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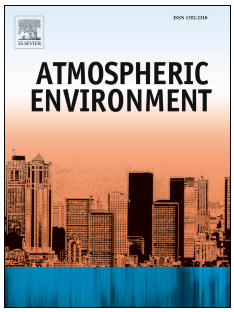

Composition and hygroscopicity of aerosol particles at Mt. Lu in South China: Implications for acid precipitation

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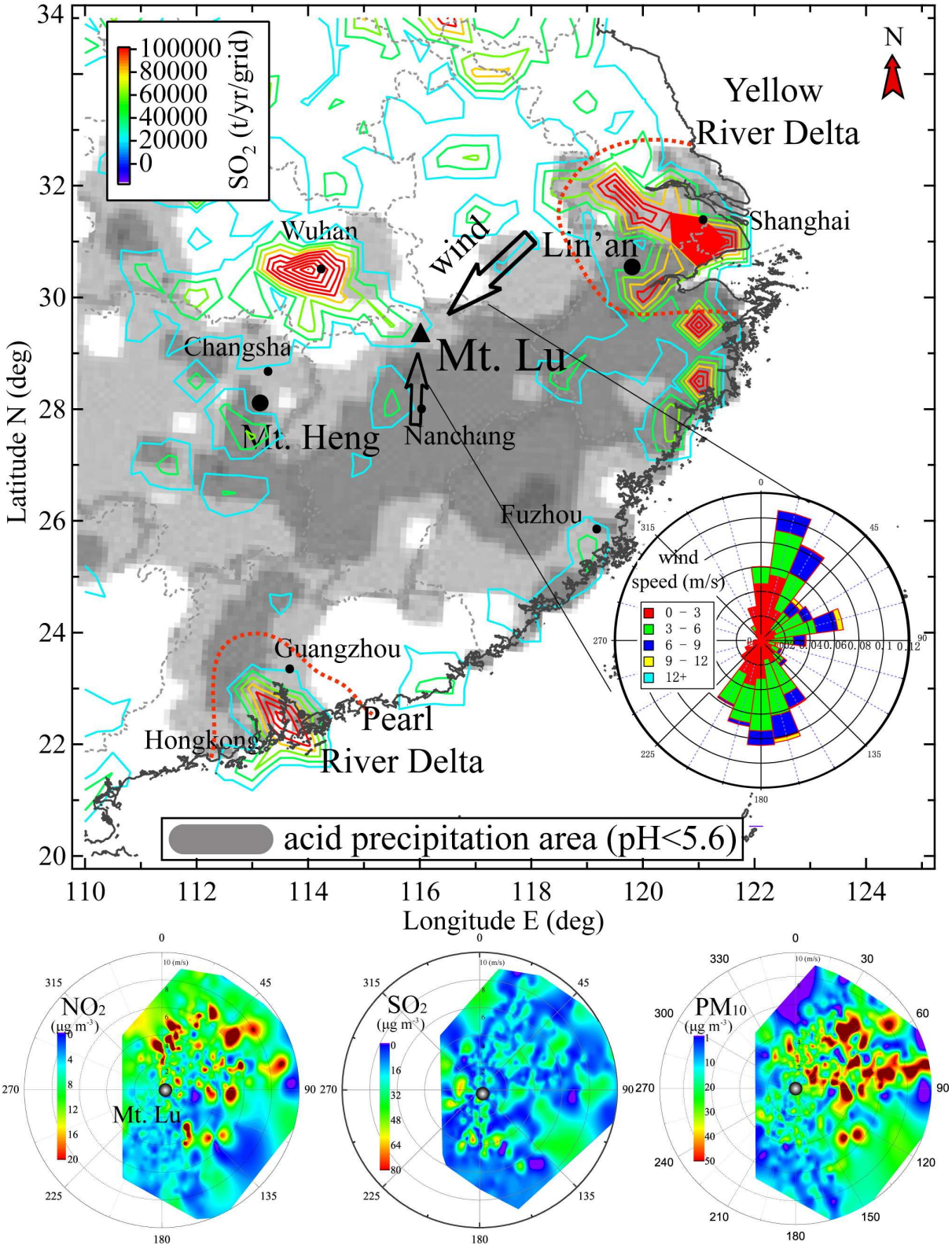
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SO2 (t/yr/grid)
N
Yellow
River Delta
Shanghai
Wuhan
wind
Lin'an
Mt. Lu
Changsha
Mt. Heng
Nanchang
Fuzhou
wind
speed (m/s)
0 - 3
3 - 6
6 - 9
9 - 12
12+
Guangzhou
Pearl
River Delta
Hongkong
acid precipitation area (pH<5.6)
Latitude N (deg)
Longitude E (deg)
NO2
(μg m-3)
Mt. Lu
SO2
(μg m-3)
PM10
(μg m-3)

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Composition and hygroscopicity of aerosol particles at Mt. Lu in South China: Implications for acid precipitation

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Abstract: Physicochemical properties of aerosol particles were studied at Mt. Lu, an elevated site (115°59′E, 29°35′N, 1,165 m) within the acid precipitation area. Northeast winds transport copious amounts of air pollutants and water vapor from the Yangtze River Delta into this acid precipitation area. NH_4^+ and SO_4^{2-} are the dominant ions in $PM_{2.5}$ and determine aerosol acidity. Individual particle analysis shows abundant S-rich and metals (i.e. Fe-, Zn-, Mn-, and Pb-rich) particles. Unlike aerosol particles in North China and urban areas, there are little soot and mineral particles at Mt. Lu. Lack of mineral particles contributed to the higher acidity in precipitation in the research area. Nano-sized spherical metal particles were observed to be embedded in 37% of S-rich particles. These metal particles were likely originated from heavy industries and fired-power plants. Hygroscopic experiments show that most particles start to deliquesce at 73-76% but organic coating lowers the particle deliquescence relative humidity (DRH) to 63-73%. The DRHs of these aerosol particles are clearly smaller than that of pure ammonium sulfate particles which is 80%. Since RH in ambient air was relatively high, ranging from 65% to 85% during our study period, most particles at our sampling site were in liquid phase. Our results suggest that liquid phase reactions in aerosol particles may contribute to SO_2 to sulfuric acid conversion in the acid precipitation area.

Keywords: acid precipitation, hygroscopicity, aerosol formation, individual particle

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1. Introduction

Airborne pollutants are deposited on the earth's surface by 1) wet deposition (rain and snow); 2) dry deposition (particles and gases). Acting as condensation cloud nuclei (CCN) and ice nuclei (IN), aerosol particles influence the climate system indirectly by altering cloud microphysics and albedo (IPCC, 2007), hydrological balance (Ramanathan et al., 2001), and the ecosystem (Bormann, 1985). In the past two decades, rapid industrialization and urbanization in China have contributed large quantities of anthropogenic pollutants into the atmosphere.

Recently, research activities in China has been directed to understand the formation of haze-fog events in East China, with the Chinese government starting to improve air quality in the megacities (Zhang et al., 2012). On the other hand, acid precipitation has been to some extent overlooked, even though it covers 12.9% of the continental area of China (AEAERC, 2011). The world's third largest acid rain area has emerged in this region in the past thirty years, following Europe and North America (Galloway et al., 1987; Wang and Wang, 1995; Li et al., 2010b; Tang et al., 2010). The impact of anthropogenic air pollutants on precipitation composition and the subsequent effects on aquatic and terrestrial ecosystems have been well recognized in North America, Scandinavia, South China, and Europe over the past decade (Bormann, 1985; Galloway et al., 1987). Progress report from the U.S. Environmental Protection Agency (EPA, 2006) showed that the developed countries in past decades that have pursued the tenets of the Clean Air Act have substantially reduced the size of the acid precipitation area. Conversely, in South China the acid precipitation area increased slightly and has been shown to occur throughout this period (Tang et al., 2010).

The largest, contiguous acid-impacted region is south of the Yangtze River, according to the AEAERC in 2011. Tang et al. (2010) suggest that the center of the severe acid rain area south of the Yangtze River moved eastwards to include Jiangxi and Zhejiang provinces. In the acidic cloud water or rain water of south China, SO_4^{2-} dominates followed by NH_4^+, NO_3^-, Ca^{2+}, Cl^-, F^-, K^+, Na^+, and Mg^{2+} (Lei et al., 1997; Cao et al., 2009; Huang et al., 2009; Huang et al., 2010; Li et al., 2010b; Sun et al.,

2010). Recently, Li et al. (2013b) showed that strongly acidic clouds (pH, ~3.5) cover Jiangxi province and form acid rain in summer. The study further suggested that the acidic cloud droplets enhance the soluble efficiency of nano-sized metals in clouds, which may lead to additional adverse impacts on the ecosystem and human health in South China.

Once aerosol particles act as CCN, chemical properties of individual aerosol particles can affect the acidity of the corresponding cloud droplet, thereby pointing out the importance of understanding the physicochemical properties of aerosol particles in the acid precipitation area. In particular, the chemical composition of aerosols among various size ranges is a key factor in determining their hygroscopicity, CCN activity, and optical properties (Hudson, 2007). Individual aerosol particles are a complex mixture of inorganic and organic species, and soluble and insoluble species contributed directly or indirectly by anthropogenic and natural sources (Li and Shao, 2009; Posfai and Buseck, 2010). When considering the influence of aerosol particles in one region, one first needs to understand their chemical composition and mixing state (Hudson, 2007; Twohy and Anderson, 2008; Posfai and Buseck, 2010; Adachi et al., 2011; Li et al., 2011a). Individual particle analysis by transmission electron microscopy (TEM) has become a reliable technique to characterize aerosol particles which range in size from nanometer to micrometer, as well as provide information on their sources, morphology, and mixing state (Li and Shao, 2009).

Hygroscopic characterization of aerosol particles has important implications for their environmental effects (Martin, 2000; Wise et al., 2009; Freney et al., 2010; Peckhaus et al., 2012). If aerosol particles contain highly hygroscopic species such as sulfates, nitrates, or soluble organic acids, they would take up water when the relative humidity (RH) is high enough and grow into cloud droplets at certain supersaturation conditions (Martin, 2000; Hudson, 2007). Water absorbing hygroscopic components can change both diameter and wavelength dependent refractive indices of individual particles (Lack et al., 2009; Adachi et al., 2011). Therefore, it is necessary to quantify the hygroscopicity of aerosol particles in acid precipitation areas with high RH.

The objective of this paper is to characterize the chemical composition and

hygroscopicity of individual aerosol particles in an acid deposition area in South China. In this study, aerosol samples were collected near the summit of Mt. Lu (115°59′E, 29°35′N, 1,165 m) in Jiangxi province, the center of the heavy acid precipitation area in South China. Chemical composition and mixing state of individual particles were investigated using transmission electron microscopy (TEM). We also studied the hygroscopicity of individual particles using a newly developed individual particle hygroscopic (IPH) system.

2. Experiments

2.1 Sampling site

Mt. Lu, covering an area of 300 km^2 (115°59′E, 29°35′N, 1,165 m), is located south of Jiujiang city in northern Jiangxi Province, China, between the Yangtze River and Boyang Lake. Mt. Lu is 700 km northwest of the Pearl River Delta (PRD) and 400 km southwest of the Yangtze River Delta (YRD) (Figure 1). Mt. Lu lies within the Asian humid continental and tropical monsoon climate zone, where cloud/fog and rain events are common from spring to autumn. Figure 1 shows that the Mt. Lu area is located within the acid precipitation area of South China. The town of Guling on top of Mt. Lu has a population of about 10,000; most residents work in tourism or related services, so relatively little local pollution is produced. There are some large steel and oil refining industries and coal-fired power plants in the YRD and non-ferrous mines associated with non-ferrous mining, smelting, and refining of pure metals in Jiangxi province. Therefore, the major SO_2 emission sources are located in the YRD but outside of Shanghai city.

2.2 Meteorology

The dominant wind direction below 1500 m during the summer season in South China is from the Northeast, which brings water vapor and pollutants into acid precipitation area (Figure S1-S4 in Supporting Information (SI)). The sampling was conducted during 11 August to 23 September, 2013. The average temperature and relative humidity (RH) were 23 ^oC and 80% during non-cloud periods, respectively. Thirty 48-h air mass back trajectories ending at Mt.Lu from 14 to 24 November were simulated by HYSPLIT model ((http://ready.arl.noaa.gov/HYSPLIT.php) (Figure S2). Most of air mass back trajecotries were from South and Northeast areas of Mt. Lu in

South China.

2.3 Aerosol sampling and analysis

Aerosol particles were collected on copper TEM grids coated with carbon film (carbon type-B, 300-mesh copper, Tianld Co., China) by a single-stage cascade impactor with a 0.5-mm-diameter jet nozzle and an air flow rate of 0.5 l min^{-1}. For these conditions, the calculated size (d_{50}) is ~ 0.5 μm (Marple et al., 1993). Because the air quality has small changes at Mt. Lu, each sampling time was set up at 4 min in non-cloud periods. Clouds or fog frequently occurred during our sampling period. After sample collection, we immediately used optical microscopy with magnification from ×500 to ×1200 to check whether the carbon film and aerosol distribution on the TEM grids were suitable for analysis. Then, the grid was placed in a sealed, dry plastic tube and stored in a desiccator at 25 ºC and 20 ± 3% RH to minimize exposure to ambient air and preserve it for analysis. Finally, nine samples collected in clear periods during 14 August - 23 September, 2013 were selected and analyzed by TEM.

Aerosol particles on the TEM grids were analyzed with a JEM-2100 TEM operated at 200 kV. Particles examined by TEM were dry at the time of observation in the vacuum of the electron microscope. The effects of water, semi-volatile organics, and NH_4NO_3 could not be considered. Elemental composition was determined semi-quantitatively by an energy-dispersive X-ray spectrometer (EDS) that can detect elements heavier than carbon. EDS spectra were collected for only 15 s to minimize radiation exposure and potential beam damage. Copper could not be analyzed because of interferences from the copper TEM grid. EDS data obtained from INCA software under channel 4-5. In this study, TEM images with magnification between ×2000 and ×5000 were quickly obtained from the center to the periphery of each sample. The procedure ensured that the aerosol distribution and morphology over the entire sample was obtained. To understand the morphology, composition, size, and mixing state of each aerosol particle, TEM images were taken and EDS was used to determine the composition of their component parts such as coatings, inclusions, and aggregates. In order to understand elemental distributions in individual aerosol particles, the elemental mapping experiments were conducted by the JEM-2100F TEM with a

scanning TEM (STEM) function. Equivalent circle diameter in two dimensions were determined using the iTEM software (Olympus soft imaging solutions GmbH, Germany) (Li et al., 2013a).

A MiniVol sampler (Airmetrics, USA) with a constant pumping rate of 5 l min^{-1} was employed to collect $PM_{2.5}$ on quartz-fiber filters for the analysis of soluble inorganics. Thirty $PM_{2.5}$ samples and two blank samples as the reference filters were collected in non-cloud periods from 11 August to 23 September, 2011. The sampling periods ranged from 4 hours to 23.5 hours depending on the cloudy and rainy periods in different days. In addition, we collected the cloud water during cloud or fog periods and cloud water was acidic, with a pH of 3.52 at Mt. Lu. The detailed information about cloud water can be found in Li et al. (2013b). The $PM_{2.5}$ samples were stored at refrigerator at Mt. Lu and were put in one icebox during the transportation from sampling site to our laboratory, which kept the temperature lower than 0 ^{o}C. Five cations (Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}) and five anions (F^-, Cl^-, NO_2^-, NO_3^-, and SO_4^{2-}) were quantified by ion chromatography (IC). Because of limitation from the IC detection, we only obtained concentration of nine ions (see section 3.2). The hourly mass concentrations of SO_2, NO_2, and PM_{10} were provided by an automatic environmental monitoring station, about 5 m from the sampling site. In this study, we obtained valid concentration data of PM_{10} (n = 1112 hours), SO_2 (972 hours), and NO_2 (493 hours) (Figure 1). Wind speed, wind direction, relative humidity (RH), barometric pressure, and ambient temperature were obtained from the local meteorological station. In this study, the wind vector maps in different altitudes in South China are shown in supplemental material (Figure S3-S4).

2.4 Hygroscopic experiments of individual aerosol particles

One individual particle hygroscopic (IPH) system was built for observing hygroscopic properties of individual particles at different relative humidities. The measurement system consisted of three steps: (1) Introducing wet and dry N_2 gas with controlled flow into one chamber, controlled by two mass control flow meters. (2) Setting the TEM grids with aerosols on the bottom of one stainless steel column chamber (size: 20mm (height)×30mm (diameter)) with two holes on top and bottom

side covered by two microscope slides. RH and temperature sensors of a digital hygrometer (Testo 645, ±1%) were inserted into the chamber from its side. (3) Obtaining images in different relative humidity through one inverted microscope (IBE2003, China) with a camera (Canon 650D). NaCl aerosols were generated from 1 M solutions. We used the same procedure from Wise et al. (2005) to make the standard samples in the laboratory. Laboratory-generated NaCl particles on TEM grids were used to calibrate the system (Figure S5). Detailed descriptions of the similar measurement system were given by Ahn et al. (2010). Similar IPH systems have successfully observed hygroscopic growth observations of field-collected and laboratory-generated aerosols with the diameter larger than 0.5 μm (Ahn et al., 2010; Peckhaus et al., 2012; You et al., 2012). Here two samples of particles with organic coating and particles with non-coating were chosen to observe particle hygroscopic growth. The IPH system observed the particle deliquescence and efflorescence at the RH range from 3% to 90% under one stable room temperature at 20 ^{o}C.

3. Results and discussion

3.1 Transport of gas and aerosol pollutants

Wind direction and wind speed are the most important factors for transport of air pollutants in the troposphere. Examining wind direction, wind speed, and pollutants at Mt. Lu, Figure 1 shows two major transport paths: from the northeast and from the south. Figure S3 shows that mean wind in August and September is from the northeast. These results were consistent with 48-h air mass back trajectories as shown in Figure S2. The northeasterly wind apparently brought air pollutants and water vapor from the coastal YRD into the acid precipitation area. 42% (by hour) PM_{10} data, 46% SO_2, and 42% NO_2 occur with northeast winds, with their average hourly concentrations at 28 μg m^{-3}, 16 μg m^{-3}, and 11 μg m^{-3}, respectively (Figure 1). Wind rose data (bottom of Figure 1) also showed a possible source of PM_{10} from the northeast direction, that is, the YRD. The southerly wind possibly brought air pollutants from Jiangxi province. 37% PM_{10} data, 31% SO_2, and 37% NO_2 occur from northeast winds, with their average hourly concentrations at 15 μg m^{-3}, 17 μg m^{-3}, and 5 μg m^{-3}, respectively. Figure 1 also shows that the SO_2 emission sources, including heavy industries and

coal-fired power plants, lie within the YRD, indicating that air pollutants from the northeast could have contributed to the air pollution on Mt. Lu. The SO_2 wind rose data did not show any particular emission source in the major wind directions. The reason can be attributed to its relatively short lifetime of SO_2 or the region emission sources.

3.2 Soluble inorganic ions in $PM_{2.5}$

Nine inorganic ions were quantified in 35 $PM_{2.5}$ samples. Figure 2 shows that the highest inorganic ion is SO_4^{2-} with a concentration of 18.4±8.0 μg m^{-3}, close to the 17.2 μg m^{-3} at the regional background station of Lin'an and more than two times higher than that at Mt. Heng in Hunan province (Xu et al., 2002; Gao et al., 2012). Sun et al. (2010) showed that SO_4^{2-} was the dominant anion, followed by NO_3^-, both of which control the acidity of cloud water at Mt. Huang in spring.

Interestingly, the mass concentration of NO_3^- at 0.71 ± 0.99 μg m^{-3} is lower than 1.5 μg m^{-3} at Mt. Heng (Gao et al., 2012). The partition of NO_3^- between the gas and particulate phases strongly depends on temperature, with lower temperatures favoring the partition of ammonium nitrate in the particulate phase. Indeed, air temperatures ranging from 19 ^oC to 29 ^oC at Mt. Lu in this study are much higher than the springtime temperatures at Mt. Heng (9.8 ^oC to 16.3 ^oC). Figure 2 shows that NH_4^+ at 6.68±3.3 μg m^{-3} is the major cation to neutralize acidic components. Additionally, K^+ concentration at 0.65±0.22 μg m^{-3} at Mt. Lu is higher than 0.43 μg m^{-3} at Mt. Heng reported by Gao et al.(2012), who suggested that biomass burning contributed potassium salts in the atmosphere over the precipitation area. The average cation/anion (C/A) ratio is 0.94 in $PM_{2.5}$ samples, suggesting that ammonium sulfate could be the dominant component in the $PM_{2.5}$.

Soluble ions of 54 cloud water samples show that SO_4^{2-} dominated 30% of the total ions in cloud water, following by NH_4^+ (24%) at Mt. Lu during this period (Yang, 2013). Therefore, SO_4^{2-} is the dominant acidic ion in both aerosol particles and cloud droplets and contribute to the acidity of cloud water and rain at Mt. Lu in summer.

3.3 Main individual particle types

Based on elemental composition and morphology of individual particles, we

identified six different particle types: S-rich, metal (including fly ash), organic matter, soot, K-rich, and mineral. S-rich particles were a dominant aerosol type in all size ranges, which are internally mixed with metal, organic matter, soot, K-rich, and mineral (Figure S6). The result is consistent with the SO_4^{2-} as the dominant ion in $PM_{2.5}$. In the internally mixed particles, various metal particles were embedded within individual S-rich particles, and secondary organic matter coated onto the surface of S-rich particles, as shown in Figure S6 and Figure 3. These observations are consistent with previous studies (Li et al., 2013b) where large amounts of nano-sized metal particles were measured in the atmosphere at Mt. Lu.

3.3.1 Sulfates

S-rich particles contained S and O, with certain amounts of K, Na, C, and N (Figure 3a). S-rich particles at Mt. Lu could be mainly composed of $(NH_4)_2SO_4$ and minor $(NH_4)HSO_4$, organic matter, and K_2SO_4. Although TEM analysis cannot give nitrate information, NH_4NO_3 cannot be excluded in this study according to the soluble ions in $PM_{2.5}$ shown in Figure 2. Many studies already show that individual secondary particles commonly contain ammonium sulfate and ammonium nitrate in the atmosphere (Whiteaker et al., 2002; Middlebrook et al., 2011; Hao et al., 2013). As a result, we can speculate that individual secondary particles could mainly contain sulfates with other minor particle species.

The second dominant type of S-rich particles contain certain amounts of K (Figure 3b). The fraction of K in S-rich particles is lower than K_2SO_4 in Figure 3c. We suggests that certain amounts of potassium salts coexisted in secondary sulfate particles, which has been commonly observed in cloud droplets at Mt. Lu (Li et al., 2013b). TEM analysis revealed that this kind of S-rich particle significantly contributed soluble K^+ to $PM_{2.5}$ shown in Figure 2. We also found that the S-rich particles were coated frequently by organic matter. Li et al. (2010a) observed similar particles in Beijing air influenced by agricultural biomass burning. In the present study, only small numbers of K_2SO_4 particles were shown in Figure 3b and abundant S-rich particles with minor K were founds at Mt. Lu. Here we can presume that particles (e.g., KCl and K_2SO_4) from biomass burning can transform into S-rich

particles with certain amounts of K through processing in cloud droplets or condensations of SO_2 and H_2SO_4.

3.3.2 Metal particles

Numerous metal particles occurred at Mt. Lu and were internally mixed with S-rich particles (Figure 4). One low-magnification TEM image displays ten S-rich particles, six of which include metal inclusions confirmed by EDS. Many metal particles look like an aggregation of several metal particles. Since small sized metal particles have a higher density, they are darker than other aerosol particle types and are therefore easy to be identified. For example, Figure 5 shows two dark dots in the S-rich particle and their composition reveals two metal particles (Fe-rich and Pb-rich). Li et al. (2013b) found four major metal types at Mt. Lu in cloud droplets: Pb-rich (35%), fly ash including minor metals (27%), Fe-rich (23%), and Zn-rich (15%). We still found that Pb, Fe, and Zn in metal particles were the dominant elements in aerosol particles. These metal particles exhibit a nearly spherical shape (e.g., Figure 5), suggesting that they likely come from industrial processes and coal-fired power generation via high-temperature combustion followed by fast cooling (Giere et al., 2006). There are various large steel and oil refining industries and coal-fired power plants in YRD and many non-ferrous smelting industries are distributed throughout Jiangxi province.

Li et al. (2013b) show that acidic cloud droplets can dissolve nano-sized metal particles into sulfates. We carefully examined the composition of individual metal-bearing particles. In this study, we found that 37% of S-rich particles had metal inclusions. For example, Figure 6 shows the Sn-O and Pb-S particles were internally mixed with S-rich particles. Once this kind of aerosol particles act as CCN, SO_2 oxidation catalyzed by metal ions could be the dominant in-cloud oxidation pathway (Harris et al., 2013).

3.3.3 Soot and mineral particles

Many studies showed that soot and mineral particles were the major particle types in the atmosphere and were commonly found in aerosol samples collected at mountain site and ground level (Li and Shao, 2009; Posfai and Buseck, 2010; Li et al., 2011b).

TEM analysis display a rather low number of soot and mineral particles at Mt. Lu (Figure 7). The typical soot particles in Figure S6g were difficult to be found at Mt. Lu and some tiny soot particles were internally mixed with organic or sulfate (Figure 3c). A few elongate regular $CaSO_4$ were detected in the samples but the $Ca(NO_3)_2$ coated on mineral particles occurring at Mt. Tai and urban cities in North China (Li and Shao, 2009) had been not found at Mt. Lu. In addition, some mineral particles mixed with metal particles as shown in Figure S6e occurred in fine and coarse particles. Such mixed mineral particles were considered as the emissions of industries and fired-power plant instead of natural soil.

3.3.4 Organic matter

Most organic matter was internally mixed with secondary particles at Mt. Lu. Most organic aerosols can not be clearly identified in secondary particles (Figure 3a) although some can be identified as the organic coatings (Figure 3b-c). Therefore, we classified the internally mixed particles of organic and sulfate in Figure 3b as S-rich particle type. Only small number of particles in the samples at Mt. Lu were dominated by organic matter, as shown in Figure S4a.

3.4 Size and mixing of different particle types

Figure 7 shows the relative abundance of 1634 particles from 80 nm to 4 μm. The S-rich particles account for 82% of all analyzed particles and are the dominant particle type in all size bins. 46% of 1388 analyzed S-rich particles were defined as internally mixed particles that include fly ash, metal, soot, or mineral, except for the organic matter that cannot be clearly identified (Figure 5). Although 18% particles were not classified as S-rich particles, they still contained certain amounts of sulfates. In all, morphology, composition, and mixing state of individual particles at Mt. Lu in South China were more homoneneous than those at Mt. Tai (1535m) in North China (Li et al., 2011b). In addition, only 6% of S-rich particles contained soot inclusions at Mt. Lu are much lower than at Mt. Tai in North China where 72% to 83% of S-rich particles included soot inclusions (Li et al., 2011b). The low percentage of soot and mineral particles at Mt. Lu differs from the aerosol distribution in North China where soot and mineral particles were dominant in sizes smaller than 1 μm and larger than 2

μm (Li and Shao, 2009; Li et al., 2011b). In addition, 6% and 3% of 1388 S-rich particles mixed soot and mineral particles.

3.5 Hygroscopic properties of individual particles

Hygroscopic properties of individual particles from two different samples exhibit different hygroscopic growth factors. Figure 8a shows that particles collected on 4 September begin to grow at 73-76% with the average grow factor (GF) at 1.006 and that dramatic growth occurs at 80% with the average GR at 1.13. Figure 8b shows that particles collected on 5 September begin to grow at 63-73% with the average GR at 1.04 but that part of them display dramatic growth at 80% with the average GR at 1.23. The dramatic changes of growth factor at 80% suggest that these secondary particles completely transformed from solid phase to liquid phase in two samples. When the humidity increase 90%, the GR values increase the largest at 1.26 in Figure 8a and 1.38 in Figure 8b. Additionally, the particles in these two samples have similar dehydration curves with the efflorescence RH (ERH) at 49-53%. Although the particles in the two samples have similar DRH and ERH, they exhibit different hygroscopic growth trends.

A number of studies have shown that hygroscopic properties of aerosol particles are dependent on their chemical composition (Martin, 2000; Choi and Chan, 2002; Shi et al., 2012). Figure 2 shows that SO_4^{2-} is the dominant ion in fine particles, consistent with the dominant S-rich particles found in individual particle analysis. Individual ambient particles normally start to deliquesce at lower RH than the DRH at 80% of the pure $(NH_4)_2SO_4$. This result can be attributable to the mixtures of two or more inorganic species (e.g., $(NH_4)_2SO_4$, $(NH_4)HSO_4$, K_2SO_4, or NH_4NO_3) within the same individual particles (discussed in section 3.3.1) (Freney et al., 2009). In particular, particles shown in Figure 8b start to deliquesce at 63-73% -- much lower than those at 73-76% shown in Figure 8a. The ion analysis and TEM observations together showed similar inorganic ions and particle types, but TEM images revealed thin organic layers coated on some particles in Figure 8b. Soluble organic species in the internally mixed particles may cause the water absorption of organic materials at low RH than inorganic materials (Varutbangkul et al., 2006) and change the

hygroscopic growth of aerosol particles (Brooks et al., 2002; Choi and Chan, 2002). Therefore, the soluble organic coatings probably induce the early deliquescence of individual particles. Shi et al. (2012) showed that the internally mixed $(NH_4)_2SO_4$-benzoic acid particles display deliquescence earlier than the DRH of pure $(NH_4)_2SO_4$ particles. Also, the ratio of organic and inorganic ions in individual particles determines their deliquescent transitions (Peckhaus et al., 2012). These results suggest that soluble organic coatings and mixtures of multi-inorganic species account for the lower DRH of individual particles at Mt. Lu compared to that of ammonium sulfate.

The ambient RH during the sampling periods ranged from 65% to 85%. Based on the hygroscopic experiments, we conclude that the some or all the aerosol particles in non-cloud periods suspended as the liquid phase or liquid-solid phase while suspended in air. Therefore, the liquid water around the deliquesced particles provide an important media for gaseous SO_2 to sulfate conversion.

3.6 Implications of acid precipitation

Heavy acid precipitation in South China mostly occurs in highland areas with altitudes of 500-1500 m, where SO_2 emissions are low (Figure S3). Figure 1 shows the largest and highest intense SO_2 emissions in South China in the YRD, one area that is upwind of Mt. Lu in summer. The dominant wind is from the east during sampling periods; therefore, the SO_2 emissions could be readily transported into the acid precipitation area and be transformed into secondary sulfates. Large amounts of secondary particles dominated by SO_4^{2-} can be formed during long-range transport and can further be CCN in acid clouds. Based on the composition and hygroscopicity of aerosols in the present study and results from Harris et al. (2013), we summarized the SO_2 oxidation during long-range transport in Figure S7a. Liquid layer formation on secondary particles due to early deliquescence probably enhance SO_2 oxidation through heterogeneous reactions in multiphase environment (Ravishankara, 1997).

Compared to small amounts of mineral and soot particles from ground-level sources such as road dust, ground soil, and vehicle emissions, the abundant metal particles at Mt. Lu suggest that the large amounts of gaseous and particulate emissions

from major industries and power plants can reach high altitudes. As a result, transition metals from anthropogenic sources could catalyze SO_2 oxidation in clouds (Harris et al. (2013). In addition, the low concentrations of Ca^{2+} and Mg^{2+} in $PM_{2.5}$ and rather low number of mineral particles from TEM analysis both suggest that the alkaline mineral particles have limited acidic buffering capacity at Mt. Lu. Therefore, absence of mineral particles in the air likely contributes to the higher acidity of aerosol particles. These phenomenon indicated above can be attributed to the seasonal meteorological situation in South China and the height of emission sources -- both critical for determining the transport distance (Kahn et al., 2008; Chen et al., 2013). Firstly, the humid air and frequent rains limit vertical transport of ground-level urban pollutants such as soil dust and vehicle emissions raise up to planetary boundary layer. Secondly, the large industries and power plants with their tall stacks can emit air pollutants into higher atmospheric levels (Chen et al., 2013). Figure S4 shows that wind speed is at 3-10 m/s at 1000 m and < 3 m/s on the ground during the sampling period. Therefore, the pollutants at high altitude can be dispersed quickly and transported for long distance. In addition, biomass burning plumes can reach the free troposphere because their buoyancy can be sufficient to lift smoke above the near-surface boundary layer (Kahn et al., 2008).

Based on our results and discussion, we devised one conceptual model that describes air pollutant emissions and their transport in Figure S7b. Massive amounts of air pollutants (e.g., SO_2 and metal) from coal-fired plants, heavy industries, and biomass burning are readily transported into upper levels of the troposphere. The summer monsoons likely drive large amounts SO_2 and water vapor from east lowland areas to west highland areas in South China. Therefore, beside pollutants' emission and transport, regional meteorological properties (i.e. wind and humidity) and terrain also significantly affect acidic cloud formation.

4. Conclusions

Soluble inorganic ions and individual aerosol particles were studied in summer at Mt. Lu. Northeast winds transported air pollutants from the YRD into the acid precipitation area, with the average hourly concentrations at 28 μg m^{-3} for PM_{10}, 16

412 μg m^{-3} SO_2, and 11 μg m^{-3} for NO_2. SO_4^{2-} is the dominant acidic ion in aerosol
413 particles and could determine the acidity of cloud water and rain at Mt. Lu. In
414 addition, absence of mineral particles in the air lead to their limited acidic buffering
415 capacity and conversely aerosol particles become more acidic at Mt. Lu.

416 The secondary particles occurred in all sizes and S-rich particles were the
417 dominant particle type, accounting for 82% of all analyzed particles. The study
418 indicates that individual particles contain multi-inorganic species with the major
419 compound being $(NH_4)_2SO_4$ with lesser amounts of NH_4HSO_4, NH_4NO_3, or K_2SO_4.
420 The hygroscopic experiments show that individual particles start to deliquesce at
421 73-76%, although the secondary particles completely deliquesce at 80%. In addition,
422 the soluble organic coatings on secondary particles can start deliquescence at 63-73%
423 of individual particles but still completely deliquesce at 80%. Considering the ambient
424 RH of 65-85%, the secondary particles should be in the liquid phase or liquid-solid
425 multiphase in air. We found large amounts of nano-sized metal particles embedded in
426 37% S-rich particles. In addition, we devised a conceptual model that describes air
427 pollutant emissions and their transport, clearly indicating the acid cloud or rain
428 formation at Mt. Lu.

429 **Auxiliary Materials Available**

430 **Figure S1** Terrain of South China and terrain profile of from PRD (East) to Mt. Lu
431 (West); **Figure S2** 48-h Back trajectories of air masses arriving at 1500 m at Mt. Lu
432 during 14 August -24 September, 2013; **Figure S3** Topography and Asian summer
433 monsoon.; **Figure S4** Wind direction and speed in different heights in August and
434 September of 2011 in South China; **Figure S5** Humidifying and dehydration curves
435 for the laboratory-generated NaCl particle collected on a TEM grid; **Figure S6**
436 Different types of individual particles based on morphology and compositions; **Figure**
437 **S7** Conceptual model summarizing acid rain or cloud formation from anthropogenic
438 pollutants; **Figure S8** Sulfate particles without/with organic coating from the two
439 different aerosol samples examined by TEM/EDS.

440 **Acknowledgments**

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587

588 **Figure Captions**

589 **Figure 1** The location of Mt. Lu (115° 59′ E, 29° 35′ N, 1,165 m) in the acid precipitation
590 area wind rose, and concentration distribution for PM_{10}, SO_2, and NO_2 associated with wind speed
591 and directions from 1 August to 26 September, 2011. Mt. Heng (27.3^o N, 112.7^o E, elevation at
592 1269 m) as one elevated site and Lin'an station (30.3^o N, 119.7^o E) as one regional background
593 site, are marked in the acid precipitation area. The data of acid precipitation area were obtained
594 from the Annual Environment Report of China in 2011 and the contours represent the SO_2
595 emission distributions in East China (units: t/year/grid, grid size: 0.5 degree, data from Zhang et
596 al.(2009)).

597 **Figure 2** Average soluble inorganic ions concentration in 33 $PM_{2.5}$ samples at Mt. Lu in summer.

598 **Figure 3** Three different types of individual S-rich particles. (a) S-rich particle with minor K
599 mixed with one As-rich particle and one Fe-rich particle. EDS data obtained from INCA software
600 under channel 5. (b) S-rich particle with moderate K coated by organics. (c) K_2SO_4 particle mixed
601 with organic coating, soot, and Pb-S. EDS data obtained from INCA software under channel 4.

602 **Figure 4** One low-magnification TEM image showing metal inclusions in S-rich

603 Figure 5 TEM image and EDS of two metal inclusions in one S-rich particle.

604 **Figure 6** Elemental mapping of an individual metal-bearing particle obtained from the STEM. A
605 dark-field TEM image of the individual particle and each elemental distribution are shown.

606 **Figure 7** Proportions of aerosol particles collected at Mt. Lu during 11 August to 23 September,
607 2011 in acid precipitation area. A total of 1634 aerosol particles were identified by their different
608 morphology and composition. The number of the analyzed aerosol particles in different size
609 ranges is shown above each column.

610 **Figure 8** Deliquescence and efflorescence of each particle with one color from 3% to 90% RH. (a)
611 the sample collected on 4 September, 2011 containing secondary particles (b) the sample collected
612 on 5 September, 2011 containing secondary particles with organic coating. Compositions of
613 individual particles in the two samples were examined by TEM/EDS as shown in Figure S6.
614 Mixing state and composition of individual particles were described in the scheme.

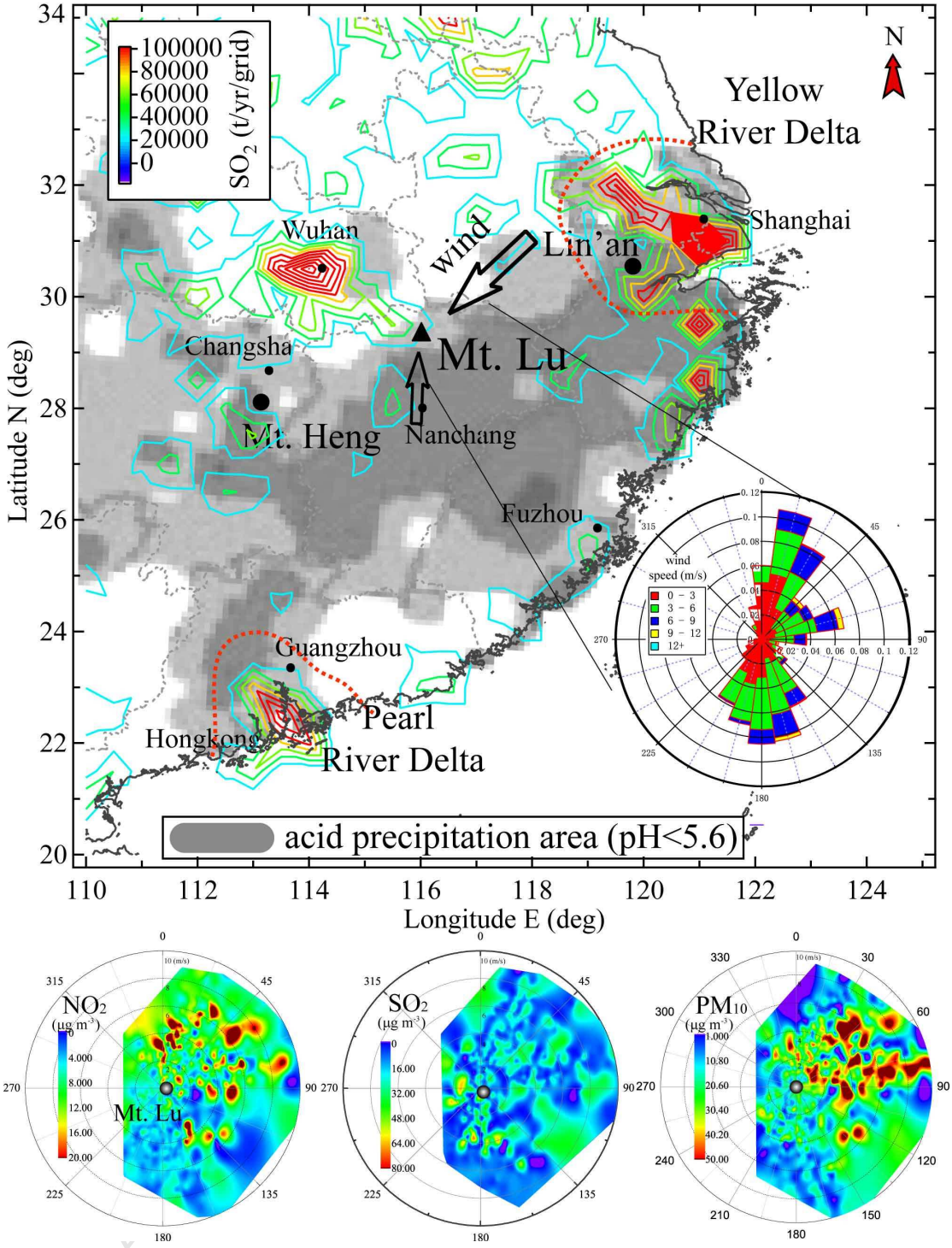

Figure 1 The location of Mt. Lu (115° 59′ E, 29° 35′ N, 1,165 m) in the acid precipitation area wind rose, and concentration distribution for PM_{10}, SO_2, and NO_2 associated with wind speed and directions from 1 August to 26 September, 2011. Mt. Heng (27.3° N, 112.7° E, elevation at 1269 m) as one elevated site and Lin'an station (30.3° N, 119.7° E) as one regional background site, are marked in the acid precipitation area. The data of acid precipitation area were obtained from the Annual Environment Report of China in 2011 and the contours represent the SO_2 emission distributions in East China (units: t/year/grid, grid size: 0.5 degree, data from Zhang et al.(2009)).

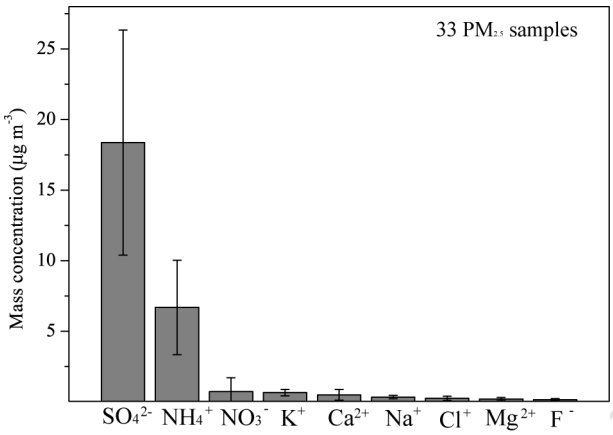

Figure 2 Average soluble inorganic ions concentration in 33 $PM_{2.5}$ samples at Mt. Lu in summer.

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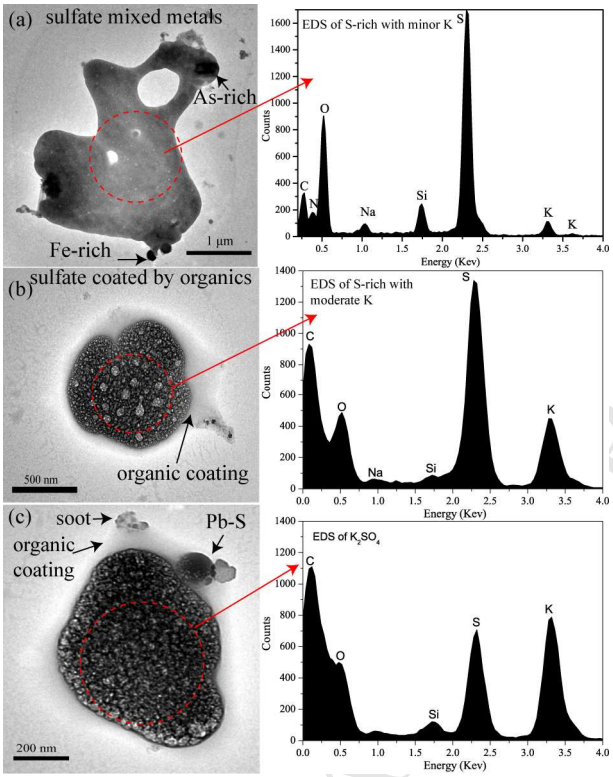

Figure 3 Three different types of individual S-rich particles. (a) S-rich particle with minor K mixed with one As-rich particle and one Fe-rich particle. EDS data obtained from INCA software under channel 5. (b) S-rich particle with moderate K coated by organics. (c) K_2SO_4 particle mixed with organic coating, soot, and Pb-S. EDS data obtained from INCA software under channel 4.

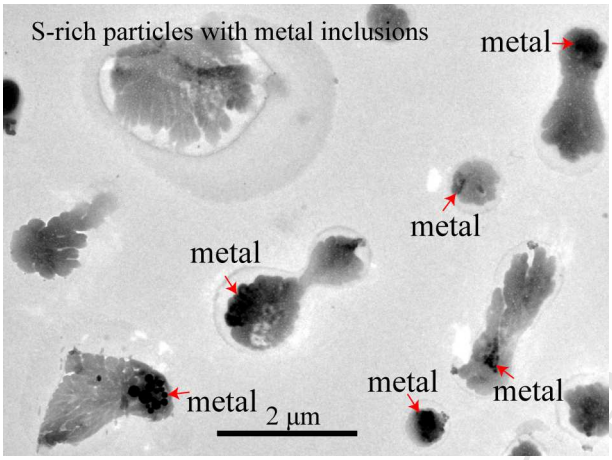

Figure 4 One low-magnification TEM image showing metal inclusions in S-rich

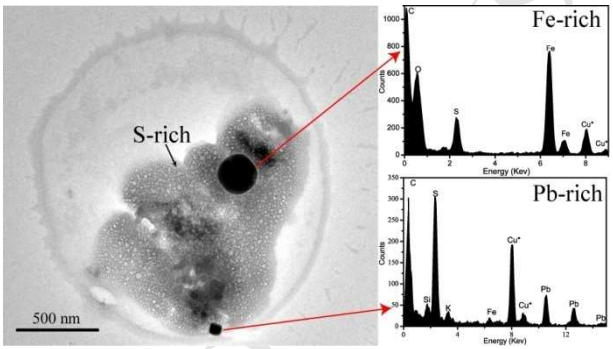

Figure 5 TEM image and EDS of two metal inclusions in one S-rich particle.

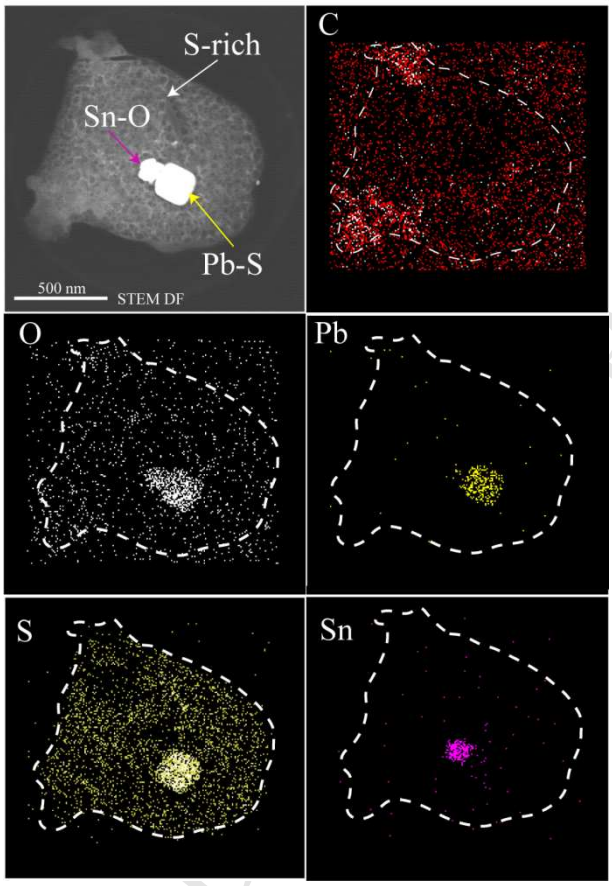

Figure 6 Elemental mapping of an individual metal-bearing particle obtained from the STEM. A dark-field TEM image of the individual particle and each elemental distribution are shown.

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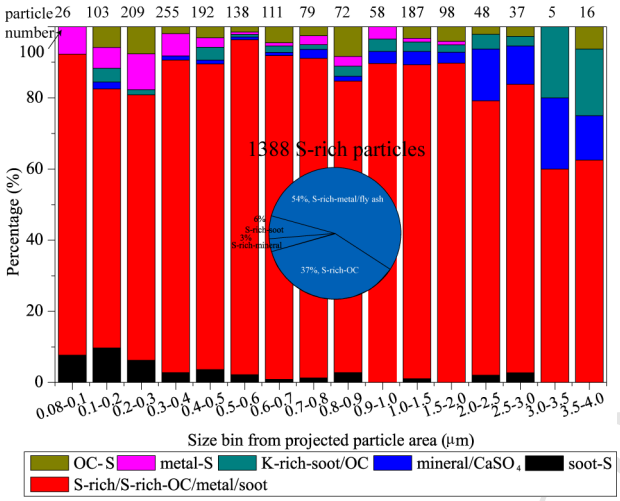

Figure 7 Proportions of aerosol particles collected at Mt. Lu during 11 August to 23 September, 2011 in acid precipitation area. A total of 1634 aerosol particles were identified by their different morphology and composition. The number of the analyzed aerosol particles in different size ranges is shown above each column.

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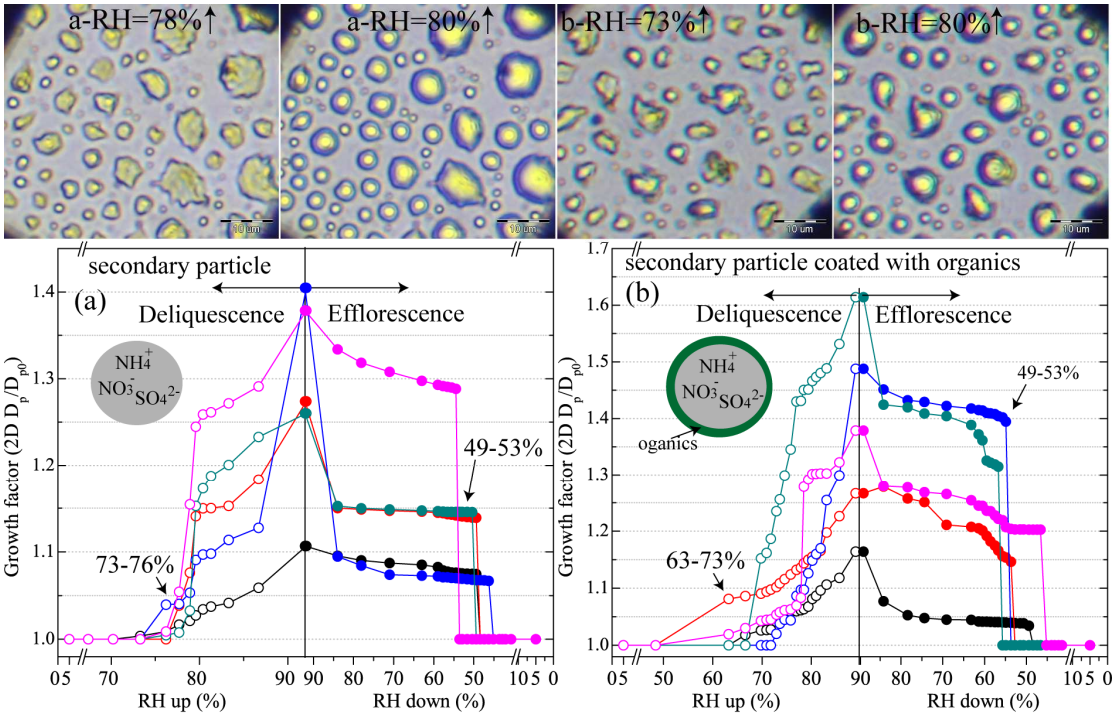

Figure 8 Deliquescence and efflorescence of each particle with one color from 3% to 90% RH. (a) the sample collected on 4 September, 2011 containing secondary particles (b) the sample collected on 5 September, 2011 containing secondary particles with organic coating. Compositions of individual particles in the two samples were examined by TEM/EDS as shown in Figure S6. Mixing state and composition of individual particles were described in the scheme.

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Highlights:

(1) SO_4^{2-} is the dominant ion in aerosol particles
(2) Aerosol particles dominated by sulfate start to deliquesce at 63-76%
(3) Large amounts of nano-sized metal particles embedded in 37% S-rich particles
(4) SO_2 of long range transport from industries and fired-power plants in the YRD.

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Composition and hygroscopicity of aerosol particles at Mt. Lu in South China: Implications for acid precipitation

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Supporting information includes 8 Figures

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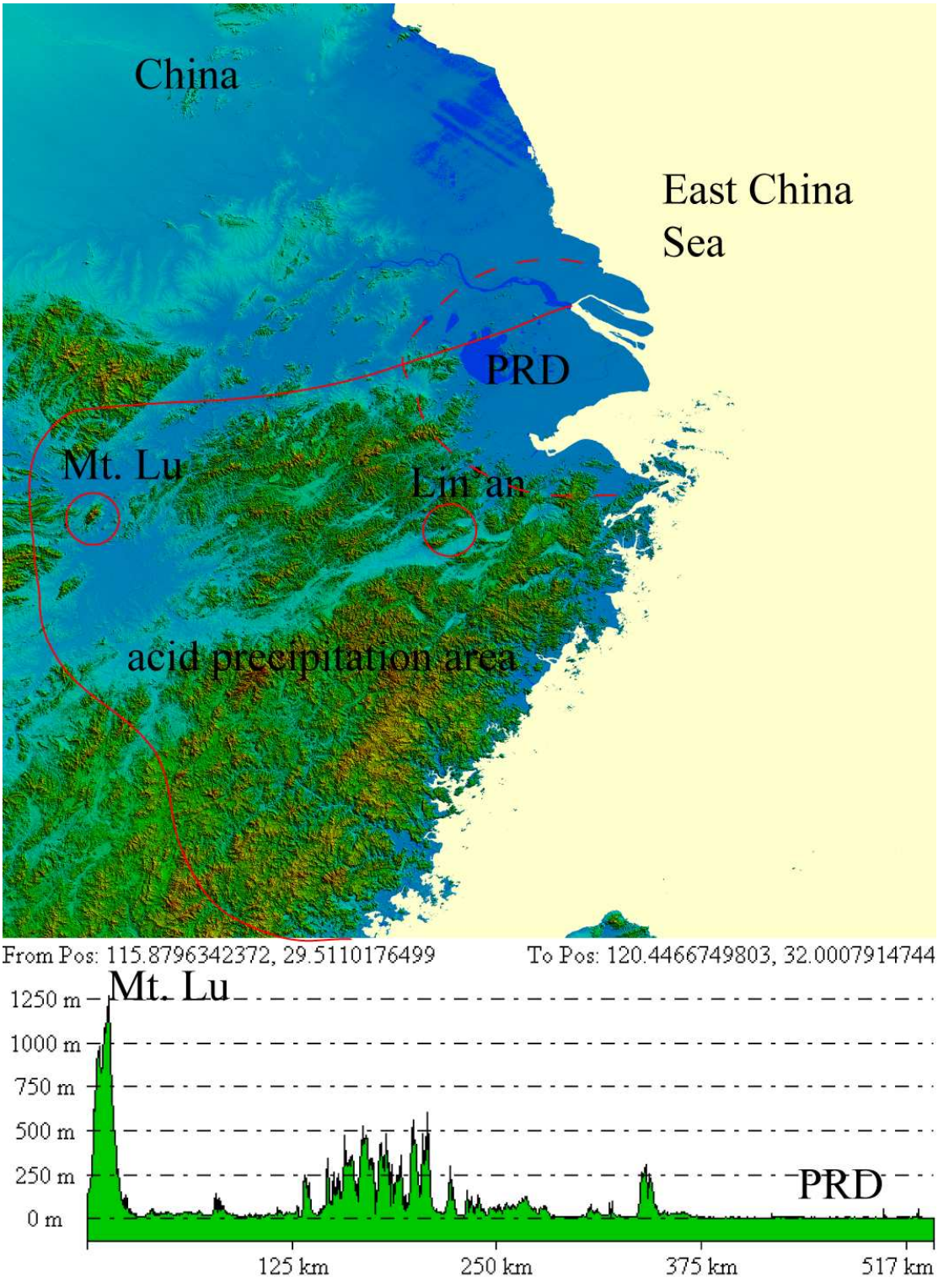

Figure S1 Terrain of South China and terrain profile of from PRD (East) to Mt. Lu (West). The map sourced from the webside at http://srtm.csi.cgiar.org/

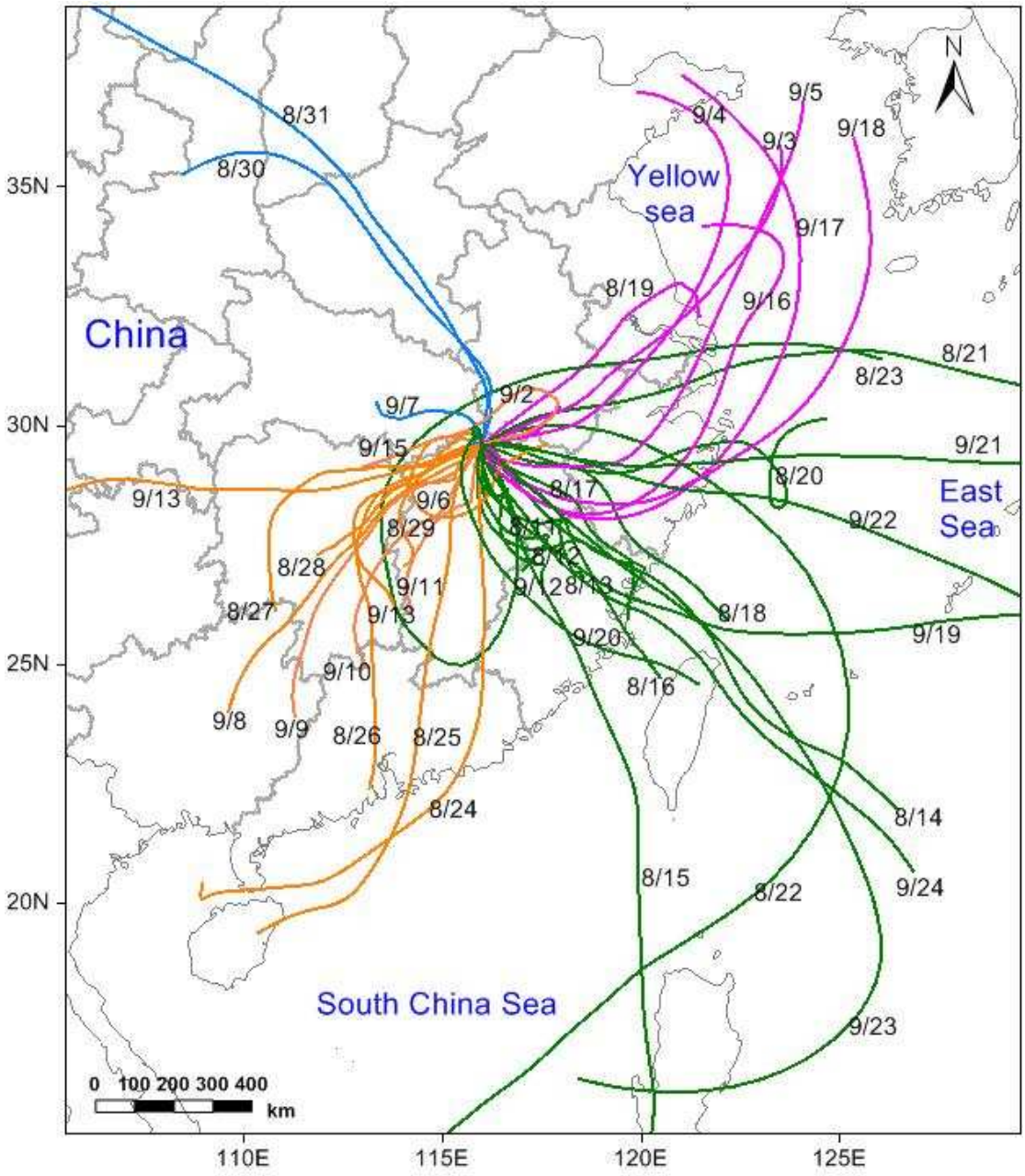

Figure S2 48-h Back trajectories of air masses arriving at 1500 m at Mt. Lu during 14 August -24 September, 2013. Most the trajectories were from South, East, and Northeast of Mt. Lu.

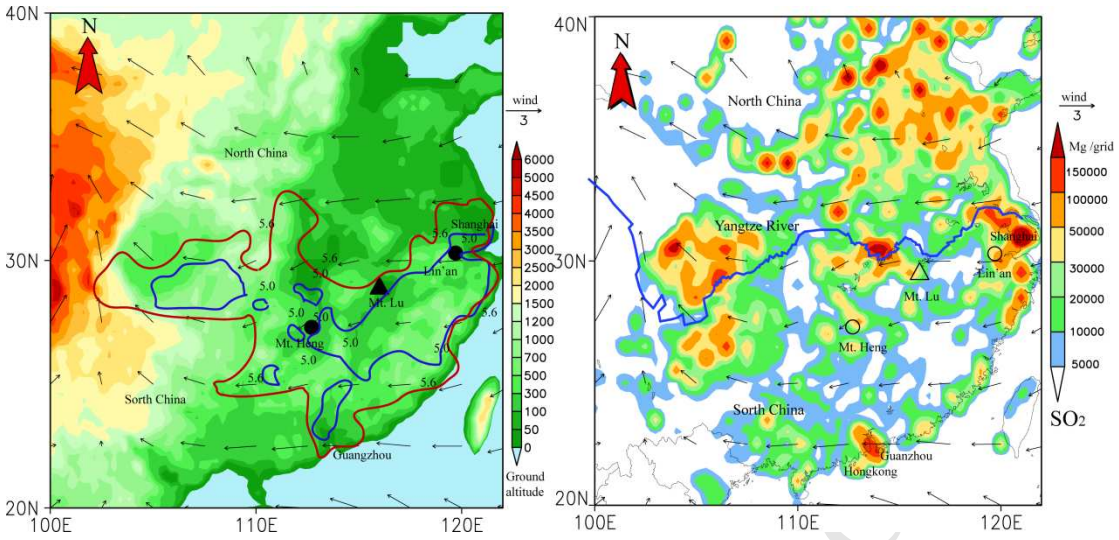

Figure S3 Topography and Asian summer monsoon. (a) Acid precipitation area over the highland area and summer wind during the sampling period (August and September of 2011 of meteorological model projection). The data of acid precipitation area were obtained from the Annual Environment Report of China in 2011 (b) SO_2 emission distributions and summer wind during the sampling period (SO_2 data from (Zhang et al., 2009)).

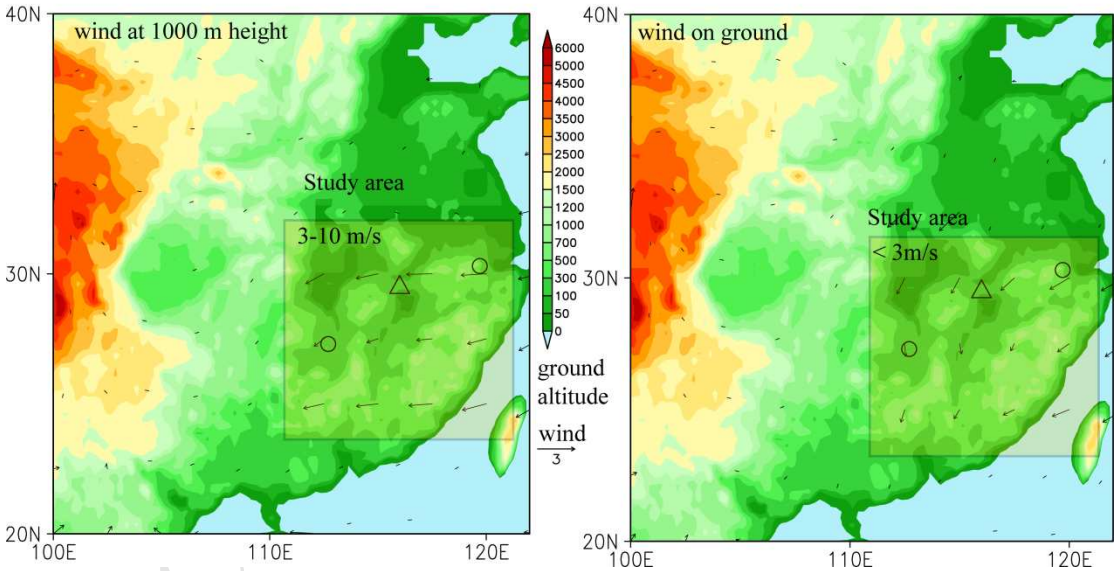

Figure S4 Wind direction and speed in different heights in August and September of 2011 in South China (a) wind at 1000 m height (b) wind on ground level. NCEP/NCAR global reanalysis data were used for projection of wind vector maps (Kalnay et al., 1996).

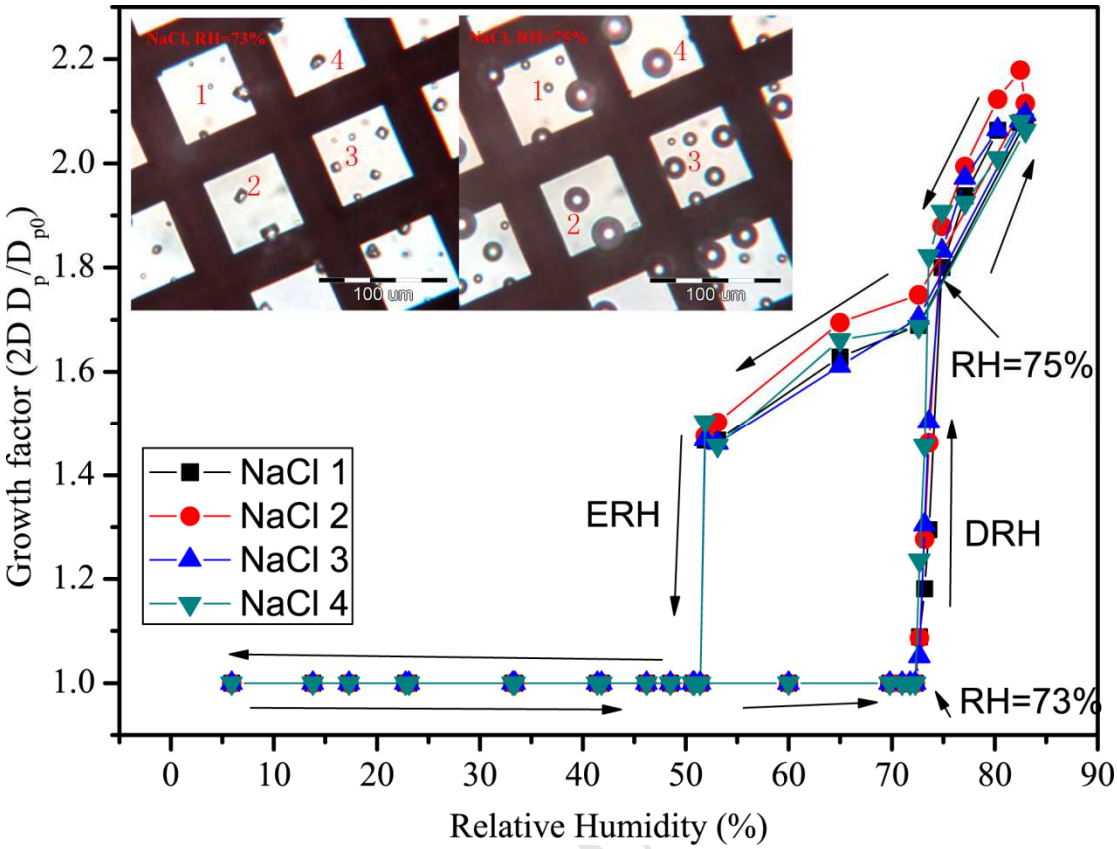

Figure S5 Humidifying and dehydration curves for the laboratory-generated NaCl particle collected on a TEM grid. Deliquescence relative humidity of pure NaCl is at 73-75%, which is consistent with the previous studies.

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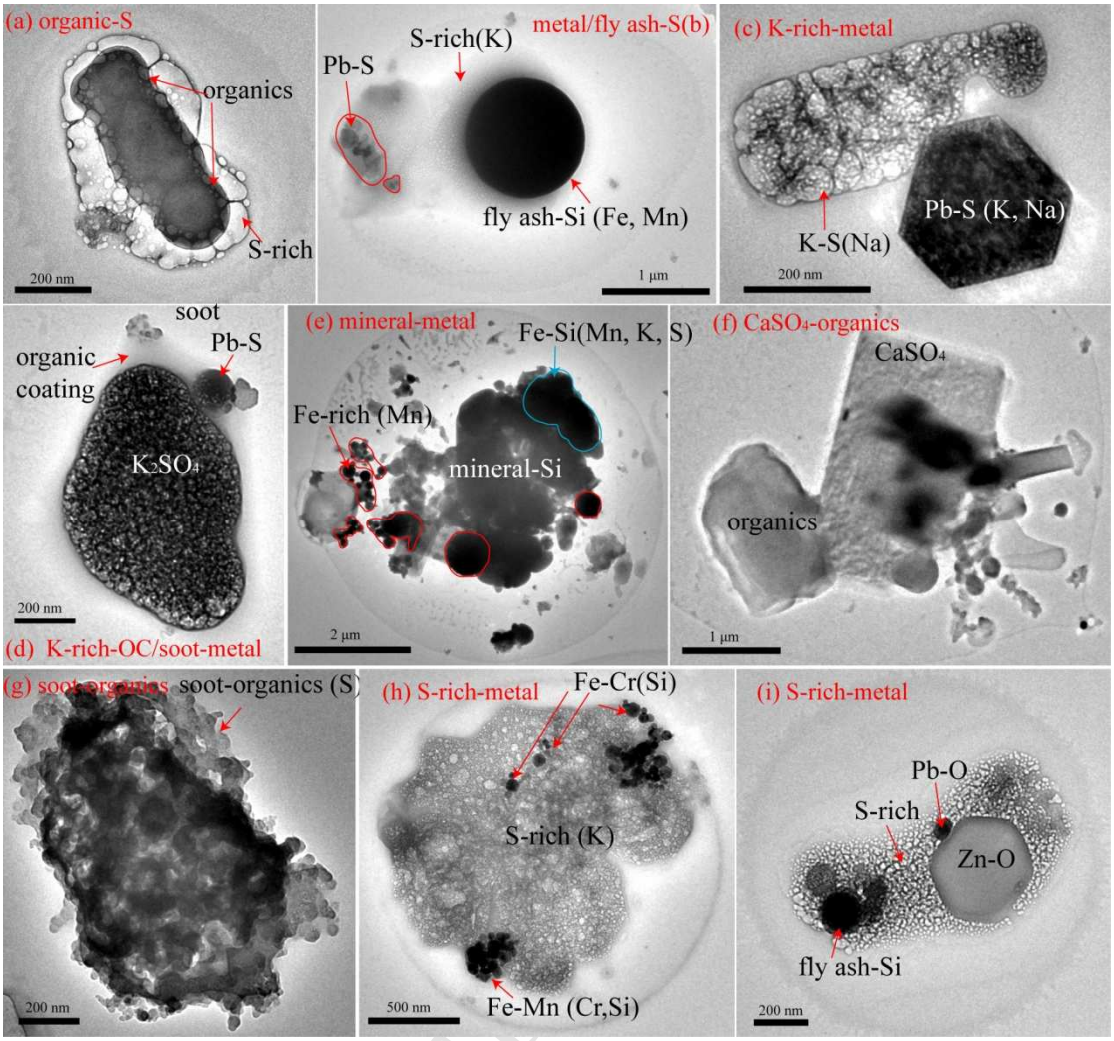

Figure S6 Different types of individual particles based on morphology and compositions

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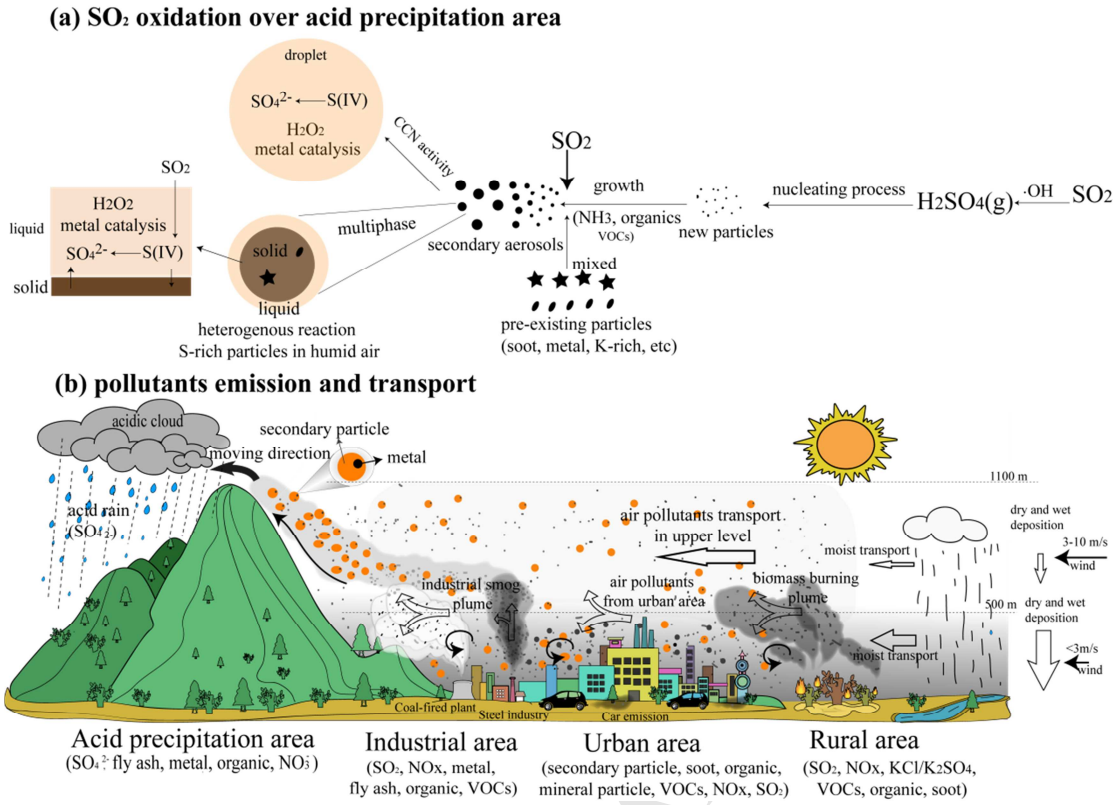

Figure S7 Conceptual model summarizing acid rain or cloud formation from anthropogenic pollutants. (a) SO_2 transformation over acid precipitation area. (b) pollutants emission and transportation. (1) air pollutants include the major gases and aerosols emitted from industrial area, urban area, and biomass burning in rural area. (2) air pollutants can be transported long distance into acid precipitation area in upper level and large amounts of secondary particles form in the air. (3) humid air and frequent rains limit vertical transport of urban pollutants from ground level into the upper atmosphere but not for smog plumes from tall stacks in industrial areas and biomass burning.

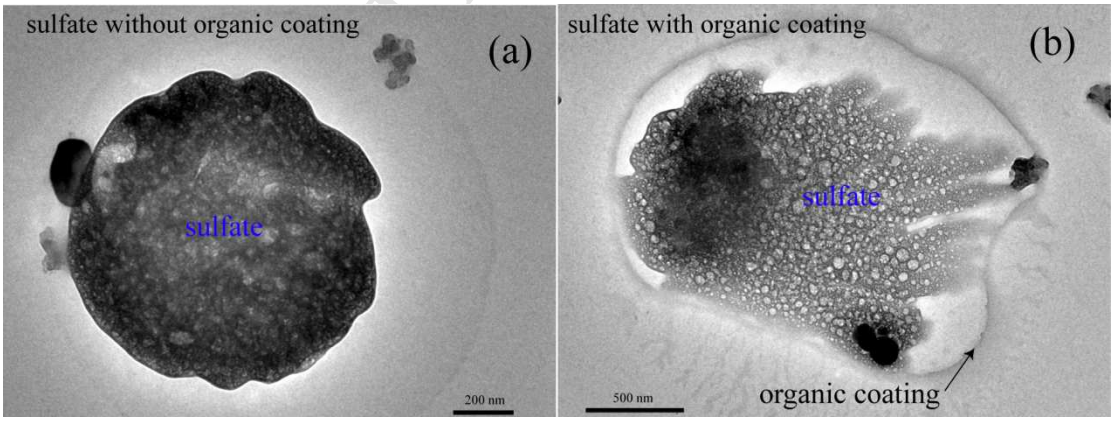

Figure S8 Sulfate particles without/with organic coating from the two different aerosol samples examined by TEM/EDS. After the TEM analysis, hygroscopic properties of aerosol particles in the two samples were studied in Figure 8.

References:

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Zhang, Q., Streets, D.G., Carmichael, G.R., He, K.B., Huo, H., Kannari, A., Klimont, Z., Park, I.S., Reddy, S., Fu, J.S., Chen, D., Duan, L., Lei, Y., Wang, L.T., Yao, Z.L., 2009. Asian emissions in 2006 for the NASA INTEX-B mission. Atmos. Chem. Phys. 9 (14), 5131-5153.

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