We greatly appreciate the reviewers for their valuable comments, which have helped us improve the paper significantly. We have addressed all of the comments carefully, as detailed below. The original comments are in black, and our responses are in blue.

Anonymous Referee #1

The authors presented field observation results of PM2.5 mass concentration, water soluble inorganic ions in PM2.5, OC/EC analysis of PM2.5, as well as reconstructed light extinction coefficient during haze events in January 2013 in the city of Suzhou, China. (1) Sources and processes leading to PM components were discussed with both back-trajectory analysis and the potential source contribution function (PSCF) method. (2) To investigate the contribution of PM species to visibility reduction, the authors attempted to link the two with the revised IMPROVE algorithm and the Koschmieder equation. (3) Finally, gas-to-particle conversion in secondary inorganic species (sulfate and nitrate) formation was briefly discussed.

The dataset itself is definitely interesting and worth exploring, and the methodologies employed by the authors were also scientifically sound. There are two reasons I don't see this version of the manuscript is publishable yet. First, for the three points summarized in the first paragraph, point (1) is just standard and should be in a short description only; point (2) is totally unnecessary since it is a two-step linkage from chemical composition to visibility (to me, it looks more like a number game if no measured extinction coefficient is shown); point (3) should be explored in greater detail, together with the distinct feature of the third haze event (30, January). This first reason will be elaborated point-by-point below in the major comments. Second, the language of the current form of the manuscript needs lots of work to enhance its readability. This second reason will be supplemented with some minor comments below (for those I have spotted). With these reasons, I suggest a major revision before the manuscript can be published in ACP.

We have made major revisions of the paper based on the reviewer's comments. We'd like to illustrate a few points here:

(1) The discussion on the backward trajectory analysis results has been simplified and improved for easy reading. We kept this discussion as one subsection due to the following considerations. Firstly, we think it's important to investigate the effects of the regional sources to the aerosol pollution in Suzhou as it is located in the typical monsoon region. Secondly, we think the results of back trajectory analysis and PSCF do not conflict with the assertion that secondary formation was responsible for high PM level. The impact of regional areas to the studied site is multifaceted. The regional transport might bring precursors or catalytic agents which could promote the secondary formation and/or the generation of PM instead of directly bring PM or secondary components to the studied site. Besides, the results of PSCF in the present study showed that Suzhou was mainly affected by local and nearby areas. Thirdly, the analysis helped the understanding of the distinct feature of the third haze event.

(2) In the revised manuscript, the reconstructed light extinction coefficients were compared

with those derived from visibility and calculated using another model. Strong correlations were observed, confirming that the reconstructed b_{ext} from IMPROVE algorithm was reliable. It's necessary to investigate the dominant contributors to the light extinction which is directly linked to the visibility. The contribution of chemical specie to light extinction might be different from that to aerosol.

(3) The discussions about the formation of secondary inorganic species and the distinct feature of the third haze event were strengthened in the revised manuscript. We have done more comprehensive analysis of the data to explore the SIA formation mechanism in the revised manuscript, such as the roles of liquid water content in aerosol, meteorological parameters and gaseous pollutants. The results suggested that the gas-phase homogeneous reaction and the heterogeneous process both responsible for the formation of nitrate and sulfate. The discussion of the distinct characteristics of the third haze was also strengthened by making comparisons with the other two haze events from more aspects such as $PM_{2.5}$ composition, light extinction coefficient, sources, etc.. The language has also been modified by professionals to enhance its readability.

Major:

1. Section 2. (a) The authors used data of SO2, CO, and NOx quite a bit later in the Results and discussion section. Measurement of these criteria pollutants should be mentioned here as part of the methodology. (b) A brief description on URG 9000 IC would be beneficial to readers since it is not as standard as TOEM. (c) A brief description on OC/EC analyzer and what method of OC/EC splitting was used (thermal OC/EC or optical OC/EC)?

The instruments used for the measurements of gaseous pollutants and meteorological parameters have been described in the revised manuscript. A brief description of instruments applied for PM, water soluble ions and OC/EC determinations has been provided in the revised manuscript.

2. Section 3.4. In this section, the authors tried to link the sources with both chemical composition and light extinction by back-trajectory analysis and PSCF. I don't see a great value of this sub-section for the following two reasons. First, if this analysis is useful, then the results just basically invalidated the authors early assertion that secondary formation was the dominant "source" for high PM levels observed (which I believe in). Second, the discussion of this sub-section is just too confusing and difficult to follow. I would suggest to talk generally about air mass origins in the general characteristics sub-section while not pushing too far to pin-point sources of those mainly secondary species.

As mentioned earlier, we think this discussion is helpful and kept this sub-section due to the following considerations. Firstly, we think it's important to investigate the effects of the regional sources to the aerosol pollution in Suzhou as it is located in the typical monsoon region. Secondly, we think the results of back trajectory analysis and PSCF do not conflict with the assertion that secondary formation was responsible for high PM level. The impact of regional areas to the studied site is multifaceted. The regional transport might bring precursors or catalytic agents which could promote the secondary formation and/or the generation of PM instead of directly bring PM or secondary components to the studied site. Besides, the results of PSCF in the present study showed that Suzhou was mainly affected by local and nearby areas. Thirdly, the analysis helped the understanding of the distinct feature of the third haze event. For your second reason, the discussion on the backward trajectory analysis results has been simplified and improved for easy reading.

3. Sub-section 3.2.3. The authors used revised IMPROVE algorithm to reconstruct light extinction coefficient and used Koshmieder equation to "reconstruct" visibility. The discrepancy is large (a factor of two), owning (in my opinion) to this two-step linkage with both steps involving a number of assumptions and uncertainties. If there is no measured extinction coefficient to support, I do not see what value this analysis would add to the manuscript.

It's meaningful to investigate the contributions of $PM_{2.5}$ component to light extinction, because the results directly manifest the dominant contributor to visibility reduction, and have policy implications. Additionally, the contribution of chemical specie to light extinction might be different from that to aerosol loading. Although the discrepancy in light extinction between those reconstructed using IMPROVE and those derived from visibility is large, the results provide useful knowledge in improving our standing of the topic. Therefore, in the revised manuscript, we have made comprehensive comparisons of light extinction coefficients calculated from using different models, and with added uncertainty analysis. The results confirmed that the reconstructed b_{ext} from the IMPROVE algorithm was reliable to a large extent.

4. Section 3.3. The discussion of secondary inorganic species formation is informative but need some cautions. (a) correlation between RH and SOR does point to the importance of aqueous-phase formation of sulfate, but RH is an indication of gas-phase water after all. It is suggested that liquid water content in PM to be estimated using E-AIM or ISORROPIA.

We agree that to get the conclusion about the importance of aqueous-phase formation to sulfate only based on the correlation between RH and SOR might hasty. So in the revised manuscript, we estimated the liquid water content in PM by using E-AIM and conducted more detailed analysis to explore the formation mechanism of nitrate and sulfate.

(b) the authors cited Pathak et al., 2004, Pathak and Chan, 2005 to back the statement that homogeneous reaction between HNO3 and NH3 was important in nitrate formation. But these two papers talked about sampling artefacts for filter sampling when particles and gases can interact for 24 hours, while the authors used continuous measurement technique to measure SNA. I don't see that is relevant.

We agree with the reviewer that it's inappropriate. We cited other references (Pathak et al., 2009; Jansen et al., 2014; He et al., 2012) to back that statement in the revised manuscript.

(c) excess ammonium is of course one way to look at nitrate formation, but partitioning equilibrium between NH4NO3 and HNO3 and NH3 is also important to considered given the low temperature and high RH in the studied period.

We explored nitrate formation mechanism from more aspects and conducted more detailed analysis. The results indicated that heterogeneous chemistry, such as equilibrium partitioning between NH_4NO_3 and HNO_3 and NH_3 (HNO_3 (g) + NH_3 (g) ↔ NH_4^+ (aq) + NO_3^- (aq)) also contributed to the formation of nitrate just as the reviewer expected.

5. The authors briefly mentioned the uniqueness of the third haze events compared to the first two in a number of places, but did not elaborate them. From the high POC and dominated air mass origins of C2 (short circulating trajectories), I believe this event was mainly contributed by primary emission from the local (surrounding) areas. It is suggested that this episode to be discussed in contrast to the other two with respect to primary/secondary fractions and meteorological parameters.

Thanks for the useful suggestion. According to the reviewer's suggestion, the discussion about the distinct feature of the third haze event has been strengthened in the revised manuscript. The characteristics of the third haze event has been compared with the other two haze events from various aspects, such as weather conditions, aerosol compositions, light extinction contributions oxidation ratio, air mass origination and etc. The results indeed indicated that the carbon components from the primary emission in local and/or nearby areas instead of secondary formation inorganic ions might be relatively more important for the visibility reduction for the third haze event.

Minor

P33409, L3: change "public" to "the public".

It has been revised accordingly.

P33409, L15: what is "artificial sampling"? should be "filter sampling"?

The phrase "artificial sampling" has been changed to "filter sampling": "Most existing studies were based on filter sampling and off-line analysis and had limitations in providing detailed insight into the roles the major chemical species played during shorter haze periods."

P33409, L26: change "close" to "similar".

It has been revised accordingly.

P33410, L3: change "salt" to "salts".

It has been revised accordingly.

P33410, L22: change "investigate the" to "investigation of".

The sentence has been revised.

P33411, L1: suffered should be suffered from.

It has been revised accordingly.

P33414, L20: change little to slightly (also in P33416, L6).

It has been revised accordingly.

P33417, L14-16: this sentence is not convincing to me. It is stated that there is difference between Suzhou and Beijing. But here it is asserted that nitrate formation may be also affected by re-volatilization of NH4NO3 as that in Beijing (similarity?).

There are both difference and similarity between Suzhou and Beijing. The NO_3^-/SO_4^{2-} ratio was higher under worst visibility conditions in Suzhou while higher under better visibility in Beijing. But similar to Beijing, the ratios of (NO_3^-/SO_4^{2-}) to (NO_X/SO_2) were lower for worse visibility period, which could indicate the effect of the re-volatilization of NH_4NO_3 on the nitrate concentrations. We have modified this paragraph hopefully to make it more understandable.

P33418, L16: change migh related to might be related.

It has been revised accordingly.

P33418, L28: change “similar profile” to a profile similar”.

It has been revised accordingly.

L33149, L3: I don’t agree that all the secondary aerosol species were “affected” by O3. O3 is just one of those oxidants that can oxidize precursors and lead to SIA formation. In fact, it is the secondary nature of O3 that makes its diurnal profile some similar to those of the secondary aerosol species.

We agree with the reviewer. We now rephrase this sentence: “The diurnal profiles of the secondary species were similar to their precursors but obviously affected by other factors such as solar radiation, which could promote the oxidation of the precursors.”

P33149, L11: also responsible should be also be responsible.

It has been revised accordingly.

L33419, L12: level should be levels.

It has been revised accordingly.

L33419, L19: “because of” should be “be due to”.

It has been revised accordingly.

P33419, L21: favored for should be favored.

It has been revised accordingly.

P33419, L22: always southwest wind? The discussion later for the first and second haze events suggests otherwise.

We assume that the later discussion the reviewer refers to is the back-trajectory analysis. We think there is no certain link between wind direction and back-trajectory results. Wind direction refers to instantaneous local weather condition. But back-trajectory results reflect the migration of air mass on a much larger temporal and spatial scale. So we don't think the results conflict with each other.

P33420, L2-7: I don't see it is necessary to repeat the equation here. In fact, I don't see it is necessary to have this analysis of reconstructed light extinction coefficient, as shown above.

We agree with the reviewer that it's unnecessary to repeat the equation. Therefore, the revised equation was not showed in the new version of manuscript. But we do think it's meaningful to have the discussion about light extinction for aforementioned reasons.

P33420, L14: "similar temporary trend" and "significantly correlated" are referring to the same thing.

We agree with the reviewer. The sentence has been rephrased in the revised manuscript: "Nevertheless, they were significantly correlated with each other ($r = 0.71$, $p < 0.001$).".

P33420, L16: were should be was.

It has been revised accordingly.

P33420, L26: were reduced should be reduced.

It has been revised accordingly.

P33421, L28: how come only NO2 (not NO + NO2) was used in calculation of NOR?

The calculation of NOR by NO_2 and NO_3^- has been used to estimate the secondary formation of nitrogen in many studies (Wang et al., 2016; Ji et al., 2014; Jansen et al., 2014; Zhao et al., 2013; Squizzato et al., 2013; Fu et al., 2008). The pathways for nitrate formation mainly include heterogeneous hydrolysis of N_2O_5 and gas-phase photochemical oxidation of NO_2. N_2O_5 is mainly produced from NO_2 ($NO_2 + O_3 \rightarrow NO_3 + O_2$, $NO_2 + NO_3 + M \leftrightarrow N_2O_5 + M$). So we think it's reasonable to only use NO_2 in the calculation of NOR.

P33422, L4-6: should be two sentences.

This sentence has been split into two sentences: "The daily variation of NOR showed similar pattern as NH_4^+ and NO_3^-. Likewise, SOR had similar diurnal change as SO_4^{2-}.".

P33422, L11-14: show the correlation.

The correlation coefficient has been provided in the revised manuscript.

P33422, L27: a variety of cities (change to different cities?); a little (change to slightly?)

The phrase "a variety of cities" should be "several" and "a little" has been changed to "slightly". The whole sentence now is "Pathak et al. (2009) also reported an intercept value of 1.5 for several cities worldwide while Jansen et al. (2014) found a slightly smaller intercept value of 1.38 for Hangzhou.".

P33424, L27: remove "differently".

It has been revised accordingly.

P33425, L13: suggest should be suggests.

It has been revised accordingly.

P33425, L14: but not should be but does not.

It has been revised accordingly.

P33426, L10: severe should be efficient.

It has been revised accordingly.

P33426, L18: were should be was.

There are many changes in this section in order to highlight the main conclusions of this article. This sentence is not included in the revised manuscript.

P33426, L24: But distinctively should be However.

There are many changes in this section in order to highlight the main conclusions of this article. This sentence is not included in the revised manuscript.

P33435: what are the shaded areas with different colors?

The shaded areas in orange refers to periods when visibility lower than 10 km and accompanied by precipitation. The shaded areas in grey refers to haze periods. We have clarified this in the revised manuscript.

P33437: it is difficult to be convinced that CO is a precursor of aerosol species; O3 might be one type of oxidants in secondary aerosol formation, but not a precursor.

We agree with the reviewer that it might be inappropriate to refer to these species as precursors. So the title of this figure has been rephrased: "Figure 6. Diurnal profiles of meteorological variables, aerosol precursors (NO_X, SO_2), CO, O_3, $PM_{2.5}$, and major aerosol compounds (NO_3^-, SO_4^{2-}, NH_4^+, EC, POC, SOC) under different visibility conditions.".

P33439: if it is a ratio, then show a ratio, not a percentage.

It has been revised accordingly in the revised manuscript.

Anonymous Referee #2

Manuscript on "Characteristics of aerosol pollution during heavy haze events in Suzhou, China" evaluates the atmospheric concentrations of PM, its chemical composition, and light extinction properties to understand the characteristics of haze events at Suzhou. Their results showed that haze events are characterized by the presence of enhanced concentration of secondary aerosol species and their precursors; further, abundance of OM, (NH4)2SO4, and NH4NO3 led to visibility impairment during the haze events. The study is useful towards understanding the role of pollutants in haze formation and visibility degradation and could help policy makers in specific control measures. This is an interesting piece of work, but in my view, the manuscript needs to be strengthened in terms of scientific analysis and its novelty. Authors should highlight in the "Introduction" and in their Results and Discussion, the gaps in understanding (what is known and what we still need to understand through this work) related to aerosol pollution during haze events and how objectives and analyses presented in the manuscript for a specific location of Suzhou is different than reported information in literature for other locations influenced by haze events, e.g. Beijing etc. Also, there is a difficulty in the readability of the manuscript, this needs to be improved checking sentences throughout.

We have made significant revisions based on the reviewer's comments to strengthen the paper. The novelty, originality and importance of this study can be summarized below. (1) Suzhou, an important city in the YRD, with annual haze days increased from only two days to more than 150 days from 1956 to 2011, has experienced the extremely serious aerosol pollution in Jan. 2013, but little is known about the chemical characteristics and sources of fine particles in this city. This paper provide basic data for implementing effective pollution control measures in Suzhou. (2) The discussion in the present study was based on high time resolution data which could provide detailed insight into the role the major chemical species in $PM_{2.5}$ played during shorter haze periods. (3) The dominant species in $PM_{2.5}$ and those responsible for the visibility reduction were identified. (4) The formation mechanism of sulfate and nitrate were explored as high secondary aerosol contributions to particulate pollution during haze events. (5) The impact of local and outside sources on aerosol pollution in urban Suzhou was discussed. We now highlighted these points in the manuscript and we have also strengthened the comparison of the haze characteristics between Suzhou and other locations such as Beijing etc. The language has also been proofread by professionals to enhance its readability.

Specific comments:

Section 2.1: Please discuss uncertainty involved in measurements using each of the equipments.

The uncertainties have been discussed for the measurement of each equipment in the revised manuscript.

Section 2.2.1: It would be helpful to the reader if you can include information on basis of "numbers" (such as 2.2 x fs(RH) and so on, what does 2.2 indicate?) used in the equation 1 (IMPROVE algorithm).

The information of the numbers have been included in the revised manuscript: "The constant numbers in the above equation are extinction efficiencies for each chemical species under dry condition."

Section 2.2.2: please provide reason for 48 h back trajectories calculation; typically, taking into account lifetime of aerosols of the order of seven-days in the lower troposphere, should you perform 7-day back trajectory calculations?

48-h back trajectory analysis has been used in many studies (Yu et al., 2014; Ji et al., 2014; Behera and Balasubramanian, 2014; Zhang et al., 2013; Huang et al., 2012; Huang et al., 2010; Wang et al., 2005). We think the back trajectory analysis is mainly used to explore the origination of the air mass in the studied area. The transport of air mass might bring aerosols and/or precursors to the target area and consequently influence the aerosol pollution. The results of this analysis basically could imply the impact of regional transport on the existing aerosol in the studied area. So we think the back trajectory analysis don't mean to calculate the lifetime trajectory of the aerosol.

Section 3.2.1: How does the chemical composition observed at Suzhou compares with that at Beijing or other places where haze events are frequent. Please discuss if sources of aerosol species are distinct between Suzhou and others.

The chemical composition observed at Suzhou has been compared with that at Beijing or other places in the manuscript, such as "These secondary inorganic components in total constitute 93% of total WSIIs, close to the result in Beijing (Gao et al., 2015; Tao et al., 2015)." and "The carbonaceous species, constituting 22% of $PM_{2.5}$, were dominated by organic carbon, which was 22.8 ± 10.6 mg m^{-3} and 3 to 29 times of that of elemental carbon (2.79 ± 2.58 mg m^{-3}), similar to those in Beijing (Tao et al., 2015).". Other results in present study have also been compared to other places, for instance, "The relatively high ratios of OC/EC (10.6 ± 4.29), which were higher than the ratios in Beijing (7.1 ± 0.5) and Jinan (7.15 ± 1.78)", "The ratio of NO_3^-/SO_4^{2-} in this study was lower than that in Beijing, but higher than those in Shanghai (0.43), Qingdao (0.35), Taiwan (0.20), and Guiyang (0.13) (Wang et al., 2006; Yao et al., 2002; Hu et al., 2002; Fang et al., 2002; Xiao and Liu, 2004).", etc.. We agree with the reviewer that to compare the sources of aerosol species between Suzhou and other places might be interesting. However, specific emission sources could not be identified only based on the existing data of species (water soluble ion, OC, EC) in $PM_{2.5}$. Some tracers of emission sources would be needed other than existing components.

Section 3.2.2: Please replace 'AM peak' and 'PM peak' by other relevant words. "It seemed that low visibility: : :southwest wind" please explain the possible reason for this.

The "AM peak" and "PM peak" have been replaced by "morning peak" and "afternoon peak". The possible explanation has been provided in the revised manuscript: "This might related to the topography. There are mountains located on the southwest which is not conducive to the diffusion of pollutants."

Section 3.2.3: "In order to appoint: : :" please change the word "appoint". Your analysis show that while OM is the largest contributor to light extinction, but its contribution to PM during haze events is lower than rest of the water soluble constituents. Please discuss the possible reason for this.

(1) The word "appoint" has been changed to "determine" in the revised manuscript: "In order to determine the contribution of $PM_{2.5}$ constituents to the visibility degradation, light extinction (b_{ext}) was reconstructed based on the revised IMPROVE algorithm." (2) There might be two possible reasons. Firstly, OM refers to organic matter which is derived from multiplying OC concentrations by a factor of 1.8 to account for unmeasured atoms. Secondly, the extinction efficiencies for each species under dry conditions are different. The extinction efficiencies of OM (2.8 for Small OM and 6.1 for Large OM) are higher than $(NH_4)_2SO_4$ (2.2

and 4.8) and NH_4NO_3 (2.4 and 5.1).

Section 3.4: Please provide insights on emission sources corresponding to paths of clusters and PSCF analysis. Please discuss why a set of clusters are found to be different than the rest.

We agree with the reviewer that discussing the emission sources (such as biomass burning, coal combustion, vehicle emission, etc.) corresponding to paths of clusters and PSCF analysis would be of great interest. However, specific emission sources could not be identified only based on the existing data of species (water soluble ion, OC, EC) in $PM_{2.5}$. Some tracers of emission sources would be needed other than existing data. Besides, the current paper is already very long and focuses on the chemical contribution, formation mechanism and regional impact. Introducing additional analysis of emission sources would weaken the overall focus, increase the length, and decrease the readability. Trajectories are calculated on basis of meteorological parameters such as wind direction and wind speed. Different meteorological parameters would result in different trajectory. The pollution characteristics (such as aerosol pollution level, chemical composition, light extinction, etc.) in clusters might differ from each other. There might be many reasons, for instance, the trajectories pass over different areas and/or the local emission sources varied.

Anonymous Referee #3

Reviewer’s comments for "Characteristics of aerosol pollution during heavy haze events in Suzhou, China" by Tian et al. The manuscript by Tian et al. presented a field study for PM2.5 mass concentration, PM2.5 chemical composition, and associated gaseous precursors during haze events in a major Chinese city located in the Yangtze River Delta. Like many other studies in China, this work highlighted the large contributions of secondary aerosol species in PM2.5. Source regions were analyzed based on the back trajectory calculations.

The new perspective (in my opinion) this paper brought to us is the results on the main contributors of the light extinction in PM2.5 components. These results are interesting and potentially have policy implications, because light extinction is directly linked to the visibility, which is one of the major public concerns in China. In the current manuscript, this assessment was based on the measured concentrations of chemical species weighted by the mass-extinction coefficients derived from the revised IMPROVE algorithm. The authors identified OM, sulfate, and nitrate as the major contributors of visibility impairment. However, I do agree with reviewer #1 that such analysis was not convincing without appropriate comparisons with other measurements. I would suggest the authors to strengthen this analysis before this paper can be published in ACP, since it seems to be crucial for the main conclusions.

A possible way to do this can be including a more comprehensive comparison between the light extinction reconstructed from chemical species with that derived from the visibility. A previous study (Chen et al. ACP, 2012) in North China has shown that the visibility-derived ambient light extinction can be well reconstructed by an optical model with measured number-size distribution, hygroscopicity, and RH. For the revision, a scatter plot and/or a time series plot could be included for comparison of the light extinction coefficients derived from both methods. Uncertainties should also be included. In the case of poor agreement, several hypotheses can be tested, including: 1) Coefficients developed based the IMPROVE data are not suitable for the aerosol populations in China, e.g., due to the differences in size distributions. In this case better parameterizations are needed for the haze over China. 2) The RH (or other key parameters) measurement may not be accurate; e.g., Fig. 2 shows severe haze events are associated with high RH (_90%), where the RH sensor may have a large error. In this case the assessment can be biased for contributions between hygroscopic inorganic species and hydrophobic OM. Some caveats should be discussed.

We have compared the light extinction coefficients reconstructed by IMPROVE algorithm with that calculated by the optical model as the reviewer suggested. Strong correlations were observed (R^2 = 0.952) with a slop of 0.837, confirming that the reconstructed b_{ext} from IMPROVE algorithm were basically reliable. We also discussed the possible reasons for the deviations between the results.

Another suggestion is that the authors can also present the contributions of different species to PM2.5 mass concentration in addition to light extinction (e.g., in Fig. 5 and 9, Table 1). This analysis will be based on measured variables and thus less ambiguous. Such results can be useful in the context of aerosol health effect, which is another major concern related to the air pollution.

Thanks for the valuable suggestion. The aerosol compositions in the three haze events have been illustrated in the pie chart in figure 3 in the revised manuscript.

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Characteristics of aerosol pollution during heavy haze events in Suzhou, China

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Abstract

~~A comprehensive measurement was carried out to analyze the heavy haze events in Suzhou in January 2013 when e~~Extremely severe haze weather events~~pollution~~ occurred in many cities in China, especially in the ~~E~~east part of the country, in January 2013. Comprehensive measurements including ~~H~~hourly concentrations of $PM_{2.5}$~~,~~ and its major chemical components~~sition~~ (~~including~~ water-soluble inorganic ions, OC, and EC)~~,~~ and related gas-phase precursors were ~~obtained~~conducted via on-line monitoring system in Suzhou, a medium size city of Jiangsu province, just east of Shanghai. ~~Based on these data, detailed aerosol composition, light extinction and gas-phase precursors were analyzed to understand the characteristics of the haze events, moreover, the formation mechanism of nitrate and sulfate in $PM_{2.5}$ and the regional sources deduced from trajectory and PSCF were discussed to explore the origin of the heavy aerosol pollution. The results showed that frequent haze events were occurred on Jan. 2013 and the concentrations of~~ $PM_{2.5}$ frequently~~often~~ exceeded 150 μg m^{-3} on hazy days~~during the haze occurrence~~, with the~~a~~ maximum reaching~~concentration of~~ 324 μg m^{-3} on Jan. 14, 2013. Unfavorable weather conditions (high RH, and low rainfall, wind speed and atmospheric pressure) were conducive for the haze formation.~~,~~ ~~h~~High concentrations of secondary aerosol species (including SO_4^{2-}, NO_3^-, NH_4^+, and SOC) and gaseous precursors were observed during the first two haze events, while elevated primary carbonaceous species emissions were found during the third haze period, pointing to different haze formation mechanisms. ~~Additionally,~~ OM, $(NH_4)_2SO_4$, NH_4NO_3 were ~~demonstrated~~ found to be the major contributors to ~~the~~ visibility impairment ~~but the share differed from haze events~~. ~~This study also found that the h~~High concentrations of sulfate and nitrate might be explained by ~~the~~ homogeneous gas-phase reactions under low RH conditions and by heterogeneous processes under relatively high RH conditions. ~~heterogeneous reactions in the aqueous surface layer of pre-existing particles or in cloud processes while nitrate might be mainly formed through homogeneous gas-phase reactions. The results of~~ Analysis of air mass trajectory clustering and potential source contribution function~~the PSCF method~~ manifested that aerosol pollutions in the studied areas were

mainly caused~~affected~~ by local activities and surrounding sources transported from nearby cities.

1. Introduction

~~High occurrence of h~~Haze~~ events (~~ is defined as visibility lower than 10 km when~~under the conditions of~~ relative humidity < 80%.~~)~~ Rapidly increased air pollution in China in the past several decades have resulted in frequent occurrences of haze events, which have caused~~is of~~ great concern to the scientific community as well as~~both scientists and~~ the public (Zhang et al., 2012). ~~in China in recent years because of its~~Haze events have~~ great~~ adverse effects on ~~the people's~~human health, traffic, climate, and other important aspects (Zhang et al., 2015; Charlson et al., 1987; Ramanathan and Vogelmann, 1997; Tegen et al., 2000; Yu et al., 2002; Tie et al., 2009a; Tie et al., 2009b). Fine particles ($PM_{2.5}$, aerosols with an aerodynamic diameter of 2.5 microns or less) are~~has a~~ largely responsible for haze formation due to their ability in~~ impact on visibility by~~ light extinction including scattering and absorbing solar and infrared radiation ~~ and is mainly responsible for the formation of haze~~(Yu et al., 2014). ~~The l~~Light extinction of $PM_{2.5}$ is highly associated with its~~the~~ chemical composition~~s~~ (Tao et al., 2014). Water-soluble inorganic ions and carbonaceous species often account for major fractions of $PM_{2.5}$ and are important contributors to visibility impairment (Tan et al., 2009; Pathak et al., 2009), and thus have been~~. Therefore, these species were emphatically~~ investigated extensively~~in researches related to haze occurrence~~ (Yang et al., 2005; Jansen et al., 2014; Pathak et al., 2009). ~~However, m~~Most ~~of these~~existing studies were based on ~~artificial ~~filter sampling and off-line analysis and had~~which has its~~ limitations ~~of~~in providing detailed insight into the roles ~~of ~~the major chemical~~these~~ species played during shorter haze periods.

High contributions of secondary inorganic aerosols (SIA, including sulfate, nitrate and ammonium), the predominant water-soluble ionic species in $PM_{2.5}$, to visibility reduction have been observed in many cities in China (Huang et al., 2014).

Gas-~~phase~~ or liquid-phase reactions of sulfur dioxide and nitrogen oxides are~~is~~ the primary mechanisms forming~~source of~~ aerosol sulfate and nitrate. For the formation of sulfate, homogeneous gas phase reaction of SO_2 with OH radical, and heterogeneous reactions in the aqueous surface layer of pre-existing particles~~,~~ and in-cloud processes are the primary mechanisms (Wang et al., 2006). The rates of gas-phase and liquid-phase reactions of SO_2 were ~~close~~ similar in summer while the heterogeneous processes were responsible for the oxidation in winter (Hewitt, 2001). Nitric acid can be formed from homogeneous gas-phase reactions of NO_2 with OH or O_3 and from heterogeneous hydrolysis of N_2O_5, which occurred predominantly during daytime and nighttime, respectively (Khoder, 2002). Both sulfuric acid and nitric acid ~~will~~ react with alkaline substance in the atmosphere, mostly ammonia under ambient conditions to produce salts (Hewitt, 2001). The neutralization of sulfuric acid by ammonia has been found to be preferred over the formation of ammonium nitrate (Warneck, 1999). Thus, the formation of ammonium nitrate in fine particles is usually under significantly neutralized or ammonium-rich ~~sulfate~~ conditions (Pathak et al., 2009). There are various factors influenc~~e~~ing the formation of aerosol sulfate and nitrate, such as the levels of gaseous precursors (SO_2, NH_3, NO_X) and oxidants, the characteristics of pre-existing aerosols, and meteorological conditions. These factors may vary by location, ~~this may~~ resulting in different formation mechanism in different areas. For instance, different formation pathways had been reported for nitrate in ammonia-rich and ammonia-deficient areas (Pathak et al., 2009).

~~Due to the rapid economic and industrial developments and urbanization in past few decades, the visibility reduction become increasingly serious in China, especially in the East (Zhang et al., 2012).~~ In January 2013, extremely severe, persistent and widespread haze weather occurred in 10 provinces~~, regions and cities~~ in central and eastern China. These serious pollution events not only had~~ve~~ great adverse effects on human health, as seen in~~caused~~ a sharp increase in respiratory diseases, but also caused immeasurable economic loss (Huang et al., 2014; Chen et al., 2013). High secondary inorganic and organic aerosol contributions to particulate pollution during these haze events were reported in a recent study based on the measurements at urban sites in Beijing, Shanghai, Guangzhou and Xi'an, which located in the northern, eastern, southern and western regions of China, respectively (Huang et al., 2014). ~~This result indicated that i~~In addition to investigating~~investigate the~~ primary particulate emissions, ~~it's also important to explore~~ the formation mechanisms ~~and effect factors~~ of these secondary species and related affecting factors also need to be understood in order to controlling $PM_{2.5}$ levels in China.

The Yangtze River Delta (YRD), ~~together with~~ the Pearl River Delta, Beijing–Tianjin–Tangshan, and the Sichuan Basin are ~~of most interesting as they are~~ the four regions with heaviest haze influence~~regions~~ in China. The characteristics and formation mechanisms of haze in the YRD are different from other haze regions, such as Beijing and the Pearl River Delta (Fu et al., 2008). Suzhou is located in the heartland of YRD region and is an important city~~ in the YRD~~. ~~Suzhou~~It suffered from the extremely serious aerosol pollution in Jan. 2013. With the tremendous economic growth over the past 30 years, Suzhou has experienced~~s~~ high levels of air pollution as reflected in the frequency of haze occurrence. The annual~~ly~~ haze days in Suzhou increased from only two days to more than 150 days from 1956 to 2011, i.e. over 40% of days ~~a~~were hazy in 2011. The low~~er~~ visibility, particularly the haze, has become a major concern of the city.~~,~~ ~~h~~However, only a few studies~~researches~~ have focused on~~been carried out to study the~~ haze events in Suzhou and~~.~~ ~~L~~little is known about the chemical characteristics and sources of fine particles in this city~~Suzhou~~. To fill these knowledge gaps~~Therefore~~, an intensified monitoring campaign was launched from December 2012 to January 2013 to collect~~get insight into the haze occurrence in urban Suzhou. On the basis of~~ high temporal resolution chemical and ~~measurements combined with~~ meteorological data.~~,~~ ~~t~~The objectives of this study are to (1) identify the dominant species in $PM_{2.5}$ and responsible for the visibility reduction; (2) explore the formation mechanism of the aerosol pollution; (3) study the impact of local, nearby and remote~~transport~~ sources on the formation of haze in urban Suzhou.

2. Methodology

2.1 Field observations

The sampling station was set up at the roof of one~~the~~ building in Suzhou Institute of Environmental Sciences (31°20'N, 120°36'E) (Fig. 1), about 300 m west to Nanyuan South Road and 360 m north to S Ring Road Elevated Bridge. There is no industrial source nearby and the~~is~~ site is representative of an urban residential and commercial environment~~ area~~. Suzhou is located in the center of Yangtze River Delta (YRD) and about 80 km east of~~to~~ Shanghai and 200 km west of~~to~~ Nanjing.

~~On-line hourly $PM_{2.5}$ mass concentrations, ionic species and OC/EC were measured by tapered element oscillating microbalance (TOEM), URG 9000 Ion Chromatography, Sunset semi-continuous OC/EC analyzer, respectively.~~ On-line hourly $PM_{2.5}$ mass concentrations were measured using tapered element oscillating microbalance (TEOM1405, Thermo Scientific Corp., MA, US) with the heating temperature of 50 °C. Some of the volatile particulate matter might be lost at 50 °C, but comparisons with collocated filters showed that the loss was less than 10%-20% of the gravimetric mass (Chow et al., 2008).

Hourly real-time concentrations of five cations (Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}) and four anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) in $PM_{2.5}$ were determined by URG Series 9000 Ambient Ion Monitor (AIM, URG Corporation, Chapel Hill, NC). The system consists of a particle collection unit and two ion chromatograph analyzers for cation and anion analyses. $PM_{2.5}$ was separated by a sharp-cut cyclone inlet operating at a flow rate of 3 L/min. The air was drawn through a liquid diffusion parallel-plate denuder to remove the interfering acidic and basic gases. A Steam-Jet Aerosol Collector was placed downstream of the denuder for collection and extraction of particles. The water extract was subsequently injected into the two ICs once an hour. The estimated uncertainties of the AIM measurements were approximately less than 15% (Trebs et al., 2004; Pathak et al., 2011). Some measures were taken out to reduce error, for instance, standards solutions were periodically injected to check the consistency of sensitivity of the detectors and air flow rate is frequently checked using a calibrated flow meter.

A semi-continuous OC/EC analyzer (Sunset Laboratory, Forest Grove, Oregon, USA) was applied to determine the carbonaceous species in $PM_{2.5}$. This instrument used the thermal-optical transmittance method based on NIOSH Method 5040. Organic compounds were vaporized in pure helium and then oxidized to CO_2 in a manganese dioxide oxidizing oven. CO_2 was then quantified by non-dispersive infrared detector. EC was then desorbed in an oxygen blend carrier gas and then oxidized and quantified using the same method as for OC. The split point between the pyrolized carbon formed from the organic carbon during the heating and EC that was originally in the sample was determined by measuring the transmission of a laser beam through the filter. Known volume of methane was injected, oxidized and quantified as an internal standard. Good correlations were found between the data measured by this instrument and filter-based laboratory analyses (Bae et al., 2004).

Visibility was monitored using the Belfort Model 6000 Visibility Sensor (Belfort Instrument Corp., MD, US). Trace O_3, SO_2, NO-NO_2-NO_X and CO gases were obtained with a resolution of 1 h by applying online analyzers (Thermo Instruments, TEI 49i, 43i, 42i and 48i, respectively)~~{Wang, 2016 #343}~~. Meteorological parameters were collected using Met Station One (Met One Corp., OR, US).

2.2 Data analysis methods

2.2.1 Reconstruction of the light extinction coefficient

The light extinction (b_{ext}) which is the sum of light scattering by particle ($b_{s,p}$), absorption by particle ($b_{a,p}$), scattering by gas ($b_{s,g}$), and absorption by gas ($b_{a,g}$), is reconstructed according to the revised IMPROVE algorithm as following (Pitchford et al., 2007):

$$b_{ext} = b_{s,p} + b_{a,p} + b_{a,g} + b_{s,g}$$

$$
\begin{aligned}
&\approx 2.2 \times f_S(RH) \times [\text{Small } (NH_4)_2SO_4] + 4.8 \times f_L(RH) \times [\text{Large } (NH_4)_2SO_4] \\
&+ 2.4 \times f_S(RH) \times [\text{Small } NH_4NO_3] + 5.1 \times f_L(RH) \times [\text{Large } NH_4NO_3] \\
&+ 2.8 \times [\text{Small OM}] + 6.1 \times [\text{Large OM}] \\
&+ 1 \times [\text{Fine Soil}] + 1.7 \times f_{SS}(RH) \times [\text{Sea Salt}] \\
&+ 0.6 \times [\text{Coarse Mass}] + 10 \times [\text{EC Mass}] \\
&+ 0.33 \times [NO_2\ (\text{ppb})] + \text{Rayleigh Scattering} \qquad (1)
\end{aligned}
$$

where $f_S(RH)$ and $f_L(RH)$ are the water growth factors for small- and large-sized distribution of sulfate and nitrate, respectively,~~;~~ and $f_{SS}(RH)$ is the water growth factor for sea salt. Water growth factors are adopted according to Pitchford~~Isakov~~ et al. (Pitchford et al., 2007)~~(Isakov et al., 2007)~~. The constant numbers in the above equation are extinction efficiencies for each chemical species under dry condition. $(NH_4)_2SO_4$ mass is estimated as 1.38 times of~~by the~~ SO_4^{2-} mass~~ multiplied by a factor of 1.38,~~ and ~~the ~~NH_4NO_3 mass ~~is estimated by the~~1.29 times of NO_3^- mass ~~multiplied by a factor of 1.29 based on the ~~assuming~~ption~~ that SO_4^{2-} and NO_3^- are fully neutralized by NH_4^+ in the forms of $(NH_4)_2SO_4$ and NH_4NO_3, respectively, according to the revised IMPROVE method. Organic matter (OM) is estimated as 1.8 times of~~derived from multiplying~~ OC concentration~~s by a factor of 1.8~~ to account for unmeasured fractions~~atoms~~.

The concentrations of sulfate, nitrate, and OM are divided into small- and large-sized fractions in this algorithm. The size modes are described by log-normal mass size distributions with geometric mean diameter and geometric standard deviations. Concentrations of sulfate, nitrate, and OM in the large- and small-mode are estimated ~~by ~~using the following equations (taking sulfate as an example):

$$[\text{Large } (NH_4)_2SO_4] = [\text{Total } (NH_4)_2SO_4]^2/20, \text{ for } [\text{Total } (NH_4)_2SO_4] < 20\ \mu g\ m^{-3} \qquad (2)$$

$$[\text{Large } (NH_4)_2SO_4] = [\text{Total } (NH_4)_2SO_4], \text{ for } [\text{Total } (NH_4)_2SO_4] > 20\ \mu g\ m^{-3} \qquad (3)$$

$$[\text{Small } (NH_4)_2SO_4] = [\text{Total } (NH_4)_2SO_4] - [\text{Large } (NH_4)_2SO_4] \qquad (4)$$

2.2.2 Air mass back trajectory

To study the impact of local and regional sources on the aerosol pollution in Suzhou, ~~the~~ 48-h back trajectories starting at 100 m from the sampling site were calculated ~~by~~ using the NOAA HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT_traj.php). The back trajectories were calculated four times per day at starting times of 04:00, 10:00, 16:00, and 22:00 UTC, i.e. 12:00, 18:00, 00:00, and 06:00 local times, respectively. The trajectory cluster analysis was based on the GIS-based software TrajStat (Wang et al., 2009).

2.2.3 Potential source contribution function

The potential source contribution function (PSCF) method is based on the results of HYSPLIT model and can be used to identify the regional sources. The zone of concern is divided into $i \times j$ small equal grid cells. The PSCF value for the ijth grid cell is calculated as: $\mathrm{PSCF}_{ij} = m_{ij}/n_{ij}$, where n_{ij} is designated as the number of trajectory segment endpoints that fall in the ijth cell and m_{ij} is defined as the number of trajectory endpoints with pollutants concentrations higher than an set criterion (Ashbaugh et al., 1985; Wang et al., 2009). In present study, the average concentrations were treated as the criterion (Hsu et al., 2003). The PSCF values were multiplied by a weighting function W_{ij} to reduce the effect of small values of n_{ij} and to better reflect the uncertainty in the values for the cells with small n_{ij} values. The weighting function W_{ij} is defined as follows (Polissar et al., 1999):

$$W_{ij} = \begin{cases} 1.00, & 80 < n_{ij} \\ 0.70, & 20 < n_{ij} \le 80 \\ 0.42, & 10 < n_{ij} \le 20 \\ 0.05, & n_{ij} \le 10 \end{cases}$$

The PSCF value can be interpreted as the conditional probability that ~~the~~ air masses with pollutants concentration greater than the set criterion pass through the ijth cell during transport to the receptor site (Wang et al., 2009). That is, cells with high PSCF values are indicative of regions having~~e~~ high potential contributions to the pollution at the receptor site.

3. Results and discussion

3.1 General characteristics of haze events

As illustrated in Fig. 2, the visibility varied from a few hundred meters to more than 50 km with a minimum value of only 322 m on Jan. 15, 2013, which was accompanied by high RH (82%). During the 2-month observation period, there were a total~~ly~~ of ten periods when visibility was below 10 km. Excluding~~ept for~~ the five periods ~~which were~~ accompanied by precipitation, the other five periods were identified as haze events~~ were identified~~ and all of these events occurred in January 2013. During the haze occurrence, ~~the~~ hourly concentrations of PM$_{2.5}$ often exceeded 150 μg m^{-3}, with a maximum concentration of 324 μg m^{-3} observed on Jan. 14, 2013.~~,~~ These concentrations were generally higher than those in normal periods. The daily concentrations of PM$_{2.5}$ on haze days varied from 148 to 196 μg m^{-3}, which were 1.97 to 2.61 times the Grade II criteria of the national ambient air quality standard (75 μg m^{-3}). These values~~is~~ were~~as~~ comparable to that observed~~the PM$_{2.5}$ concentrations~~ in Nanjing where the ~~with~~ average PM$_{2.5}$ ~~value of~~was 175.6 μg m^{-3}~~,~~, but slightly~~little~~ higher than those in some other cities in YRD where ~~with the~~ mean values were generally lower than 147.3 μg m^{-3} when haze occurred in Jan. 2013 (Wang et al., 2014a; Wang et al., 2014d). The aerosol pollution happened in northeast China such as in Beijing, Tianjin, and Shijiazhuang were much severer, for instance, the daily and hourly concentrations of PM$_{2.5}$ were up to 368 μg m^{-3} and 462 μg m^{-3} in Tianjin in January 9 to 13, 2013, and~~;~~ the ~~hourly~~ maximum hourly value~~s~~ of approximately 1000 μg m^{-3} was~~ere~~ recorded in Beijing and Shijiazhuang in Jan. 2013 (Ji et al., 2014; Han et al., 2014; Wang et al., 2015).

~~The duration of haze events comprised a~~Approximately 40% of the time in~~whole~~

January 2013 met haze weather criteria, whereas no haze appeared in December 2012. ~~Less~~Low amount of rainfall in ~~the ~~January might be one of the factors causing~~es~~ the long duration of haze. ~~The r~~Relative humidity (RH) was reported to be an important contributor to the visibility reduction. In the present study, ~~the RH increased with the reduction of ~~visibility decreased with increasing RH, e.g. when RH increased from 42% to 78%, ~~the ~~visibility decreased from 42 km at 2:00 p.m. on 17 January to 4 km at 7:00 a.m. on 19 January. Statistically, ~~the ~~RH was relatively higher during haze occurrence than clear periods. Low wind speed, smaller than 5 m s^{-1}, was~~ere~~ frequently observed during this winter. Furthermore, ~~the ~~wind speed~~s~~ was~~ere~~ mostly less than 1 m s^{-1} during the haze events, lower than those in Beijing (Yang et al., 2015). Besides, atmospheric pressure was also found to be relatively low during the haze occurrences. The stagnant air, due to low wind speed and pressure, was unfavorable for ~~the ~~aerosol horizontal transport or vertical diffusion~~ of aerosols~~, and therefore resulted in~~leading to the increase of~~ aerosol accumulation~~concentration~~. Therefore, unfavorable weather conditions (high RH, and low rainfall, wind speed and atmospheric pressure) were among the causes ~~might provide external caused beneficially for the ~~forming~~ation of~~ haze in January 2013 in Suzhou as well as in many other cities (Wang et al., 2014b; Wang et al., 2014c; Wang et al., 2014d; Han et al., 2014; Yang et al., 2015).

In order to get more insights of the haze formation in this region, three haze events, which occurred on Jan. 19, from Jan. 21 to 26, and on Jan. 30, respectively, were further discussed below. Generally, the meteorological parameters and aerosol pollution level were comparable during these three haze occurrences, except for the relatively lower RH and higher temperature in the third haze events.

3.2 PM$_{2.5}$ chemical composition and light extinction

3.2.1 PM$_{2.5}$ chemical composition

The temporal variations of the concentrations of water-soluble inorganic ions (WSIIs) ~~we~~are illustrated in Fig. 3. The mean concentration of WSIIs (including four anions and five cations) was 48.8 ± 24.6 $\mu g\ m^{-3}$, accounting for 40% of $PM_{2.5}$ mass concentration, slightly~~little~~ lower than that in Beijing which was 69.4 ± 55.8 $\mu g\ m^{-3}$ and accounted for 43% of $PM_{2.5}$ (Tao et al., 2015). SO_4^{2-} was the most abundant species in WSIIs, with averaged value of 21.1 ± 13.5 $\mu g\ m^{-3}$, followed by NH_4^+ (13.9 ± 5.69 $\mu g\ m^{-3}$) and NO_3^- (10.7 ± 6.75 $\mu g\ m^{-3}$), accounting for 43%, 29% and 21% of WSIIs, respectively. These secondary inorganic components in total~~ly~~ constitute 93% of total WSIIs, close to the result in Beijing (Gao et al., 2015; Tao et al., 2015). The rest of ions, Na^+ (1.36 ± 0.43 $\mu g\ m^{-3}$), K^+ (0.85 ± 0.45 $\mu g\ m^{-3}$), Cl^- (0.54 ± 1.28 $\mu g\ m^{-3}$), Ca^{2+} (0.34 ± 0.27 $\mu g\ m^{-3}$), F^- (0.06 ± 0.72 $\mu g\ m^{-3}$), Mg^{2+} (0.05 ± 0.07 $\mu g\ m^{-3}$), each had minor contribution (< 3%) to WSIIs.

NO_3^- and SO_4^{2-} are mainly formed from the transformation of their respective gaseous precursor~~s~~ of NO_X and SO_2 (Wang et al., 2005). The emission ratio of NO_X to SO_2 was 17.2–52.6 for motor vehicles and 0.527–0.804 for stationary sources in the Yangtze River Delta, which means that the emissions of SO_2 from motor vehicles were much less than NO_X, but the emissions of SO_2 from stationary sources such as power plants, industrial boilers and furnaces were relatively higher than NO_X (Fu et al., 2008). Thus, the mass ratio of NO_3^-/SO_4^{2-} could be used as an indicator of the relative importance of mobile and stationary sources of sulfur and nitrogen in the atmosphere (Arimoto et al., 1996). In the present study, the averaged ratios of NO_3^-/SO_4^{2-} and NO_X/SO_2 were 0.59 and 5.68, respectively, indicating that emissions from vehicles and stationary sources were both important in Suzhou. The ratio~~s~~ of NO_3^-/SO_4^{2-} in this study was~~ere~~ lower than that~~the ratio~~ in Beijing, but higher than those ~~reported ~~in Shanghai (0.43), Qingdao (0.35), Taiwan (0.20), and Guiyang (0.13) (Wang et al., 2006; Yao et al., 2002; Hu et al., 2002a; Fang et al., 2002; Xiao and Liu, 2004).

The NO_3^-/SO_4^{2-} ratio was relatively higher for 20% worst visibility hours (0.58) than 20% best visibility hours (0.54)~~, which were 0.58 and 0.54, respectively~~, suggesting that vehicle emission might play an important role in haze pollution. This was in agreement with the result in Guangzhou, where the NO_3^-/SO_4^{2-} ratio was 1.02 under stagnation and 0.55 in normal days, but contrary to that in Beijing, where the ratio in haze days (0.~~64~~89) was lower than in normal days (0.96~~83~~) (Tan et al., 2009; Wang et al., 2006). In present study, NO_X concentration greatly exceeded that of SO_2 during haze period, coincided with the result in Guangzhou, but disagreed with that in Beijing (Tan et al., 2009). Previous studies have indicated that high NO_X emission may reduce the formation of OH and H_2O_2, and further decrease the possibility of SO_4^{2-} formation (Tan et al., 2009). Thus, the elevation of NO_3^- concentration under worse visibility conditions was greater than that of SO_4^{2-} in both Suzhou and Guangzhou. ~~Besides of lower NO_3^-/SO_4^{2-} ratio, Wang et al. also found lower NO_2/SO_2 ratio and lower ratio of (NO_3^-/SO_4^{2-}) to (NO_2/SO_2) in haze days than that in clear days in Beijing, and summarized that the formation rate of nitrate might not be the controlling factor for the nitrate concentrations in $PM_{2.5}$ (Wang et al., 2006). The low NO_3^-/SO_4^{2-} ratios found in haze days in Beijing was considered to be related to the thermodynamic characteristic of NH_4NO_3 (Wang et al., 2006). The ratios of NO_X/SO_2 in present study were 6.89 for 20% worst visibility period higher than 4.30 for 20% best visibility period.~~ The ratios of (NO_3^-/SO_4^{2-}) to (NO_X/SO_2) were~~ also~~ lower for worse visibility period~~ in present study~~, in accordance with that in Beijing, ~~suggesting~~ showing that the nitrate concentrations may be also greatly affected by the re-volatilization of NH_4NO_3 (Tan et al., 2009)~~ as those in Beijing~~.

The carbonaceous species, constituting 22% of $PM_{2.5}$, were dominated by organic carbon~~s~~, which was~~ere~~ 22.8 ± 10.6 μg m^{-3} and 3 to 29 times of that of elemental carbon (2.79 ± 2.58 μg m^{-3}), similar to those in Beijing (Tao et al., 2015). The relatively high ratios of OC/EC (10.6 ± 4.29), which were higher than the ratios in Beijing (7.1 ± 0.5) and Jinan (7.15 ± 1.78), demonstrated the existence of secondary organic carbon (SOC) (Ji et al., 2014; Zhang et al., 2014). The concentrations of SOC were estimated by applying the EC tracer method, which has been widely used to estimate the secondary organic aerosol contribution to $PM_{2.5}$

concentrations (Castro et al., 1999; Yang et al., 2005). The minimum ratio of OC/EC was 3.09 in the present study. ~~So t~~The estimated ~~concentrations of~~ SOC was~~ere~~ 14.2 ± 5.69 μg m^{-3}, contributing 65% on average to OC. The ~~ratios of~~ SOC/OC was~~ere~~ higher than 0.5 during almost the whole sampling period~~time~~ except on~~for the periods around~~ Jan. 30~~,~~ when the third haze event occurred. This ratio was higher than most of the results found in other areas such as in Beijing and Guangzhou (Yang et al., 2005; Tan et al., 2009).

~~Overall, according to the percentage of each species in $PM_{2.5}$ mass, the m~~Major components in $PM_{2.5}$ were found to be SO_4^{2-} (17%), SOC (14%), NH_4^+ (12%), NO_3^- (8%), and POC (6%)~~ with total percentage of 57%~~. ~~It is noted that t~~The top~~first~~ four components~~species~~ were mainly from secondary sources. ~~In addition, the concentrations of~~ $PM_{2.5}$ was~~ere~~ significantly correlated with these secondary species, revealing that gas to particle conversion ~~during winter in this region~~ was severe in winter and had great impact on aerosol pollution in this region. It's worth noting that the aerosol composition in the third haze event was distinct from the other two (Fig. 3) as seen from the higher proportion of carbon species from primary emissions (POC and EC) and lower fraction of secondary formation components (SIA and SOC), indicating different haze formation mechanism in the third haze event.

~~3.2.2 Variations of aerosol particles and precursors~~

~~Fig. 4 diagrammed the diurnal variation of meteorological parameters, various aerosol components and, the precursors and some other important gaseous species under three different visibility conditions (i.e., (1) all data, (2) visibility ≤ 10 km, (3) visibility > 10 km). The daily variation of gas phase compounds were different between species and were mainly controlled by the direct surface emissions (such as NO_X, SO_2, and CO) or photochemical process (O_3). There were a distinct AM morning peak and a less distinct afternoonPM peak, consistent with morning and afternoonPM rush hours for NO_X and CO. This might related to the heavy traffic emission in the rush hours~~

~~and the strong elevation of the Planetary Boundary Layer heights at noon. In contrast, there was only one mid-day peak for SO_2. This diurnal profiles were similar to those observed in Guangzhou (Hu et al., 2002b) and Maryland (Antony Chen et al., 2001). In the latter study, the dominant source of SO_2 was considered to be the long range transport from the industrialized Midwest and with the deep boundary layer around noon, SO_2 aloft mixed more effectively down to the surface and thus caused the mid-day peak of SO_2. The reasons for the diurnal variation of SO_2 observed in present study need further investigation. Similar to the diurnal distribution of SO_2, O_3 also showed one distinct peak around noon due to the strong photochemistry at that time (Quan et al., 2014).~~

~~For the aerosol components, EC which was also produced by the surface emissions showed similar profile to NO_X and CO. Furthermore, EC had significantly positive correlation with NO_X and CO, demonstrating that they had common sources, mainly from vehicular exhaust. However, tThe diurnal profiles of the secondary species were similar to their precursors but obviously affected by O_3 concentrationsother factors such as solar radiation, which could promote the oxidation of the precursors, as these species were mainly produced by chemical processes. For instance, there was a 2-hour delay for sulfate to reach its peak compared to SO_2 due to the transformation. This pattern was also observed in Guangzhou (Hu et al., 2002b). NO_3^- and SOC exhibited similar diurnal variation as their precursors had common sources and they both formed from secondary photochemical oxidation. The daily profiles of NO_3^-, NH_4^+ and SOC showed lower concentrations around 15:00 (local time) probably due to the high boundary layer and/or low concentration of precursors. Besides, for NO_3^- and NH_4^+, high temperature, which enhanced the evaporative loss, and low relative humidity may also responsible for the low level.~~

~~Fig. 4 also suggested that both gas-phase compounds and aerosol components all showed similar pattern of diurnal variation but had different magnitudes of concentrations for different visibility levels. These components except for O_3 all showed relatively higher concentrations under low visibility especially for the~~

~~secondary inorganic species, indicating the important impact of the formation of secondary components on the visibility reduction. The relatively low levels of O_3 under low visible conditions might because of the decreased photochemical production and the chemical conversions of SO_2 and NO_X to sulfate and nitrate. It is worth noting that relatively high humidity which favored for the formation of sulfate and nitrate was observed under low visibility conditions. In addition, it seemed that low visibility was associated with southwest wind. This might related to the topography. There are mountains located on the southwest which is not conducive to the diffusion of pollutants.~~

3.2.2~~3~~ Light extinction coefficient

In order to ~~appoint~~ determine the contribution of $PM_{2.5}$ constituents to the visibility degradation, light extinction (b_{ext}) was reconstructed based on the revised IMPROVE algorithm. In the present study, the impact of fine soil and coarse mass were not included because of the lack of metal elements and coarse matter concentrations. ~~Thus, the revised IMPROVE algorithm was modified as following:~~

~~$b_{ext} = b_{s,p} + b_{a,p} + b_{a,g} + b_{s,g}$~~

~~$\approx 2.2 \times f_S(RH) \times [\text{Small } (NH_4)_2SO_4] + 4.8 \times f_L(RH) \times [\text{Large } (NH_4)_2SO_4]$~~

~~$+2.4 \times f_S(RH) \times [\text{Small } NH_4NO_3] + 5.1 \times f_L(RH) \times [\text{Large } NH_4NO_3]$~~

~~$+2.8 \times [\text{Small OM}] + 6.1 \times [\text{Large OM}]$~~

~~$+1.7 \times f_{SS}(RH) \times [\text{Sea Salt}] + 10 \times [\text{EC Mass}] + 0.33 \times [NO_2 \text{ (ppb)}] + \text{Rayleigh Scattering}$~~

The estimated b_{ext} ~~in present study~~ was~~ere~~ 664 ± 288 Mm^{-1}~~,~~ and was significantly correlated with $PM_{2.5}$ concentrations ($r = 0.94$, $p < 0.001$), demonstrating the strong influence of fine aerosols on visibility degradation.~~.~~

The reconstructed light extinction coefficient was compared with that derived from visibility and that calculated using a regression model developed by Chen. Extinction coefficient is inversely correlated with visibility according to the

Koschmieder equation (Vis = K/b_{ext}) (Seinfeld and Pandis, 2012). By using a K value of 3.912, t~~A comparison of the light extinction coefficients derived from different methods. ~~he calculated b_{ext}~~Visibility is inversely correlated with the extinction coefficient according to the Koschmieder equation (Vis = K/b_{ext}). By using a K value of 3.912~~, ~~we further calculated the visibility based on the reconstructed b_{ext}. The estimated visibilities ~~was~~ere~~ ~~7.47~~371 ± ~~4.12~~234 Mm^{-1}~~ km, ranged from 2.57 km to 23.41 km.~~, ~~Although this was~~much lower than the ~~measured visibility, which were 15.0 ± 8.50 km,~~coefficients obtained from IMPROVE algorithm. Nevertheless, ~~the estimated and measured visibility~~they~~ had similar temporary trend and~~ were significantly correlated with each other ($r = 0.71$, $p < 0.001$). Another method applied here to estimate b_{ext} was a 2-factor parameterization regression model based on RH and aerosol volume concentration (Chen et al., 2012). The volume concentration can be acquired from the mass concentration divided by an average particle density of 1.7 g cm^{-1} (Wehner et al., 2008). A comparison of b_{ext} reconstructed by IMPROVE algorithm and the regression model is presented in Fig. 4. Generally, a strong correlation was evident with a correlation coefficient higher than 0.97 ($R^2 = 0.952$), confirming that the reconstructed b_{ext} from the IMPROVE algorithm was reliable. The majority of b_{ext} was clustered near the 1:1 line for $b_{ext} < 500$ Mm^{-1}, with the corresponding RH~~s~~ mainly below 75%. However, for $b_{ext} > 500$ Mm^{-1}, the dispersion of b_{ext} gradually increased, and most of the corresponding RH was higher than 75%. There are two possibilities causing these deviations. The first one is the ignorance of the impact of particle size distribution on light extinction in the 2-factor parameterization model applied here, as the variation of aerosol mass or volume fractions of different size particles can influence b_{ext} value especially under high RH (Chen et al., 2012). The second one is from the uncertainties of in situ measurements since RH sensor may have large errors under high RH condition. The regression model result was directly controlled by the RH value, and the hygroscopic growth factor in the IMPROVE algorithm depends on RH.

The light extinction was~~were~~ mostly influenced by aerosol light scattering as the estimated $b_{s,p}$ was~~ere~~ 609 ± 277 Mm^{-1}, accounting for 91% of ~~the~~ b_{ext}~~ (at least 75%)~~, while $b_{a,p}$ and the extinction coefficient by gaseous were only 27.9 ± 25.8 Mm^{-1} and 26.6 ± 4.87 Mm^{-1}, respectively. The largest contributor to b_{ext} from the~~of~~ reconstructed chemical species in fine particles ~~to b_{ext}~~ was organic matter (OM), accounting for 40%, followed by $(NH_4)_2SO_4$, 34%, NH_4NO_3, 16%, and EC~~, with their shares of 34%, 16% and~~ 4%~~, respectively~~. ~~Fractions of these~~However, the percentage contributor~~s~~ varied greatly during~~over~~ the study period, e.g. the contributions of NH_4NO_3 ranged from only 3% to up to 40%. Generally, the contributions of $(NH_4)_2SO_4$ and NH_4NO_3 were higher under low visibility period, increased from 30% and 11%, respectively, during the~~under~~ 20% best visibility periods to 39% and 19%~~-~~, respectively, during the~~under~~ 20% worst visibility period~~, increased 1.3 and 1.7 times, respectively~~. ~~While~~Correspondingly, the contributions of OM and EC ~~were~~ reduced from 46% and 5%, respectively, ~~under 20% best visibility period~~ to 35% and 4%, respectively, during the same periods~~under 20% worst visibility period~~. These results indicated the important role ~~of~~ sulfate and nitrate played on haze formation.

The percentage~~s~~ contribution to light extinction from individual~~of the~~ aerosol components ~~contribute to the light extinction were~~ also varied with~~experienced different variations in their fractions during different~~ haze event~~s~~ and visibility conditions. ~~We compared t~~The percentage contributions of individual~~these~~ components during the best and worst~~under~~ 20% ~~best~~ visibility hours in each of the three haze events are compared and shown in Fig. 5~~conditions to those under 20% worst visibility conditions to investigate the controlling factor for the haze formation (Fig. 5)~~. During the first haze event (on Jan. 19), the contribution~~s~~ of NH_4NO_3 was~~increased from only~~ 8% ~~under 20% best visibility to~~and 24% during the~~under~~ 20% best and worst visibility hours, respectively, while the corresponding numbers are~~percentage of OM decreased from~~ 48% and~~to~~ 37% for OM. ~~For~~There were no significant differences between the two visibility categories for the contributions of $(NH_4)_2SO_4$ or~~and~~ EC~~, there was no significant change~~. During~~For~~ the second haze event (from Jan. 21 to 26), the fractions were 1.8, 1.5 and 1.3 times higher for NH_4NO_3, $(NH_4)_2SO_4$ and EC respectively but 1.2 times lower for OM under ~~worse~~ 20% worst visibility condition than those under 20% best visibility condition during this time. Overall, $(NH_4)_2SO_4$ made great contribution to the light extinction and NH_4NO_3 had largest difference between 20% best and worst visibility conditions during these two haze events. Therefore, secondary inorganic aerosols especially NH_4NO_3 was likely the key component for the impaired visibility for these two haze events. The elevated proportion of $(NH_4)_2SO_4$ and NH_4NO_3 during the heavy polluted period was also observed in Beijing (Tao et al., 2015; Wang et al., 2015; Zheng et al., 2015). A different trend of comparison between the best and worst visibility periods was found in the third haze event (on Jan. 30) than in the first two. In the third event, the percentage contributions of ~~Contrarily, during the third haze (on Jan. 30) increasing proportions of~~ OM and EC increased during the worst visibility period compared to the best visibility period (from 40% to 49% and 6.8% to 11%, respectively), while that of ~~accompanied with decreasing percentage of~~ $(NH_4)_2SO_4$ decreased (from 28% to 19%). ~~were found under worse visibility period, indicating that the~~ ~~e~~Carbonaceous components ~~might be relatively~~played a more important role for ~~the~~ visibility reduction in the third event. Therefore, there seems to be different formation mechanisms for haze events~~formation~~ in Suzhou.

3.3 Conversion from gas to particle phase

3.3.1 Variations of aerosol particles and precursors

Fig. 6~~4~~ diagrammed the diurnal variations of meteorological parameters, various aerosol components, ~~the~~gaseous precursors, and some other important gaseous species under three different visibility conditions: ~~(i.e.,~~ (1) all data, (2) visibility ≤ 10 km, and (3) visibility > 10 km~~)~~. The daily variations of gas-phase compounds were different between species and were mainly controlled by the direct surface emissions (such as NO_X, SO_2, and CO) or photochemical process (O_3). There were a distinct morning peak and a less distinct afternoon peak, consistent with morning and afternoon rush hours for NO_X and CO. This might be related to the heavy traffic emissions in the rush hours and the strong elevation of the Planetary Boundary Layer heights at noon. In contrast, there was only one mid-day peak for SO_2. This diurnal profiles were similar to those observed in Guangzhou (Hu et al., 2002b) and Maryland (Antony Chen et al., 2001). In the latter study, the dominant source of SO_2 was considered to be the long range transport from the industrialized Midwest and with the deep boundary layer around noon;~~,~~ SO_2 aloft mixed more effectively down to the surface and thus caused the mid-day peak of SO_2. The reasons for the diurnal variation of SO_2 observed in the present study need further investigation. Similar to the diurnal distribution of SO_2, O_3 also showed one distinct peak around noon due to the strong photochemistry at that time (Quan et al., 2014).

For the aerosol components, EC which was also produced by the surface emissions showed a profile similar~~ profile~~ to NO_X and CO. Furthermore, EC had significantly positive correlation with NO_X and CO, demonstrating that they had common sources, mainly from vehicular exhaust. The diurnal profiles of the secondary species were similar to their precursors but obviously affected by other factors such as solar radiation, which could promote the oxidation of the precursors. For instance, there was a 2-hour delay for sulfate to reach its peak compared to SO_2 due to the transformation processes. This pattern was also observed in Guangzhou (Hu et al., 2002b). NO_3^- and SOC exhibited similar diurnal variation as their precursors had common sources and they both formed from secondary photochemical oxidation. The daily profiles of NO_3^-, NH_4^+ and SOC showed lower concentrations around 15:00 (local time) probably due to the high boundary layer and/or low concentration of precursors. Besides, for NO_3^- and NH_4^+, high temperature, which enhanced the evaporative loss, and low relative humidity may also be responsible for the low levels.

Fig. 64 also suggested that both gas-phase compounds and aerosol components all showed similar patterns of diurnal variations but had different magnitudes of concentrations for different visibility levels. These components except for O_3 all showed relatively higher concentrations under low visibility especially for the secondary inorganic species, indicating the important impact of the formation of secondary components on the visibility reduction. The relatively low levels of O_3 under low visible conditions might be due to~~because of~~ the decreased photochemical production and the chemical conversions of SO_2 and NO_X to sulfate and nitrate. It is worth noting that the relatively high humidity which favored~~ for~~ the formation of sulfate and nitrate was observed under low visibility conditions. In addition, it seemed that low visibility was associated with southwest wind. This might related to the topography. There are mountains located on the southwest which is not conducive to the diffusion of pollutants.

In consideration of the distinct aerosol composition during the third haze, the comparison of gaseous pollutants between the third and the first two haze episodes were made. The concentrations of SO_2 and O_3 were comparable for these three haze event. Contrarily, much higher levels of NO, CO and NO_2 were evident during the third haze, in accordance with the high concentrations of POC and EC. These species (NO, CO, NO_2, POC and EC) ~~were ~~had good correlations with each other. Furthermore, they had similar diurnal variations and exhibited extremely high levels in the morning rush hours ~~i~~on January 30 when the third haze occurred. These results implied that there were common sources for these species, mainly from vehicle exhaust emission.

3.3.2 Formation mechanisms of sulfate and nitrate

As discussed earlier, the chemical formation of sulfate and nitrate from SO_2 and NO_2 respectively, should play important roles for visibility reduction, especially for the first two haze events. The sulfur oxidation ratio, defined as SOR = $n\text{-}SO_4^{2-}/(n\text{-}SO_4^{2-} + n\text{-}SO_2)$ and the nitrogen oxidation ratio, defined as NOR = $n\text{-}NO_3^-/(n\text{-}NO_3^- + n\text{-}NO_2)$ were used as indicators of the secondary transformation processes. The daily variations of NOR showed similar patterns as those of NH_4^+ and NO_3^-. Likewise, SOR had similar diurnal changes as SO_4^{2-}. The values of SOR and NOR increased more than 1.3 and 2.0 times, respectively, during the first two haze periods compared to clear periods, ~~Both SOR and NOR were higher with lower visibility (Fig. 6),~~ implying greater oxidation of gaseous species and more elevated secondary aerosols. This was supported by the evidently higher concentrations of SO_4^{2-}, NH_4^+, and NO_3^- ~~under worse visibility conditions~~in the first two haze events. Almost no elevating levels of SOR, NOR or SIA were observed in the third haze, again confirming that the SIA formation may not be the predominant factor controlling the occurrence of this haze event.

The formation of SO_4^{2-} from SO_2 was mainly ascribed to the gas-phase oxidation ~~with~~by OH and H_2O_2 radical or heterogeneous oxidation (Wang et al., 2006; Zhao et al., 2013). The gas-phase reaction is a strong function of temperature and heterogeneous reactions always associated with high RH (Sun et al., 2006; Sun et al., 2014; Sun et al., 2013a). However, weak correlations were found between SOR and either temperature ($r = 0.174$, $p < 0.01$) or RH ($r = 0.150$, $p < 0.01$) in the present study, indicating the complex formation mechanism of sulfate.

Many studies suggested that sulfate from aqueous SO_2 oxidation catalyzed by transition metals was more significant during winter haze rather than gas-phase oxidation (Li et al., 2011; Sun et al., 2013b; Zhao et al., 2013). Our measurement also found that the heterogeneous oxidation was an important sulfate formation pathway in this study area. As shown in Fig. 7, high concentrations of NO_2 accompanied with ultralow level of O_3 less than 10 ppb and low amount of solar radiation were observed during most of the time in the haze period, such as from 12 PM to 10 AM on 19 January and from 21 to 34 January. These results revealed the rather weak photochemical activities during these time windows. The high levels of NO_2 and weak photochemical activities could result in insufficient production of oxidants (OH and H_2O_2 radicals) for gas-phase oxidation (Hua et al., 2008). Thus, other oxidation reactions other than gas-phase oxidation likely explained the formation of abundant secondary sulfates during the haze episode. The high RH (> 70%) during these haze period was a beneficial factor for aqueous-phase oxidation of SO_2 to sulfate. Besides, the calculation results using the Extended AIM Aerosol Thermodynamic Model (E-AIM, Model II) (Clegg et al., 1998) (http://www.aim.env.uea.ac.uk/aim/aim.php) showed a significant increase of the liquid water content when RH > 70%. These results highlight the importance of aqueous-phase reaction to the secondary transformation of SO_2.

The concentrations of O_3 were not extremely low during the whole haze period, such as during daytime on January 23 and 25; the O_3 levels were as usual and had obvious diurnal variations with one distinct peak around noon. RH was lower than 70% and sulfate was primarily in the solid phase at these times, indicating that gas-phase oxidation was probably the dominant pathway for sulfate formation. Aqueous-phase oxidation likely became predominant at night. This could explain the high SOR in the afternoon and the sustained high level at night.

~~The daily variation of NOR showed similar pattern as NH_4^+ and NO_3^-, likewise, SOR had similar diurnal change as SO_4^{2-}, indicating the influence from NO_X or SO_2 and O_3. Additionally, it is interesting to notice that under low visibility conditions during nighttime when O_3 concentrations were extremely low, there was still a rapid chemical conversion from gaseous to particle phase especially for sulfate particles. This conversion might mainly be produced through the processes other than the photochemical activities such as heterogeneous reactions in the aqueous surface layer of pre-existing particles or in cloud processes. The higher humidity during that time and the significant positive correlations between SOR and humidity through the whole study period again seem to validate that the heterogeneous process likely dominate the sulfate formation. This was consistent with the finding by Hewitt that liquid phase chemical conversion process was responsible for the formation of sulfate particles in winter (Hewitt, 2001).~~

~~Compared to the formation of sulfate, the contributions of various conversion pathways to nitrate formation were less known (Pathak et al., 2009). In this section,~~

~~we examined in detail the possible causes of nitrate in $PM_{2.5}$.~~Nitrate formation is mainly through gas-phase oxidation of NO_2 by OH during daylight and the heterogeneous reactions of nitrate radical during nighttime (Seinfeld and Pandis, 2012). ~~Figure~~ Fig. ~~7~~ 8 showed the nitrate-to-sulfate molar ratio ($[NO_3^-]/[SO_4^{2-}]$) as a function of the ammonium-to-sulfate molar ratio ($[NH_4^+]/[SO_4^{2-}]$), which can provide an insight into the formation pathway of the secondary species (Jansen et al., 2014; Pathak et al., 2009; He et al., 2012).

The relative abundance of nitrate linearly increased with the increasing ammonium-to-sulfate molar ratio. Fitting a linear regression line resulted in an intercept of $[NH_4^+]/[SO_4^{2-}]$-axis of 1.51, indicating that nitrate formation via homogeneous reaction of HNO_3 with NH_3 became significant at $[NH_4^+]/[SO_4^{2-}] > 1.51$ (Pathak et al., 2009; Jansen et al., 2014; He et al., 2012)~~ (Pathak et al., 2004; Pathak and Chan, 2005)~~. Pathak et al. (2009) also reported an intercept value of 1.5 for ~~a variety of~~several cities worldwide while Jansen et al. (2014) found a ~~little~~ slightly smaller intercept value of 1.38 for Hangzhou. The ammonium concentration in excess of the amount at which nitrate formation became evident was defined as excess ammonium ($[NH_4^+]_{exc} = ([NH_4^+]/[SO_4^{2-}]-1.51)\times[SO_4^{2-}]$). The concentrations of excess ammonium were always higher than 0 and linearly correlated with nitrate concentration, as shown in Fig.~~ure~~ 8. This indicated that the formation of nitrate was strongly associated with ammonium formation. In other words, when the excess ammonium was > 0, the gas-phase homogeneous reaction between the ambient ammonia and nitric acid was responsible for forming nitrate (Pathak et al., 2009; Jansen et al., 2014). The slope of 0.37 for the regression and the scattering of the data indicated that the excess ammonium was bound to species other than nitrate, such as chloride, bisulfate, etc. The significance of gas-phase homogeneous reaction to nitrate formation has been reported for many cities (Jansen et al., 2014; Pathak et al., 2009). However, as mentioned above, in some cases during haze period, the conditions (ultralow ozone concentrations, low solar radiation and high NO_2) were not favorable for the gas-phase oxidation. Relatively high RH were often observed in those cases, which may have favored the gas to particle partitioning of nitrate acid and ammonia (Sun et al., 2011). Furthermore, the E-AIM calculation results manifested that the nitrate partly or completely existed in the aqueous phase during those conditions. Therefore, we assumed that heterogeneous chemistry, such as heterogeneous hydrolysis of N_2O_5 ($N_2O_5 + H_2O$ (aq) → $2HNO_3$) or equilibrium partitioning (HNO_3 (g) + NH_3 (g) ↔ NH_4^+ (aq) + NO_3^- (aq)) also contributed to the formation of nitrate under high RH conditions. This was supported by the fact that in Fig. 8 more plots were deviated from the regression line when RH were relatively high. The importance of ~~Besides, a model study also verified that aqueous-phase oxidation of NO_x was of minor importance for nitrate production in the atmosphere (Pandis and Seinfeld, 1989). But contrarily,~~ heterogeneous reactions for nitrate formation were ~~considered to be significantly important in the production of both sulfate and nitrate~~also reported in other studies (Sun et al., 2011; Zheng et al., 2015) ~~(Sun et al., 2011)~~.

3.4 Regional sources deduced from trajectory and PSCF analyses

The regional sources and transport of air pollutants exert a profound impact on local air quality in YRD region as it is located in the typical monsoon region (Ding et al., 2013). Therefore, trajectory clustering method was employed to examine the pathway of air masses and to look into the chemical composition~~s~~ and light extinction coefficients among the air masses with different origination. The calculated 48-~~-~~h back trajectories were clustered into six clusters (Fig. 9 and Table 1), i.e. six air mass transport pathways. As can be seen, ~~Table 1 summarized the percentage of trajectories for each trajectory cluster and the corresponding mean concentrations of $PM_{2.5}$ and major aerosol species.~~ air masses reaching at Suzhou mainly came from local areas, the nearby provinces (cluster 2, accounting 31.7%), and the northwestern areas (cluster 1 and 3, both accounted for 20.6%).

High aerosol concentrations were associated with these trajectories. This was reasonable considering that these air masses passed over some highly industrialized cities, such as Hefei, Nanjing, and Hangzhou (Fig. 1). ~~The trajectory clusters were dominated by cluster 2, accounting for 31.7%, followed by cluster 1 and 3, both accounted for 20.6%, and the rest clusters, cluster 4, 5 and 6 accounted for 12.7%, 6.3% and 7.9%, respectively. Obviously, air masses mainly originated from the north and southwest (cluster 1 to 4).~~

~~The mean concentrations of PM$_{2.5}$ and main aerosol species varied with certain types of air masses. The highest mean concentration of PM$_{2.5}$ (167 μg m^{-3}) was associated with C3 cluster with the air masses originating from northwest and passed over Anhui and Jiangsu provinces. The air from the C1, C2 and C4 areas were also related to relatively high PM$_{2.5}$ concentrations, which were 129 μg m^{-3}, 117 μg m^{-3} and 103 μg m^{-3} respectively. These air masses all passed over some highly industrialized cities, such as Qingdao, Nanjing, and Hangzhou (Fig. 1).~~ Relatively low ~~concentrations~~ levels of PM$_{2.5}$ were ~~associated with~~related to clusters ~~C~~5 ~~(84 μg m^{-3})~~ and ~~C~~6 ~~(87 μg m^{-3})~~. ~~The trajectories of C5 and C6 mostly originated from southeast and northeast respectively.~~ Based on the pathways and origins, these air masses were expected to bring in relatively clean air from the East China Sea and the Yellow Sea and consequently reduced the aerosol pollution in Suzhou.

Aerosols had high fractions of secondary inorganic ions (39%-42%) and relatively low contributions of OC (15%-16%) when the air masses fell in the C1, C3 and C4, while had relatively high percentage of OC (36%) when the air masses fell into the C5. These differences of aerosol concentrations and composition in different clusters may result in distinct light extinction coefficients and species contributions to visibility reduction when air masses originated from different directions (Fig. 9). Similar to PM$_{2.5}$, the reconstructed b_{ext} was the highest when air masses originated from the Northwest area (C3) and was relatively low when air masses fell into C5 and C6 areas. However, the lowest value of b_{ext} was in the C6 instead of C5 for the lowest PM$_{2.5}$ level, because of the higher contribution of OM in the C5. ~~For the major components in PM$_{2.5}$, the highest averaged concentrations were associated with C3 cluster for sulfate, nitrate and ammonium but with C5 cluster for both OC and EC.~~

~~Accordingly, the composition profiles of these major species were different between clusters. C1, C2, C3 and C4 trajectory clusters had similar composition with relatively higher fractions of secondary inorganic ions (secondary inorganic ions > 35%, OC < 19%) compared to C5 and C6 clusters which both had relatively high contribution of OC (secondary inorganic ions < 30%, OC > 23%).~~

~~These differences of $PM_{2.5}$ concentrations and compositions in different clusters may result in distinct light extinction coefficients and species contributions to visibility reduction when air mass originated from different directions (Fig. 9). Similar to $PM_{2.5}$, b_{ext} values were higher when the air masses originated from the Northwest area (C3), , whereas b_{ext} were relatively low when air masses fell into C5 and C6 areas.~~ AS and OM were the dominant~~ted~~ species determining the light extinction for all clusters. However, ~~differently,~~ AS was the predominant contributor to light extinction for trajectories from north and northwest (C1, C3, C4), while in other cases the light extinction was primarily affected by OM. AN was the third highest contributor in all trajectory clusters with the largest contribution when air masses originated from northwest.

The origins of air masses in different haze events were further analyzed to interpret the relative contributions of chemical species to visibility reduction that differed between~~in~~ haze events. Most air masses fell into C1 and C3 (air masses from north and northwest, respectively) in the first two haze occurrence while all air mass trajectories were in C2 (air masses from ~~south~~local and nearby areas) for the third haze event. The contribution of OM to the total light extinction was higher in the third haze event than in the first two as discussed early, consistent with the results for cluster analysis that the light extinction was primarily impacted by AS for C1 and C3 but by OM for C2. These results manifested that the third haze event was mainly contributed by the primary emission of carbon species from the local and/or surrounding areas.

~~the air mass originated from southwest and passed over Zhejiang province might play a key role in the high contribution of OM in the third haze event.~~

It should be noted that air mass back trajectory analysis only suggests the originations and pathways of air masses but does not directly reveal the exact sources. Based on the results of trajectory analysis, the PSCF method was applied to explore the likely regional sources of major components in $PM_{2.5}$, including sulfate, nitrate, OC, and EC, as illustrated in Fig. 10. Generally, $PM_{2.5}$ and the five aerosol species in Suzhou were mainly affected by local sources and nearby cities. Specifically, the higher value for $PM_{2.5}$ and the aerosol components were all localized in northwest to the south, covering surrounding cities in Jiangsu and near the border of Anhui and Zhejiang provinces. Additionally, these species were all affected by pollutions from Anhui province. Sulfate, nitrate and ammonium had similar spatial distributions, and relatively more affected by the north and northwest cities in Shandong, Jiangsu and Anhui provinces while pollutions from south cities in Zhejiang province had more impact on OC and EC in studied area than sulfate, nitrate and ammonium.

4. Conclusions

Heavy aerosol pollution occurred in Suzhou in January 2013 with daily $PM_{2.5}$ concentrations on haze days 1.97 to 2.61 times higher than Grade II criteria of the national ambient air quality standard (75 $\mu g\ m^{-3}$) and maximum value of 324 $\mu g\ m^{-3}$ on Jan. 14, 2013. Unfavorable weather conditions (high RH, low rainfall, wind speed and atmospheric pressure) especially high RH together with increased air pollutants produced from local and nearly sources were responsible~~might provide beneficial conditions~~ for these haze formation.

During the first two haze periods, ~~WSII and carbonaceous species both increased during the haze events and~~ the major aerosol components~~sitions~~ were SO_4^{2-}, NO_3^-, NH_4^+, and SOC, which were mainly from secondary sources. Furthermore, SOR and NOR both increased under worst visibility conditions, revealing efficient~~severe~~ gas to particle conversion~~ during winter in this region~~. Additionally, ~~The conversion mechanisms were further analyzed for sulfate and nitrate. Rapid chemical conversion from gas to particle phase for sulfate particles under extremely low O_3 concentrations~~

~~and significant correlations between SOR and humidity demonstrated that heterogeneous process might dominate the sulfate formation. However, the result of ($[NO_3^-]/[SO_4^{2-}]$) as a function of ($[NH_4^+]/[SO_4^{2-}]$) showed that the formation of ammonium nitrate via the homogeneous gas-phase reaction was favored.~~

~~The reconstructed light extinction coefficients based on the revised IMPROVE algorithm were 664 ± 288 Mm^{-1}, and mainly contributed by OM (40%), $(NH_4)_2SO_4$ (34%), NH_4NO_3 (16%), and EC (4%). The contributions of these species experienced different variations in their fractions under different visibility conditions. Generally, t~~the contributions~~share~~ of $(NH_4)_2SO_4$ and NH_4NO_3 to the reconstructed b_{ext} based on IMPROVE were higher under low visibility conditions while those~~the percentages~~ of OM and EC were higher~~increased~~ under high visibility conditions, indicating that secondary inorganic aerosols especially NH_4NO_3 seemed to be very important for the impaired visibility. Gas-phase homogeneous reaction might dominate the formation of sulfate and nitrate under low RH conditions while heterogeneous process might be responsible when RH were relatively high.

~~But d~~Distinctively, high proportion of carbon species from primary emission and lower fraction of secondary formation components were observed in the third haze. The SOR and NOR during the third haze episode were comparable to clean days. Moreover, increasing proportions of OM and EC accompanied with decreasing percentage of $(NH_4)_2SO_4$ were found under worst visibility conditions when the third haze occurred. These results~~,~~ suggested~~suggesting~~ that the carbon components from the primary emission might be relatively important for the visibility reduction for this haze event.

~~These differences in different haze events might be greatly affected by the pathways of air masses according to trajectory clustering analysis.~~

~~The result of t~~Trajectory clustering analysis showed that the air quality in Suzhou was mostly affected by air masses originating from North and Southwestern areas which were associated with high aerosol concentrations. Distinct aerosol composition profiles, light extinction coefficients and species contributions to visibility reduction were observed when air masses originated from different directions, e.g. AS was the predominant contributor to light extinction for trajectories from north and northwest, while in other cases the light extinction was primarily affected by OM.

The likely sources of aerosol and the major species based on the PSCF method were mainly from local anthropogenic activities and source emissions transported from nearby cities. The northwestern to southern regions may be important sources of aerosols and the major components. The northern and northwestern areas were predominant source regions for sulfate, nitrate and ammonium aerosols, whereas the southern area could be the common source region for carbonaceous species. This information has the implications for the importance of collaborative air pollution control strategy in the Yangtze River Delta Region.

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Table 1. The percentages of air masses from each trajectory cluster and associated~~the mean b_{ext} (Mm^{-1}) and~~ mean concentrations (μg m^{-3}) of $PM_{2.5}$ and its major chemical components, and mean b_{ext} (Mm^{-1})~~selected aerosol species in the identified trajectory clusters~~.

	1	2	3	4	5	6
Percent (%)	20.6	31.7	20.6	12.7	6.3	7.9
$PM_{2.5}$	129	117	167	103	84.0	87.4
OC	21.1	22.8	25.3	16.4	30.5	20.3
EC	2.05	3.87	2.21	1.45	3.90	1.86
Sulfate	22.9	18.2	32.4	23.1	8.85	8.39
Nitrate	11.5	10.0	16.9	7.84	3.26	7.91
Ammonium	15.2	12.3	18.9	12.4	7.93	9.88
b_{ext}	675	597	921	556	548	463

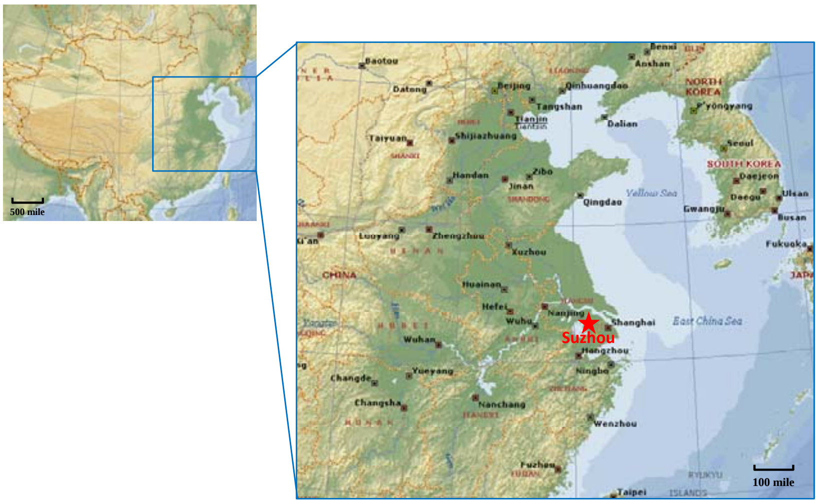


Figure 1. The sampling site in Suzhou. The locations of ~~some~~ major cities with a population of more than 1 million (such as Qingdao, Nanjing and Hangzhou) are marked with a square symbol. The topographical map was derived from Microsoft® Encarta® 2009 © 1993－2008.

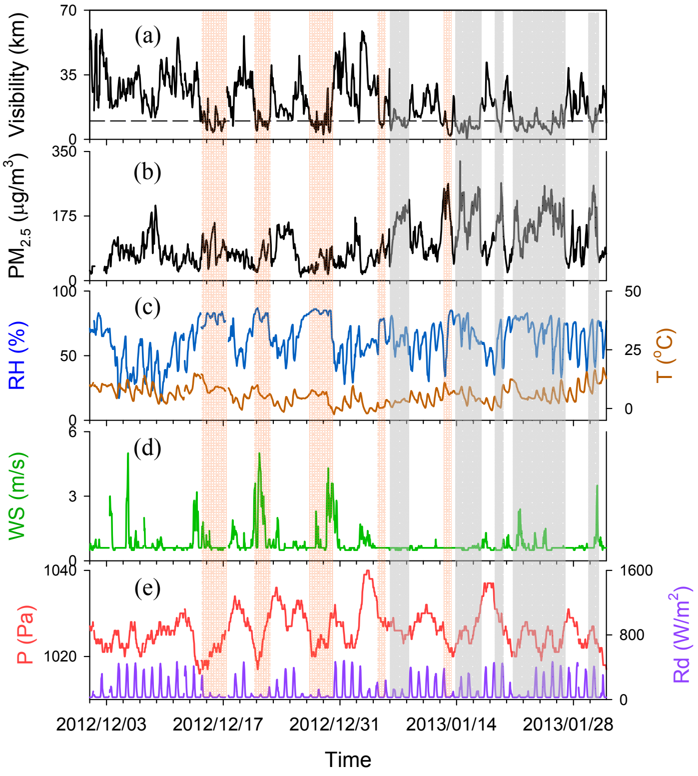


Figure 2. Time series of (a) visibility; (b) $PM_{2.5}$ concentration; (c) relative humidity (RH) and temperature (T); (d) wind speed (WS) and pressure (P); and (e) solar radiation (Rd). The shaded areas in orange represent periods when visibility were

lower than 10 km and accompanied by precipitation. The shaded areas in grey represent haze periods.

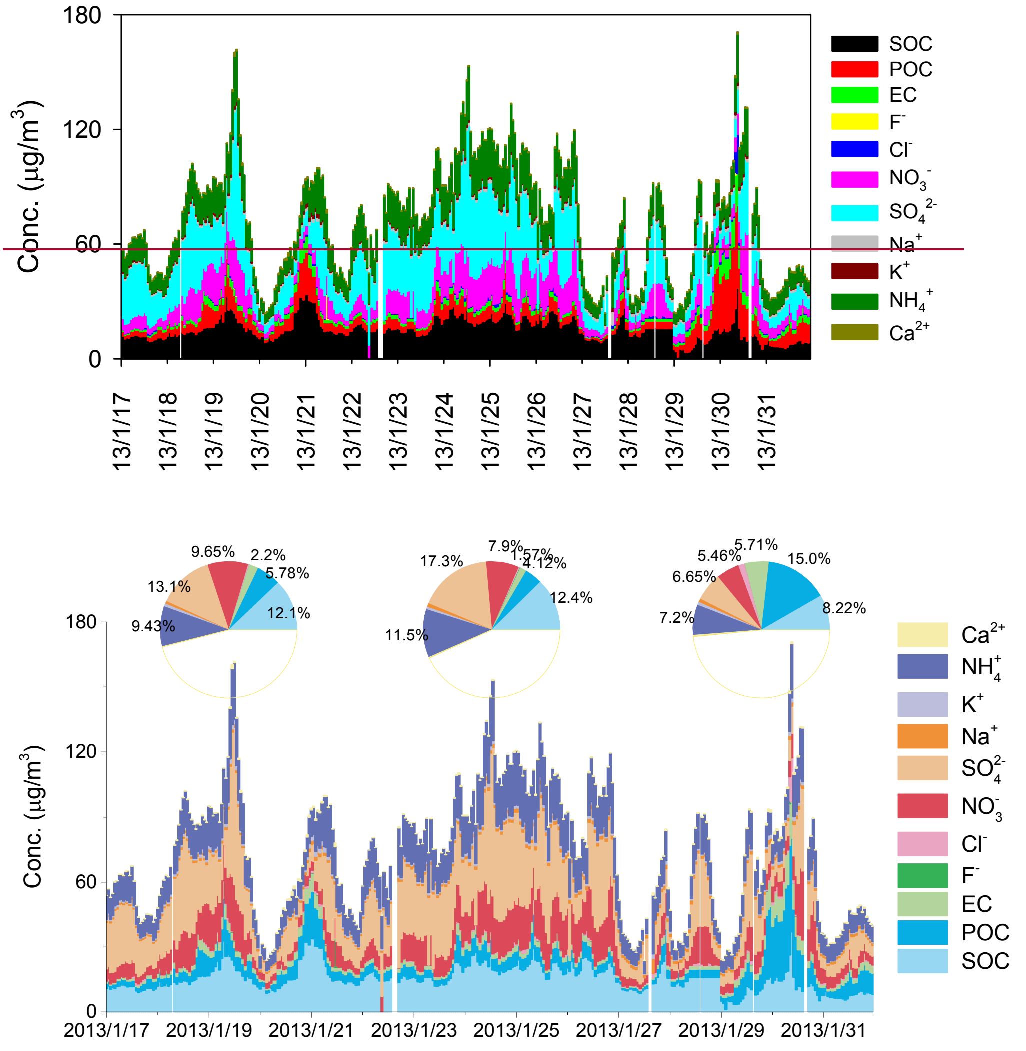
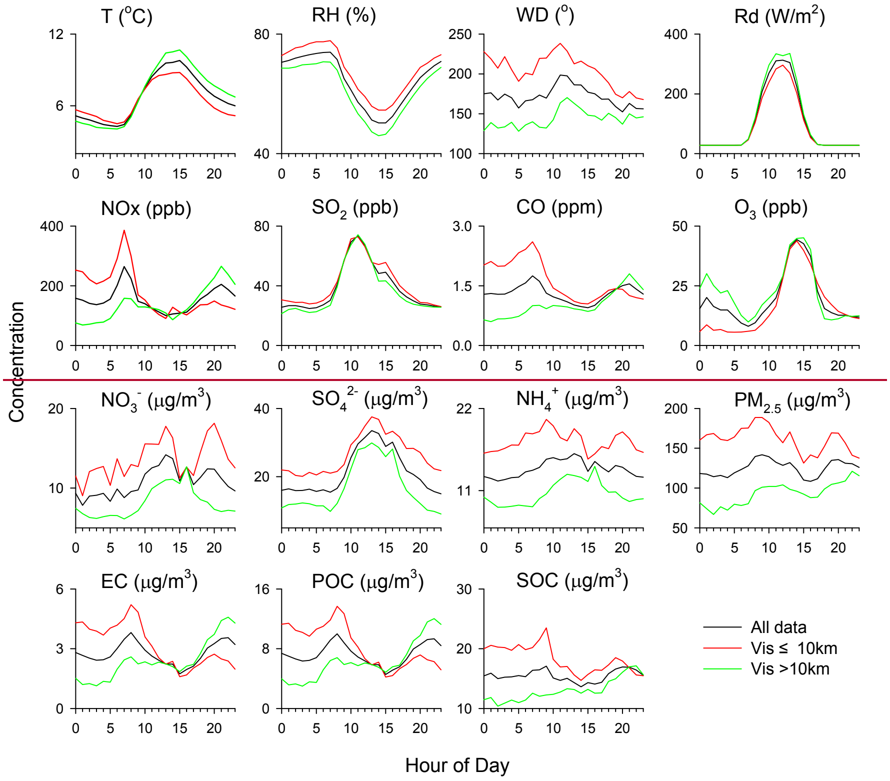


Figure 3. Temporal distribution of water soluble inorganic ions and carbonaceous species. The aerosol composition in the three haze events was also illustrated in the pie chart.



~~Figure 4. Diurnal profiles of meteorological variables, aerosol precursors (NO_X, SO_2,),~~ ~~CO, O_3), $PM_{2.5}$, and major aerosol compounds (NO_3^-, SO_4^{2-}, NH_4^+, EC, POC, SOC)~~ ~~under different visibility conditions.~~

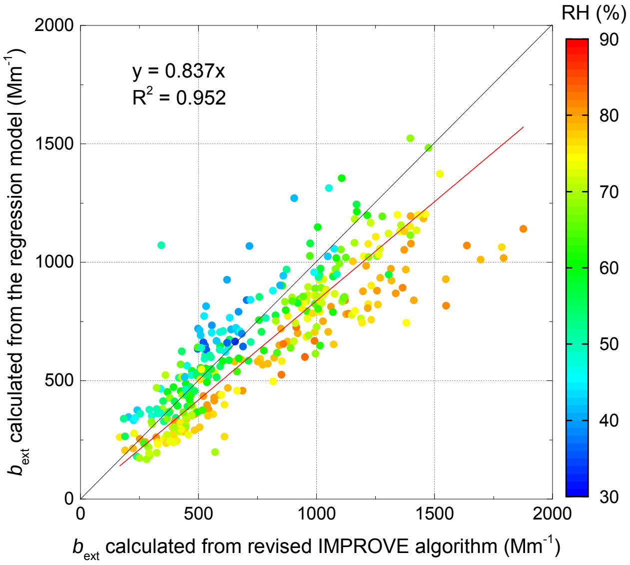


Figure 4. Comparison of the calculated b_{ext} between those obtained from the regression equation and those from the IMPROVE algorithm.

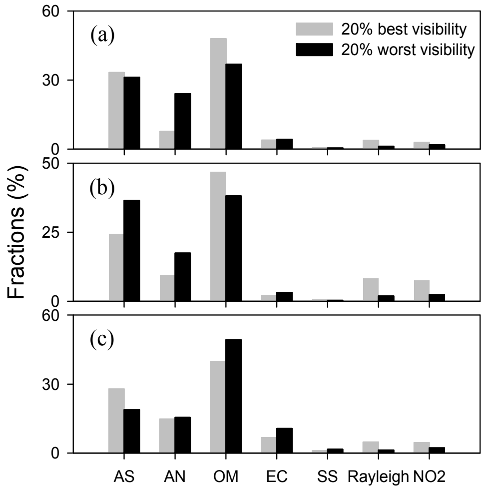


Figure 5. Relative contributions of various chemical components in $PM_{2.5}$ (ammonium sulfate (AS), ammonium nitrate (AN), OM, and EC) to the total light extinction under 20% best and 20% worst visibility conditions during the first (a), second (b), and third (c) haze events.

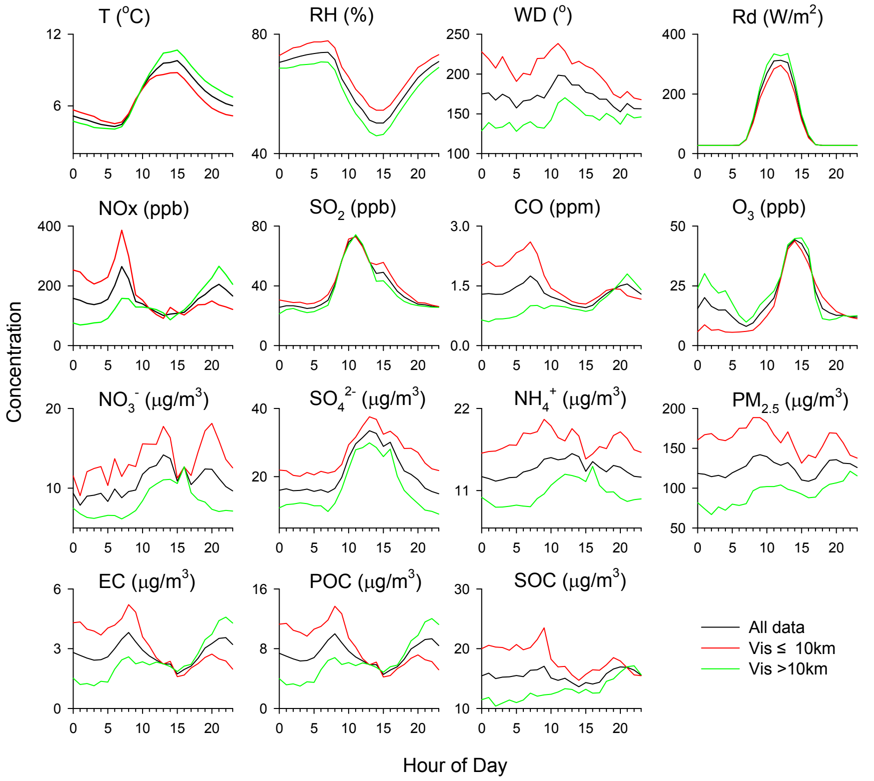
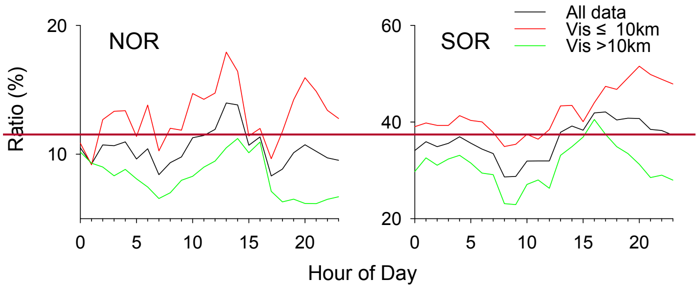


Figure 6. Diurnal profiles of meteorological variables, aerosol precursors (NO_X, SO_2),

CO, O_3, $PM_{2.5}$, and major aerosol compounds (NO_3^-, SO_4^{2-}, NH_4^+, EC, POC, SOC) under different visibility conditions.



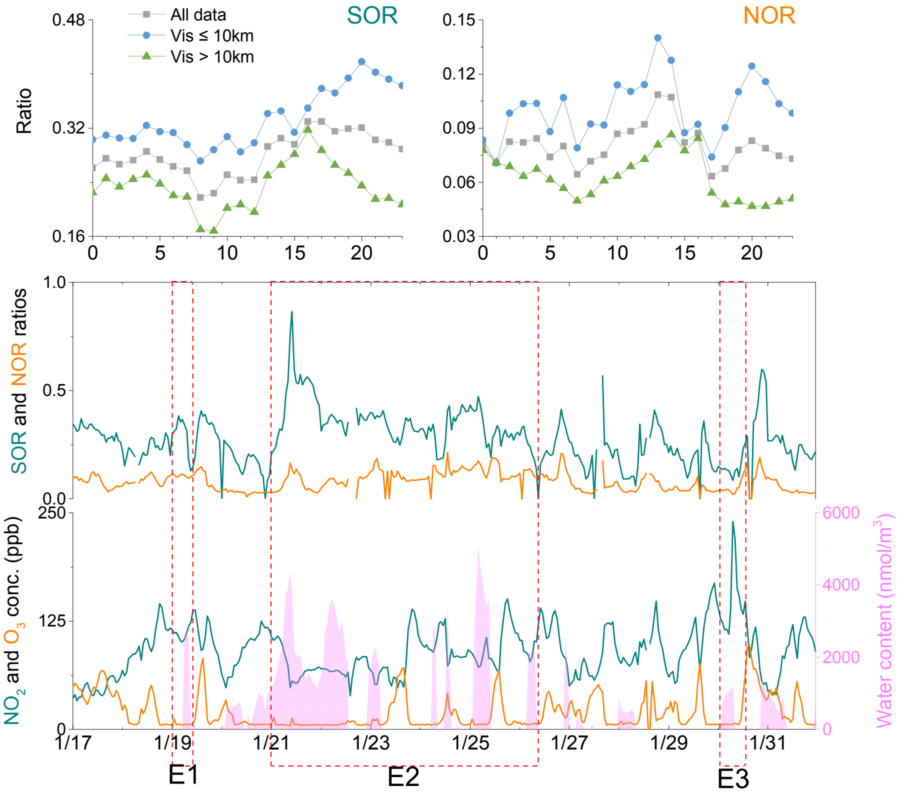
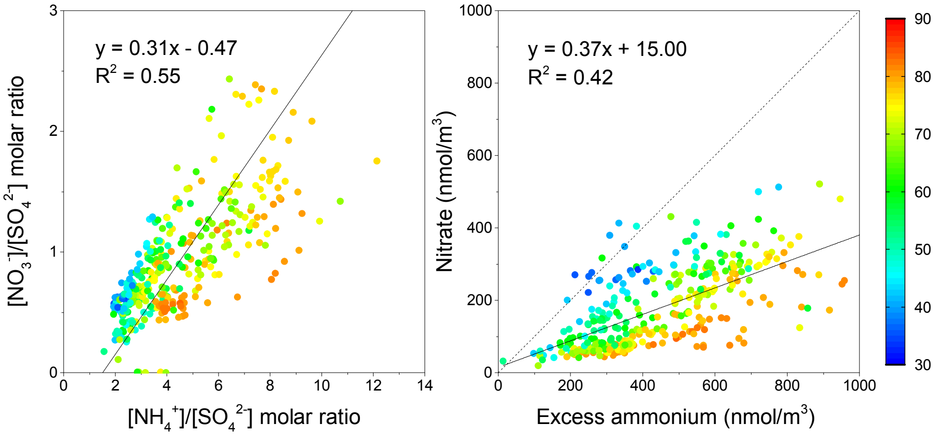


Figure 7~~6~~. Temporary distributions of SOR, NOR, NO_2, O_3 and aerosol water content. Diurnal profiles of NOR and SOR ratios under different visibility conditions.



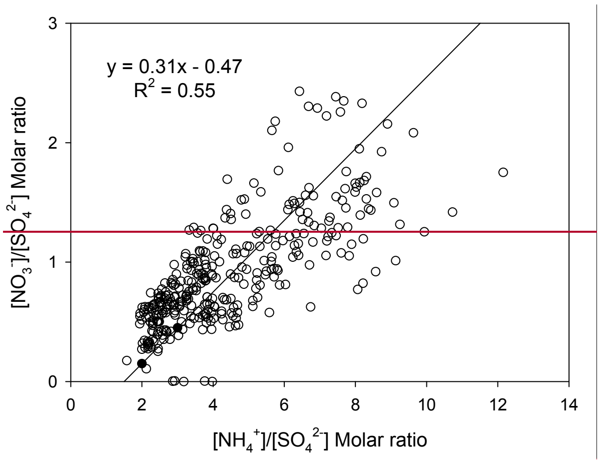
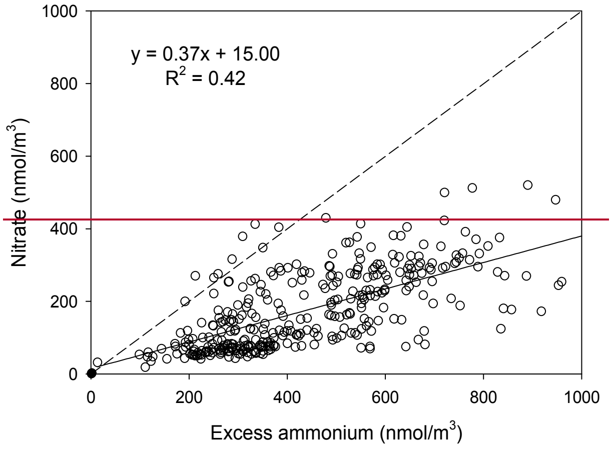


Figure ~~7~~8. Nitrate to sulfate molar ratio as a function of ammonium to sulfate molar ratio~~.~~ (left) and relationship



~~Figure 8. Relationship~~ between molar concentrations of nitrate and excess ammonium (right).

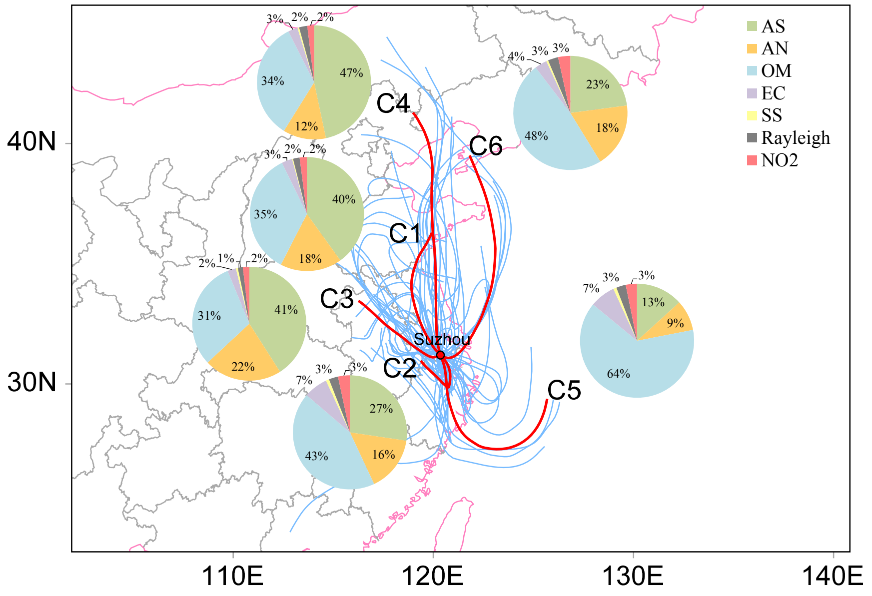


Figure 9. Backward air mass trajectories and six mean trajectories after the cluster analysis at the sampling site during Jan. 17 to 31. Relative contributions of various chemical components to the total light extinction in different clusters are illustrated.

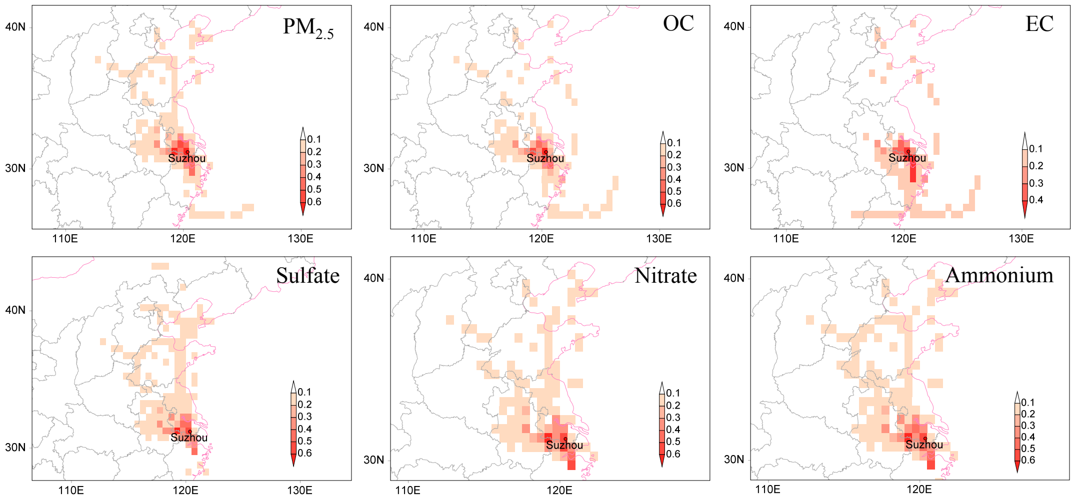


Figure 10. The PSCF maps for $PM_{2.5}$, OC, EC, sulfate, nitrate, and ammonium.