can the values from two methods for the two sites be compared? Are there any errors or deviations between the results from offline bulk sample analysis and online analysis for urban site?

Response: Thanks for the comment. In this paper, we mainly focused on the microscopic properties and aging process of primary organic particles through the individual particle analysis. Due to the limited instruments, we collected offline PM_{2.5} filter samples at the Gucheng rural site and used the Aerosol Mass Spectrometer (AMS) to continuously monitor the chemical species at the Beijing urban site. The bulk analysis results were used as solid evidence to support the individual particle analysis results. We mainly focused on the relative changes of different chemical species but not the absolute concentration changes. The detailed comparison of bulk analysis results between the two sites is not intended. Therefore, we did not compare the bulk analysis results between the two sites in this paper. The deviations between the offline bulk sample analysis and the online analysis at the urban site were not determined because of the lack of offline samples.

3. The analysis shows that fossil fuel burning and biomass burning are the main sources of pollution. What is the difference between POT particles produced by these two sources?

Response: The previous papers reported that tar balls can be emitted from biomass burning (Pósfai et al., *J. Geophys. Res.*, 108, D13, 8483, 2003) and coal combustion (Zhang et al., *J. Geophys. Res.*, 123, 12964-12979, 2018). These papers reported similar characteristics such as spherical morphology, high viscosity, and C/O composition of tar balls. Therefore, it is difficult to distinguish the tar balls emitted from biomass burning and coal combustion, which is out of the main objective of this manuscript. Therefore, we did not identify their exact sources, and as referee#2 suggested, we refer to them as the burning-related primary organic particles. We think that the reviewer's comments might be our next aim to work on it.

References:

Pósfai, M., Simonics, R., Li, J., Hobbs, P. V., and Buseck, P. R.: Individual aerosol particles from biomass burning in southern Africa: 1. Compositions and size distributions of carbonaceous particles, *J. Geophys. Res.-Atmos.*, 108, 8483, 10.1029/2002JD002291, 2003.

Zhang, Y., Yuan, Q., Huang, D., Kong, S., Zhang, J., Wang, X., Lu, C., Shi, Z., Zhang, X., Sun, Y., Wang, Z., Shao, L., Zhu, J., and Li, W.: Direct observations of fine primary particles from residential coal burning: insights into their morphology, composition, and hygroscopicity, *J. Geophys. Res.-Atmos.*, 123, 12964-12979, 10.1029/2018JD028988, 2018.

4. It is concluded that the particle size of the rural point is larger than that of the urban point, because the particles with small particle size are easier to be transmitted. However, in this transportation process, the formation of new particles or secondary chemical reaction (aging) may occur, which would increase the particle sizes, do the authors take into account this factor.

Response: We appreciate the referee's comment. Indeed, the whole aged particle sizes increased due to the production of secondary aerosols on their surfaces during the particle aging process as we have shown in the manuscript. What we refer to is that the sizes of uncoated POA particles slightly decreased during the regional transport.

5. The second paragraph of the conclusion: "The primary pollutants from the intense coal and biomass burning in rural areas can also pose serious threats to human

health.....”. This looks unnecessary as the health effects are not the focus of this current study and it may need to be removed.

Response: According to the referee’s suggestion, we removed this part.

6. Line 251 “Figure S2a shows higher fractions of OM, EC, and Cl^- at nighttime than daytime during the whole haze episode at the GC rural site, suggesting the continuous strong local combustion emissions at nighttime”. We notice that the whole haze period was from November 22 to 27, and Figure 2A shows that the EC quality score was higher at nighttime than in the daytime on November 22. Please also explain why the nighttime would have higher level combustion emissions.

Response: As we have written in the manuscript, at the GC rural site the $\text{PM}_{2.5}$ concentration began to increase at 18:00 on 22 November and the air quality was changed from the clean period to heavily polluted period during the 22–27 November. The EC concentration at the nighttime ($12.1 \mu\text{g m}^{-3}$) was much higher than that ($1.8 \mu\text{g m}^{-3}$) in the daytime on November 22 (Figure 2a). In rural areas, people may work out and the heating activities stopped in the daytime. But at nighttime people all stayed at home and consumed more biomass and coal for cooking and heating, especially the heating activities with coal maintained several hours during the nighttime, which can release large amounts of pollutants into the air. Therefore, the primary emissions were much higher during the daytime than the nighttime.

7. Figure S2b shows only the ion concentration of 5 parameters, and the concentration of other ions at the rural points should also be listed.

Response: As we have mentioned above, at the Gucheng rural site, offline $\text{PM}_{2.5}$ filter samples were collected to obtain the concentrations of water-soluble inorganic ions (i.e., Cl^- , SO_4^{2-} , NO_3^- , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) using the ion chromatograph and obtain the OC and EC concentrations using the OC/EC analyzer. However, at the Beijing urban site offline $\text{PM}_{2.5}$ filter samples were not collected. Instead, we used the online Aerosol Mass Spectrometer (AMS) which can only obtain five chemical species (i.e., OM, Cl^- , SO_4^{2-} , NO_3^- , and NH_4^+). Therefore, we provided 10 chemical species at the Gucheng rural site and five chemical species at the Beijing urban site. We should note that the lack of Na^+ , Mg^{2+} , Ca^{2+} , K^+ , and EC at the Beijing urban site did not influence the main content and conclusions of this paper, because the primary organic aerosols and secondary

inorganic aerosols were mainly discussed in this study.

8. It is better to have discrimination of the ion concentration between daytime and nighttime for Figure S2 and Figure 2. In addition, the variation trend of CO concentration in Figure 2 may needs to be put together with gaseous pollutants such as SO₂ and O₃.

Response: According to the referee's suggestion, we added the comparison of chemical species concentrations between the daytime and nighttime, also we put the CO line with gaseous pollutants together. Moreover, the figure showing variation trends of gaseous pollutants were moved to the Supplementary Information (Figure S2), as has mentioned in question 1.

9. The specific calculation formula of light absorption cross section needs to be provided in methodology section.

Response: As the reviewer suggested, we provided the calculation formula of light absorption cross sections in the methodology section.

Please refer to Line 211-222 :

After running the Mie calculation, the attenuation efficiency (Q_{atn}), scattering efficiency (Q_{sca}), and absorption efficiency (Q_{abs}) of an individual particle were output with their definitions as follows (Aden and Kerker, 1951; Toon and Ackerman, 1981):

$$Q_{\text{atn}} = \left(\frac{2}{x^2}\right) \sum_{n=1}^{\infty} (2n+1) [\text{Re}(a_n + b_n)] \quad (1)$$

$$Q_{\text{sca}} = \left(\frac{2}{x^2}\right) \sum_{n=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2) \quad (2)$$

$$Q_{\text{abs}} = Q_{\text{atn}} - Q_{\text{sca}} \quad (3)$$

where $x = \frac{\pi D}{\lambda}$, is the dimensionless size parameter of the particle diameter D and the wavelength of light λ ; a_n and b_n are calculated from Riccati–Bessel functions of the particles sizes and refractive indices (Bohren and Huffman, 1983); The symbol Re denotes the real part of the complex quantity $a_n + b_n$.

The ACS of a particle can be obtained via multiplying the Q_{abs} by the geometric cross section of the particle as follow:

$$\text{ACS} = Q_{\text{abs}} \times \frac{\pi D^2}{4} \quad (4)$$

References:

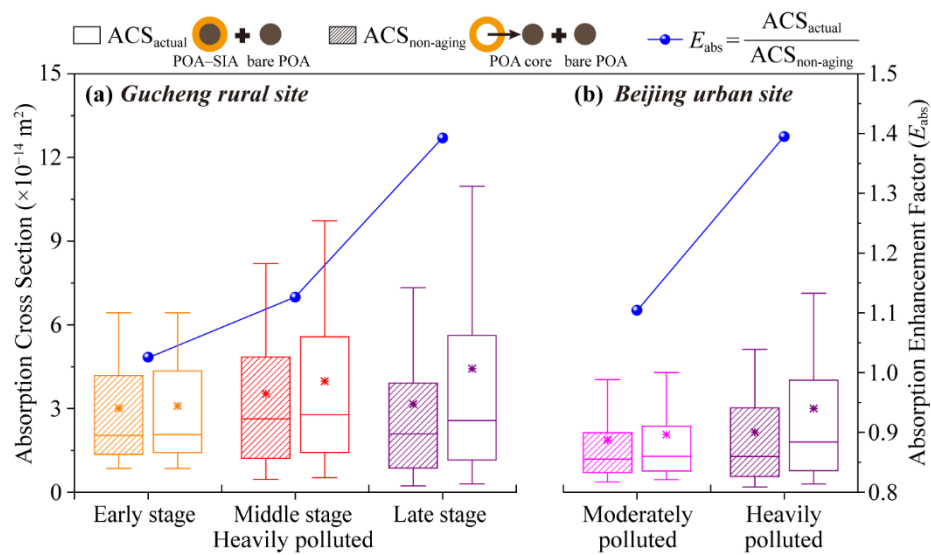
Aden, A. L., and Kerker, M.: Scattering of Electromagnetic Waves from Two Concentric Spheres, *Journal of Applied Physics*, 22, 1242-1246, 10.1063/1.1699834, 1951.

Toon, O. B., and Ackerman, T. P.: Algorithms for the calculation of scattering by stratified spheres, *Appl. Opt.*, 20, 3657-3660, 10.1364/ao.20.003657, 1981.

Bohren, C. F., and Huffman, D. R.: Absorption and scattering of light by small particles, John Wiley & Sons, New York, 1983.

10. Figure 9. Legend error. Ratio should be replaced by Eabs.

Response: Corrected.



11. Line 390: “pore” may be core.

Response: Corrected.