## Response to Reviewers' comments

We are thankful to the two referees and Dr. Lin for their thoughtful and constructive comments which help improve the manuscript substantially. Following the reviewers' suggestions, we have revised the manuscript accordingly. Listed below are our point-by-point response in blue to each comment that was offered by the reviewers.

### Response to Dr. Chunshui Lin

1. **General comments**

The study by Lei et al., entitled "Fine particle characterization in a coastal city in China: composition, sources, and impacts of industrial emissions", characterizes the aerosol composition and sources near two large steel plants in a coastal city in Shandong using a $PM_{2.5}$ TOF-ACSM. While it is generally well presented, I have a few concerns about the data interpretation which is sometimes questionable. Specifically, in the OA Source Apportionment section, HOA was apportioned to traffic which was shown to have a pronounced morning and evening rush hour peaks. However, HOA was also shown to have a good correlation with $NO_x$ ($R^2$ =0.82-0.87). The tight correlation between HOA and $NO_x$ means $NO_x$ also had such diurnal trends and could be exclusively from traffic. However, contrasting results appeared in the Industrial Plumes Section where it shows $NO_x$ was also correlated with CO ($R^2$ =0.83). Later, Lei et al., stated that CO, $NO_x$, and $SO_2$ were co-emitted from steel plants. So my question, how is the correlation between CO and HOA, and what on earth $NO_x$ is from. If $NO_x$ is from traffic then other correlated species (i.e., CO and $SO_2$) are also from traffic, which means the $NO_x/SO_2$ ratios or $NO_x$/CO ratios would be invalid diagnostic ratios for steel plant emissions. If $NO_x$ was indeed from steel plant, then the source apportionment of OA factor is questionable. Because the tight correlation between HOA and $NO_x$, HOA would also be from steel plant, however, which shows morning and evening rush hour peaks. This would be more questionable.

We thank Dr. Lin's comments on our manuscript. First, the correlation coefficient $r^2$ between HOA and $NO_x$ was incorrectly written, and it was corrected into "$r^2$ =0.52-0.65" in the revised manuscript. CO and HOA were poorly correlated ($r^2$=0.04-0.05) and showed quite different diurnal variations (Fig. R1), suggesting their different emission sources. On the contrary, the tight correlation between HOA and $NO_x$ ($r^2$ =0.52-0.65) and the similarity in their diurnal patterns suggested their common sources. As proved by previous studies, $NO_x$ is produced from the reaction of nitrogen and oxygen gases in the air during combustion, especially at high temperatures. Transportation, industrial activities, power plants and domestic combustion could contribute significantly to $NO_x$ in the atmosphere (Streets and Waldhoff, 2000). The characteristics of diurnal patterns of $NO_x$ in our study indicated that traffic emissions were the main source of $NO_x$ near the sampling site during plume excluded period. As shown in Fig. 8 in the manuscript, the tight correlation between $NO_x$ and CO, $NO_x$ and $SO_2$ were only found during periods with clear influences from steel plant plumes, suggesting that a large fraction of the three gaseous species were co-emitted from steel plants during plume periods, while they were affected by multiple and different sources during non-plume periods. And due to the high instant concentrations in the plumes, other sources like transportation or domestic coal combustion play minor roles during plume periods, so we concluded reasonably that the ratio of $NO_x$/CO and $NO_x/SO_2$ can be used as indicators for steel plant emissions.

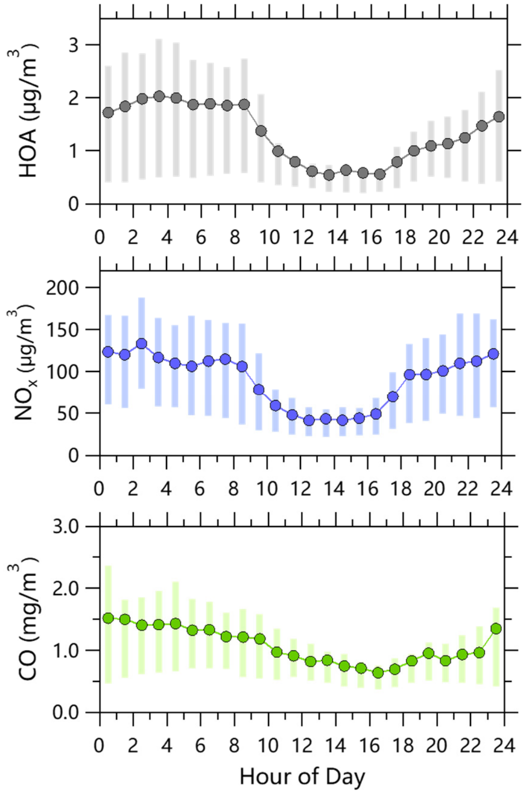

Figure R1. Average diurnal variations of mass concentrations of HOA, $NO_x$ and CO in March 2019, the plume periods have been excluded. The error bars indicate 25th and 75th percentiles.

## 2. Specific comments

1. My other major concern is how to prove that $SO_4$ are exclusively from power plant, but not regionally transported. The good correlation between LO/MO-OOA and $SO_4/NO_3$ indicates regional transport. And the increase of $SO_4$ above background level before and after the plume could be stronger secondary production during transport. The wind rose only shows a huge source from the southwest region which could be other sources (e.g., general industries

activities) other than power plant. You need more evidence to show the sulfate/ammonium were exclusively from the power plants.

It is a good point. If sulfate was dominantly from regional transport, all aerosol species would be expected to vary similarly. However, during periods with significant influences of steel plants, we only observed substantial increases in ammonium and sulfate, while the mass concentrations of organics and $NO_3$ remained small changes. Therefore, the sharp increases in mass concentrations of $SO_4$ and $NH_4$ were unlikely from the regional transport. The bivariate polar plots also showed that the periods with large increases of sulfate were dominantly from the southwest where the industrial region is located. Based on the available measurements in this study, we cannot quantify the exact contributions of each industry to the increase of sulfate. Considering the dominant industrial emissions in this region, sulfate and ammonium were expected dominantly from the emissions of steel plants.

The correlation coefficients between $SO_4$ and MO-OOA in Fig. 4 were performed by excluding the periods with significant industrial influences, which is now clarified in figure caption as "Note that the periods with influences from steel plants were excluded when performing correlation analysis between MO-OOA and $SO_4$ in (a) and (b)." It can be seen that sulfate was generally well correlated with MO-OOA, consistent with the fact that the two components of MO-OOA and $SO_4$ were mainly from regional transport during periods with small influences of industrial plumes. As shown in Fig. 4, we didn't observe simultaneously large increase in MO-OOA as the plume-related sulfate (Fig. 2), further supporting that the large increases in sulfate could not be from strong secondary production during transport.

2. Are these two power plants coal-powered? Could you comment why CCOA was only resolved in March but not in September. Does it mean the CCOA was actually not from the power plants but from residential sectors? What is the correlation between CCOA and $NO_x$/CO/$SO_2$ during the industrial plume? What are the mass spectra during industrial plume, any sign of CCOA? If no sign of CCOA, does it mean the SO4 was not from power plants?

   Yes, they were coal-powered steel plants. According to previous studies, the emission factors of carbonaceous aerosol from industrial boilers were significantly lower than those from residential coal combustion by a factor of more than 2 (Zhang et al., 2008). Therefore, CCOA was not resolved in September when residential heating was not important. This is also consistent with many observations in China, e.g., Beijing. For example, CCOA was only resolved in heating season when residential coal combustion was important. However, it cannot be identified in other seasons even the industrial emissions are one of the important aerosol sources (Sun et al., 2016;Sun et al., 2018;Xu et al., 2019). In comparison, CCOA was resolved in March because of the enhanced coal combustion emissions for domestic heating in this season. Thus, we concluded that CCOA was mainly from residential coal combustion instead of steel plants.

Figure R2 shows the correlation of CCOA with $NO_x$/CO/$SO_2$ during the periods with clear industrial plumes. It can be seen that CCOA was almost completely irrelevant with $NO_x$/CO/$SO_2$ ($r^2$=0.02-0.10), suggesting their different emissions during industrial plume periods. Considering that a large fraction of $NO_x$, CO and $SO_2$ were emitted from the steel plants during plume episodes, the poor correlation between CCOA and $NO_x$/CO/$SO_2$ further supported that CCOA could not be dominantly from steel plants.

Figure R3 shows the average OA spectra during the periods with the influences of industrial plume in March. No pronounced PAHs signals were observed in the spectra suggesting that the industrial activities appear not emit CCOA significantly. Even there was no sign of CCOA, it does not mean that sulfate was not from steel plants as well. For example, carbonaceous aerosols can be burned out completely to CO and $CO_2$ during the high-temperature processes of steel making, while the emissions of $SO_2$ and $SO_3$ are still significant which can form ammonium sulfate rapidly in the atmosphere.

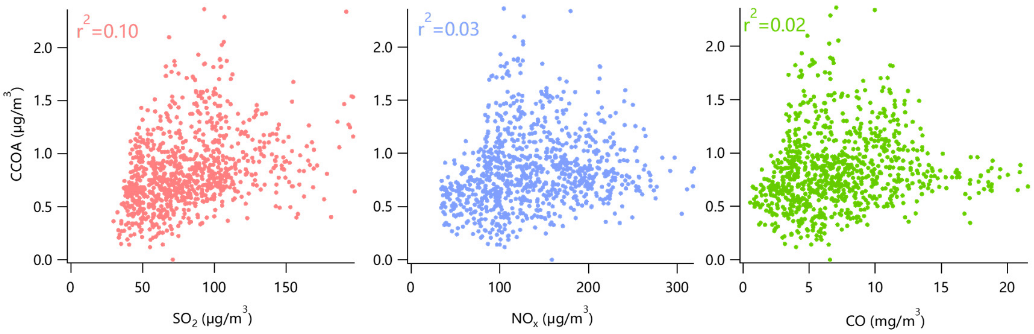

Figure R2. Scatter plots of CCOA with (a) $SO_2$, (b) $NO_x$ and (c) CO during periods with significant influences from steel plant plumes in March 2019.

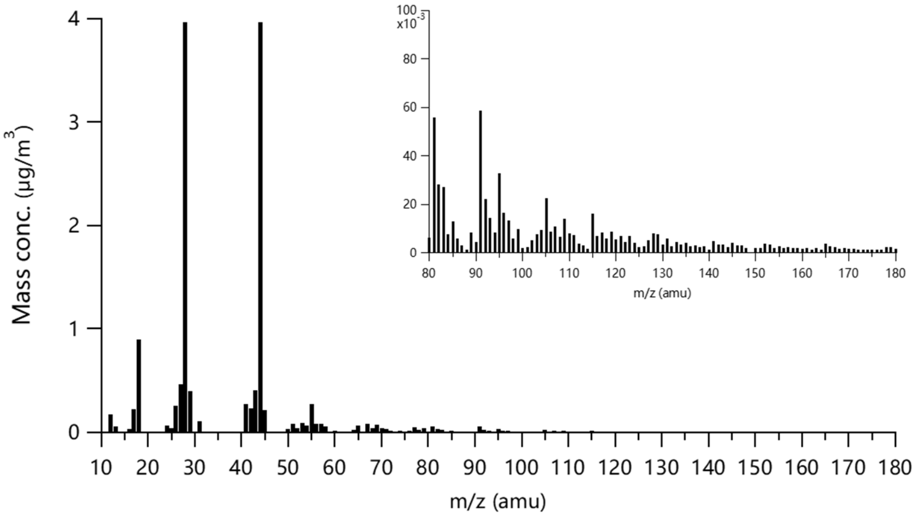

Figure R3. Average OA mass spectra during periods with significant influences from steel plant plumes in March 2019.

3. What are the tools to perform the PMF analysis? How the factors are systematically evaluated? In the Method section, it states “Considering the limited sensitivity of the ToF-ACSM, m/z’s larger than 120 and 180 were excluded in PMF analysis” However, in the PMF Section, and Fig. 4, it states “Compared with HOA, CCOA presented a higher mass fraction of larger m/z’s (>120) indicating that coal combustion can be an important source of high molecular-weight organic matter during heating period.” Is m/z’s >120 really excluded?

The PMF analysis on the organic mass spectra from ToF-ACSM were performed by using the Igor PMF evaluation tool (PET, version 3.04A) (Paatero and Tapper, 2010;Ulbrich et al., 2009), following the data-processing and factors-selecting steps given by Zhang et al. (2011). Factor numbers from 1 to 10 were run in the model with different rotational parameter ($f_{peak}$) values (i.e., -0.6 to 0.6, stepped by 0.2), and a 3-factor solution with $f_{peak}$=0 and a 4-factor solution with $f_{peak}$=0 were determined in September 2018 and March 2019, respectively. More factor solutions would lead to clear splitting of the factors and thus are not selected. We performed PMF analysis on the organic mass spectra in September 2018 and March 2019, and we excluded *m/z’s* >120 in September 2018 and *m/z’s* > 180 in March 2019, respectively, due to (1) their low signal-to-noise ratios and low contributions to the total OA mass, and (2) low contribution of CCOA in September. Such explanations have been clarified in the manuscript “Considering the limited sensitivity of the ToF-ACSM, *m/z’s* larger than 120 and 180 were excluded in PMF analysis in September 2018 and March 2019, respectively due to their low signal-to-noise ratios, and low contributions to the total OA mass.”

## Response to Reviewer #1

Lei et al. presented time-of-flight aerosol chemical speciation monitor (ToF-ACSM) measurements of fine particles in a coastal city in China that is affected by two large steel plants. The instrument was equipped with the newly developed $PM_{2.5}$ size cut and capture vaporizer. From data sets in spring and fall, differences in mass concentration and species concentration were discussed with both diurnal pattern analysis and positive matrix factorization (PMF). Potential source analysis using bivariate polar plots revealed impacts from the steel plants. Specifically, six plumes were analyzed in detail, and results suggest that ammonium sulfate, $NO_x$/CO ratio, and $NO_x/SO_2$ ratio could be used to evaluate the impacts from steel plant emissions. The measurements are new in that 1) a focus on the effects of industrial plumes; and 2) with newly developed $PM_{2.5}$ size cut and capture vaporizer. The analysis is rigorous for standard aerosol mass spectrometric (AMS) practice and PMF analysis, but lacks in verification of certain potential differences between the capture vaporizer (CV) and standard vaporizer (SV), as indicated in Major Comment #1 below. The manuscript is fairly well written, but has some room for improvement. Minor Comments below list a few examples for the authors to consider changing. Overall, I have concerns in the assertions that certain inorganic and gaseous species can be used as diagnostics for steel plant emissions (see Major Comments below). Therefore, I suggest Major Revision, for the authors to lean the discussion more on other major conclusions (which are by themselves quite useful), instead of focusing too much on using these diagnostic indicators that might not be specific to steel plant emissions.

We thank the reviewer's positive comments.

**Major Comments:**

1. P11, L14. The authors suggested that there were two plumes in which ammonium bisulfate accounted for 70-80% of PM mass. I suppose the conclusion that the "sulfate" detected by the ToF-ACSM was bisulfate is from the observation that "sulfate" measured was much higher than the ammonium measured on an equivalent basis. If so, the authors should specify that in the manuscript. Another concern I have is whether that was partly due to the usage of CV as compared to the commonly found nearly "neutral" NR-PM in previous AMS studies using SV. There might be difference in both RIE and fragmentation patterns for CV compared to SV, as indicate by Hu et al. (AMT, 2017 and AST, 2017). The authors need to clarify whether these would affect quantification of sulfate using the ToF-ACSM that comes with a CV.

We thank the reviewer's comments. It was a mistake, and the correct conclusion should be that ammonium bisulfate accounted for ~20%-40% of total PM mass during steel plant plumes. In consideration of the negligible contribution of $NO_3$ and Chl in the plumes, which was demonstrated by the pie charts in Fig. 7, it is reasonable to estimate the relative fraction of ammonium sulfate and ammonium bisulfate based on the $NH_4$_meas/$NH_4$_pred ratios, which was discussed in detail in Zhang et al. (2007). The plots of $NH_4$ balance for different periods are presented in Fig. R4. As for the quantitation of sulfate by CV ToF-ACSM, it has been validated in both laboratory studies and field campaigns that, even the fragmentation patterns and RIE may be different, the sulfate mass concentrations measured by CV and SV instruments agreed well with each other, as long as the RIE could be calibrated correctly (Hu et al., 2016;Hu et al., 2017). In addition, we calibrated RIEs of ammonium and sulfate before and after the two campaigns, and found that the RIE of sulfate was fairly robust which was 1.1, while that of ammonium changed from 3.1 in September 2018 to 3.8 in March 2019.

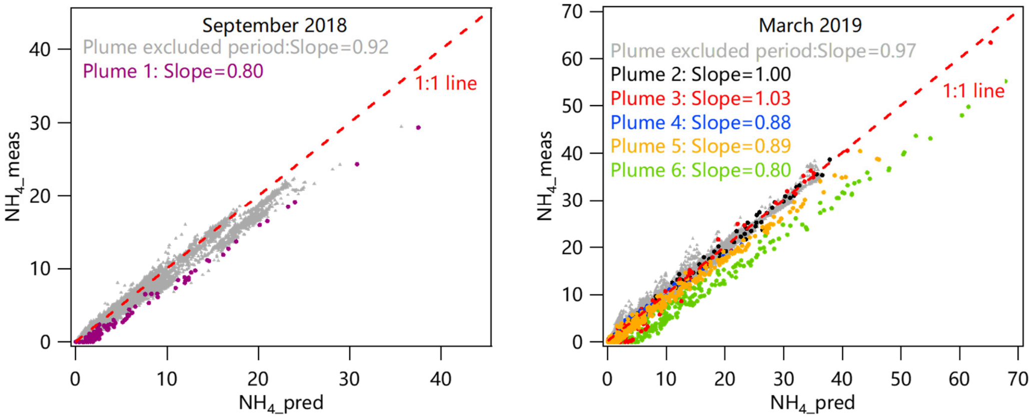

Figure R4. Scattering plots of measured $NH_4$ vs. predicted $NH_4$ in steel plant plumes (after subtracting background concentrations, $NH_4$_pred=18*(2*$SO_4$/96+$NO_3$/62+Chl/35.5)).

2. P12, L5-8. The authors suggested that the $NO_x/SO_2$ and $NO_x$/CO ratios can be used as diagnostics for impacts of steel plant emissions. First, it is ok for $NO_x/SO_2$ ratio with both ug/$m^3$ as the mass concentration unit, and end up in a dimensionless ratio. But CO has a unit of mg/$m^3$. Should the $NO_x$/CO ratio be the number stated * 10^-3? Second, the low ratios observed in plumes in this study do not exclude possibilities of similar low ratios from other plumes (such as traffic emissions, power plants, and biomass burning). Can the authors summarize literature values for other typical primary sources before making such a statement that low ratios of these gaseous species can be indicators of steel plant emissions?

We thank the reviewer's comments. We have changed the $NO_x$/CO ratios into the correct order of magnitude accordingly. We referred to relevant articles and summarized the literature values of $NO_x$/CO and $NO_x/SO_2$ ratios in Table R1. The $NO_x$/CO ratios in different emission types including vehicle, biomass burning, urban site, rural background site, etc., were investigated relatively more extensively. As presented in Table S1, the $NO_x$/CO values obtained from other emission sources were apparently higher than that in the steel plant plumes in this study (Schürmann et al., 2007;Fujita et al., 2012;Tiwari et al., 2015;Santos et al., 2018). It’s worth noting that the values of $NO_x/CO$ for on-road motor vehicle emissions (Fujita et al., 2012) were quite close to the values during non-plume period in our study, which supported that our results are reliable. The $NO_x/SO_2$ value of 1.04 obtained from the fresh flue-gas plume from a coal-fired power plant when FGD and fabric filter were used (Mylläri et al., 2016), which was similar to the flue-gas cleaning conditions of RSP, is close to 1.24 in this study. Unfortunately, the investigations on $NO_x/SO_2$ were relatively fewer and there are not enough comparable literature values. However, it has been proved by Parrish et al. (1991) that lower $NO_x/SO_2$ is characteristic of the emissions from coal burning, e.g., in power generation plants or steel making plants, while higher $NO_x/SO_2$ is generally attributed to vehicle emissions, which is consistent with our conclusions in this study. It needs to be clarified that we treated the steel plant (RSP or SSP) as a whole in this study, rather than focusing on detailed or specific production process including coking, sintering, pickling, etc., or the small-scale coal-fired power plant for the power supply of steel production. Another important thing to note is that plumes emitted by steel plants and power plants are supposed to have common characteristics, such as close values of $NO_x/SO_2$ as mentioned above, that is because the main source of pollutants emitted from the two kinds of industrial plant could be attributed largely to coal combustions. However, take the fact that there is no any other power plant around our sampling site into consideration, we can conclude reasonably that the lower ratio of $NO_x/SO_2$, supported also by lower values of $NO_x/CO$ and sharp increase in mass concentration of sulfate and ammonium, can be used as indicators of steel plant emissions. We have also clarified this important conclusion in more detail in the revised manuscript.

Table R1. Summary of literature values of $NO_x$/CO and $NO_x/SO_2$.

| | **Emission type** | **$NO_x$/CO** | **$NO_x/SO_2$** |
|---|---|---|---|
| Schurmann et al., AE, 2007. | Airport | 0.20-0.25 | - |
| Tiwari et al., AR, 2015. | Urban background site | 15.0 | - |
| Fujita et al. J. Air Waste Manage. Asso, 2012. | On-road motor vehicle | 0.04-0.05 | - |
| Santos et al., ACP, 2018. | Biomass burning | - | - |
| | Forest background | 0.33-1.48 | - |
| | Fresh plume | 0.056-8.33 | - |
| | Anged plume | 0.1-6.33 | - |
| Mylläri et al., ACP, 2016. | Coal-fired power plant | - | - |
| | Fabric filter on | - | 1.04 |
| | Fabric filter off | - | 4.69 |
| ***This study*** | Steel plant | | |
| | Non-plume period | 0.04 | 1.55 |
| | ***Plume period*** | ***0.01*** | ***1.24*** |

3. P13, L4. The statement that ammonium sulfate can be used to evaluate and quantify the impacts of steel plant emissions is even less convincing. There would be ubiquitously existence of ammonium sulfate in most environments, many of which with ammonium sulfate as the dominating NR-PM species. If the authors can justify Major Comment #1 above, then it makes a little bit more sense to say that ammonium bisulfate (typo?) can be used for this purpose. Still, other sources (e.g., power plants) can emit (directly or indirectly) large amounts of ammonium bisulfate too. Please clarify.

   We thank the reviewer's comments. First, the quantification of sulfate by CV-AMS has been proved to be highly consistent with SV-AMS. Second, it's true that sulfate and ammonium are ubiquitous in the atmosphere and may be the dominating NR-PM species, and that's why we deducted the background concentrations, which were determined as the average of 1 hr data before and after steel plant plumes to remove the background interference. Besides, the increases in sulfate and ammonium mass concentration are sharp and significant relative to non-plume periods. It's also true that other sources like power plants can emit large amounts of sulfate and ammonium as we stated in the reply of *Major comment 3*, but there is no such possible source emissions near our sampling site, and such rapid and significant increase in mass concentration of sulfate and ammonium is unlikely from secondary formation during the transport.

We totally agree with the reviewer that it was not convincing enough to use ammonium sulfate as a tracer for the impacts of steel plant emissions considering the ubiquitous existence of ammonium sulfate in most environments. In fact, ammonium sulfate can be used as tracer for industrial impacts only in regions nearby, while it would have a large uncertainty in regions far from the steel plants because of the rapid dilution during the transport. In the revised manuscript, we toned town the implications of our results as "Our results might have significant implications for better quantification of industrial emissions using ammonium sulfate and the ratios of gaseous species as tracers in industrial regions and nearby in the future."

**Minor Comments:**

1. P1, L13: a new sentence should start after "China".

   Corrected.

2. P1, L14: change "have" to "present".

   Corrected.

3. P1, L16: no need to use "seasons". Spring and fall contain the meaning of "season". There are a number of similar cases later. Please check.

   More appropriate expressions were used in the revised manuscript.

4. P1, L21: put a "," after "seasons".

   Corrected.

5. P2, L12: change "important one" to "important sources".

   Corrected.

6. P2, L16: add "concentrations of" before "toxic".

   Corrected.

7. P3, L1: change "contributions" to "effects".

   Revised.

8. P3, L22: add "a" before "capture vaporizer".

   Corrected.

9. P4, L9: change "new" to "newly". There are some similar cases later too. Please check.

   We replaced "new" with "newly" in our revised manuscript.

10. P4, L10: delete “those,”?

    Revised.

11. P4, L15: I would suggest either using “SO4” as the shorthand notation or using the right ionic formula.

    Thank the reviewer’s suggestion.

12. P5, L9: delete “for”.

    Modified.

13. P7, L2: delete “was” before “decreased”.

    Corrected.

14. P7, L5: change “small, less than 2%” to “small at less than 2%”?

    Modified.

15. P8, L4: I would suggest using the right ion formula for the alkyl ion series.

    Modified.

16. P8, L17: a new sentence should start before “for example”.

    Modified.

17. P11, L8: change “nearby” to “near”.

    Modified.

18. P12, L17: add “a” before “higher contribution”.

    Corrected.

19. P12, L18: which one is higher? Daytime or nighttime? It seems contradictory to what was said previously.

    Corrected. It should be “Most aerosol species showed similar diurnal variations in the two seasons with higher concentrations at nighttime and lower values during daytime,”.

20. P13, L4: change “steel plants emissions” to “steel plant emissions”

    Modified.

**Response to Reviewer #2**

Lei et al. presented a unique dataset on submicron aerosol composition in an area heavily influenced by industrial emissions during two seasons. They conducted PMF analysis for source apportionments using a $PM_{2.5}$-ACSM. They also analyzed several plume events and concluded that the low $NO_x/CO$, $NO_x/SO_2$ and the dominance of ammonium sulfate and/or ammonium bisulfate in PM may be used as tracers for identification of emissions from steel plants. This paper is within the scope of ACP. However, there are several areas of ambiguity that should be addressed/clarified in the revision.

**Major comments:**

1. How did the authors exclude the influences from industrial activities from coal-fired power station, coking state, and pickling process that are also within the region?

   Thank the reviewer's comments. Our study treated the various steelmaking processes as a whole to evaluate the effects of steel plant emissions on air quality instead of evaluating a specific production process separately and precisely. With the available measurements in this study, it is very challenging to separate and quantify the contributions from different plants and processes. Considering that the steel plants, especially RSP, is the largest industry in this area, the impacts of industrial emissions we observed are expected be dominantly from the steel plants as well.

2. Figure 7: Based on the wind rose plots, all six plumes were associated with southerly or southwesterly winds and therefore were not likely to be from the Shandong power plant. How do the authors determine the $NO_x/CO$, $NO_x/SO_2$ and ammonium sulfate concentration from the SSP?

   The steelworks plumes from RSP were characterized by dramatic increases in sulfate and ammonium mass concentrations, while maybe due to more advanced purification and emission control technologies, such distinct characteristic was not observed for SSP during northeast wind periods. In order to figure out the impacts of SSP emissions on the air quality nearby, we furtherly explored the gaseous pollutants including $NO_x$, CO and $SO_2$ from different directions, and we found some common characteristics during the southwest and northeast wind periods. Specifically, although the SSP emits much less ammonium sulfate particles, and gaseous CO and $NO_x$, the ratios of $NO_x$ /$SO_2$ and $NO_x$ /CO were similar between these two steel plants. Thus, we suggested that we can use the combination of sharp increase of sulfate and ammonium, $NO_x/CO$ and $NO_x/SO_2$ ratios to capture and quantify the effects of steel plant emissions more precisely. The wind rose plots for plume periods and plume excluded periods are shown in Fig. R5 to make a clearer explanation.

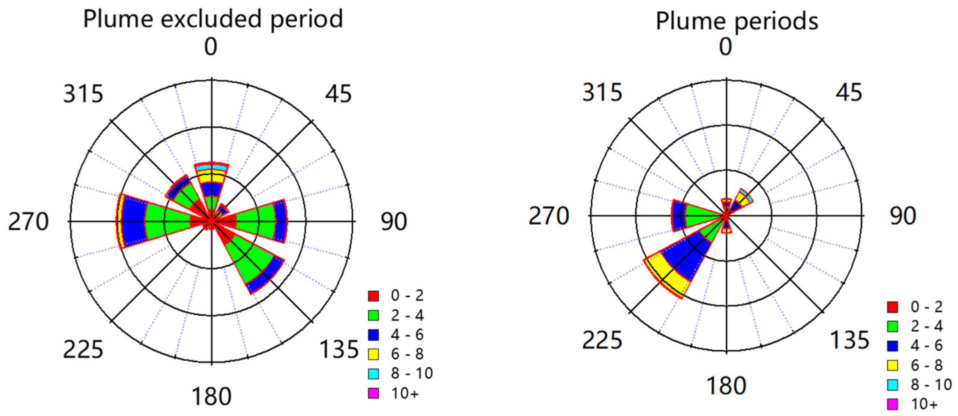

Figure R5. Wind rose plots for plume excluded period and plume periods in March 2019.

3. The authors need to confirm that buildings and street canyons do not affect their wind speeds and direction measurements.

   Thank the reviewer's comments. There are no dense and tall buildings near our sampling site that can affect the wind fields substantially. The west of the sampling site is a large wasteland, and the east is the Yellow Sea, and the north and south of the site are the buildings of steel plants.

**Minor comments:**

1. Page 2, Line 13: grammatical error in "one of the most important one"

   We revised the expression as "one of the most important sources".

2. Page 4: Line 19: It is usually called electron ionization these days. The electrons don't actually hit the molecules, so "impact" is disfavored.

   Thank the reviewer's comments. The non-refractory constitutes in the particles would be flash vaporized by the vaporizer and subsequently ionized by impacting with electrons emitted by filament (Fröhlich et al., 2013), so "electron impact" is actually a suitable expression in studies with aerosol mass spectrometer.

3. Page 5: Line 13: What about metals?

   The concentrations of metals were not measured in our study.

4. Page 4: Line 7: "while they were dominantly from the north in September and from the west in March" at night?

Yes, it’s the description of prevailing winds at night, we have clarified this in the revised manuscript.

5. Figure 1: As a key element of a map, the scale should always be included.

   The scale was added on the maps in the revised manuscript.

6. Figure 2: The units for $SO_2$ and $NO_2$ are missing.

   Corrected.

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# Fine particle characterization in a coastal city in China: composition, sources, and impacts of industrial emissions

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**Abstract.** Aerosol composition and sources have been extensively studied in developed regions in China~~, however~~. However, aerosol chemistry in coastal regions of eastern China with high industrial emissions remains poorly characterized. Here we ~~have~~present a comprehensive characterization of aerosol composition and sources near two large steel plants in a coastal city in Shandong in fall and spring ~~seasons~~ using a $PM_{2.5}$ Time-of-Flight Aerosol Chemical Speciation Monitor. The average (±1σ) mass concentration of $PM_{2.5}$ in spring 2019 (54~~ ± ~~±44 μg/m$^3$) was approximately twice that (26~~ ± ~~±23 μg/m$^3$) in fall 2018. Aerosol composition was substantially different between the two seasons. While organics accounted for ~30% of the total $PM_{2.5}$ mass in both seasons, sulfate showed a considerable decrease from 28% in September to 16% in March, which was associated with a large increase in nitrate contribution from 17% to 32%. Positive matrix factorization analysis showed that secondary organic aerosol (SOA) dominated the total OA in both seasons, on average accounting for 92% and 86%, respectively, while the ~~contributions~~contribution of traffic-related hydrocarbon-like OA ~~were~~was comparable (8-9%). During this study, we observed significant impacts of steel ~~plants~~plant emissions on aerosol chemistry nearby. The results showed that aerosol particles emitted from the steel plants were overwhelmingly dominated by ammonium sulfate/ammonium bisulfate with the peak concentration reaching as high as 224 μg/m$^3$. Further analysis showed similar mass ratios of $NO_x$/CO (~~13.7~~0.014) and $NO_x/SO_2$ (1.24) from the two different steel plants, which were largely different from those during periods in the absence of industrial plumes. Bivariate polar plot analysis also supported the dominant source region of ammonium sulfate, CO and $SO_2$ from the southwest steel plants. Our results might have significant implications for better quantification of industrial emissions using ammonium sulfate and the ratios of gaseous species as tracers in industrial regions and nearby in the future.

## 1 Introduction

Atmospheric fine particles ($PM_{2.5}$, particles with an aerodynamic diameter less than 2.5 μm) have great impacts on visibility (Reddy and Venkataraman, 2000;Jinhuan and Liquan, 2000), climate forcing~~ ~~(Lohmann and Feichter, 2005;Carslaw et al., 2010), and human health (Laden et al., 2000;Pope III et al., 2002). Among the sources of aerosol particles, industrial emissions have become one of the most important ~~one~~sources in rapidly developing countries, e.g., China (Cao et al., 2011;Huang et al., 2014). However, previous studies on chemical composition and sources were mostly conducted in densely populated urban environments and remote/rural areas (Allan et al., 2009;Aiken et al., 2009;Sun et al., 2012), while industrial plumes that can have a large impact on urban air quality and residents nearby are much less characterized. Aerosol particles in regions under the influences of industrial emissions contain much higher concentration of toxic substances than those observed at urban and rural areas (Osornio-Vargas et al., 2003;Lage et al., 2014), leading to much higher health risks for people living nearby. Therefore, it is critically important to characterize the chemical composition and sources of fine particles in the vicinity of industrial plants, and to have a better understanding of their formation mechanisms, evolution processes and potential health effects (Davidson et al., 2005).

Industrial activities in steelmaking such as coke production and ore-sintering emit a large amount of gaseous species, e.g., $SO_2$, $NO_x$, and CO (Brock et al., 2003;Weitkamp et al., 2005), and particulate matters (Almeida et al., 2015;Taiwo et al., 2014). Heavy metals including Fe, Mn, Pb, etc., (Wong et al., 2006;Yang et al., 2018), specific polycyclic aromatic hydrocarbons (PAHs) (Athanasios et al., 2011;Leoni et al., 2016), secondary inorganic species (Setyan and Jing, 2017;Wu et al., 2018), and OC/EC (organic-to-elemental carbon) ratio (Chow et al., 2011) have been used as tracers to identify various industrial processes and to estimate ~~the contributions to~~their influences on air quality. During the last decade, real-time measurement instruments including aerosol time-of-flight mass spectrometer (ATOFMS) and Aerodyne aerosol mass spectrometer (AMS) ~~have~~has been used to measure the rapid changes in ~~particles~~particle mixing states and chemical composition of industrial particles (Dall'Osto et al., 2008;Setyan et al., 2019). Dall'Osto et al. (2008) found several unique types of particles such as Fe-rich, Pb-rich, Zn-rich, and Ni-rich from steelmaking progresses, and Setyan et al. (2019) found a large increase in non-refractory chloride from the Fe-Mn plant and the adjacent steelworks based on the measurements of a high-resolution time-of-flight AMS. Although the real-time measurements of fine particles are important for understanding the rapid evolutionary processes of aerosol composition, size distributions, and mixing states from industrial plumes, few studies have been conducted in highly industrialized areas in China.

Rizhao, located to the west of Yellow Sea is one of the most important steel production bases in Shandong, China. The steel production in 2018 was approximately 26 million tons, ~40% of the total production in Shandong. In addition to emissions from the steel plants, the air pollution in Rizhao is subject to multiple influences from local emissions, regional transport from Linyi to the west and Weifang to the northwest, and sea-land breezes. According to the Environment Statement of Shandong Province, the air quality in Rizhao was improved significantly with the annual average $PM_{2.5}$ decreasing from ~70 μg/m$^3$ in 2013 to ~50 μg/m$^3$ in

2017. However, the $PM_{2.5}$ still exceeds the National Ambient Air Quality Standard (35 μg/$m^3$ as an annual average) by more than 40%, and severe haze episodes were also frequently observed in winter. Although aerosol composition, sources and formation mechanisms have been widely characterized in Beijing-Tianjin-Hebei, Yangtze River Delta, and Pearl River Delta during the last decade (Li et al., 2017), aerosol chemistry in the coastal city of Rizhao, and chemical characteristics of steel plant emissions are rarely characterized. Therefore, it is of importance to investigate the composition, sources and variations of aerosol particles near industrial areas, and to better understand their impacts on urban air quality and human health.

In this work, we conducted two campaigns in the vicinity of steel plants in Rizhao in September 2018 and March 2019 using an Aerodyne Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM) that was equipped with a $PM_{2.5}$ aerodynamic lens and a capture vaporizer. Aerosol particle composition, diurnal variations, and potential sources are characterized, and the sources of organic aerosol are analyzed with positive matrix factorization. In particular, the chemical characteristics of pollutants from the emissions of steel plants, and their impacts on air quality are elucidated.

## 2 Experimental methods

### 2.1 Sampling site and measurements

All measurements were carried out at a site near two steel plants in a coastal city Rizhao, Shandong (35°10’59” N, 119°23’57” E) from 2 to 29 September 2018, and 2 to 29 March 2019. As shown in Fig. 1, the sampling site is located approximately 2 km northeast of the Rizhao steel plant (RSP), ~1 km southwest of the Shandong steel plant (SSP), and ~1 km from the Yellow Sea. As shown in Figs. 1c and 1d, the prevailing winds were from the east and southeast during daytime in both September and March, while they were dominantly from the north in September and from the west in March~~.~~ during nighttime. As a result, the sampling site was subject to~~ a~~ significant influence from sea-land breeze. Also note that the two steel plants have differences in technologies for controlling the emissions of pollutants. The ~~new~~newly built SSP uses more advanced purification and ~~emissions~~emission control technologies, e.g., dry desulfurization technology with the advanced activated coke compared with ~~those, mainly~~ wet limestone-gypsum flue gas desulfurization (FGD) used in RSP. According to the National Bureau of Statistics of China, the annual steel production of RSP was ~18 million tons, and that of SSP was ~ 8 million tons.

An Aerodyne ToF-ACSM, that is equipped with a $PM_{2.5}$ aerodynamic lens and a capture vaporizer (CV), was deployed for real-time measurements of non-refractory aerosol species in fine particles (NR-$PM_{2.5}$) including organics (Org), sulfate ($SO_4$), nitrate ($NO_3$), ammonium ($NH_4$) and chloride (Chl) at a time resolution of 2 min. Briefly, ambient aerosol particles were first drawn into the sampling line at a flow rate of ~3 L/min after passing through a $PM_{2.5}$ cyclone (URG-2000-30EH). Aerosol particles were then dried with a nafion dryer, and sampled into the ToF-ACSM at a flow rate of ~0.1 L/min. After focusing into a narrow particle beam and flying through the vacuum chamber, non-refractory aerosol species were flash vaporized at ~540 °C and then ionized immediately by the 70 eV electron impact. The ions were analyzed using the time-of-flight mass analyzer and detected by an SGE dynode detector (Fröhlich et al., 2013). Similar to Quadrupole-ACSM (Ng et al., 2011b), the mass concentrations of aerosol species were derived from the differences between sampling mode and filter mode. The ionization efficiency (IE) and relative ionization efficiencies (~~RIE~~RIEs) were calibrated using pure $NH_4NO_3$ and $(NH_4)_2SO_4$ before and after the campaigns. The RIE of sulfate was fairly robust which was 1.1, while that of ammonium changed from 3.1 in September 2018 to 3.8 in March 2019. The default RIE values of 1.1, 1.4, and 1.3 were used for nitrate, organics, and chloride, respectively.

In addition to NR-$PM_{2.5}$ aerosol species, a 7-wavelength Aethalometer (Model AE33, Magee Scientific) was used to measure black carbon (BC) at a time resolution of 1 min. The gaseous species including $SO_2$ (Model 43i), CO (Model 48i) and $NO_x$ (Model 42i) were measured by various gas analyzers from Thermo Fisher Scientific, and the meteorological parameters including temperature ($T$), relative humidity (RH), wind speed (WS) and wind direction (WD) were measured by WS500-UMB Smart Weather Sensor (Lufft).

### 2.2 Data analysis

The mass concentration and chemical composition were analyzed using the standard ToF-ACSM data analysis software (Igor-based Tofware_2_5_13_ACSM, www.tofwerk.com/tofware). A collection efficiency (CE) of ~1 ~~for~~ was used for mass quantifications as indicated by previous studies that AMS or ACSM with CV has a fairly robust CE of ~1 (Hu et al., 2016a;Hu et al., 2018b, a). Our results showed that NR-$PM_{2.5}$ + BC was well correlated with the total $PM_{2.5}$ mass in both spring and fall ($r^2$ = 0.54 and 0.86), and the regression slopes of 0.89 and 0.78 suggested that the mass quantification of the ToF-ACSM was reasonable considering that mineral dust was not measured in this study.

The bilinear model positive matrix factorization (PMF) (Paatero and Tapper, 2010) has been widely used to deconvolve organic aerosol (OA) into different factors (Lanz et al., 2007;I. M. Ulbrich et al., 2009;Sun et al., 2011). In this study, PMF analysis was performed to the organic mass spectra from ToF-ACSM measurements to determine the potential OA ~~factors~~ from different sources and process. The detailed procedures for pretreatment of the data and error matrices were presented in Zhang et al. (2011). Considering the limited sensitivity of the ToF-ACSM, *m/z*'s larger than 120 and 180 were excluded in PMF analysis in September 2018 and March 2019, respectively due to their low signal-to-noise ratios, and low contributions to the total OA mass. After careful evaluations of mass spectral profiles, diurnal variations and correlations with external tracers, three OA factors including a hydrocarbon-like OA (HOA), a less oxidized oxygenated OA (LO-OOA) and a more oxidized OOA (MO-OOA) were determined in September 2018, and four ~~factors~~factor, i.e., HOA, LO-OOA, MO-OOA and a coal combustion OA (CCOA) were identified in March 2019. Compared with previous OA factors identified from PMF-AMS analysis (Ng et al., 2011a), the mass spectra of both primary and secondary OA factors showed much higher $f_{44}$ (fraction of *m/z* 44 in OA) in this study due to increased thermal decomposition on the surface of CV (Hu et al., 2018b, a). Hu et al. (2018a) also found that the previous AMS tracer *m/z's* are still present and usable in mass spectra although the fragmentation in CV tends to shift towards small *m/z's* due to additional thermal decomposition. Comparisons of PMF results further showed consistent time series of OA factors between CV and standard vaporizer (SV), yet the CV may introduce higher uncertainty in separating different types of OOA (Hu et al., 2018b).

## 3 Results and discussion

### 3.1 Mass concentrations, chemical composition and diurnal variations

Figure 2 shows the time series of aerosol species, gaseous species, and meteorological parameters during the two seasons. The average (±σ) RH and *T* was 62~~% (±~~%(±15%) and 23 °C (±3 °C) in September 2018, which were overall higher than those (60±4% and 10±4 °C, respectively) in March 2019, while the average WS was comparable between the two seasons (2.8±1.1 m/s vs. 3.2±1.9 m/s). One of the major differences in meteorological conditions is wind direction. While the prevailing winds were both from the east and southeast during daytime, they were mainly from the north in September and the west in March at ~~nighttime~~night. We also noticed a considerable frequency of southwesterly winds in spring of 2019 suggesting a high potential impact of RSP on the sampling site.

The average $PM_{2.5}$ (NR-$PM_{2.5}$ + BC) concentration was ~26 (±23) μg/m$^3$ for the entire study in September 2018, which was approximately half of that (54±44 μg/m$^3$) in March 2019. This result suggested that air quality in March was much worse than that in September, and the PM loading was even more than 50% higher than the National Ambient Air Quality Standard (35 μg/m$^3$ as an annual average). According to the measurements at the Environmental Monitoring Station of Rizhao, the average $PM_{2.5}$ mass concentration in September showed a continuous decrease from 50 μg/m$^3$ in 2013 to 22 μg/m$^3$ in 2018, suggesting a significant improvement in air quality in September. However, the $PM_{2.5}$ mass concentration remained at relatively high levels ranging from 54 to 78 μg/m$^3$ in March during the years of 2013 – 2018, indicating a great challenge in reducing PM in this season.

Figure 2 shows the average aerosol composition during fall and spring~~ seasons~~. While organics contributed approximately one-third of the total $PM_{2.5}$ mass in both spring and fall~~ seasons~~, large differences in secondary inorganic species were observed. For example, sulfate was the second largest component in $PM_{2.5}$ in fall accounting for 28%, and its contribution ~~was ~~decreased to 16% in spring. In contrast, nitrate showed ~~a ~~largely elevated ~~contribution~~contributions from 17% to 32%. These results indicate that the formation mechanisms and sources of secondary inorganic species could be different ~~between~~during the two seasons. BC contributed similar fractions to $PM_{2.5}$ in both seasons, which was 7 – 8%, and chloride was generally small~~,~~ at less than 2%. We noticed that the average composition in spring was similar to that observed at a receptor site (Changdao Island) in north coast of Shandong province in spring 2011 (Hu et al., 2013). These results might suggest that aerosol composition did not change significantly although the PM levels decreased substantially during the last decade. We further compared aerosol composition during and after the heating season in March, and observed remarkably similar mass concentrations and aerosol compositions during the two periods. One of the major reasons was that the residents near the steel company were all relocated to other places. As a result, the emissions from residential coal combustion were small. Further support is that the coal combustion OA only accounted for ~5% to the total OA mass as discussed in Section 3.2.

Although the mass concentrations and aerosol compositions were substantially different, the diurnal patterns were overall similar for all aerosol species during the two seasons, indicating that the factors driving the diurnal variations were similar. As shown in Fig. 3, higher mass concentrations at nighttime and in the early morning than ~~those~~ in the daytime were observed for the most aerosol species. Such diurnal patterns can be explained by the rising boundary layer height during daytime and the prevailing winds from the east and southeast that brought relatively clean air from the ocean. In contrast, sulfate presented similar and relatively flat diurnal patterns in both fall and spring, consistent with the fact that sulfate was mainly formed over a regional scale. Despite the rising boundary layer height, the sulfate concentrations remained relatively high during daytime. One reason was likely due to the sea-land breeze that brought the potentially high sulfate concentrations over the Yellow Sea (Li et al., 2018) to the sampling site. Organics in ~~autumn~~fall also showed a relatively flat diurnal pattern due to the dominance of MO-OOA that was highly correlated with sulfate.

### 3.2 OA composition and sources

The mass spectra, time series and diurnal variations of OA factors in ~~autumn~~fall and spring are shown in Figs. 4 and 5. The mass spectra of HOA in both seasons resembled those of primary emissions reported previously (Canagaratna et al., 2004;Lanz et al., 2007;Mohr et al., 2009) showing the typical characteristics of hydrocarbon ion series of $C_nH_{2n-1}^{+}$ and $C_nH_{2n+1}$~~.~~$^{+}$. However, the HOA spectra showed generally higher $f_{44}$ compared with previous studies (14% in spring and 6% in ~~fall). One reason is~~autumn) due to the increased thermal decomposition in CV. Indeed, Hu et al. (2018b) also observed much higher $f_{44}$ in HOA spectrum from CV than that from SV. HOA was ~~highly~~well correlated with $NO_x$ ($r^2$ = 0.~~87~~52-0.~~82~~65) and BC ($r^2$ = 0.~~63~~66-0.~~79~~75) in both fall and spring, supporting that HOA was mainly from traffic emissions. This is further supported by the pronounced diurnal cycles of HOA showing higher mass concentrations during morning and evening rush hours. The average mass concentration of HOA was 0.7 μg/m$^3$ and 1.3 μg/m$^3$ in September and March, respectively. Although the mass concentration had a difference by a factor of 2 ~~between~~during the two seasons, the HOA contribution to total OA was comparable (8% vs. 9%), which is also close to that ~10% reported in Beijing (Zhang et al., 2014;Hu et al., 2016b;Sun et al., 2016).

A coal combustion OA factor was identified in March 2019 (Figs. 4b and 4c). The CCOA spectrum showed some similarities to that of HOA at small *m/*~~*z* range~~*z*'s yet was featured by pronounced PAHs-related *m/z*'s such as *m/z* 91, 115, 152, 165, 178, etc. (Dzepina et al., 2007). Despite the high thermal decomposition in CV, the PAHs signatures can be well retained as those in previous studies (Sun et al., 2016;Hu et al., 2013;Hu et al., 2016b). In fact, CCOA was highly correlated with these PAHs-related *m/z*'s~~, for example~~. For instance, CCOA was tightly correlated with *m/z* 115 (mainly $C_9H_7^+$, $r^2$ = 0.~~79~~76). Compared with HOA, CCOA presented a higher mass fraction of larger $m/z$'s (>120) indicating that coal combustion can be an important source of high molecular-weight organic ~~matter~~matters during heating period. CCOA on average accounted for 5% of the total OA mass in March with an average concentration of 0.8 μg/m$^3$. Compared with previously reported CCOA at urban sites, e.g., Beijing (~20%) and the receptor site Changdao in Shandong (~9%) (Sun et al., 2016;Hu et al., 2013), CCOA in this study seemed not an important contributor to OA although it presented a pronounced diurnal pattern with higher concentration and fraction at night. This is consistent with the fact that local residents were all relocated to other places, and the residential coal combustion emissions could not be significant.

Two SOA factors with different oxidation levels were determined in both September 2018 and March 2019. The total SOA (LO-OOA + MO-OOA) correlated well with secondary inorganic components, (SIA, i.e., sulfate + nitrate), and the ratios of SOA to SIA were 0.37 and 0.41 in September and March, respectively, which were close to those reported in Beijing (0.36-0.42) (Huang et al., 2010;Sun et al., 2010). The mass spectra of the two SOA factors were both characterized by a prominent $m/z$ 44 (mainly $CO_2^+$) peak, and the $f_{44}$ in MO-OOA was higher than that in LO-OOA (~36% vs. ~25%). Comparatively, $f_{29}$ and $f_{43}$ were notably higher in LO-OOA than MO-OOA, suggesting that MO-OOA was more oxidized than LO-OOA. Indeed, the MO-OOA tracked better with sulfate ($r^2$ = 0.45-0.~~70~~71) while the LO-OOA correlated better with nitrate ($r^2$ = 0.56-0.~~63~~60). The diurnal patterns of MO-OOA and LO-OOA were also different. LO-OOA showed similar and pronounced diurnal variations in both September and March with much higher mass concentration at nighttime than daytime. Such diurnal patterns were very similar to nitrate suggesting the similar semi-volatile properties of LO-OOA as nitrate (Docherty et al., 2011). In contrast, MO-OOA presented relatively flat diurnal cycles that were remarkably similar to those of sulfate, supporting that MO-OOA was highly aged and formed over a ~~reginal~~regional scale. SOA together accounted for 92% and 86% of the total OA mass in September and March, respectively. These results highlight an overwhelming dominance of SOA in OA during both seasons even our sampling site is located nearby the steel plants. However, we also found a change in SOA composition from March to September. In particular, MO-OOA showed ~10% higher contribution to OA in September than March (60% vs. 51%), while the fraction of LO-OOA was comparable (32% vs. 34%).

### 3.3 Potential sources of aerosol species

Figure 6 shows the bivariate polar plots of aerosol components and gaseous species in September and March. In general, high concentrations near the center area is associated with local sources, while that far away from the center area is indicative of regional transport (Carslaw and Ropkins, 2012). It can be seen that high concentration of $PM_{2.5}$ in September was mainly located in the region to the west (Fig. 6a) suggesting that regional transport played the most important role for air pollution in Rizhao. Comparatively, two high potential source regions for $PM_{2.5}$ were observed in March including local emissions and transport from the southwest region where RSP is located. The source regions were also substantially different for different aerosol species in September and March. As indicated in Fig. 6a, high mass concentrations of sulfate, ammonium, and chloride were mainly located in the southwest region in both September and March, suggesting the large impacts of the emissions from the RSP. High concentration of chloride likely existed mainly in the form of ammonium chloride considering that sea salt particles cannot be detected efficiently at a vaporizer temperature of ~ 540°C. We also observed high potential source regions to the west of the sampling site for sulfate, ammonium, and chloride in September. This result indicated that regional transport from the west, e.g., Linyi, can also be a significant contribution to air pollution in Rizhao. Comparatively, organics and nitrate showed very different sources between September and March. While organics and nitrate were dominantly from regional transport from the west in September, they were mainly from local emissions and production in March. BC showed similar source regions in the two seasons which were from both local emissions and regional transport.

HOA and LO-OOA showed similar potential source regions ~~as~~to those of organics and nitrate, i.e., mainly transported from the west in September 2018 with an increased contribution from local emissions in March 2019. In addition, a potential source region located to the northwest was also observed for LO-OOA in March. Similar to HOA and LO-OOA, the major source region of CCOA was located to the west with an additional source region to the southwest. The high potential source regions of MO-OOA were more complicated and have much differences between the two seasons. As shown in Fig. 6b, regional transport played a significant role for the high mass concentrations of MO-OOA in both September and March. While MO-OOA was mainly transported to the sampling site from the west in fall, the transport from the southwest and northwest also contributed substantially to the high mass loading of MO-OOA in spring elucidating the diverse sources of MO-OOA during this season. Overall, the regional transport from the west was the most significant and common source for all OA factors in September and March although that from the northwest and southwest also played a role in spring. The large differences in sources between sulfate, ammonium and OA factors in spring also demonstrated that the industrial plumes with high concentrations of ammonium sulfate were not associated with correspondingly high OA.

The potential source regions for high concentrations of CO and $SO_2$ were located to the southwest region in both September and March, which were also similar to those of sulfate and ammonium. These results illustrated the similar and significant impacts of the emissions from the RSP on CO an $SO_2$ as those of ammonium sulfate. We also noticed relatively high concentrations of CO and $SO_2$ in the northeast region in March suggesting the potential impacts of the SSP. However, the impacts appeared to be much smaller than that of RSP. One reason is that the current steel production of the SSP was much smaller than that of RSP. Another reason could be due to the different FGD (Saarnio et al., 2014) and emission control technologies. Compared with CO and $SO_2$, $NO_2$ was subject to multiple influences from steel plants, regional transport from the west and south, and local production.

### 3.4 Industrial plumes

Six clear industrial plumes, one in September and five in March, were observed during this study. Depending on meteorological conditions, the duration of plumes lasted from ~2 to 13 hours. As shown in Fig. 7, the steelworks plumes were characterized by dramatic increases in sulfate and ammonium, while the changes in organics and nitrate were small. This result was consistent with a study ~~nearby~~near a steel plant in Wales (UK), which also showed sharp increases in sulfate and sulfur-containing particles (Dallosto and Harrison, 2006). For example, the sulfate concentrations varied significantly during the plume period with the highest concentrations being 108 μg/m$^3$ and 189 μg/m$^3$ in September and March, respectively. By subtracting the background concentration that was determined as the average of 1 hr data before and after the plume, we found that the average mass concentration of PM$_{2.5}$ emitted from steel plants varied from 18 to 55 μg/m$^3$ during the six plumes suggesting a large impact of steel plant emissions on the air quality nearby. Figure 7 shows that aerosol particles from the steel plants were overwhelmingly dominated by ammonium sulfate ~~except the two plumes on September 3,~~ and ~~March 26 when~~ the contribution of ammonium bisulfate ~~accounted for ~70-80% of~~ to the total mass~~.~~ was in the range of ~20-40%. We noticed that the occurrence of six plumes were all associated with the southerly and southwesterly winds (Fig. 7), suggesting that ammonium sulfate and bisulfate particles were dominantly from RSP, while the emissions from the SSP appeared to be small. One reason is that more advanced purification and emission control technologies are used for the ~~new~~newly built SSP. Unfortunately, whether ammonium sulfate and bisulfate were directly emitted from the steel plants or from the reactions of SO$_3$ with NH$_3$ during the transport from the steel plant to the sampling site were unknown.

We also observed large increases in gaseous species of CO, SO$_2$, and NO$_x$ from steel plants during the plume periods. As shown in Fig. 8, CO was highly correlated with NO$_x$ ($r^2 = 0.83$), and NO$_x$ was also moderately correlated with SO$_2$ ($r^2 = 0.51$) during the periods of six plumes, while such correlations were much weaker during periods in the absence of plume influences ($r^2 = 0.26$-$0.17$). These results suggest that a large fraction of CO, NO$_x$, and SO$_2$ were co-emitted from the steel plants, while these gaseous pollutants were subject to multiple influences from different sources during other periods. ~~For example, BC, a tracer from incomplete combustion, was highly correlated with NO$_x$ during periods with small influence from steel plants ($r^2 = 0.66$), suggesting that BC and NO$_x$ were mainly from traffic and coal combustion emissions because steel plants unlikely emit a large amount of BC. As shown in Fig. 8, the average mass ratios of NO$_x$/SO$_2$ and NO$_x$/CO from the steel plant plumes were significantly lower than those during periods in the absence of plumes (1.24 vs. 1.55 and 13.7 vs. 41.0, respectively). Although the SSP emits much less ammonium sulfate particles, and gaseous CO and NO$_x$, we found that the ratios of NO$_x$/SO$_2$ and NO$_x$/CO were similar between these two steel plants. Our results highlight that NO$_x$/SO$_2$ and NO$_x$/CO ratios can be used as good diagnostics for evaluating the impacts of steel plant emissions on air quality~~For example, BC, a tracer for incomplete combustion, was highly correlated with NO$_x$ during periods with small influences from steel plants ($r^2 = 0.66$), suggesting that BC and NO$_x$ were mainly from traffic emissions because steel plants unlikely emit a large amount of BC. As shown in Fig. 8, the average mass ratios of NO$_x$/SO$_2$ and NO$_x$/CO from the steel plant plumes were significantly lower than those during periods in the absence of plumes (1.24 vs. 1.55 and 0.014 vs. 0.04, respectively). Although the SSP emits much less ammonium sulfate particles, and gaseous CO and NO$_x$, we found that the ratios of NO$_x$/SO$_2$ and NO$_x$/CO were similar between these two steel plants. The previously reported values of NO$_x$/CO from other emission sources, e.g., biomass burning (0.056-8.33), on-road motor vehicles (0.04-0.05), etc., were significantly larger than the NO$_x$/CO ratio during steel plant plumes in this study (Schürmann et al., 2007;Fujita et al., 2012;Tiwari et al., 2015;Santos et al., 2018). Moreover, the $NO_x$/CO ratio during plume excluded period was close to the values from vehicle emissions (0.04 vs. 0.04-0.05) (Fujita et al., 2012). The lower $NO_x/SO_2$ ratio was found to be characteristic of emissions from coal burning, e.g., in power generation plants or steel making plants, while higher values were generally attributed to vehicle emissions (Parrish et al., 1991). For example, the $NO_x/SO_2$ value of 1.04, obtained from the fresh flue-gas plume from a coal-fired power plant when FGD and fabric filter were used (similar to the flue-gas cleaning conditions of RSP), is close to the value of 1.24 during steel plant plumes in this study (Mylläri et al., 2016). In conclusion, our results highlight that $NO_x/SO_2$ and $NO_x$/CO ratios combined with significant increase of ammonium sulfate can be used as good diagnostics for evaluating the impacts of steel plant emissions on air quality in industrial regions and nearby.

## 4 Conclusions

We conducted two campaigns in the vicinity of two steelworks in a coastal city in Shandong, China using a $PM_{2.5}$ ToF-ACSM and various collocated instruments to investigate aerosol composition and sources in coastal regions and chemical characteristics of air pollutants from the emissions of steel plants. Our results showed that the mass concentrations of $PM_{2.5}$ varied greatly in the two seasons, and aerosol composition was also substantially different. The average $PM_{2.5}$ concentration in March 2019 (54±44 μg/m$^3$) was approximately twice that in September 2018 (26±23 μg/m$^3$) with nitrate being the largest fraction (32%) followed by organics (29%). Comparatively, aerosol composition in September showed high contribution of sulfate (28%) and correspondingly low nitrate (17%). PMF analysis showed the dominance of SOA in both March and September (86% vs. 92%). While LO-OOA contributed similarly to OA (32% vs. 34%), MO-OOA in September showed higher contribution than that in March (60% vs. 51%). Most aerosol species showed similar diurnal variations in the two seasons with higher concentrations during ~~daytime~~nighttime and lower values at ~~nighttime~~daytime, which were primarily driven by boundary layer dynamics and sea-land breeze. Sulfate and MO-OOA however presented relatively flat diurnal patterns because they were formed ~~over~~overall a regional scale. Bivariate polar plots reveal the two major sources of air pollutants in this study including the regional transport from the west, and the impacts of steel ~~plants~~plant emissions from the southwest. By analyzing six industrial plumes, we found that the emissions of steel plants were characterized by large increases in sulfate and ammonium, and also in gaseous species of CO and $SO_2$. In fact, aerosol particles of the six plumes were overwhelmingly dominated by ammonium sulfate and ammonium bisulfate. Although the SSP appeared to emit low concentrations of sulfate and ammonium, we found that the ratios of $NO_x$/CO and $NO_x/SO_2$ were close to those from RSP, and they were both significantly different from those during periods in the absence of industrial plumes. Our results highlight that ammonium sulfate, $NO_x$/CO and $NO_x/SO_2$ ratios can be used to evaluate and quantify the impacts of steel ~~plants~~plant emissions on air quality ~~downwind~~in industrial regions and nearby. Also, our results demonstrated a need for RSP to reduce sulfur emissions using more effective and advanced emission control technologies in the future.

***Data availability.*** The data in this study are available from the authors upon request (sunyele@mail.iap.ac.cn).

***Author contributions.*** YS~~ and ZW~~ designed the research. LL, CX, QW, YC and DW conducted the measurements. LL, YH, WZ and YS analyzed the data. PF, WH, XP, ZW and YS reviewed and commented on the paper. LL and YS wrote the paper.

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

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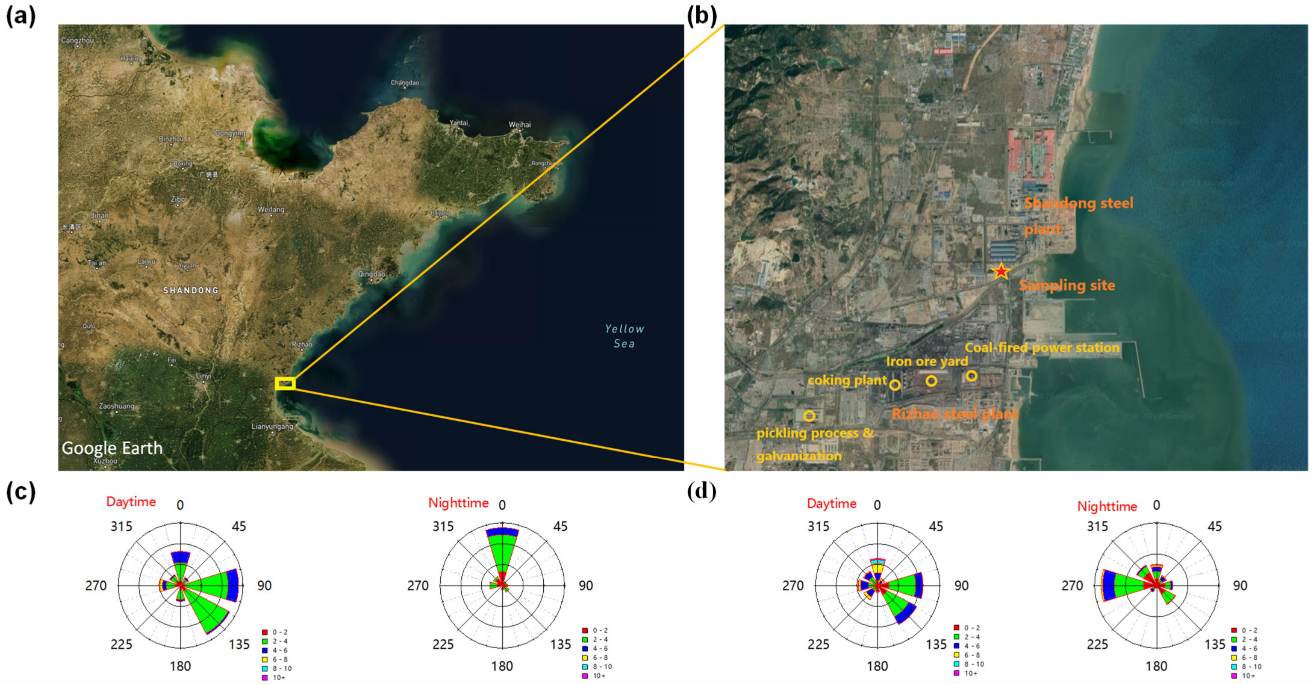


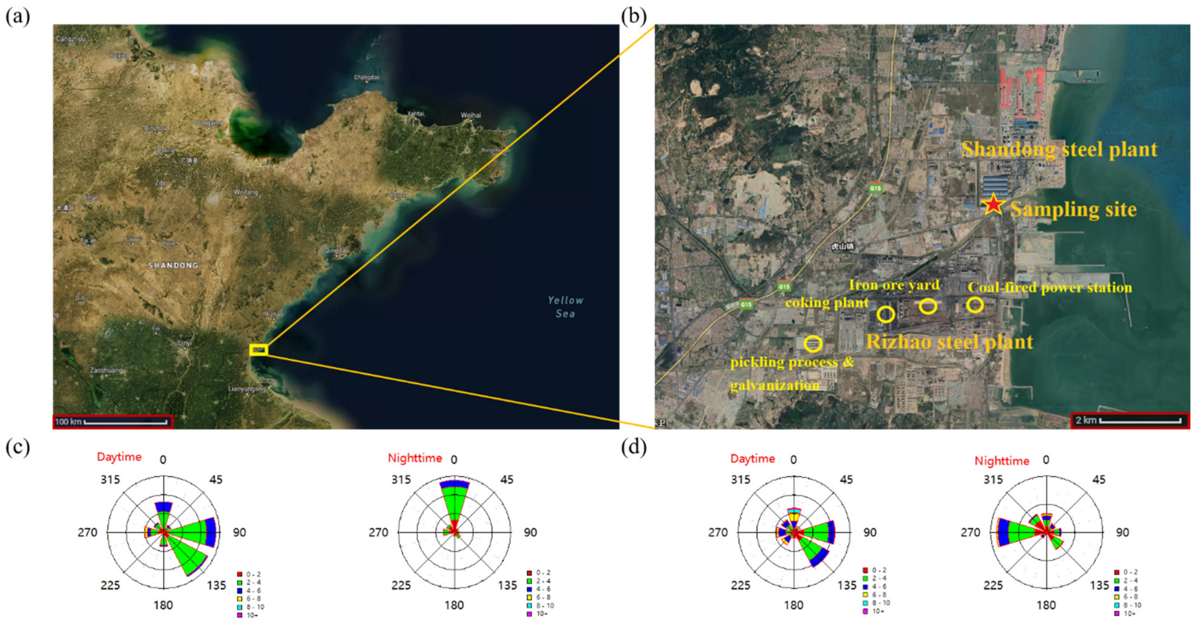
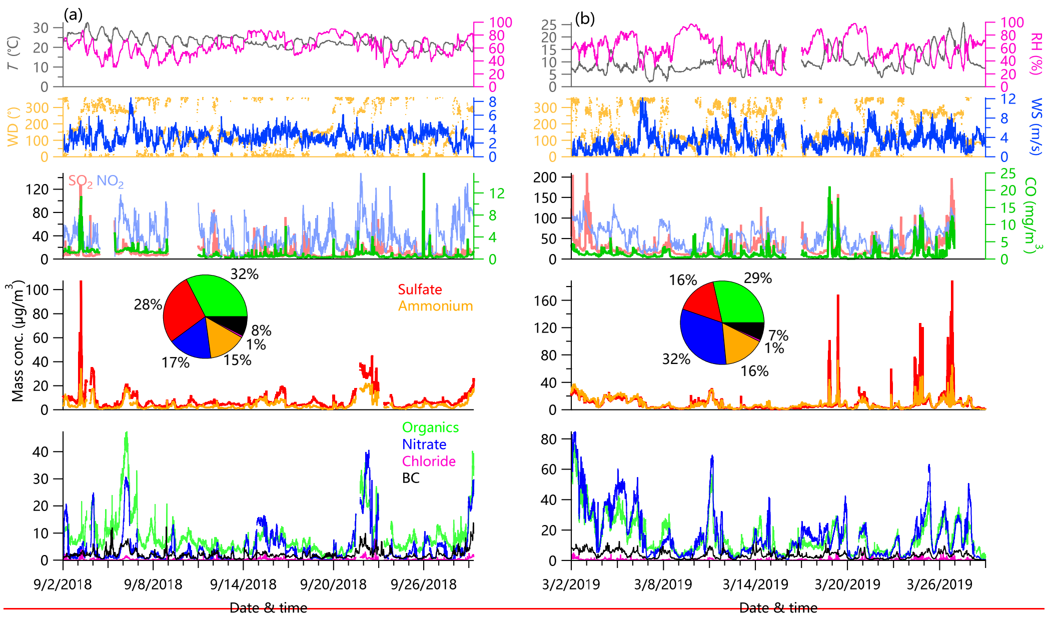


**Figure 1. (a, b) Location of the sampling site. (c, d) show wind rose plots of daytime and nighttime for the entire study in September 2018 and March 2019, respectively. ©Google Earth.**



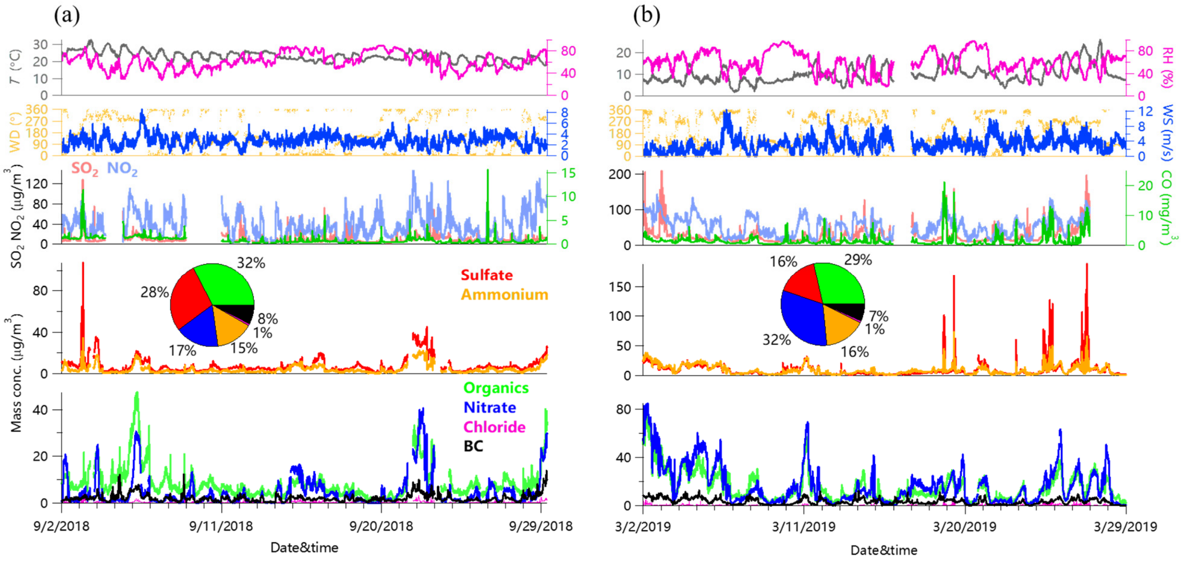


**Figure 2. Time series of meteorological variables including *T*, RH, WD and WS, mass concentrations of gaseous species including $SO_2$, $NO_2$ and CO, and chemical species in $PM_{2.5}$ in (a) September 2018 and (b) March 2019, respectively. The pie charts show the average chemical composition for the entire campaign.**

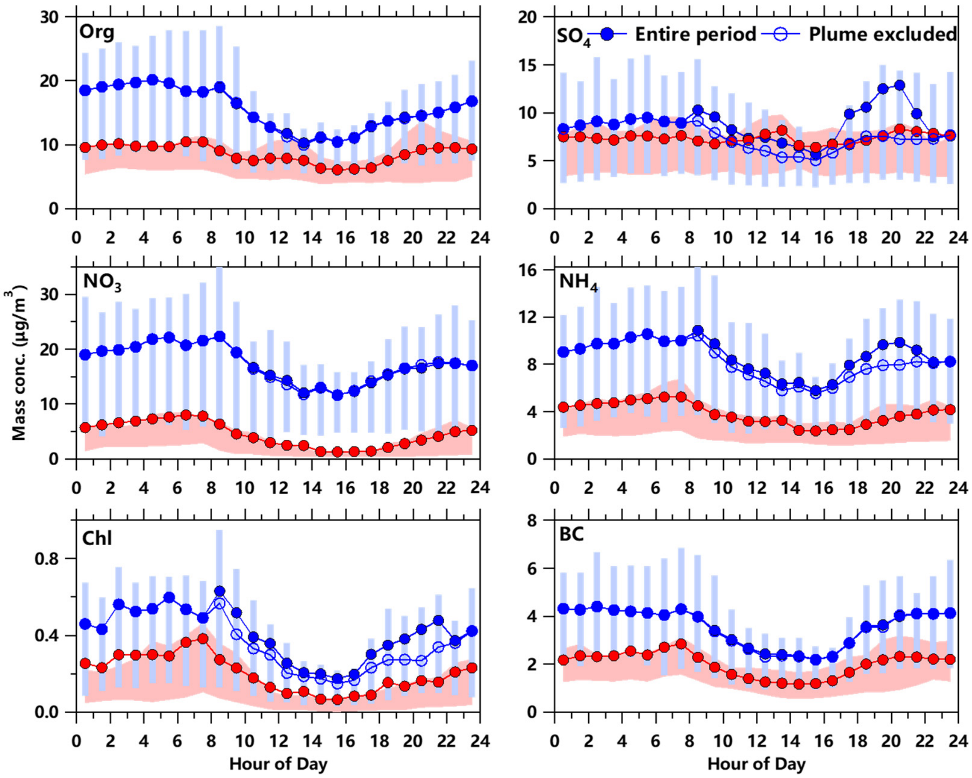
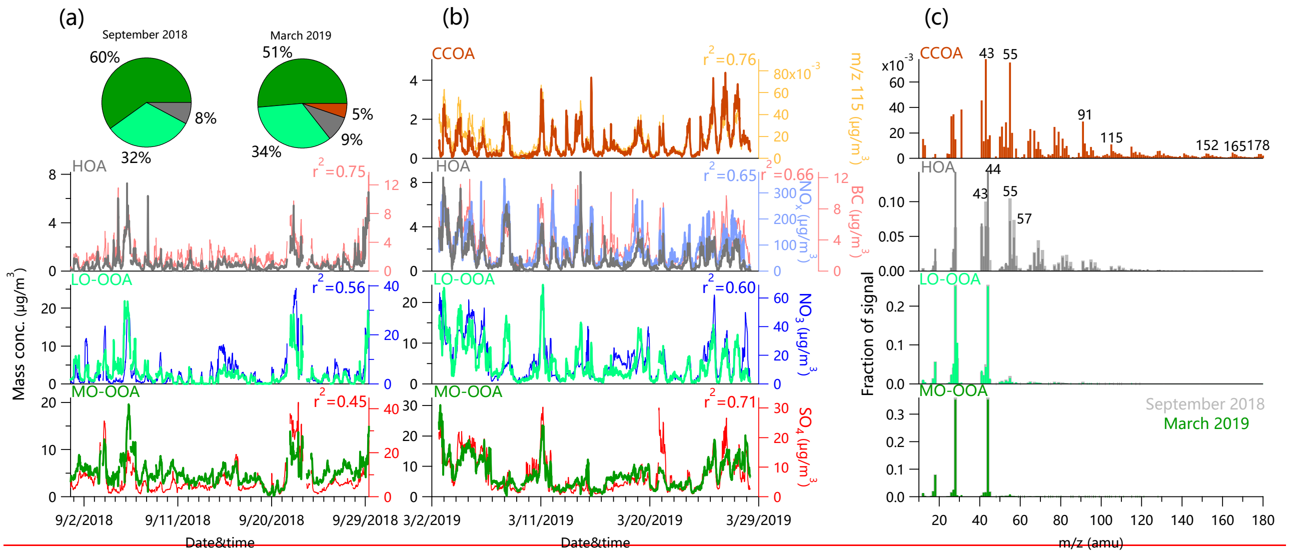


**Figure 3. Average diurnal variations of mass concentrations of chemical species in $PM_{2.5}$ in September 2018 (red) and March 2019 (blue), respectively. The shaded areas and error bars indicate 25th and 75th percentiles. Also, the diurnal cycles of aerosol species by excluding the periods with the influences from steel plants in March are shown as blue open circles.**



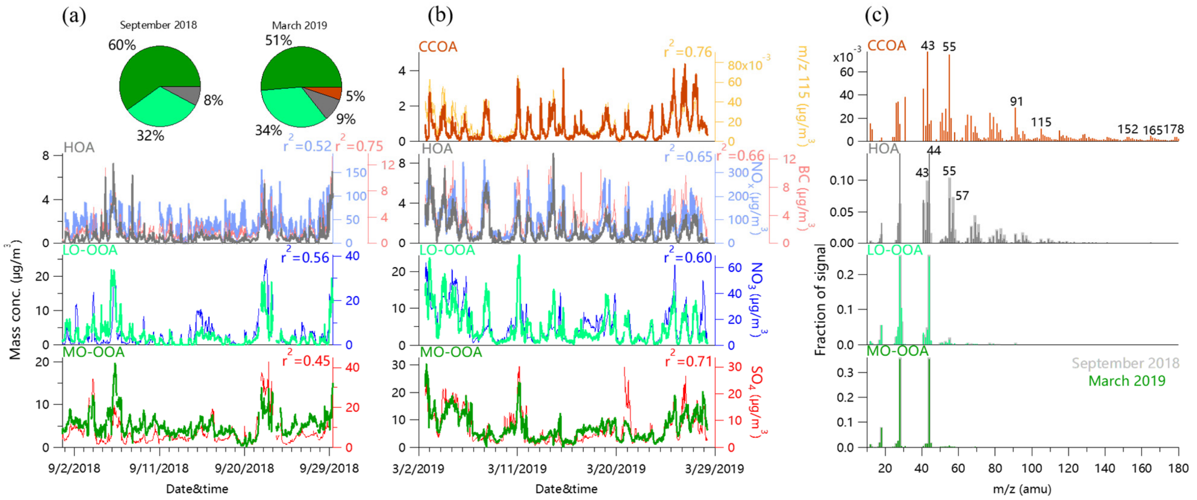
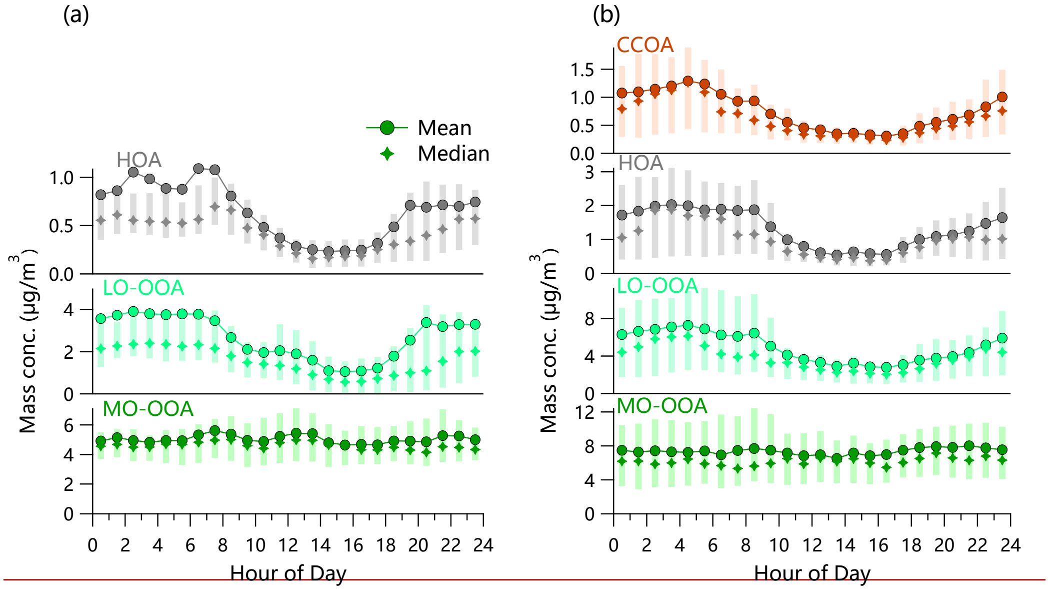


**Figure 4. (a, b) Time series and (c) mass spectral profiles of OA factors in September 2018 and March 2019. The time series of external tracer species are also shown for comparisons. The two pie charts present the average OA composition in September and March, respectively. Note that the periods with the influences from steel plants were excluded when performing correlation analysis between MO-OOA and $SO_4$ in (a) and (b).**



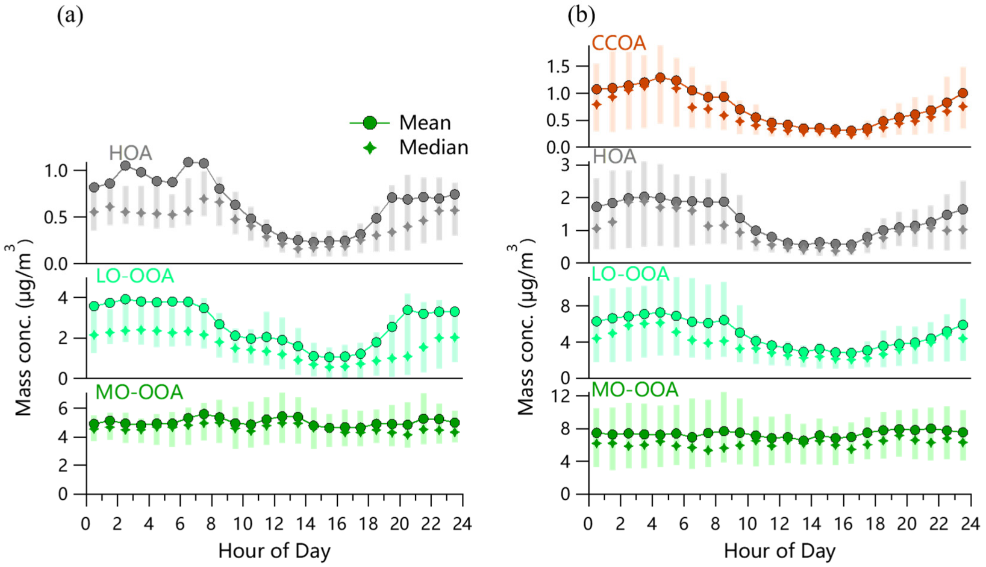
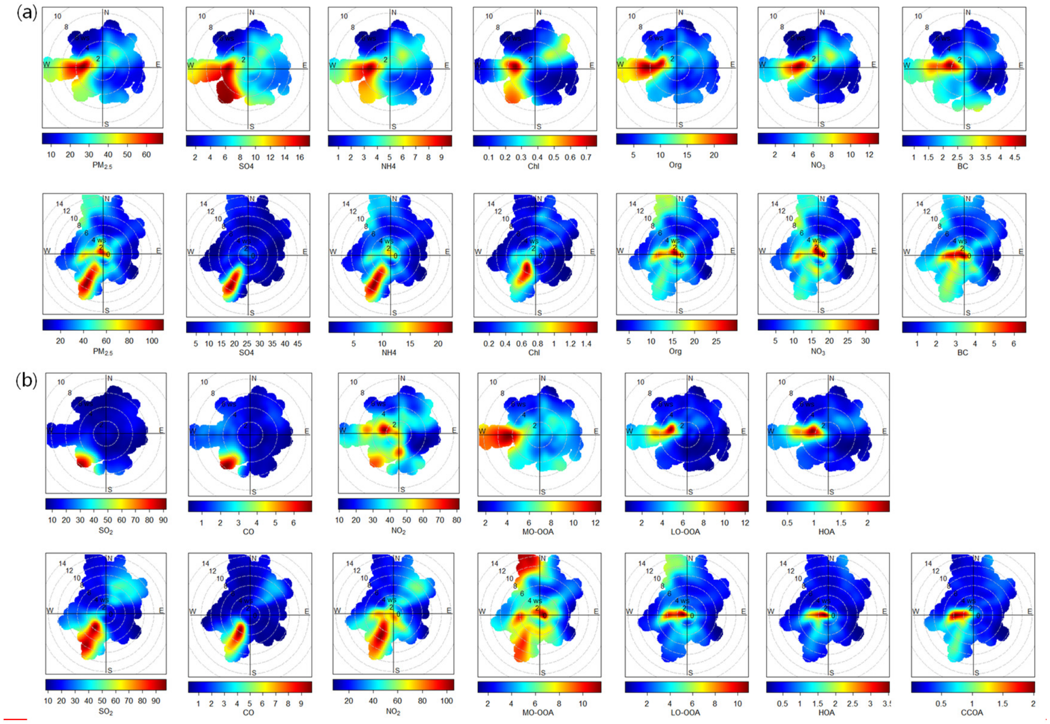


**Figure 5. Diurnal variations of mass ~~concentrations~~concentration of OA factors in (a) September 2018 and (b) March 2019. The error bars indicate 25th and 75th percentiles.**



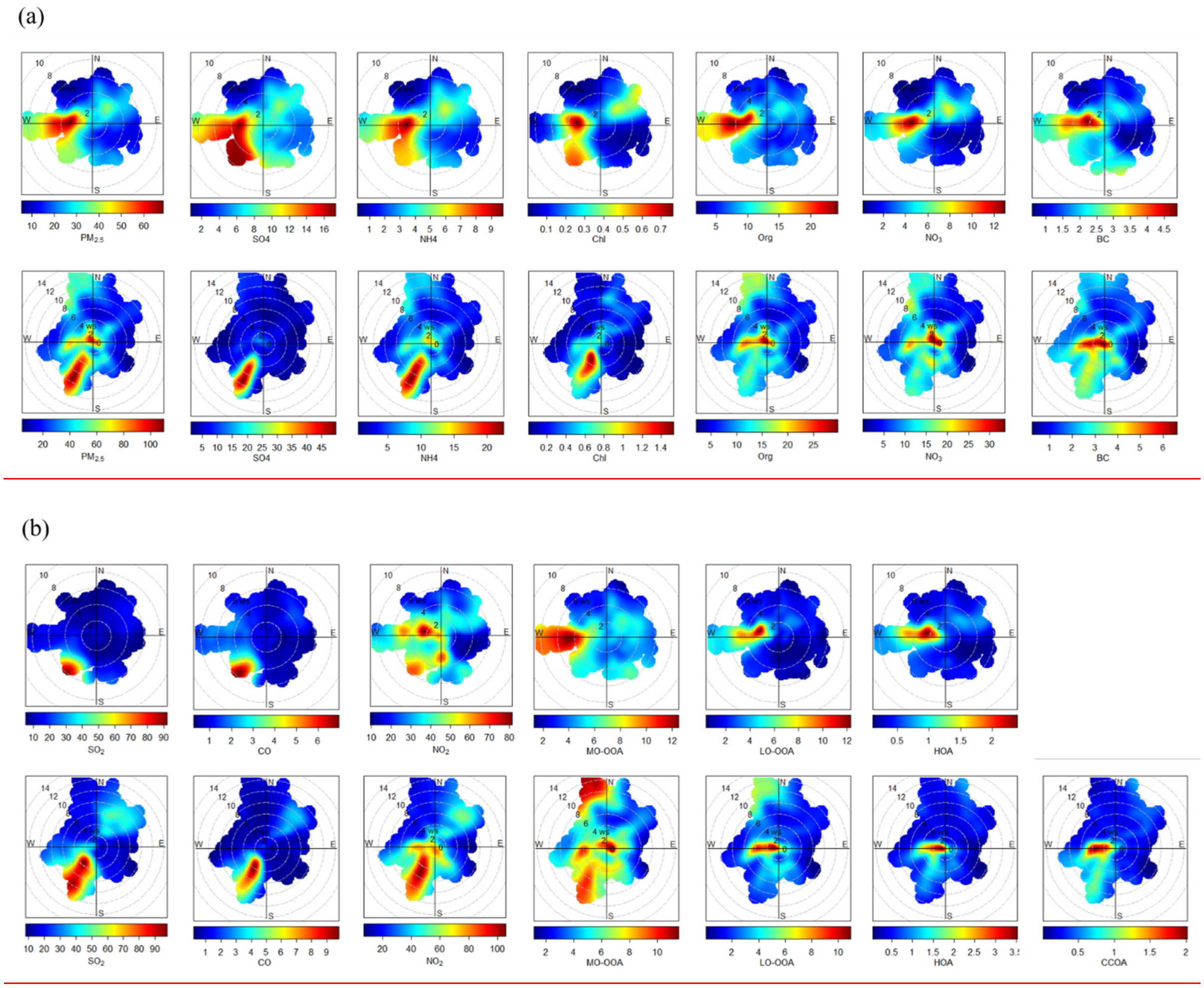
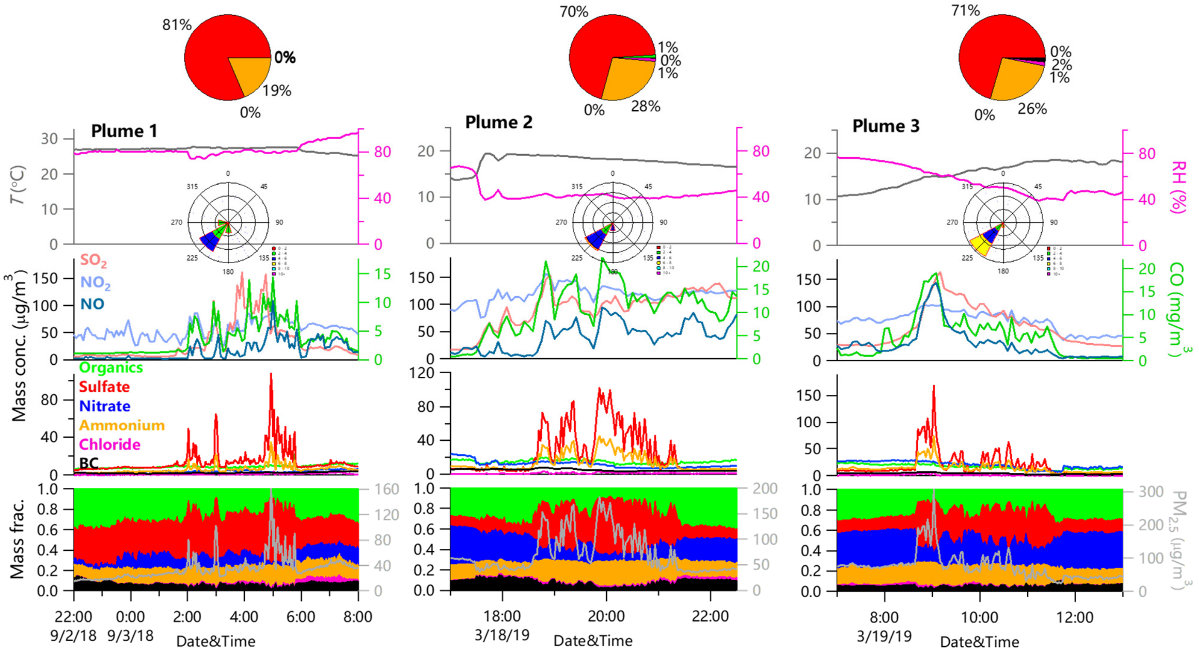


**Figure 6. Bivariate polar plots of (a) $PM_{2.5}$ and aerosol species; (b) $SO_2$, CO, $NO_2$, and OA factors in September 2018 (top) and March 2019 (bottom), respectively.**



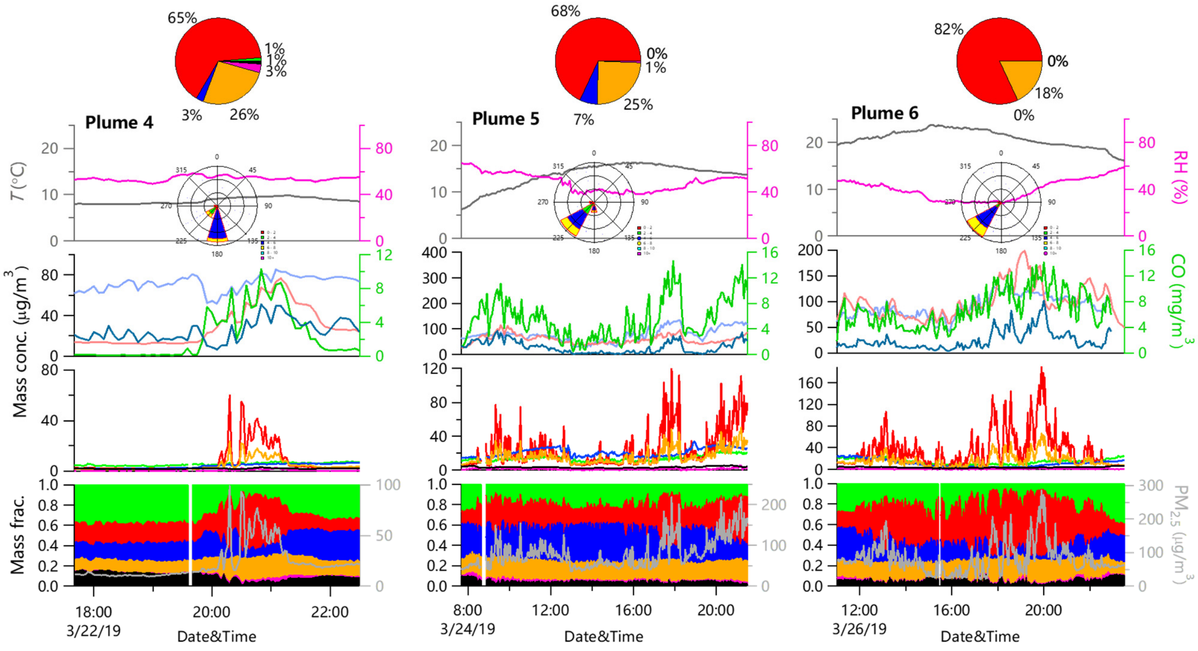
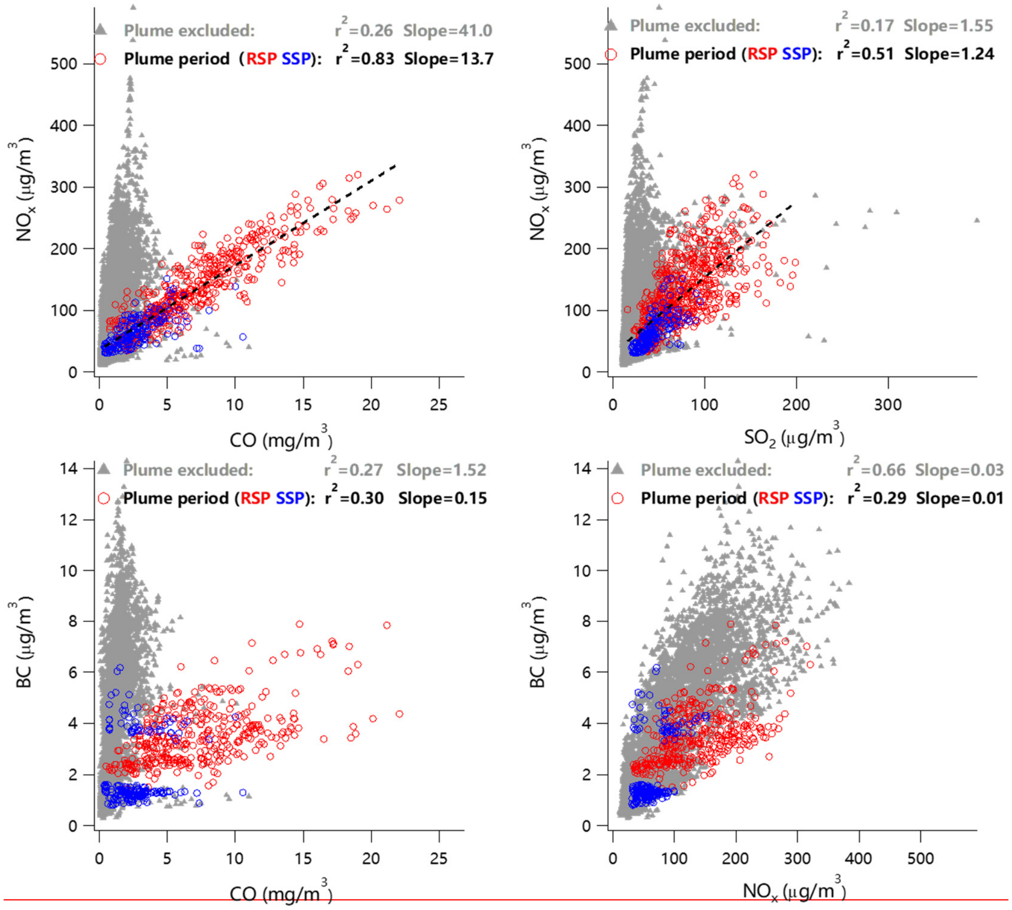


**Figure 7. Evolution of meteorological parameters including *T* and RH, gaseous species, mass concentrations and mass fractions of chemical species in PM$_{2.5}$ during six steelworks plume episodes. The pie charts show the contribution of each species emitted completely from steel plants. The wind rose plots depict the prevailing wind direction during each plume period.**



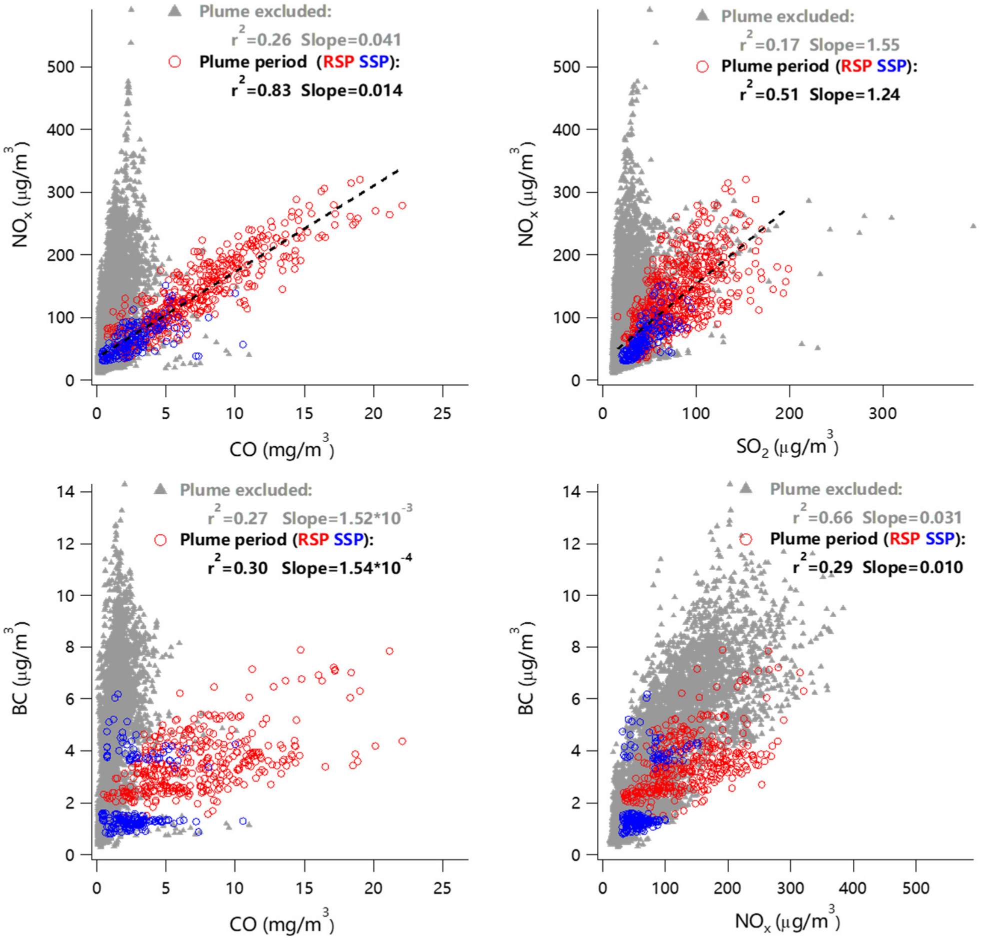


**Figure 8. Correlations between (a) $NO_x$ and CO, (b) $NO_x$ and $SO_2$, (c) BC and CO, and (d) BC and $NO_x$ during periods with (open circles) and without (gray triangle) influences of the emissions from the steel plants. RSP = Rizhao steel plant, SSP = Shandong steel plant.**