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, aerosol chemistry in coastal regions of eastern China with high industrial emissions remains poorly characterized. Here we have a

15   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 ($\pm 1\sigma$) mass concentration of $PM_{2.5}$ in spring 2019 (54 ± 44 μg/m³) was approximately twice that (26 ± 23 μg/m³) 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

20   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 of traffic-related hydrocarbon-like OA were comparable (8-9%). During this study, we observed significant impacts of steel plants 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) 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

5   implications for better quantification of industrial emissions using ammonium sulfate and the ratios of gaseous species as tracers

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

10   (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 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

15   urban air quality and residents nearby are much less characterized. Aerosol particles in regions under the influences of industrial

emissions contain much higher 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).

20   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 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 been used to measure the rapid changes in particles 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

5   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

10   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 $\mu g/m^3$ in 2013 to ~50 $\mu g/m^3$ in 2017. However, the $PM_{2.5}$ still exceeds the National Ambient Air Quality Standard (35 $\mu g/m^3$ as an annual average) by more

15   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.

20   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 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. 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 built SSP uses more advanced purification and emissions 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) 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, 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

5   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   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. We also

noticed a considerable frequency of southwesterly winds in spring of 2019 suggesting a high potential impact of RSP on the

sampling site.

15   The average $PM_{2.5}$ (NR-$PM_{2.5}$ + BC) concentration was ~26 (±23) μg/m³ for the entire study in September 2018, which was

approximately half of that (54±44 μg/m³) 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/m³ 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/m³ in 2013 to 22 μg/m³ in 2018, suggesting a significant

20   improvement in air quality in September. However, the $PM_{2.5}$ mass concentration remained at relatively high levels ranging from

54 to 78 μg/m³ 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 from 17% to 32%. These results indicate that the formation mechanisms and sources of secondary inorganic species could be different between the two seasons. BC contributed

5   similar fractions to PM$_{2.5}$ in both seasons, which was 7 – 8%, and chloride was generally small, 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

10   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

15   Fig. 3, higher mass concentrations at nighttime and in the early morning than those in the daytime were observed for 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

20   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 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 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 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 correlated with NO_x ($r^2 = 0.87$-0.82) and BC ($r^2 = 0.63$-0.79) 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/m³ and 1.3 μg/m³ in September and March, respectively. Although the mass concentration had a difference by a factor of 2 between 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 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, CCOA was tightly correlated with m/z 115 (mainly $C_9H_7^+$, $r^2 = 0.79$). 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. CCOA on average accounted for 5% of the total OA mass in March with an average concentration of 0.8 μg/m³. 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

5   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) while the LO-OOA correlated better with nitrate ($r^2 = 0.56$-0.63). 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

10   relatively flat diurnal cycles that were remarkably similar to those of sulfate, supporting that MO-OOA was highly aged and formed over a reginal 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%

15   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

20   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.,

5   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 those of organics and nitrate, i.e., mainly transported from the west

10   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

15   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

20   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

5   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 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

10   concentrations being 108 $\mu g/m^3$ and 189 $\mu g/m^3$ 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 $\mu g/m^3$ 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 ammonium bisulfate accounted for

15   ~70-80% of the total mass. 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 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.

20   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 ($r^2 = 0.26\text{-}0.17$). 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

5   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.

4 Conclusions

10   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/m³) was approximately twice that in September 2018 (26 ± 23 μg/m³) with nitrate being the largest fraction (32%) followed by organics

15   (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 and lower values at nighttime, which were primarily driven by boundary layer dynamics and sea-land breeze. Sulfate and MO-OOA

20   however presented relatively flat diurnal patterns because they were formed over 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 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 emissions on air

5   quality downwind. 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

10   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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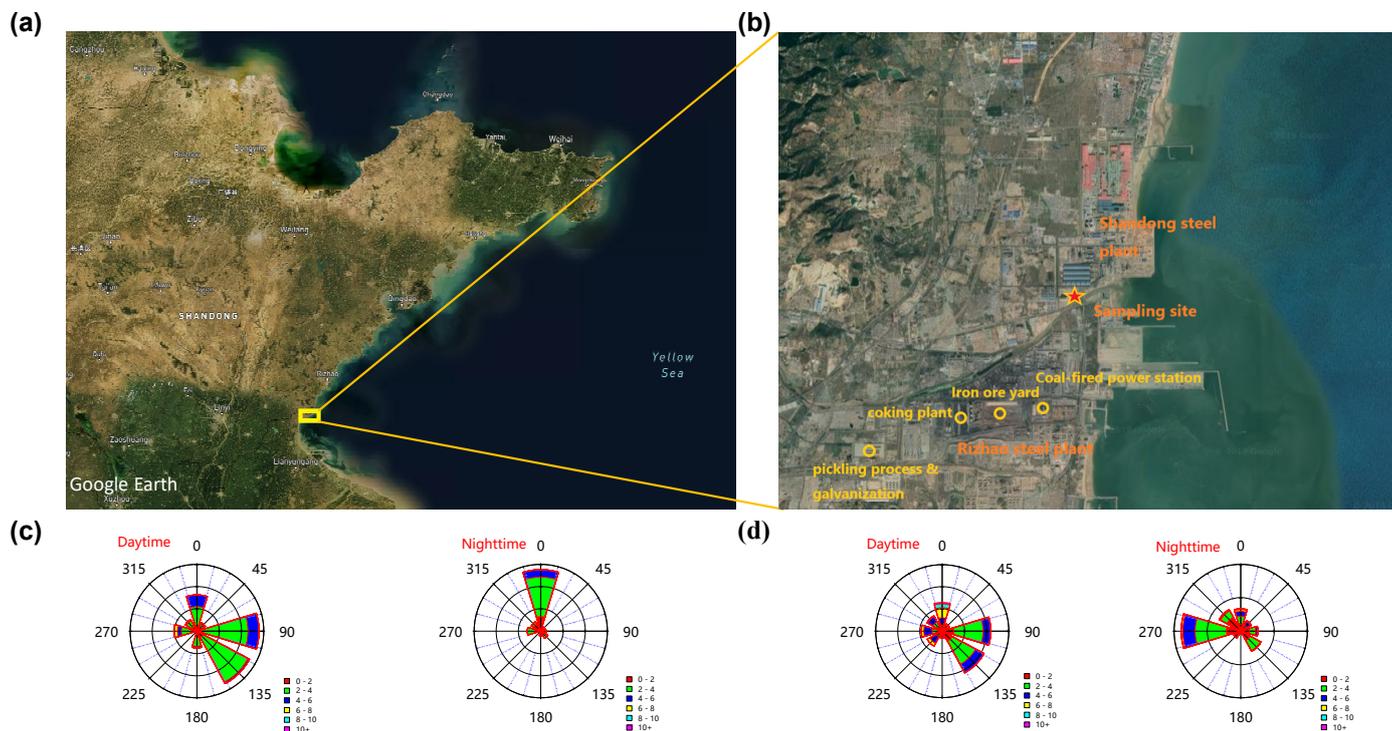


Figure 1. (a, b) Location of the sampling site. (c, d) show wind rose plots of daytime and nighttime for the entire study in September 2018 and March 2019, respectively. ©Google Earth.

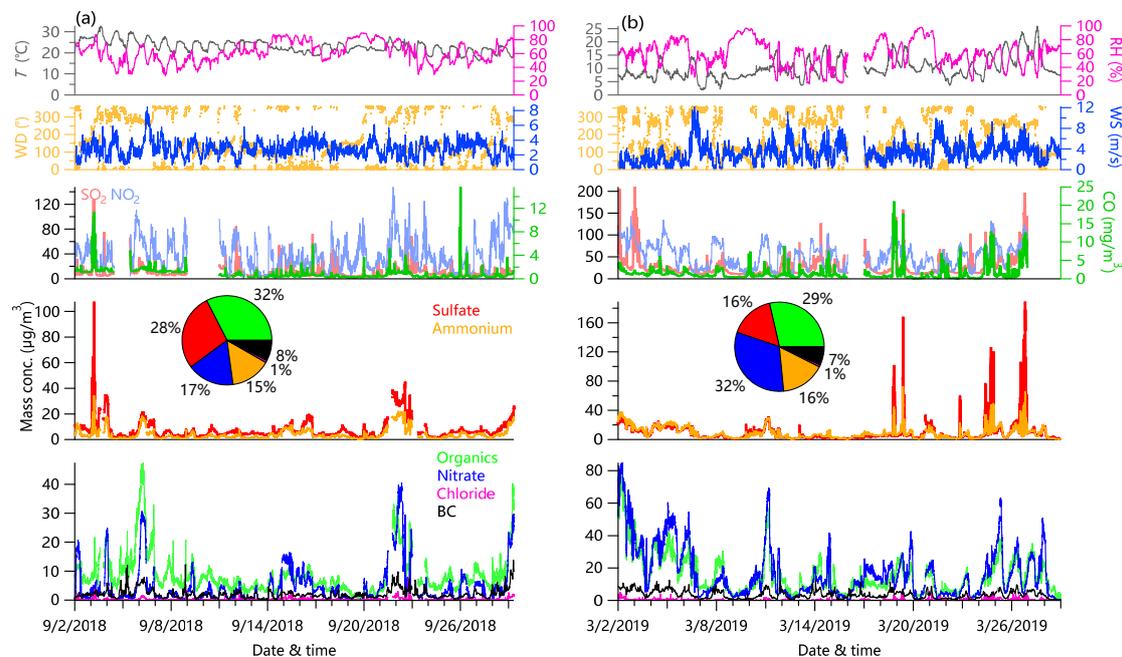



Figure 2. Time series of meteorological variables including *T*, RH, WD and WS, mass concentrations of gaseous species including SO₂, NO₂ and CO, and chemical species in PM₂.₅ in (a) September 2018 and (b) March 2019, respectively. The pie charts show the average chemical composition for the entire campaign.

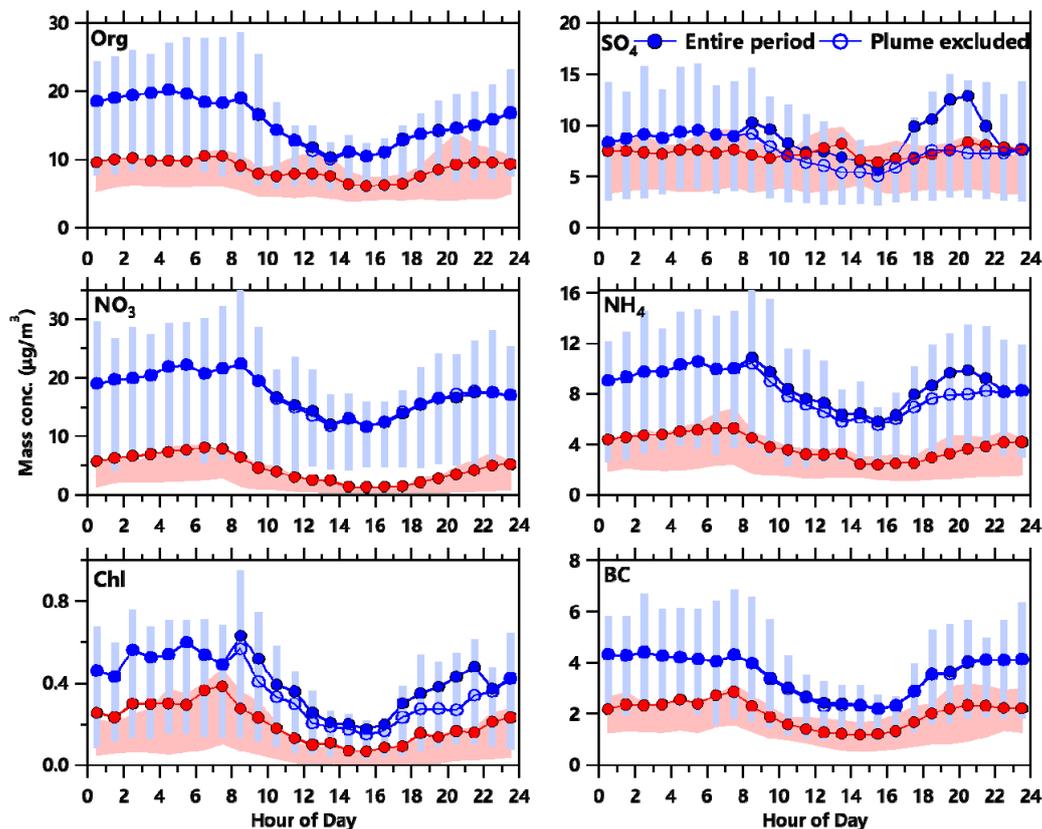



Figure 3. Average diurnal variations of mass concentrations of chemical species in PM$_{2.5}$ in September 2018 (red) and March 2019 (blue), respectively.

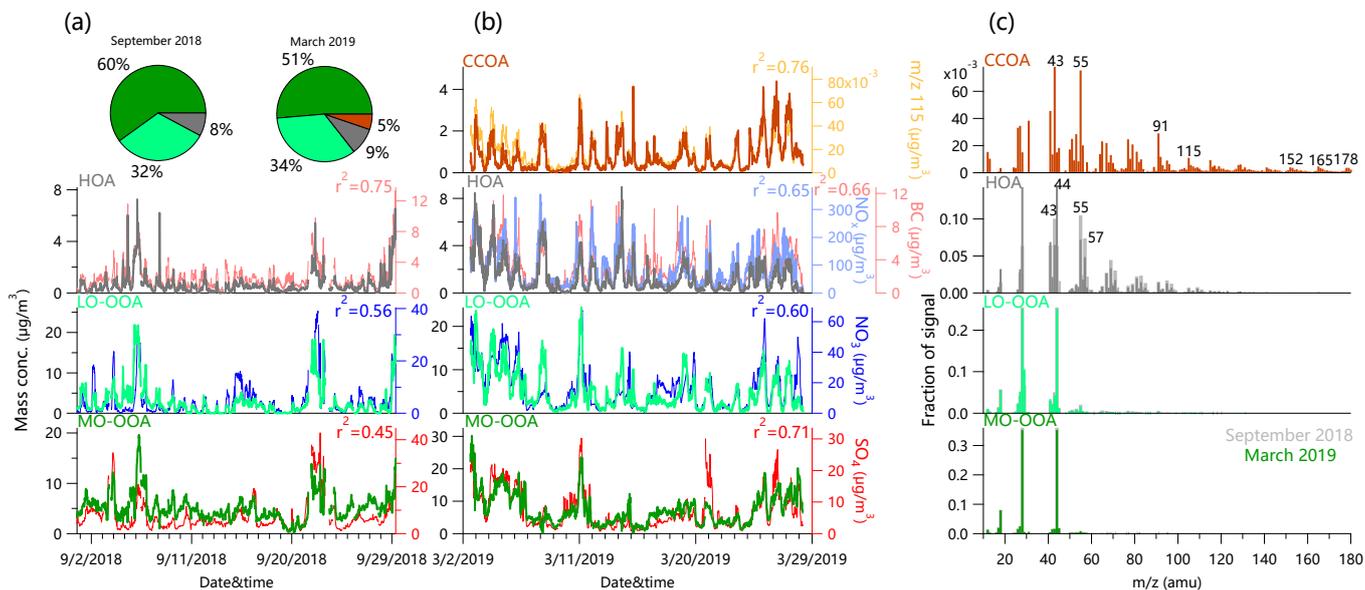
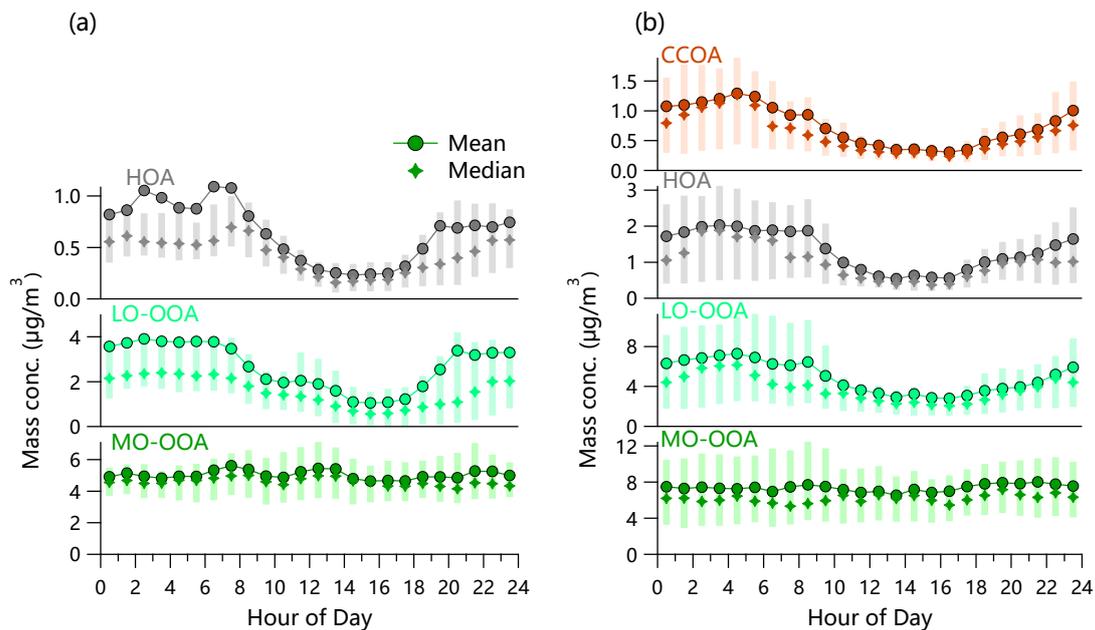



Figure 4. (a, b) Time series and (c) mass spectral profiles of OA factors in September 2018 and March 2019. The time series of external tracer species are also shown for comparisons. The two pie charts present the average OA composition in September and March, respectively.

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

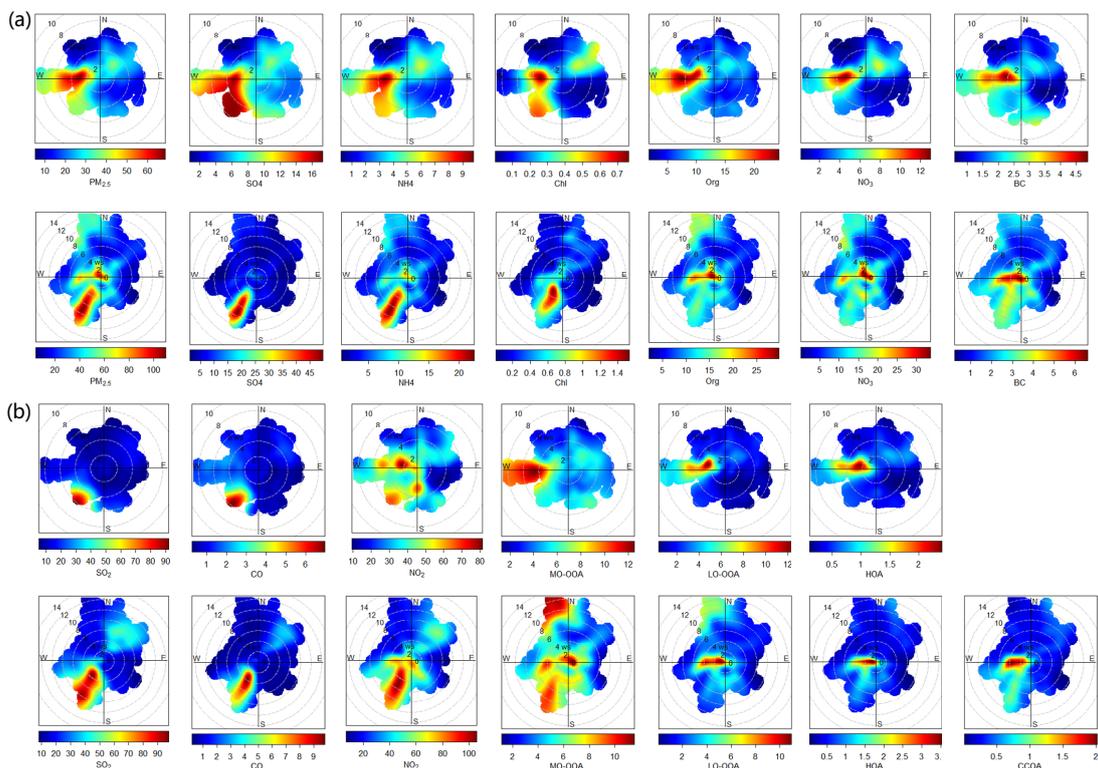



Figure 6. Bivariate polar plots of (a) PM₂.₅ and aerosol species; (b) SO₂, CO, NO₂, and OA factors in September 2018 (top) and March 2019 (bottom), respectively.

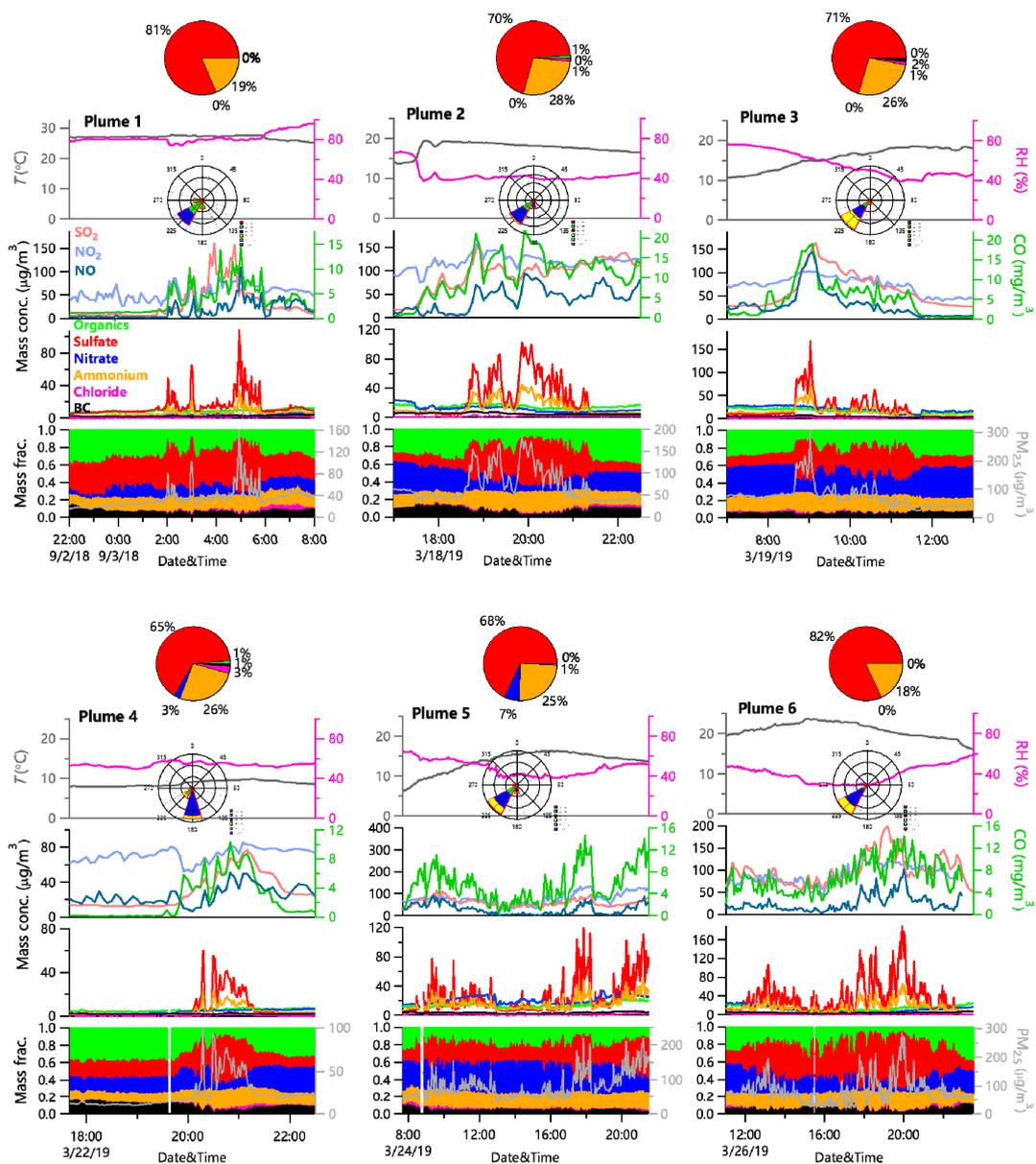



Figure 7. Evolution of meteorological parameters including *T* and RH, gaseous species, mass concentrations and mass fractions of chemical species in PM₂.₅ during six steelworks plume episodes. The pie charts show the contribution of each species emitted completely from steel plants. The wind rose plots depict the prevailing wind direction during each plume period.

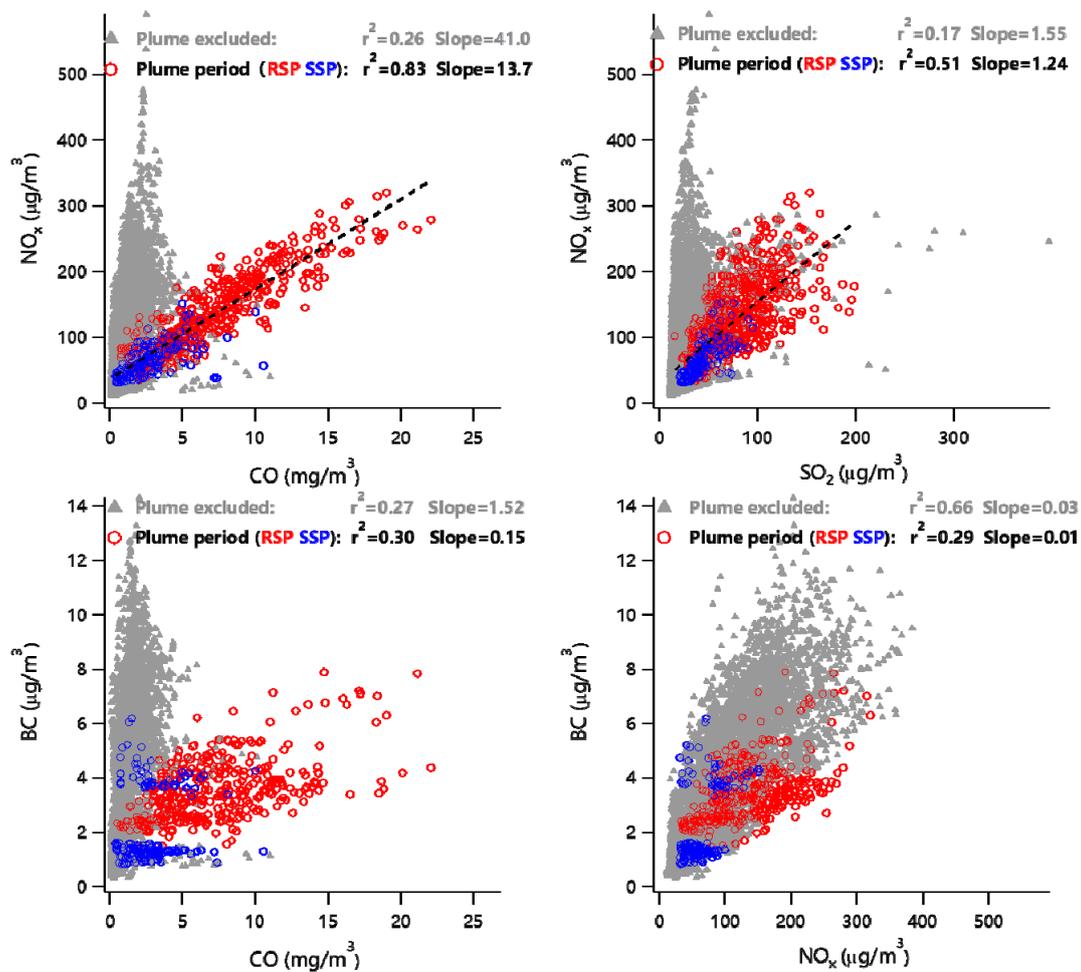



Figure 8. Correlations between (a) NO$_x$ and CO, (b) NO$_x$ and SO$_2$, (c) BC and CO, and (d) BC and NO$_x$ during periods with (open circles) and without (gray triangle) influences of the emissions from the steel plants. RSP = Rizhao steel plant, SSP = Shandong steel plant.