Dear Editor and Referees,

Thank you very much for your great efforts and suggestions for improving the quality of our paper. We have carefully considered all the referees' comments and revised the manuscript. According to the co-authors' suggestion, we deleted the word "abundant" from the title as "Cloud scavenging of anthropogenic refractory particles at a mountain site in North China".

Below are the detailed point-by-point responses to the referee comments. In the revised paper, the red color was marked as the revised places.

We look forward to receiving further evaluation of our work!

Sincerely

Weijun Li on behalf of all the coauthors

Reply to Referee#1:

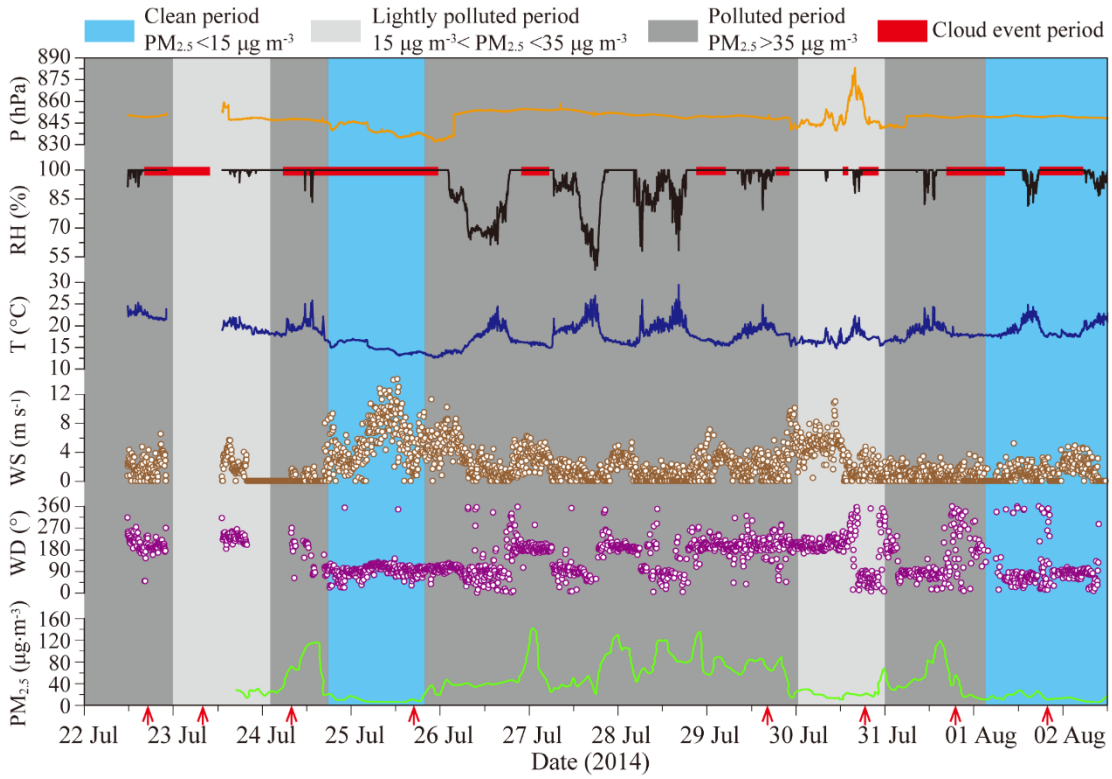
1. Overall, the article investigated cloud residual and interstitial particles and addressed the potential impact of aerosol particles on environment (including human health) and climate over one of China's heavily polluted regions. The study (or campaign) was carried out in a mountain site 1500 m a.g.l. by in-situ sampling followed by lab analysis employing TEM-EDS. The research gained some valuable data to unveil some of the chemical properties and mixing states of cloud residual and interstitial particles in a uniquely polluted area. The underlying logic is sound and the structure of the article is appropriate. The figures are clear and appropriate. However, there is room for grammar improvement and concept clarification.

   Response: We thank the referee#1' critical comments. All the comments and concerns raised by the referee have been explicitly considered and incorporated into the revised manuscript.

2. Table 1: There is a gap in individual particle sampling between July 25 and July 29. Is this because of instrument down time or other reasons? If it is the former, it could be appropriately addressed in the manuscript. If it is due to other reasons, they need to be justified.

   Response: All the individual particle samples in this study were collected during cloud events. As shown in the Figure below, we missed the collection in the late midnight of 26 July and no cloud event occurred between 27 July and 28 July. To avoid this puzzled question, we add one sentence in section 2.2 Line 126-127:

   "When cloud events occurred at the summit of Mt. Tai, individual particle samples were collected during the cloud events except one cloud event in the late midnight of 26 July"



3. Line 16: The statement of "our knowledge about aerosol-cloud interaction in heavily polluted conditions is weak" is not convincing. It might be difficult to accurately describe or explain the aerosol-cloud interaction in polluted regions, as the pollution type could vary from region to region. However, scientific communities are aware of the possible pollution sources and how these sources could influence aerosol-cloud interaction. It's just a matter of how complicated the particles could be in terms of its chemical composition and how active it could serve as CCN. Nevertheless, the NCP could be a unique area for particle pollution and well deserve sufficient scientific investigations.

   Response: We appreciated that you can point it out. We carefully revised this sentence. Please see Line 17-18:

   "Few studies have been conducted to characterize the aerosol-cloud interactions in heavily polluted conditions worldwide"

4. Line 20: Mixing state should only refer to aerosol or particle as an ensemble. When it comes to an individual particle, you can only describe it as a pure material or a mixture based on chemical composition. You can definitely describe the mixing state after investigating chemical composition of all the individual particles sampled. Therefore, I would express Line 20 as…used to investigate size and chemical composition of individual cloud RES and INT particles, and

study the mixing states of these particles.

For definition of aerosol/particles mixing state, please refer to:

N. Riemer and M.West [2013], Quantifying aerosol mixing state with entropy and diversity measures, Atmos. Chem. Phys., 13, 11423-11439, DOI: 10.5194/acp-13-11423-2013

For how to use individual particle chemical composition to describe mixing state, please refer to:

Deng, C., Brooks, S. D., Vidaurre, G., and Thornton, D. C. O.: Using Raman Microspectroscopy to Determine Chemical Composition and Mixing State of Airborne Marine Aerosols over the Pacific Ocean, Aerosol Science and Technology, 48, 193-206, 10.1080/02786826.2013.867297, 2014.

Response: Thank you for your comments. Definitely, the difference about definition of mixing state of aerosol particles should be clarified in this context. We revised the sentence in Line 20 according to the suggestion and added more content in section 3.2 Line 184-191 to explain it. As the referee's suggestion, we cited these two important papers. Please see:

Line 20-22: "Transmission electron microscopy (TEM) was used to investigate size and chemical composition of individual cloud RES and INT particles, and study the mixing states of these particles."

Section 3.2 Line 184-191: "Mixing state of aerosol particles is currently classified into population mixing state (Riemer and West, 2013) and single particle mixing state (Deng et al., 2014;Li et al., 2016b). Riemer and West (2013) defined the population mixing state as the distribution of the aerosol chemical species among the particles in a given population. However, based on the single particle mixing state of an individual particle acquired by TEM (Li et al., 2016b), this study emphasizes the distribution of different types of aerosol components within and on particle surface. Furthermore, single particle mixing state can be further divided into externally mixed particle and internally mixed particle (i.e., individual particles containing two or more types of aerosol components) (Li et al., 2016b)."

5. Line 30 to 32, The readers have to understand the relationships built on three "from"s, there must be a better grammar expression for this segment. Additionally, the article needs to discuss more about biogeochemical cycle if it is to be emphasized in abstract.

Response: We revised the sentence and deleted biogeochemical cycle here because the issue seems far away from the interactions of aerosol-cloud. Please see Line 31-33:

"Our findings provide an insight into the potential impacts on cloud radiative forcing from black carbon and metal catalyzed reactions of SO_2 in micro-cloud droplets containing soluble metals released from fly ash and metals over polluted air."

6. The article didn't measure black carbon but discussed its potential impacts. The researches of this study need to define the relationship of black carbon and the TEM measured species, e.g., soot. The authors should justify the interchangeable use of black carbon and soot identified by TEM if this is the case.

Response: Thank you for your comments. We added more explanation to show that soot and black carbon can be interchangeable in this study in Line 204-208:

"In much of the climate-change and environmental literature, "soot" and "black carbon" are commonly used interchangeably, and "black carbon" is the most commonly used term in the climate-science community (Andreae and Gelencsér, 2006;Buseck et al., 2014). In the following sections, we use the term "soot" for the classification of particle types and the term "black carbon" for the discussion of the climate issues."

Andreae and Gelencsér [2006] have given a clear definition about soot and black carbon in their paper. "Soot" is formed by combustion process and presents in the atmosphere as fine particles. Soot particles usually have chain-like structure composed of aggregates of spherules made of graphene layers, consisting almost purely of carbon. "Black carbon" generally implied to have optical properties and composition similar to soot carbon. In the literature, "black carbon" or "soot carbon" are often used synonymously for the major light-absorbing component of combustion aerosols. Buseck et al. [2014] also mentioned that black carbon and soot are commonly used interchangeably in much of the climate-change and environmental literature and no consensus exists in the atmospheric science community about whether soot is a part of black carbon, black carbon is a part of soot, or black carbon is equivalent to soot.

In the current knowledge, "Black carbon" is the most commonly used term in the climate-science community. So for aerosol particle classification, we used the term "soot", when we discussed the climate issues we used the term "black

carbon".

References:

Andreae, M. O., and A. Gelencsér (2006), Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmos. Chem. Phys., 6(10), 3131-3148, doi:10.5194/acp-6-3131-2006.

Buseck, P. R., Adachi, K., Gelencsér, A., Tompa, É., and Pósfai, M. (2014), Ns-Soot: A material-based term for strongly light-absorbing carbonaceous particles, Aerosol Sci. Tech., 48, 777-788, doi:10.1080/02786826.2014.919374.

7. Line 48: Is chemical composition of clouds important? Isn't cloud droplet mainly composed of water in terms of mass? It is understandable that chemical composition of aerosol is important for cloud nucleating, not as important as particle size though according to Dusek et al., 2006. It seems that the authors of this manuscript mean chemical composition of cloud RES and INT particles here.

   Response: We agreed with the referee#1. We revised this sentence according to the suggestion. Please see Line 47-50:

   "Owing to the rapid industrialization and urbanization in Asia, large quantities of aerosol particles from anthropogenic sources are released into the atmosphere, which can dramatically affect the chemical composition of CCN, and furthermore change the properties of clouds such as radiative forcing, lifetime, and precipitation patterns"

8. Line 58-59: The impact of Fe-bearing particles on oceans is undeniable but seems to beyond the discussion of this research. There is no measurement about how much Fe-particles are transported to ocean. Therefore, it seems to be not very relevant and insignificant to be mentioned.

   Response: We deleted this statement according to the suggestion.

Technical corrections:

1. Line 74: "Field observations are requested to…", so, who has requested field observations? I think it would be more appropriate to say "Field observations are needed to…"

   Response: Changed.

2. Line 79: I would recommend changing “Many studies…” to “Numerous studies…” or “Several studies…” “Many” sounds just vague and exaggerating.
   Response: Changed.
3. Line 79 to Line 83: From “Many studies…” on, it would be better if these can be incorporated into one sentence.
4. Line 92: “Capture interactions” is questionable and sounds exaggerated.
   Response: We used “reveal” to replace “capture”.
5. Line 101: Similar to a previous comment about Line 79, there are two occurrence of “many”. First, it would be better to have some vocabulary variations. Second, “many” doesn’t sound academically accurate.
   Response: We replaced the first “many” by “several”, and the second “many” by “a number of”.
6. Line 124-125: Recommend changing to “More detailed information about the setup of a modified sampler can be found in Li et al., 2011a.”
   Response: We changed the sentence according to the suggestion.
7. Line 142: Recommend changing to “…interstitial particles mostly distributed on the peripheral areas of TEM grid…”
   Response: Changed.
8. Line 145: Recommend changing “separate” to “distinguish between”.
   Response: Changed.
9. Line 146: Recommend changing “In a word, many previous” to “Generally, a number of previous”
   Response: Changed.
10. Line 154: “(see the supplement)” to “(refer to the supplement)”
    Response: Changed.
11. Line 191: Recommend changing from “such as steel mills and smelters.” to “such as production activities in steel mills and smelters.”
    Response: Changed.
12. Line 233: “we can still identify them…” to “they can still be identified…”
    Response: Changed.
13. Line 243 to Line 244: It can be challenged mathematically that 76% is 3.5 times higher 22%. Generally, it is preferred to express it as “76% is 2.5 times higher than 22%” or “76% 3.5 times of 22%”
    Response: We rewrote the sentence. Please see Line 260:

"we found that 76% of cloud RES were a mixture of sulfates and refractory particles, which is 3.5 times of 22% in cloud INT"

14. Line 259: "reveals" should be changed to "reveal"

    Response: Corrected.

15. Line 270: "the particle number" to "particle number"

    Response: Corrected.

16. Line 280 and Line 293: Better to rephrase the expression of "We believe". It is too subjective to be overused in a scientific journal paper.

    Response: Line 280 "We believe" was replaced by "The present study reveals". Line 293 "We believe" was replaced by "It is highly probable".

17. Line 285: It would be better to just use "black carbon" instead of "BC", even though it has been defined earlier. "BC" has only been discussed in introduction section and hasn't been discussed ever since. It won't take much more space though.

    Response: Changed.

18. Line 309: "If they are" to "If they were". The verb is in the subjunctive.

    Response: Changed.

19. Line 321: "is still a mystery in polluted air" to "is still unresolved"

    Response: Changed.

20. Line 322: "should be further considered" to "should be further studied"

    Response: Changed.

Reply to Referee#2:

1. In this study cloud residual and cloud interstitial particles were collected at a site and analyzed to obtain insight into the aerosol-cloud interactions. Properties such as size, morphology, composition and the mixing state were studied to highlight the salient differences in clout RES and INT particles. The researchers also propose a model to further explain the cloud-aerosol interactions.

   Overall, the background, scientific rationale and the data presented in the study are sound. The presentation style is clear and easy to follow. However, there are a couple minor issues which need to be addressed.

   Response: We thank the referee#2' nice comments. All the comments and concerns raised by the referee have been explicitly considered and incorporated into the revised manuscript.

2. In Results, there is a section 3.2 and 3.4 but there is no section 3.3. It seems that section 3.4 needs to be changed to 3.3.

   Response: Corrected.

3. In section 3.2, the authors classify the particles as (1)S-rich, (2)OM, (3)Soot, (4)mineral and (5)fly-ash and (6)metal. Furthermore, they say (2)-(6) can be classified as refractory particles owing to their refractory behavior under electron beams. The authors then say that "Based on the mixing properties of individual particles, they can be further classified into four categories: S-mineral, S-soot, S-fly ash/metal, S-fly ash/metal-soot" together defined as S-refractory particles. While the classification seems reasonable, the use of the term "mixing properties" is a bit vague here unless more information is provided. What are the mixing properties to which the authors are referring? Are S-refractory particles formed from refractory particles? If so, how? Is it a probabilistic phenomenon or is there a fundamental difference between the refractory particle in itself as opposed to a component of S-refractory particle?

   Response: Thank you for your comments. We added more information about the mixing state in section 3.2. Please see Line 184-191:

   "Mixing state of aerosol particles is currently classified into population mixing state (Riemer and West, 2013) and single particle mixing state (Deng et al., 2014;Li et al., 2016b). Riemer and West (2013) defined the population mixing state as the distribution of the aerosol chemical species among the particles in a

given population. However, based on the single particle mixing state of an individual particle acquired by TEM (Li et al., 2016b), this study emphasizes the distribution of different types of aerosol components within and on particle surface. Furthermore, single particle mixing state can be further divided into externally mixed particle and internally mixed particle (i.e., individual particles containing two or more types of aerosol components) (Li et al., 2016b)."

The explanation is helpful for the potential readers to understand how we classify the mixing state in this study.

To better answer the question, we give more explanations as below:

About the mixing state of individual particles, we have detailed discussion and clear definition in our previous paper (Li, W., et al., 2016a, 2016b). The mixing state of an aerosol particle can be classified as either internally mixed (whether distinct, homogeneous entities occur within the same particles) or externally mixed (whether they are separated entities in the air), please see the figure below.

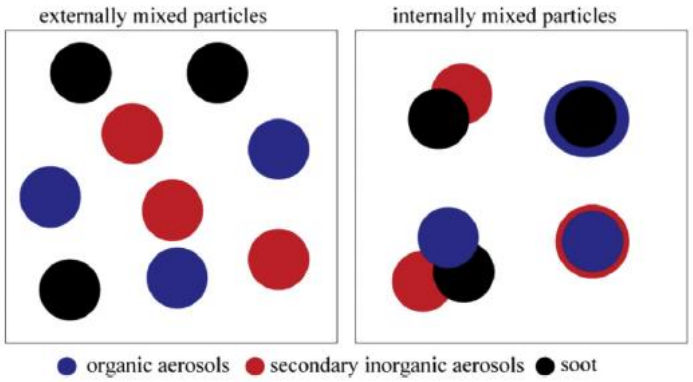


Fig. 14. Schemes of externally mixed and internally mixed particles.

The basic types of aerosol components (i.e., (1) S-rich, (2) OM, (3) soot, (4) mineral, (5) fly-ash and (6) metal) refer to the externally mixed individual particles. For the individual particles containing two or more basic types of aerosol components, they can be further classified into S-mineral, S-soot, S-fly ash/metal, and S-fly ash/metal-soot as internally mixed particles.

Refractory particles are directly emitted from natural or anthropogenic sources, such as mineral dust particles from deserts, soot and primary organic aerosol particles (POA) from incomplete combustion of fossil fuel and biomass, fly ash from coal combustion, and metals from heavy industries. The internally mixed particles such as S-mineral, S-soot, S-fly ash/metal, and S-fly ash/metal-soot are formed through condensation, coagulation, and cloud process of refractory

particles with secondary particles (i.e., S-rich) during atmospheric transports. Therefore, in this study, we used S-refractory particle representing internally mixed particle between secondary sulfate and primary refractory particles (e.g., mineral, soot, POM, fly ash, and metal).

References:

Li, W., J. Sun, L. Xu, Z. Shi, N. Riemer, Y. Sun, P. Fu, J. Zhang, Y. Lin, and X. Wang (2016a), A conceptual framework for mixing structures in individual aerosol particles, *J. Geophys. Res.-Atmos.*, 121(22), 13784-13798.

Li, W., L. Shao, D. Zhang, C.-U. Ro, M. Hu, X. Bi, H. Geng, A. Matsuki, H. Niu, and J. Chen (2016b), A review of single aerosol particle studies in the atmosphere of East Asia: morphology, mixing state, source, and heterogeneous reactions, *J. Clean Prod.*, 112, 1330-1349.

Cloud scavenging of anthropogenic refractory particles at a mountain site in North China

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Abstract. Aerosol-cloud interactions remain a major source of uncertainty in climate forcing estimate. Few studies have been conducted to characterize the aerosol-cloud interactions in heavily polluted conditions worldwide. In this study, cloud residual (cloud RES) and cloud interstitial (cloud INT) particles were collected during cloud events under different pollution levels from 22 July to 1 August, 2014 at Mt. Tai (1532 m above sea level) located in the North China Plain (NCP). Transmission electron microscopy (TEM) was used to investigate size and chemical composition of individual cloud RES and INT particles, and study the mixing states of these particles. Our results show that S-rich particles were predominant (78%) during clean periods ($PM_{2.5}$ < 15 μg m^{-3}), but a large amount of anthropogenic refractory particles (e.g., soot, fly ash, and metal) and their mixtures with S-rich particles (named as S-refractory) were observed during polluted periods. Cloud droplets collected during polluted periods were found to become an extremely complicated mixture by scavenging of abundant refractory particles. We found that 76% of cloud RES were S-refractory particles and that 26% of cloud RES contained two or more types of refractory particles. Soot-containing particles (i.e., S-soot and S-fly ash/metal-soot) were the most abundant (62%) among cloud RES, followed by fly ash/metal-containing particles (i.e., S-fly ash/metal and S-fly ash/metal-soot, 37%). The complicated cloud droplets have not been reported in clean continental or marine air before. Our findings provide an insight into the potential impacts on cloud radiative forcing from black carbon and metal catalyzed reactions of SO_2 in micro-cloud droplets containing soluble metals released from fly ash and metals over polluted air.

1. Introduction

Clouds play a crucial role in various physical and chemical processes occurring in the lower troposphere and hence affect the Earth's radiation budget (Seinfeld et al., 2016;Tilgner et al., 2014). Aerosol particles, including primary and secondary ones generated from natural and anthropogenic sources, either directly alter radiative forcing or act as cloud condensation nuclei (CCN) to indirectly influence it. At present, aerosol-cloud interactions unquestionably affect radiative forcing and global climate (McFiggans et al., 2006;Seinfeld and Pandis, 2006;Rosenfeld et al., 2014). CCN become cloud droplets through the condensation of water vapor when the relative humidity (RH) of an air parcel increases above saturation (Farmer et al., 2015). Size, chemical composition, and mixing state are main factors affecting the ability of a particle to act as CCN (Dusek et al., 2006;Li et al., 2011a;Fan et al., 2016;Rosenfeld, 2000;Hudson, 2007). In addition, aerosol particles incorporated into cloud droplets can be easily lifted into the free troposphere during cloud development and further extend their influence on cloud precipitation and regional climate (Fan et al., 2016).

Owing to the rapid industrialization and urbanization in Asia, large quantities of aerosol particles from anthropogenic sources are released into the atmosphere, which can dramatically affect the chemical composition of CCN, and furthermore change the properties of clouds such as radiative forcing, lifetime, and precipitation patterns (Li et al., 2011b;Drewnick et al., 2007;Ervens, 2015;Twohy and Anderson, 2008). High concentrations of aerosol particles increase the number of cloud droplets and reduce their size, which further results in the reduction of precipitation efficiency and in extending the lifetime of clouds (McFiggans et al., 2006;Qian et al., 2009;Fan et al., 2016;Li et al., 2017a;Rosenfeld, 2000). Moreover, anthropogenic aerosol particles - especially fly ash, metal, and soot particles - are incorporated into cloud droplets, and be transported long distances to affect ecosystems, human health, and radiative forcing (Li et al., 2013;Rosenfeld et al., 2014). Especially the toxic and bioaccumulative metals can deposit into the ecosystem following fog or precipitation and further cause severe health problems to human beings (Liu et al., 2012). Moreover, transition metals such as iron (Fe) and manganese (Mn) can enhance the in-cloud oxidation of sulfur dioxide to sulfate (Harris et al., 2013).

Recently, many studies have been performed worldwide to investigate aerosol-cloud interactions and the composition of cloud droplets. Schroder et al. (2015) investigated the activation of refractory

black carbon particles in stratocumulus clouds at a marine boundary layer site using a counterflow virtual impactor and single particle soot photometer. Ueda et al. (2014) reported the effects of in-cloud processes on the compositional changes of sea salt particles by collecting individual aerosol particles in and below clouds, respectively. Pierce et al. (2015) calculated size distribution changes and radiative forcing effects due to the scavenging of interstitial particles by cloud droplets in a clean, remote region. Roth et al. (2016) analyzed the composition and mixing state of cloud residues and out-of-cloud aerosol particles by single particle aerosol mass spectrometry on a mountain site and found that soot particles internally mixed with sulfate and nitrate were the dominant ones in cloud residues. All of the above studies were carried out in clean atmosphere; they could not observe the clear interactions between abundant anthropogenic particles and cloud droplets. However, the latest satellite observations indicated that large amounts of anthropogenic fine particles assembled in cloud base and might modify cloud properties in heavily polluted air influenced by industrial and urban emissions (Eck et al., 2018). Field observations are needed to confirm it and understand the interactions of aerosol-cloud over polluted areas, especially in North and South Asia.

Mt. Tai, the highest mountain in the NCP, is surrounded by several medium-sized industrial cities. The altitude of Mt. Tai is close to the top of the planetary boundary layer (PBL) above the NCP. Therefore, Mt. Tai is an ideal site to study the effects of regional transport and local emissions of anthropogenic aerosols on cloud properties. Numerous studies have been conducted on Mt. Tai, but virtually all the researchers mainly focus on the variation of chemical composition and size distribution of aerosol particles (Zhang et al., 2014) and chemical composition of cloud water (Li et al., 2017a;Wang et al., 2011). Because of the limitation of sampling and analyzing techniques, these studies did not consider the aerosol-cloud interactions at the top of Mt. Tai in North China.

Transmission electron microscopy (TEM) has become a powerful technique to characterize the morphology, composition, size, and mixing state of individual aerosol particles in recent years (Li et al., 2016a;Ueda et al., 2014). Many studies used single particle aerosol mass spectrometry (SPAMS) to characterize the composition and mixing state of residual particles of individual cloud droplets (Zhang et al., 2017;Lin et al., 2017;Pratt et al., 2010). Compared to the SPAMS, TEM can directly observe the morphology and mixing state of individual cloud droplet residual (cloud RES) and interstitial particles (cloud INT) (Ueda et al., 2014;Twohy and Anderson, 2008;Li et al., 2011a;Kojima et al., 2004). Therefore, TEM technique can not only be used to identify cloud RES and cloud INT collected in a

same cloud event but also reveal interactions between aerosol-clouds based on mixing state of individual particles. In this study, we collected individual particles during cloud events at the summit of Mt. Tai and applied TEM to obtain and compare the size, morphology, composition, and mixing state of cloud RES and cloud INT. This is helpful to understand the influence of anthropogenic sources on cloud properties above the heavily polluted region.

2. Experimental methods

2.1 Sampling sites

Field observations were carried out at Mt. Tai (36.251°N, 117.101°E; 1532 m above sea level (a.s.l)) from 22 July to 1 August 2014. Mt. Tai is the highest mountain in the central NCP and is surrounded by several medium-sized industrial cities (Fig. 1). A number of large coal-fired power plants, oil refinery plants, steel plants, and cement plants are located in these industrial cities (Jinan, Zibo, Laiwu, Liaocheng, Jining, Tai'an etc.) within a radius of 120 km around Mt. Tai (Fig. 1b). Jinan city is the capital of Shandong Province and is situated 60 km north of Mt. Tai. Tai'an city is located at the southern foot of Mt. Tai. Therefore, the local and regional emissions may have a large contribution to the air quality at the summit of Mt. Tai. Mt. Tai's altitude is close to the top of planetary boundary layer over the NCP, and local cloud events frequently occur at its summit, especially in summer.

As shown in Fig. 1c, individual particle samples were collected at a sampling site near the summit of Mt. Tai. The sampling site was usually covered by clouds when cloud events occurred during the sampling periods. The 24-h air mass backward trajectories arriving at Mt. Tai at 1500 m above ground level (a.g.l) (Fig. 1a) were calculated using the Hybrid Single-Particles Lagrangian Integrated Trajectory (HYSPLIT) model available at the NOAA Air Resources Laboratory's web server (Draxler and Rolph, 2003).

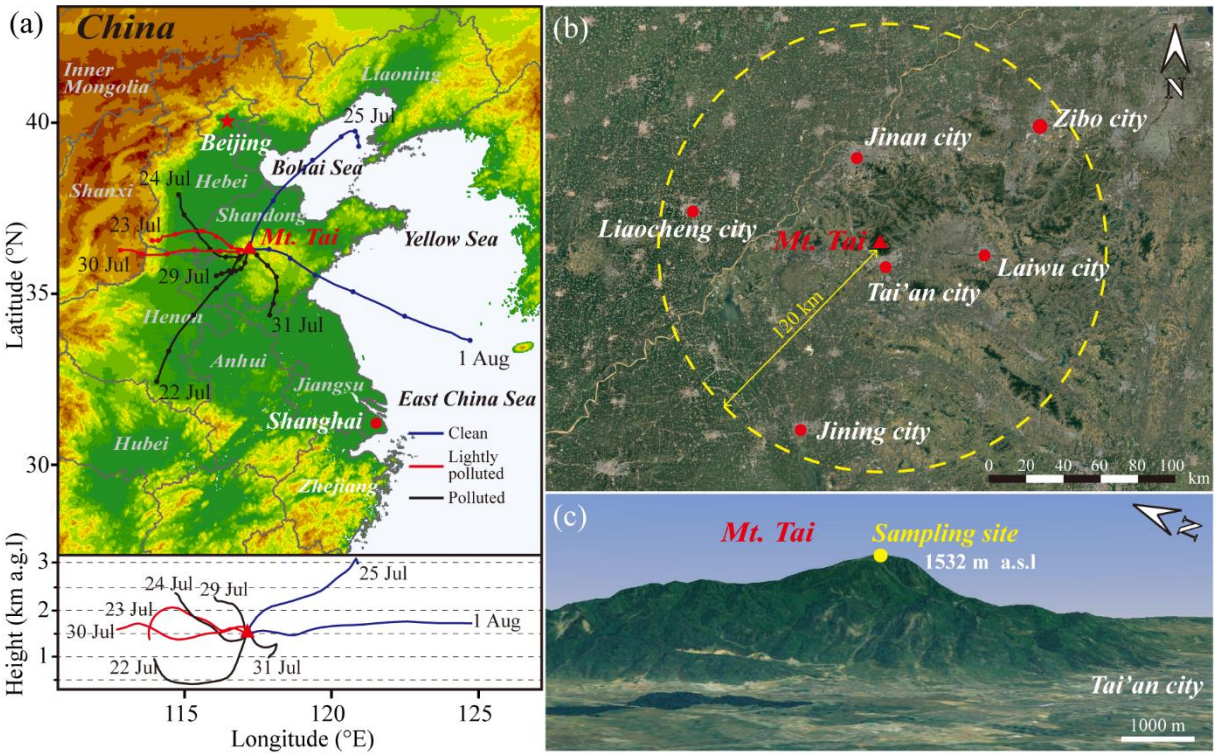


Figure 1. (a) Location of Mt. Tai in the North China Plain and the 24-h air mass backward trajectories arriving at Mt. Tai at 1500 m a.g.l during the sampling period. (b) The medium-sized industrial cities distributed within a radius of 120 km around Mt. Tai. (c) The expanded topographic view of Mt. Tai and the sampling site near the summit of Mt. Tai.

2.2 Individual particle collections

Individual aerosol particles were collected onto carbon films supported by TEM copper grids (carbon type-B, 300-mesh copper, Tianld Co., China) using a single-stage cascade impactor with a 0.5 mm diameter jet nozzle at a flow rate of 1.0 L min^{-1}. The aerodynamic diameter of particles collected with a 50% efficiency (cutoff diameter, d_{50}) by this individual sampler is 0.24 μm if particle density is 2 g cm^{-3}. More detailed information about the setup of a modified sampler can be found in Li et al. (2011a). When cloud events occurred at the summit of Mt. Tai, individual particle samples were collected during the cloud events except one cloud event in the late midnight of 26 July (Fig. 3). The sample information in the present study is listed in Table 1.

During the sampling period, meteorological data at the summit of Mt. Tai including pressure (P), relative humidity (RH), temperature (T), wind speed (WS), and wind direction (WD) were measured and recorded every 5 min by a pocket weather meter (Kestrel 4500, Nielsen-Kellermann Inc., USA). $PM_{2.5}$ concentrations on Mt. Tai were monitored on-line by a beta attenuation and optical analyzer

(model 5030 SHARP monitor, Thermo Scientific, USA).

Table 1. Information on individual particle samples collected on Mt. Tai.

Sample ID	Sampling time (local time)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	T (°C)	RH (%)	P (hPa)	WS ($m\ s^{-1}$)
1	22 Jul. 2014 16:04	51.6	22.8	100	849.1	0.9
2	23 Jul. 2014 08:00	24.2	20.4	100	849.4	2.5
3	24 Jul. 2014 07:43	74.3	19.2	100	848.0	0
4	25 Jul. 2014 17:00	11.8	13.9	100	838.0	5.5
5	29 Jul. 2014 16:18	72.9	20.8	95.7	848.0	1.1
6	30 Jul. 2014 19:24	24.2	17.5	100	844.2	0.8
7	31 Jul. 2014 17:30	56.4	18.1	100	849.0	0.9
8	01 Aug. 2014 17:56	14.7	18.8	100	849.1	1.8

2.3 TEM analysis

Individual aerosol particles collected on TEM grids were analyzed by a transmission electron microscope (TEM, JEM-2100, JEOL Ltd., Japan) at a 200 kV accelerating voltage. TEM is equipped with an energy-dispersive X-ray spectrometer (EDS, INCA X-Max^N 80T, Oxford Instruments, UK). EDS semi-quantitatively detects the elemental composition of individual particles with atomic number greater than six ($Z > 6$). However, Cu peaks in the EDS spectra were not considered because of the interference from the copper substrate of TEM grids. We acquired morphology, composition, and mixing state of individual particles through the combination of TEM and EDS (TEM/EDS).

The distribution of aerosol particles on TEM grids was not uniform, with particle size decreasing from the center to the edge of the TEM grids. Cloud droplets with larger size normally impacted on the center and interstitial particles mostly distributed on the peripheral areas of TEM grids (Li et al., 2011a). Moreover, cloud RES had large rims compared with cloud INT, suggesting that cloud RES were droplets before being captured (Zhang et al., 2006). According to the distribution and morphology of individual particles on the substrate, we can distinguish between cloud RES and cloud INT particles. Figure 2 generally displays typical TEM images of cloud RES and cloud INT particles. Generally, a number of previous studies using the cascade impactor have successfully captured individual interstitial particles and cloud droplets on the substrate during cloud events (Ueda et al., 2014;Zhang et al.,

2006;Kojima et al., 2004;Li et al., 2011a).

To obtain the size of cloud RES and cloud INT particles, we measured the area and equivalent circle diameter (ECD) of these analyzed particles by iTEM software (Olympus soft imaging solutions GmbH, Germany). It should be noted that we measured ECD of the core of individual cloud RES excluding the water rim because water rim only contains trace organics (Li et al., 2011a). The ECD can be further converted to equivalent spherical diameter (ESD) according to the AFM analysis (refer to the Supplement Fig. S1).

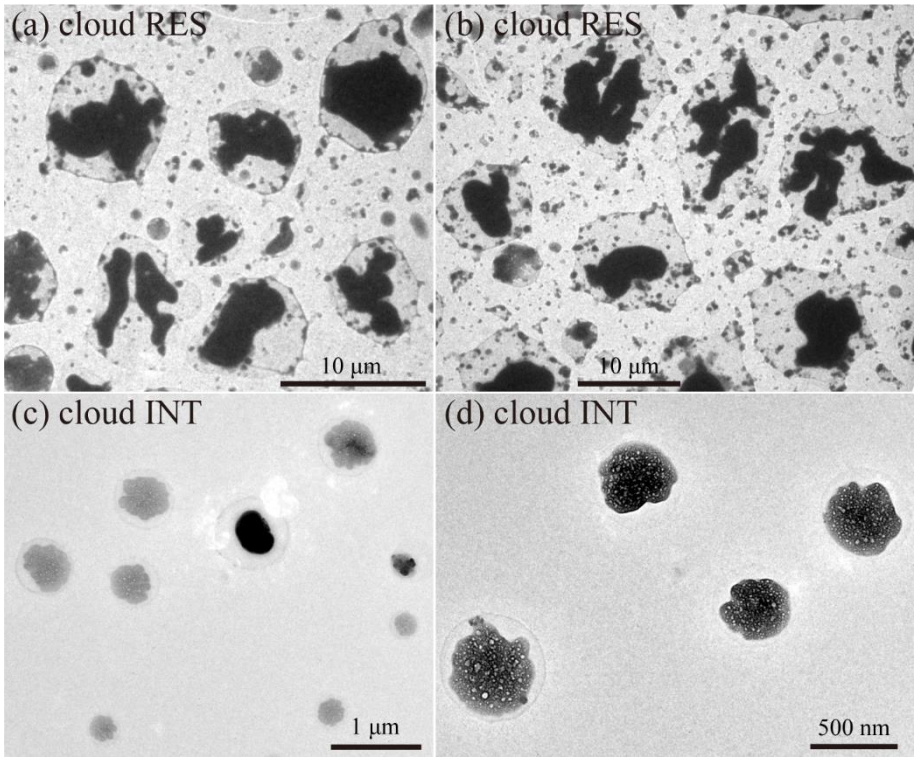
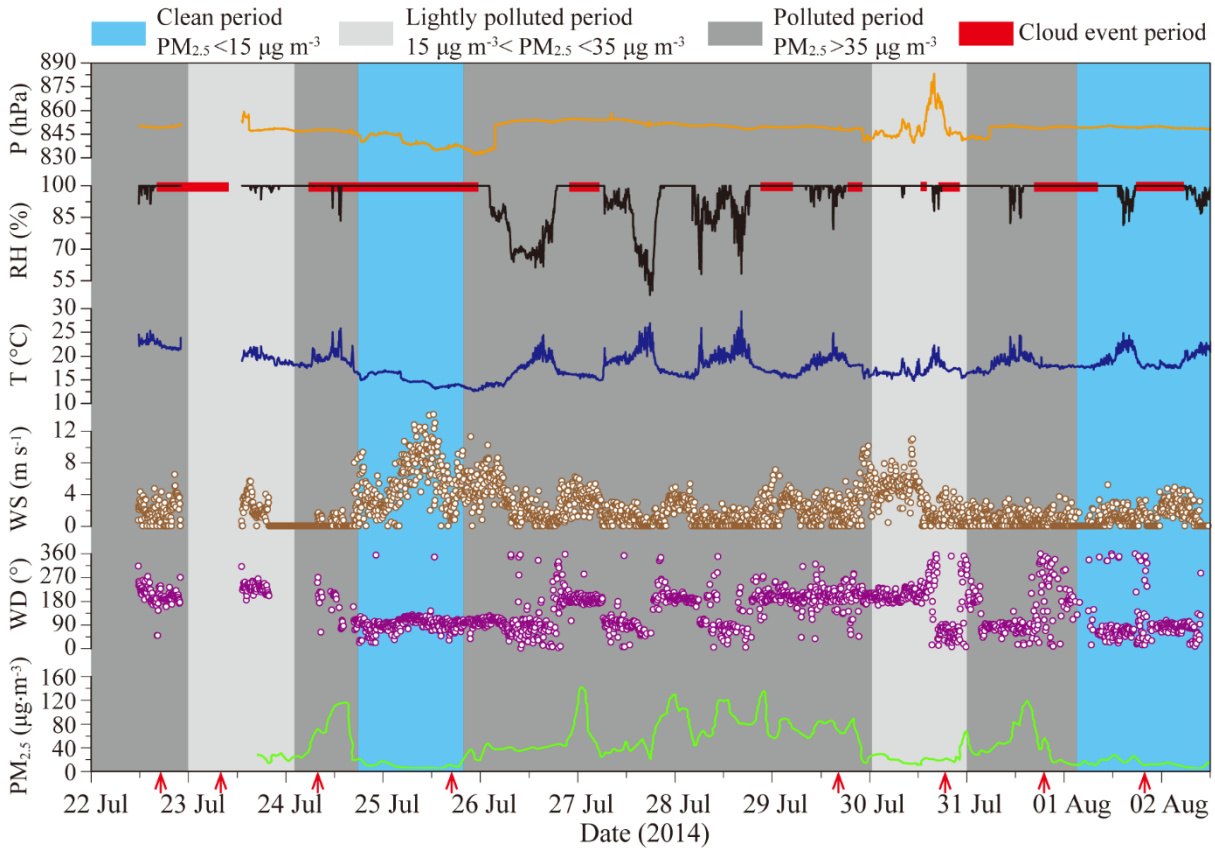


Figure 2. Low magnification TEM images of cloud RES (a-b) and cloud INT (c-d) particles collected on Mt. Tai.

3. Results

3.1 Meteorological conditions and backward trajectories

Temporal variations of pressure (P), relative humidity (RH), temperature (T), wind speed (WS), wind direction (WD), and $PM_{2.5}$ concentration were measured on Mt. Tai from 22 July to 2 August 2014 (Fig. 3). During the sampling period, the temperature ranged from 12.6 to 29.4 $^{\circ}C$, and the RH varied between 48.2% and 100%. Each day during the sampling period, the RH reached 100% as temperatures decreased from the late afternoon into the evening (Fig. 3). We noticed that $PM_{2.5}$ concentrations on the mountaintop were closely related to wind direction and speed during the regional transport of hazes. Based on backward trajectories of air masses and $PM_{2.5}$ concentrations, the whole sampling period can be divided into three categories: *clean period* ($PM_{2.5} < 15$ μg m^{-3}), the prevailing winds were from the northeast to east and air masses were from higher altitudes above the marine areas which lead to the lowest $PM_{2.5}$ concentration; *lightly polluted period* (15 μg $m^{-3} < PM_{2.5} < 35$ μg m^{-3}), the prevailing winds were from the west, and air masses originating from higher altitudes above continental areas brought regional pollutants to the summit of Mt. Tai; *polluted period* ($PM_{2.5} > 35$ μg m^{-3}), air masses originating from northwest, southwest, or south went through Tai'an city. Back trajectories as shown in Fig. 1a during polluted days suggest that air pollutants from industrialized cities might be lifted along the southern slope up to Mt. Tai's summit.



179

180 **Figure 3**. Temporal variations of pressure (P), relative humidity (RH), temperature (T), wind speed
181 (WS), and wind direction (WD) measured on Mt. Tai from 22 July to 2 August 2014. The red arrows
182 indicate collection times of individual particle samples during the cloud events.

3.2 Mixing state of anthropogenic refractory particles

Mixing state of aerosol particles is currently classified into population mixing state (Riemer and West, 2013) and single particle mixing state (Deng et al., 2014;Li et al., 2016b). Riemer and West (2013) defined the population mixing state as the distribution of the aerosol chemical species among the particles in a given population. However, based on the single particle mixing state of an individual particle acquired by TEM (Li et al., 2016b), this study emphasizes the distribution of different types of aerosol components within and on particle surface. Furthermore, single particle mixing state can be further divided into externally mixed particle and internally mixed particle (i.e., individual particles containing two or more types of aerosol components) (Li et al., 2016b).

Based on the elemental composition and morphology of individual particles, six basic types of externally mixed particles were classified: S-rich (Fig. S2a), soot (Fig. S2b), organic matter (OM, Fig. S2c), mineral (Fig. S2d), and fly ash/metal (Figs. S2e-h). The classification criteria of different particle types and their sources have been described in our previous study (Li et al., 2016a). S-rich particles representing secondary inorganic particles (e.g., SO_4^{2-}, NO_3^-, and NH_4^+) are transformed from gaseous SO_2, NO_x, and NH_3. OM can be divided into primary organic matter (POM) and secondary organic matter (SOM). POM is directly emitted from coal or biomass burning and normally has spherical or irregular shapes (Liu et al., 2017), whereas SOM is produced from the chemical oxidation of volatile organic compounds (VOCs) and exhibits OM-coating on S-rich particles (Li et al., 2016b). Fly ash (e.g., Si, Al, and O) and metal particles (e.g., Fe, Mn, Zn, and Pb) normally are emitted from coal-fired power plants and heavy industrial activities, such as production activities in steel mills and smelters. Soot particles are generated from incomplete combustion processes of biomass burning and fossil fuels in both industrial activities and vehicular emissions. In much of the climate-change and environmental literature, “soot” and “black carbon” are commonly used interchangeably, and “black carbon” is the most commonly used term in the climate-science community (Andreae and Gelencsér, 2006;Buseck et al., 2014). In the following sections, we use the term “soot” for the classification of particle types and the term “black carbon” for the discussion of the climate issues. Mineral particles come from construction activities, resuspended road dust, and natural soil. Among these types of particles, soot, POM, fly ash, mineral, and metal particles were refractory under electron beams and were thus termed as refractory particles (Ebert et al., 2016).

Based on the composition and mixing state of internally mixed particles (Figs. 4 and 5), they can be further classified into four categories: S-mineral (Figs. 4a and 5a), S-soot (Figs. 4b and 5b), S-fly ash/metal (Figs. 4c and 5c), S-fly ash/metal-soot (Figs. 4d and 5d). Here, these four types of particles with refractory inclusions are generally defined as "S-refractory" particles.

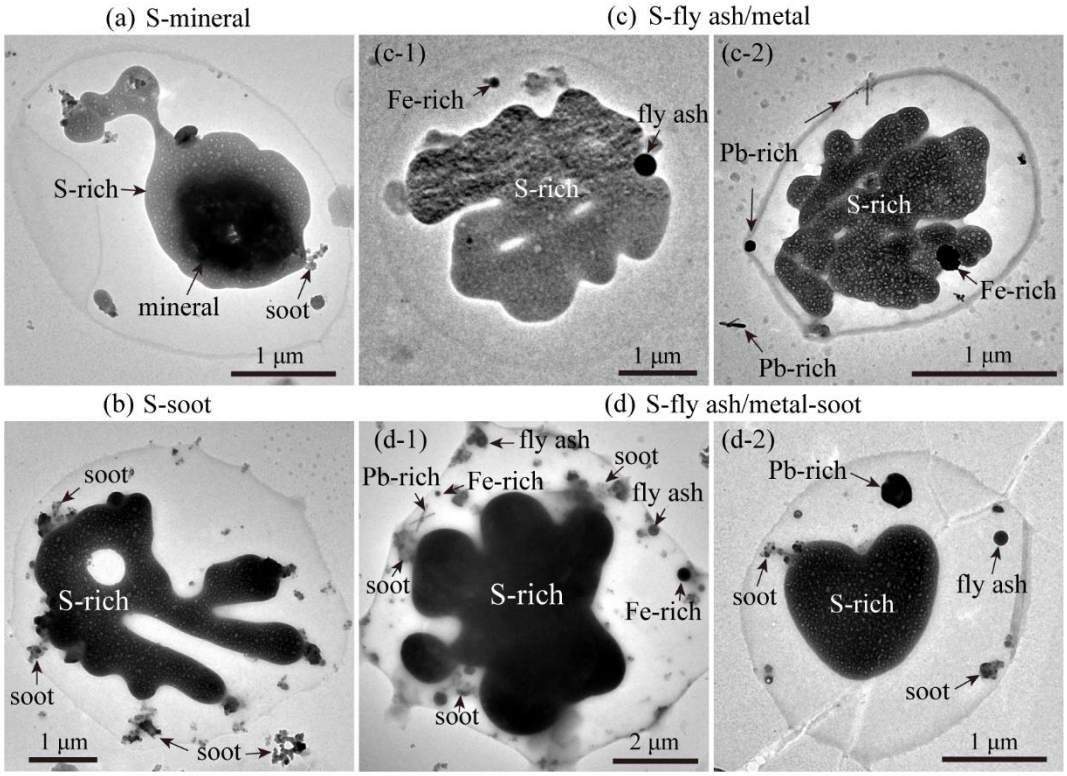


Figure 4. Typical TEM images of individual internally mixed cloud RES particles: (a) a mixture of S-rich and mineral; (b) a mixture of S-rich and soot; (c) a mixture of S-rich and fly ash/metal; (d) a mixture of S-rich, soot, and fly ash/metal.

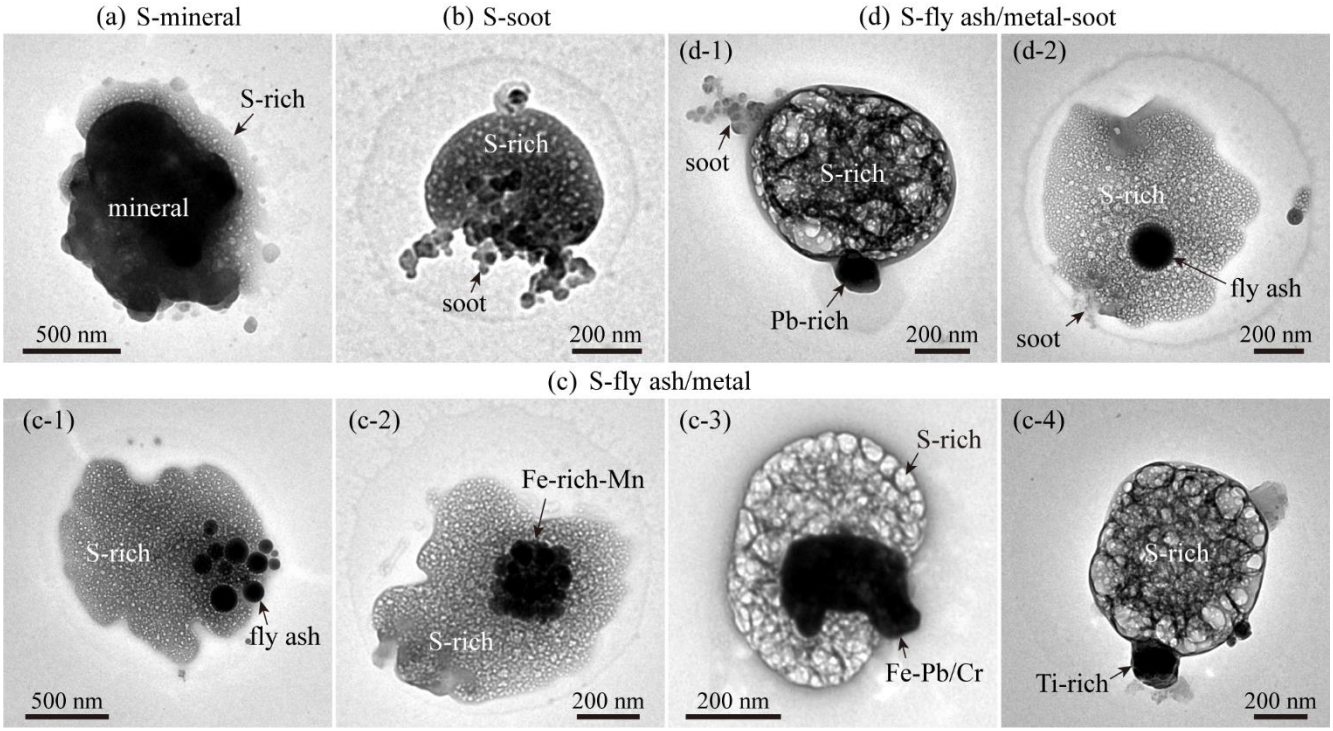
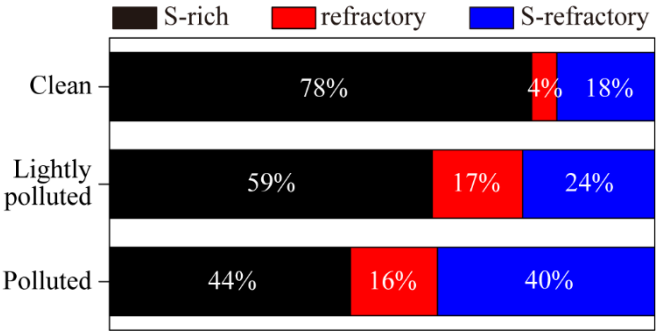


Figure 5. Typical TEM images of individual internally mixed cloud INT particles: (a) a mixture of S-rich and mineral; (b) a mixture of S-rich and soot; (c) a mixture of S-rich and fly ash/metal; (d) a mixture of S-rich, soot and fly ash/metal.

Figure 6 shows number fractions of S-rich, refractory, and S-refractory particles in clean, lightly polluted, and polluted periods on Mt. Tai. In clean periods, S-rich particles had the highest proportion (78%), followed by a 22% contribution of the refractory and S-refractory particles. This may be attributed to the clean air masses that originated from the clean marine area and arrived at the summit of Mt. Tai through high-altitude transport (above 1500 m) (Fig. 1). Because the air masses did not contact the ground surface, the local anthropogenic pollutants (e.g., soot, fly ash, and metal) could not be lifted to the summit of Mt. Tai. Hence, secondary particles like S-rich were dominant in the clean period. In the lightly polluted and polluted periods, the fraction of S-rich particles decreased to 59% and 44%, respectively; meanwhile, the fractions of refractory and S-refractory increased up to 41% and 56%, respectively (Fig. 6). The backward trajectories suggest that these air masses went through the most heavily polluted areas before they arrived at the mountaintop (Fig. 1). Air masses on two polluted days (e.g., 22 and 31 July) were lifted from ground level to the atmospheric boundary layer. Our study shows that number fractions of refractory and S-refractory particles significantly increased from clean to polluted periods (Fig. 6). This result shows that large amounts of primary refractory particles from

239 ground-level anthropogenic sources were lifted into the upper air and were further internally mixed with
240 S-rich particles.



241

242 **Figure 6.** Number fractions of S-rich, refractory, and S-refractory particles at different pollution levels.

3.3 Comparisons of cloud RES and INT particles

During the sampling period, a fog monitor was used to measure the size of cloud droplets during cloud events (Li et al., 2017a). This study reveals that in the cloud events all the cloud droplets displayed particle size larger than 2 μm in which size range the interstitial particles were absent. Based on their different size, we can know that these cloud droplets and interstitial particles impacted on different positions on the substrate. Although cloud droplets and interstitial particles became dry after the collection, they can still be identified based on the distribution and morphology of individual particles in TEM images (Li et al., 2011a;Ueda et al., 2014;Zhang et al., 2006;Kojima et al., 2004). Cloud RES display larger size and large rims around their CCN (Figs. 2 and 4) which has not been observed in non-cloud events. In contrast, cloud INT impacted on the position away from the center of sampling spot and their morphology looks like individual particles collected in non-cloud events. According to the rule, we can identify cloud RES and cloud INT in the samples collected during the cloud events.

Figure 7a shows that 100% of cloud RES and 83% of cloud INT contained S-rich species (i.e., S-rich and S-refractory). In other words, none of cloud RES were soot, fly ash/metal, and mineral particles but 17% of cloud INT were. Soot particles mainly distributed in the finer size bins (< 600 nm) of cloud INT (Fig. S3a). Interestingly, we found that 76% of cloud RES were a mixture of sulfates and refractory particles, which is 3.5 times of 22% in cloud INT (Fig. 7a). Furthermore, 26% of cloud RES had two or more types of inclusions (i.e., S-fly ash/metal-soot in Figs. 4d and 5d) but only 3% of cloud INT did. Therefore, we can conclude that cloud RES are extremely complex mixtures formed when cloud droplets act like a collector to scavenge these refractory particles.

The size-resolved number fractions of different particle types in cloud RES and cloud INT indicate that S-rich particles were predominant from 60 nm to 1.2 μm in cloud INT (Fig. S3a), and S-refractory particles (indicated by the red box) dominated from 400 nm to 5.5 μm in cloud RES (Fig. S3b). Figure 7b shows that the median diameters of cloud RES and cloud INT were 1.19 μm and 422 nm, respectively. The size of cloud RES was much larger than that of cloud INT, suggesting that size is an important factor affecting the CCN ability (Dusek et al., 2006).

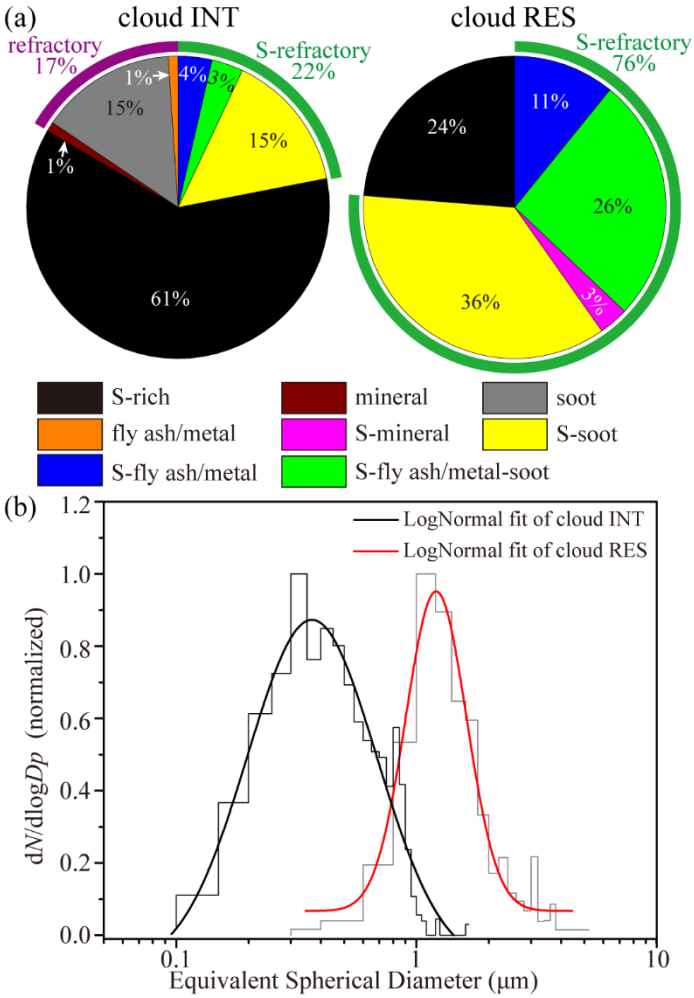


Figure 7. Number fractions of different particle types in cloud RES and INT particles (a) and size distributions of cloud RES and cloud INT particles (b). The measured particle sizes exclude the effects of water rims in TEM images. In total, 292 cloud RES and 1161 cloud INT particles were analyzed.

4. Discussion

TEM observations in this study reveal that cloud RES contained large amounts of refractory-containing particles primarily emitted from various anthropogenic sources in the heavily polluted NCP. As much as 76% of cloud RES were identified as S-refractory particles (Fig. 7a). We found that soot-containing particles (i.e., S-soot and S-fly ash/metal-soot) were the most abundant (62%) among the cloud RES, followed by the relatively abundant fly ash/metal-containing particles (i.e., S-fly ash/metal and S-fly ash/metal-soot, 37%) compared with 18% and 7% in the cloud INT, respectively (Fig. 7a). Although these refractory particles such as soot with hydrophobic properties could not be CCN directly, they can be easily accumulated by the existing cloud droplets as inclusions (Zuberi et al., 2005). In the heavily polluted NCP, large amounts of soot and fly ash/metal particles are released from anthropogenic sources (e.g., industrial activities and vehicular exhaust). During cloud events, abundant

refractory particles can be efficiently entrained into existing liquid cloud droplets by wet scavenging. Li et al. (2011a) reported that particle number decreased dramatically during cloud formation at Mt. Tai with a scavenging ratio of 0.54, which demonstrated that aerosol particles could efficiently be incorporated into cloud droplets. Physical coagulation of interstitial particles with cloud droplets is an important process in developing clouds, which can lead to the reduction of cloud INT number and a size increase of cloud RES after the cloud dries (Pierce et al., 2015). As we know so far, the extremely complicated mixture of secondary and primary particles observed in the present study has seldom been found in cloud droplets in clean air over developed countries (Ueda et al., 2014;Schneider et al., 2017;Hao et al., 2013;Kojima et al., 2004), remote areas (Hiranuma et al., 2013), and ocean (Twohy and Anderson, 2008;Hopkins et al., 2008;Zhang et al., 2006). For example, Zhang et al. (2006) reported that S-rich particles were predominant in the cloud RES with a small number fraction of sea salt particles over the Sea of Japan and soot or fly ash/metal particles were not observed. The present study reveals that individual cloud droplets are a far more complicated system in polluted air in North China than in the pristine continental and clean ocean air of the world.

The cloud properties such as albedo and lifetimes could be largely modified by the aerosol-cloud interactions, especially in heavily polluted regions (Wang et al., 2010;Wang et al., 2013). The model simulation revealed that black carbon aerosols had a noticeable impact (up to nearly 20%) on cloud droplet number concentration in polluted black carbon source regions (Cherian et al., 2017). Especially, abundant black carbon particles incorporated into cloud droplets could lead to a decrease in cloud albedo by absorbing radiation and an increase of temperature in troposphere, then accelerate the evaporation of the cloud droplets (Zuberi et al., 2005;Ackerman et al., 2000;Adachi et al., 2010;Wang et al., 2013). In the past few decades, precipitation was significantly reduced over east-central China due to the large amounts of anthropogenic aerosols (Zhao et al., 2006;Qian et al., 2009). Because an excess of aerosols in clouds could reduce precipitation, the non-precipitating clouds in the NCP tend to evaporate back to aerosol particles by solar radiation. It is highly probable that abundant black carbon particles presenting in the cloud droplets in the heavily polluted NCP in this study (e.g., particle 1 and 2 in Fig. 8) significantly affected the cloud properties and regional climate.

Fly ash and metal particles are a typical “fingerprint” pointing to the coal-fired power plants and boilers in factories and heavy industries (e.g., steel plant and smelting factory) (Chen et al., 2012;Moffet et al., 2008;Li et al., 2016a). Indeed, the most intense emissions from various industries in the world

315 occur in Hebei and Shandong provinces in the NCP (Qi et al., 2017). It is well known that these
316 industrial activities continuously release anthropogenic pollutants via high stacks into the upper air. Liu
317 et al. (2012) reported that the concentration of Zn reached 249.1 μg L^{-1} in the cloud/fog water samples
318 at Mt. Tai, followed by Al (157.3 μg L^{-1}), Fe (105.8 μg L^{-1}), Pb (46.2 μg L^{-1}), and Mn (42.8 μg L^{-1}),
319 which were extremely higher than those values reported at Mt. Schmücke in Germany (Fomba et al.,
320 2015). Combining these results with our present study, we infer that fine primary particles emitted from
321 these industrial activities might spread and be lifted to the upper air more easily than at ground level.
322 These metal particles, especially Pb and Zn of nanometer size, can harm ecosystems and human health
323 (Roberts et al., 2004). The fly ash and metal particles incorporated into cloud droplets (e.g., particle 1 in
324 Fig. 8) could go through the atmospheric acid Fe dissolution processes during long-range transport
325 reported by Li et al. (2017b). If they were further transported to remote oceanic regions, soluble Fe
326 species in the aerosol particles can fertilize plankton on the surface of ocean (Li et al., 2017b;Ito and Shi,
327 2016). Therefore, these anthropogenic fly ash/metal particles in polluted air contaminate cloud droplets
328 and further amplify potential impacts of fine metal particles on the biogeochemical cycle in the
329 troposphere.

330 Some studies suggested that the aqueous oxidation of SO_2 to sulfate by H_2O_2 and O_3 in cloud
331 droplets was dominant at Mt. Tai (Shen et al., 2012). However, cloud water collected on Mt. Tai
332 contained high concentrations of soluble Fe, Mn, Zn, and Pb (Liu et al., 2012). These soluble metals in
333 cloud droplets are released from aqueous reactions between metal particles and acidic sulfates in cloud
334 droplets (Li et al., 2017b). Harris et al. (2013) estimated that the oxidation of SO_2 in cloud droplets
335 catalyzed by natural transition metal ions (TMIs) in mineral dust was dominant at Mt. Schmücke in
336 Germany. For this study, how the soluble anthropogenic TMIs drive sulfate formation through TMI
337 catalysis in micro-cloud droplets is still unresolved in polluted air. We propose that anthropogenic TMI
338 catalysis contributing to sulfate production should be further studied in cloud droplets in the polluted
339 NCP.

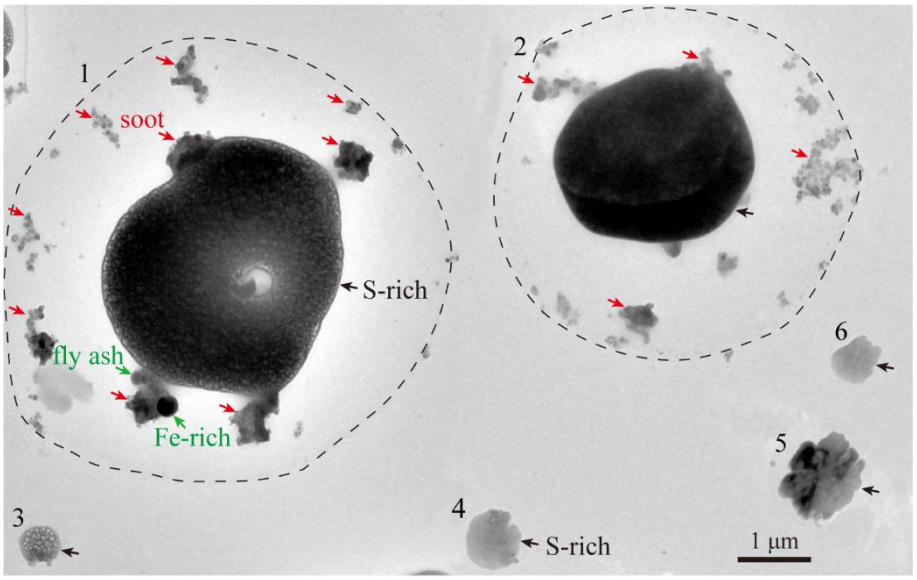


Figure 8. TEM image of cloud RES and INT particles collected during the cloud event occurred on the polluted day of 31 July. Particle 1 and 2 are cloud RES and particle 3, 4, 5, and 6 are cloud INT. The dashed lines indicate the water rims that were left after the cloud droplets impacting on the substrate become dry.

The non-precipitating cloud processes over the polluted air of NCP quickly change the mixing state and composition of aerosol and cloud droplets in the upper air, potentially causing various effects such as human health, regional climate, and biogeochemical cycle at the larger regional scale. To better understand the aerosol-cloud interactions in this study, we offer the conceptual model of Fig. 9. The tall stacks of plants can emit smoke plumes that contain fine refractory particles and gaseous pollutants to the upper air. A portion of particles in urban areas can also be lifted to the mountaintop by prevailing valley winds. Once the clouds form on a mountaintop (or later are transported in other directions), these cloud droplets act as collectors to scavenge the refractory particles. These refractory particles as inclusions might complicate the cloud chemistry in micro-cloud droplets. Gaseous pollutants such as SO_2, NO_x, and VOCs may have enhanced aqueous oxidation potential in the complex cloud droplets. Our study is designed to better understand the aerosol-cloud interactions on the mountaintop in polluted industrial and urban areas. Recently, a study showed that the major aerosol pollution events with very high fine mode AOD (>1.0 in mid-visible) in the China-Korea-Japan region are often observed to be associated with significant cloud cover (Eck et al., 2018). Therefore, we expect that large amounts of fine refractory particles from polluted areas scavenging in clouds have important impacts not only at

local but also in large regional scale.

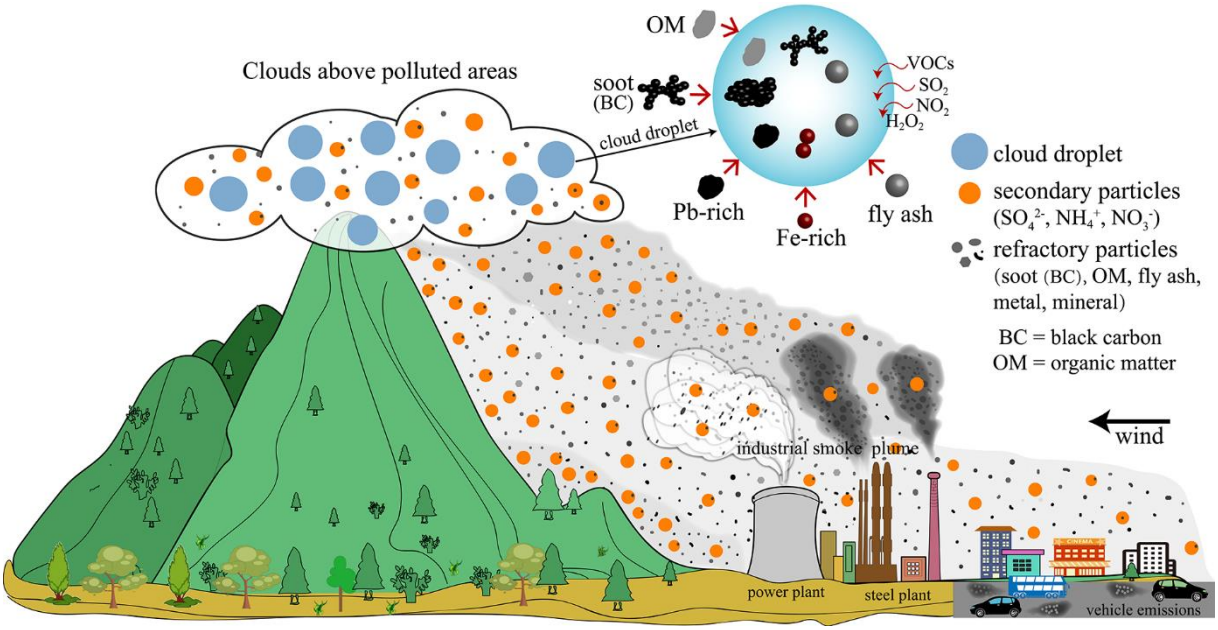


Figure 9. A conceptual model illustrating mechanisms of aerosol-cloud interactions on mountaintop influenced by anthropogenic pollutants from heavy industrial and urban emissions.

5. Conclusions

Individual aerosol particles were collected during cloud events on Mt. Tai from 22 July to 1 August, 2014. Cloud RES and INT particles were separated by their distribution on TEM grids and their composition was identified by TEM/EDS. Individual particles were classified into S-rich, refractory (i.e., mineral, soot, fly ash/metal) and S-refractory (i.e., S-mineral, S-soot, S-fly ash/metal, and S-fly ash/metal-soot). According to air mass backward trajectories and $PM_{2.5}$ concentrations on Mt. Tai, the entire sampling period was divided into three classes: a clean period ($PM_{2.5}$ < 15 μg m^{-3}), a lightly polluted period (15 μg m^{-3} < $PM_{2.5}$ < 35 μg m^{-3}), and a polluted period ($PM_{2.5}$ > 35 μg m^{-3}). In the clean period, individual particles were dominated by S-rich particles (78%), whereas the fraction of refractory particles and S-refractory particles increased significantly and dominated during the polluted periods. This suggested that anthropogenic pollutants from tall stacks of coal-fired power plants and heavy industries and vehicular exhaust in cities could be lifted to the summit of Mt. Tai under the prevailing southerly winds in summer.

TEM observations showed that 76% of cloud RES were S-refractory particles contaminated by anthropogenic refractory particles, compared with only 22% of cloud INT. Cloud RES displayed a larger size than cloud INT, which indicates that particle size decidedly affects CCN ability. Our study

reveals that large amounts of anthropogenic refractory particles were incorporated into cloud droplets through in-cloud processes. Especially important is that abundant black carbon particles in cloud droplets could alter radiative forcing of clouds and accelerate the evaporation of cloud droplets. The high concentrations of transition metal ions might favor the aqueous-phase oxidation of SO_2 by O_2 in cloud droplets under the heavily polluted conditions in the NCP. Fly ash/metal-containing cloud droplets could be transported long distance and harm ecosystems and human health through wet deposition. We propose a conceptual model to show the aerosol-cloud interactions on mountaintops influenced by heavily polluted air.

Data availability. All data presented in this paper are available upon request. Please contact the corresponding author (liweijun_atmos@gmail.com).

Competing interests. The authors declare that they have no conflict of interest.

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