We have addressed peer-referees' comments and put together the response document for acp-2020-113, which includes detailed responses to all the referees and a revised change-tracked manuscript and supplementary material.

Response to Referee #1

Comments are in black and responses are in blue.

General comments:

This is a very fine study, presenting crucial insights into the occurrence of severe haze episodes in the North China Plain during winter. Convincing evidence is provided that hydroxymethanesulfonate (HMS) is a key player in this process. Use is made of aerosol time-of-flight mass spectrometry for the real-time detection of HMS in ambient aerosols and a novel and accurate analytical method has been developed for the measurement of HMS in fine particulate matter ($PM_{2.5}$). This method has the advantage that it does not suffer from overestimation of sulfate. A comprehensive dataset has been obtained and interpreted in great detail. The results obtained in this study should be very useful for pollution abatement measures in Beijing. The scientific content of this manuscript is in a very good shape but the English usage should be improved. A list of suggested technical corrections is provided below.

Response: We thank the referee for the positive comments and correction suggestions that improve the readability of our manuscript. Our responses to the specific comments and corresponding revisions made in the revised manuscript are provided below.

Technical corrections:
Line 20 (and many places elsewhere, e.g. line 23, 31, 32, ...): ..... winter haze ..... occurs ..... and threatens ....[Note: "haze" should be in singular].
Line 24: ..... single particle mass spectrometry and an optimized ion chromatography method, ...
Line 25: ..... in Beijing during winter.
Line 29: .... using traditional ion chromatography.
Line 41: .... in the NCP during winter. .....
Line 46: ..... in the NCP during winter, which increase .....
Line 53: ..... overestimation of the observed .....
Line 55: ..... evidence for the presence of HMS .....
Line 59: ..... haze, unambiguous identification and accurate quantification .....
Line 65: .... mass spectrometry ..... and an optimized ion .....
Line 66: .... in Beijing during winter and ......

Lines 67-73: I suggest to use the present tense here: "We demonstrate ..... water is an important pathway that contributes to ....., not only accounting for a ....winter haze favor heterogeneous HMS formation. ...... to 2016 indicate that ....Finally, we discuss the ....."

Line 76: ..... located at Tsinghua .....

Line 85: ..... the ATOFMS instrument ......

Line 90: .... A bipolar reflectron mass analyzer. [Note: the abbreviation "MS" stands for "mass spectrometry" and should not be used to denote a mass analyzer or the instrument. See the IUPAC guidelines for terms relating to mass spectrometry: K. K. Murray, R. K. Boyd, M. N. Eberlin, G. J. Langley, L. Li, Y. Naito. Definitions of terms relating to mass spectrometry. IUPAC Recommendations 2013. Pure Appl. Chem., 85, 1515-1609, 2013].

Line 93: .... of the ATOFMS instrument .....

Line 95 (and many places elsewhere, e.g., lines 163, 165, ...): It is more correct to write "..... the peak at *m/z* 111 in the negative ion mode as .....". [Note: the *m/z* value is not negative].

Line 101: Here, we .....

Line 102: .... in the day- and nighttime.

Line 103: ..... baked in a Muffle ......, put in the cassettes, and packed .....

Line 106: ..... , ultrasonic agitation for ......

Line 108: ..... overestimation, whereas extraction with .....

Line 113: ..... under conventional conditions ....

Line 114: .... Here, we used .....

Line 117: HMS dissociates into ....

Line 118: ...., and the HMS concentration ....

Line 119: Thus, the ion chromatography ....

Line 151: .... in previous work .....

Line 162: .... In aerosols from Beijing during winter. We found that ......

Line 165: According to the natural isotopic distribution, the contribution of KCl_2^- was found to be insignificant.

Line 170: ....., the peak at *m/z* 111 unlikely corresponds to methylsulfate ......

Line 172: Therefore, the peak at *m/z* 111 in ambient particles can safely be assigned to .....

Line 173: .... in Beijing during winter contain ....

Line 179: I suggest to use the past tense consistently in this section. Thus: "We found that the HMS ...."

Line 180: The HMS concentration ..... , and was consistent with the variation of the relative humidity (RH).

Line 178: ....., we determined the HMS concentration .....

Line 180: .... also showed a similar HMS evolution as that of ....

Line 183: .... , the HMS concentration ....

Line 184: ....., and the HCHO concentration increase, while the O_3 concentration ....

Line 199: ..... during severe winter haze could be overestimated . . ..

Line 199: S(IV) oxidation reactions compete with .....

Line 213: ....., whereas it decreases the ....

Line 215: ..... of the reaction rate constant .....

Line 220: ... The HMS concentration ....

Line 222: With the increase of RH, the atmospheric sulfur distribution shifts toward the particle phase and more particulate sulfur exists in . . ..

Line 229: The calculations based .....

Line 233: .... conditions, HMS formation is favored, whereas decomposition of ....

Line 233: ..... under high HCHO concentrations, low oxidant levels, ...

Line 239: ..... , the atmospheric oxidation .... with the weak photochemical activity.

Line 248 .... (Niu et al., 2016); in this study, we further ....

Line 253: ..... from primary emissions and .....

Line 256: ..... formation, should be considered in future pollutant control ....

Line 261: .... In Beijing during winter.

Figure 1, legend: The peak at *m/z* 111 in the negative ion mode is .... The peaks at *m/z* 80 ..... [Note: see comment made above with regard to the omission of the minus sign].

Response: We have made corrections as recommended.

Response to Referee #2

Comments are in black and responses are in blue.

This paper discusses filed measurements of aerosol composition of HMS, one of important S(IV) and organic species, which obtains more attention recently. They did very rigorous work to identify and quantify HMS from the atmospheric particles. The main finding is that HMS, which was usually observed in cloud/fog events, is ubiquitous in Beijing winter. The HMS concentration, its mole ratio to sulfate and contribution to organic matter increased with the deterioration of winter haze. And discussed the reasons for such a high abundance of HMS in winter Beijing. While the results are interesting and novel, and very important to improve the prediction of OM and sulfate. The study relies on a combination of single particle mass spectrometry and IC. It mainly focuses on bulk measurements. The analysis and interpretation of the main results is valid and almost satisfied most of my curious of HMS in winter Beijing. However, I still have more questions about this study and look forward to some further investigations. A minor revision is required for finalizing the manuscript.

Response: We thank the referee for the constructive comments, which have helped us to improve the manuscript. Our responses to the specific comments and corresponding revisions made in the revised manuscript are provided below.

Major comments:

1. The author did very rigorous work to isolate and quantify HMS from other easily mixed species. That is very good job. But I am curious, the filter extraction found just using water as extraction may overestimate the sulfate concentration due to the transformation of HMS to sulfate over time. I am wondering how about the MARGA data? Looks like the author used MARGA sulfate to estimate the pH of particles. Will the data be influenced by the overestimation if MARGA has the same problem?

Response: Due to the slow conversion of HMS to sulfate during water extraction, the concentration of sulfate determined by MARGA could be somewhat overestimated. Assuming that HMS were completely converted to sulfate during the MARGA measurement, we could evaluate the maximum impact of sulfate overestimation on aerosol pH estimation. As described in our manuscript, the observed sulfate concentrations during severe winter haze in 2016 could be overestimated at most by 15% under the assumption of complete conversion of HMS to sulfate. We modified the sulfate concentration measured by MARGA by a factor 0.85 and recalculated the aerosol pH. The recalculated average aerosol pH value during severe winter haze was 4.6, 0.1 unit higher than the pH (4.5) calculated based on the original MARGA data. In other words, the overestimate of the sulfate concentration could cause at maximum an average aerosol pH deviation of 0.1. Such small deviation of pH estimation would not affect the point of this article: Moderately acidic pH in Beijing winter haze favors the HMS formation.

2. The author can generally compare the data observed in this study with previous studies. For the first impression, I was surprised by such a high abundance of HMS measured by ATOFMS. Previous studies usually found HMS only during cloud/fog event and only account for a small portion to the particle, usually with only several to hundreds' particles of HMS by number, or no more than 4% to the total particle number during the events. However, the characteristics of HMS is kind of very typical HMS particles. But I do think it is necessary to compare the spectrum of HMS observed in Beijing with other studies. As the HMS particles observed in this study is very mixed with other species (e.g. nitrate, elemental carbons…) no matter in the average spectrum or the digital spectrum. Is there any other data can be compared?

Response: The spectrum of HMS-containing particles observed in this study is similar to that observed in Beijing (Song et al., 2019) during haze events, and San Joaquin Valley, California (Whiteaker and Prather, 2003) and London (Dall'Osto et al., 2009) during fog events. In general, carbonaceous and inorganic components are most frequently associated with HMS in individual particles. The positive mass spectra

are characterized by the presence of ammonium (m/z 18 NH_4^+), elemental carbon (m/z 12 C^+, 36 C_3^+, 48 C_4^+, and 60 C_5^+), and organic carbon (m/z 27 $C_2H_3^+$, 37 C_3H^+, 39 $C_3H_3^+$, and 43 $C_2H_3O^+$), whilst the peaks at m/z 46 (NO_2^-), 62 (NO_3^-), 80 (SO_3^-), 81 (HSO_3^-), and 97 (HSO_4^-) are common in the negative mass spectra. We have added the comparison between the spectrum of HMS observed in Beijing with other studies in the revised manuscript (Line 179−184).

Higher concentrations of precursors (i.e., SO_2 and HCHO) coupled with higher aerosol water content and pH in severe winter haze in Beijing compared to the United States and Europe facilitate the HMS formation, leading to higher levels of aerosol HMS measured in Beijing.

References:

Dall'Osto, M., Harrison, R. M., Coe, H., and Williams, P.: Real-time secondary aerosol formation during a fog event in London, Atmos. Chem. Phys., 9, 2459–2469, https://doi.org/10.5194/acp-9-2459-2009, 2009.

Song, S., Gao, M., Xu, W., Sun, Y., Worsnop, D. R., Jayne, J. T., Zhang, Y., Zhu, L., Li, M., Zhou, Z., Cheng, C., Lv, Y., Wang, Y., Peng, W., Xu, X., Lin, N., Wang, Y., Wang, S., Munger, J. W., Jacob, D. J., and McElroy, M. B.: Possible heterogeneous chemistry of hydroxymethanesulfonate (HMS) in northern China winter haze, Atmos. Chem. Phys., 19, 1357–1371, https://doi.org/10.5194/acp-19-1357-2019, 2019.

Whiteaker, J. R., and Prather, K. A.: Hydroxymethanesulfonate as a tracer for fog processing of individual aerosol particles, Atmos. Environ., 37, 1033–1043, https://doi.org/10.1016/s1352-2310(02)01029-4, 2003.

3. Moderate pH is one of the critical factors to promote HMS formation. Have you compared the difference of pH between clean, high pollution and severe haze period? Is there any finding? Clean days with high solar radiation and less RH usually have very low particle water which decreases the aerosol pH. Compared with 2015, does the pH also influence the high contribution and concentration of HMS in 2016?

Response: The HMS concentrations were high in severe winter haze, thereby we discussed the aerosol pH during severe haze periods in the manuscript. Here, we further investigate the relationship between pH and $PM_{2.5}$ concentrations, as shown in the following figure. On clean days, some higher pH values appeared and were generally accompanied by a higher mass fraction of crustal ions (Mg^{2+} and Ca^{2+}). In Beijing during winter, clean days are generally accompanied by strong northern winds, which can raise dust in which the crustal ion species (Ca^{2+} and Mg^{2+}) are higher. The difference in pH under polluted and heavily polluted conditions is small. Our finding is consistent with previous studies (Ding et al., 2019).

As described in our manuscript, the average pH value is 4.5 (from 4 to 5) in severe winter haze in 2016, consistent with recent studies in the North China Plain (Liu et al., 2017; Song et al., 2018; Ding et al., 2019; Ge et al., 2019; Li et al., 2019). Due to the lack of MARGA data, we cannot obtain the pH data in 2015 winter. Song et al. reported that aerosol pH in Beijing winter haze events was usually in the range of 3.5−5.5 and had increased by about 0.3−0.4 unit during 2014/2015−2018/2019 mainly due to rising ammonia (Song et al., 2019), which favors the formation of HMS.
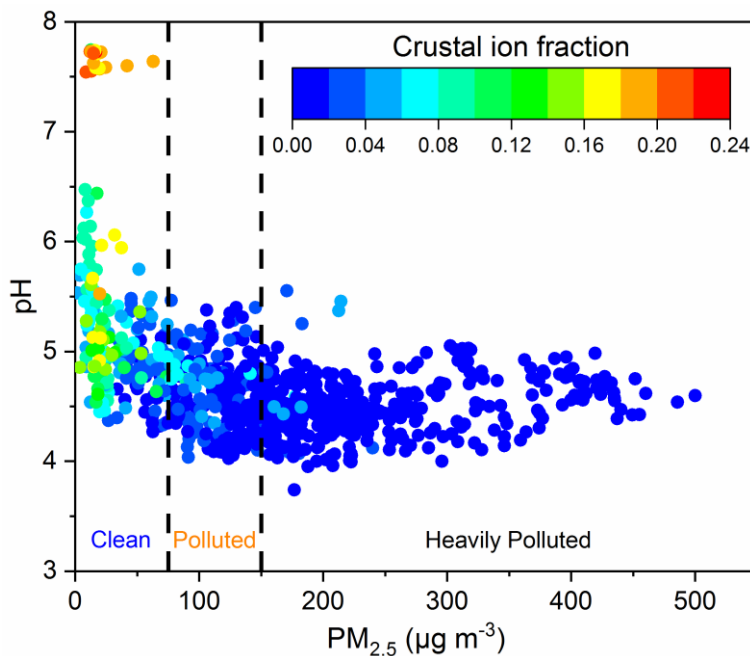
Figure R1. Relationship between pH and $PM_{2.5}$ concentrations, colored by crustal ion fraction. The crustal ion fraction represents the mass ratio of the sum of Mg^{2+} and Ca^{2+} to total ions measured by MARGA.

References:

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, Atmos. Chem. Phys., 19, 7939−7954, https://doi.org/10.5194/acp-19-7939-2019, 2019.

Ge, B., Xu, X., Ma, Z., Pan, X., Wang, Z., Lin, W., Ouyang, B., Xu, D., Lee, J., Zheng, M., Ji, D., Sun, Y., Dong, H., Squires, F. A., Fu, Q., and Wang, Z.: Role of Ammonia on the Feedback Between AWC and Inorganic Aerosol Formation During Heavy Pollution in the North China Plain, Earth and Space Science, 6, 1675−1693. https://doi.org/10.1029/2019ea000799, 2019.

Li, H., Cheng, J., Zhang, Q., Zheng, B., Zhang, Y., Zheng, G., and He, K.: Rapid transition in winter aerosol composition in Beijing from 2014 to 2017: response to clean air actions, Atmos. Chem. Phys., 19,

11485–11499, https://doi.org/10.5194/acp-19-11485-2019, 2019.

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in northern China, Geophys. Res. Lett., 44, 5213–5221, https://doi.org/10.1002/2017gl073210, 2017.

Song, S. J., Gao, M., Xu, W. Q., Shao, J. Y., Shi, G. L., Wang, S. X., Wang, Y. X., Sun, Y. L., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423–7438, https://doi.org/10.5194/acp-18-7423-2018, 2018.

Song, S., Nenes, A., Gao, M., Zhang, Y., Liu, P., Shao, J., Ye, D., Xu, W., Lei, L., Sun, Y., Liu, B., Wang, S., and McElroy, M. B.: Thermodynamic Modeling Suggests Declines in Water Uptake and Acidity of Inorganic Aerosols in Beijing Winter Haze Events during 2014/2015–2018/2019, Environ. Sci. Tech. Lett., 6, 752–760, https://doi.org/10.1021/acs.estlett.9b00621, 2019.

4. The author noted for some periods day and night samples were sampled separately. Is there any difference between these D and N samples?

Response: The average HMS concentration of the night samples is higher than that of the day samples. In general, the atmospheric conditions at night, i.e., low oxidant level, low temperature, high relative humidity, and high pH, are more favorable for the HMS formation. In this study, we only analyzed 3 daytime samples and 5 nighttime samples, and more sample analysis is needed to investigate the diurnal variation of HMS.

5. Since HMS is so easy to transform from S(IV) to sulfate, what's the fate of HMS in the urban atmosphere?

Response: HMS is easy to transform from S(IV) to sulfate in water extraction, rather than in aerosols. Given the aerosol pH (4–5) in severe winter haze, the HMS is stable in aerosols and could exist as a salt with ammonium or other cations as the counter ion. Previous studies indicate that the possible fate of HMS is to be oxidized by aqueous OH radicals to form sulfate (Olson and Fessenden, 1992). Considering the low OH radical concentrations in winter, especially during severe winter haze, the reaction removal should be relatively slow compared with the HMS formation, since significant levels of HMS were measured in particles. Actually, the quantitative rate evaluation of HMS loss needs further study.

Reference:

Olson, T. M., and Fessenden, R. W.: Pulse-radiolysis study of the reaction of OH-bullet radicals with methanesulfonate and hydroxymethanesulfonate, J. Phys. Chem., 96, 3317–3320, https://doi.org/10.1021/j100187a027, 1992.

Minor comments:

1. Section 2, total numbers of filter samples should be noted in the experiment section. In the discussion section, clean polluted and severe haze day should be also noted with the sample number. The reader may be confused when find some figures show the winter data, some figures show the filter information for four seasons.

Response: We added the number of filter samples in the experiment and discussion section. This study focused on the HMS measurements during winter in Beijing, thereby we removed the sample information in spring, summer, and autumn of 2015 in the main text and Fig. S4 to avoid confusion.

2. The figure caption of Figure 2, 95th, 75th, 50th …superscript

Response: We changed the figure caption of Figure 2 from "95th, 75th, 50th, 25th, 5th percentiles" to "95th, 75th, 50th, 25th, 5th percentiles".

3. Line 219, atmospheric sulfur distribution shifts toward particle/liquid phase….?

Response: The atmospheric sulfur in the particle phase refer to the sulfate and HMS in $PM_{2.5}$.

4. Figure 3. Evolution of sulfur distribution with the increase of RH in the winter of a) 2015 and b) 2016. (Solid circle stands for the molar ratio of HMS to sulfate, with colored by the HMS concentrations and sized by the PM2.5 concentrations; The gray crosses represent the particulate sulfur molar percentage. Particulate sulfur molar percentage….) Or Figure 3. Relationship between the molar ratio of HMS to sulfate, particulate sulfur molar percentage, and RH in the winter of a) 2015 and b) 2016. (………..)

Response: We have made corrections as recommended.

Contribution of hydroxymethanesulfonate (HMS) to severe winter haze in the North China Plain

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Abstract. Severe winter haze~~s~~ accompanied by high concentrations of fine particulate matter ($PM_{2.5}$) occurs frequently in the North China Plain and threatens public health. Organic matter (OM) and sulfate are recognized as major components of $PM_{2.5}$, while atmospheric models often fail to predict their high concentrations during severe winter haze~~s~~ due to incomplete understanding of secondary aerosol formation mechanisms. By using a novel combination of single particle mass ~~spectrometer~~ spectrometry and an optimized ion chromatography ~~measurement~~method, here we show that hydroxymethanesulfonate (HMS), formed by the reaction between formaldehyde (HCHO) and dissolved SO_2 in aerosol water, is ubiquitous in Beijing during winter. The HMS concentration and the molar ratio of HMS to sulfate increased with the deterioration of winter haze. High concentrations of precursors (SO_2 and HCHO) coupled with low oxidant levels, low temperature, high relative humidity, and moderately acidic pH facilitate the heterogeneous formation of HMS, which could account for up to 15% of OM in winter haze and lead to up to 36% overestimates of sulfate when using traditional ion chromatography ~~measurements~~. Despite the clean air actions have substantially reduced SO_2 emissions, the HMS concentration and molar ratio of HMS to sulfate during severe winter haze~~s~~ increased from 2015 to 2016 with the growth of HCHO concentration. Our findings illustrate the significant contribution of heterogeneous HMS chemistry to severe winter haze~~s~~ in Beijing, which help to improve the prediction of OM and sulfate, and suggest that the reduction in HCHO can help to mitigate haze pollution.

1 Introduction

35   Severe winter haze pollution with high $PM_{2.5}$ (particles with aerodynamic diameter ≤ 2.5 μm) concentration occurs frequently in the North China Plain (NCP), exerting adverse impacts on the environment and human health (Huang et al., 2014; Lelieveld et al., 2015). Secondary components, constituting a large fraction of $PM_{2.5}$, are key drivers of haze formation (Huang et al., 2014), however, atmospheric models with known formation mechanisms often fail to predict high levels of secondary organic matter (OM) and sulfate during severe winter hazes.

40   Traditional models with gas-phase photochemical mechanisms and aqueous chemistry involving glyoxal and methylglyoxal significantly underestimate the high OM levels observed in the NCP during winter (Wang et al., 2014; Zheng et al., 2015a). Adding heterogeneous reactions involving isoprene epoxide, glyoxal, and methylglyoxal, and accounting for organic aerosol aging and oxidation of intermediate-volatility organic compounds can improve the model predictions of OM (Hu et al., 2017; Zhao et al., 2016; Hu et al., 2017; Yang et al., 2018), however, high OM concentrations observed in Beijing winter are still

45   underpredicted (Hu et al., 2017), especially during the periods with low oxidant concentrations and weak photochemical activity.

In addition to OM, high levels of particulate sulfate are often observed in the NCP during winter and it, which increases sharply with increasing $PM_{2.5}$ pollution levels (Zheng et al., 2015b). Traditional atmospheric models containing both gas-phase oxidation of SO_2 by OH radicals and aqueous-phase reaction pathways involving H_2O_2, O_3, and O_2 catalyzed by Fe^{3+} and Mn^{2+}

50   fail to reproduce the observed high sulfate levels, and revised models with heterogeneous chemistry greatly improve the sulfate simulation (Wang et al., 2014; Zheng et al., 2015a). Cheng et al. (2016) and Wang et al. (2016) reported that the oxidation of SO_2 by NO_2 in aerosol water under high pH could explain the difference between modeled and observed sulfate (Cheng et al., 2016; Wang et al., 2016). On the other hand, the misidentification of organosulfur compounds as inorganic sulfate in conventional measurements can lead to overestimation in of the observed particulate sulfate (Chen et al., 2019). Recently,

55   Moch et al. (2018) and Song et al. (2019) reported the potential contribution of hydroxymethanesulfonate (HMS, $HOCH_2SO_3^-$) to particulate sulfur during winter haze in Beijing (Moch et al., 2018; Song et al., 2019). However, there is no direct observational evidence for the content presence of HMS in haze particles, and the formation mechanism of HMS in NCP winter hazes is still unclear.

HMS was previously found at appreciable concentrations in cloud and fog (Munger et al., 1986; Rao and Collett, 1995),

60   whereas the HMS concentrations observed in atmospheric aerosols in the United States, Germany, and Japan were low (Dixon and Aasen, 1999; Suzuki et al., 2001; Scheinhardt et al., 2014; Suzuki et al., 2001). If HMS does play a role in NCP winter haze, unambiguous accurate identification and accurate quantification of aerosol HMS are essential. Low oxidant concentrations, high water content, moderate pH, and low temperatures for typical cloud and fog environments conditions together with the presence of SO_2 and formaldehyde (HCHO) favor HMS formation (Boyce and Hoffmann, 1984; Deister et

65   al., 1986; Boyce and Hoffmann, 1984; Kok et al., 1986; Lagrange et al., 1999). Such conditions are common during severe winter hazes in the NCP, such as Beijing (Zheng et al., 2015b; Cheng et al., 2016; Rao et al., 2016).

In this study, combining aerosol time-of-flight mass spectrometry ~~spectrometer~~ (ATOFMS) measurement and an optimized ion chromatography method, we identified the ubiquity of HMS in Beijing during winter and quantified its contribution to severe winter haze~~s~~. We demonstrate~~d~~ that the reaction between HCHO and dissolved SO_2 to form HMS in aerosol water ~~was~~ is an important pathway that ~~contributed~~ contributes to winter haze pollution in Beijing, not only accounting for ~~contributing~~ a substantial mass of OM but also leading to overestimation of sulfate in conventional measurements. High concentrations of precursors (i.e., SO_2 and HCHO) coupled with appropriate conditions (i.e., low oxidants, low temperature, high relative humidity, and moderately acid~~ic~~ pH) in severe winter haze~~s~~ favor~~ed~~ ~~the~~ heterogeneous HMS formation. Furthermore, two-year continuous winter measurements from 2015 to 2016 indicate~~d~~ that HMS concentrations increased with the increase of HCHO. Finally, we discuss~~ed~~ the implications of heterogeneous HMS chemistry for haze chemistry and control strategies.

2 Methods

2.1 Sampling site

Field measurements were conducted in urban Beijing in the winter of 2015 and ~~the winter of~~ 2016. The observational sites are located ~~in~~ at Tsinghua University (40.00° N, 116.34° E), the Chinese Academy of Meteorological Sciences (39.95° N, 116.33° E), and the Chinese Research Academy of Environmental Sciences (40.05° N, 116.42° E), respectively (Fig. S1 in the Supplement). Details of the measurements and analysis are described below.

2.2 ATOFMS measurement and data analysis

Real-time ATOFMS (model 3800-100, TSI, Inc.) measurement in Beijing was carried out from December 21, 2015 to January 8, 2016. The observation site was on the tenth floor of the School of Environment, Tsinghua University, approximately 35 m above ground level. Details of ATOFMS measurements have been described in previous studies (Furutani et al., 2011). Briefly, ATOFMS simultaneously measures the size and chemical composition of individual particles. The inlet flow rate is $0.1\ \mathrm{L\,min^{-1}}$. Ambient aerosols between 100 nm and 3000 nm enter the ATOFMS instrument through an aerodynamic focusing lens and are accelerated to their size-dependent terminal velocities. The particle velocity is determined by measuring the time-of-flight between two solid state green lasers (λ = 532 nm, 50 mW, CL532‑050‑L, CrystaLaser, NV, USA). The particle size is calculated from the measured velocity based on the calibration curve between particle size and velocity. In addition, the velocity is used to trigger the 266 nm Nd:YAG laser (~1 mJ/pulse), which desorbs and ionizes the particle. The generated positive and negative ions are detected using a bipolar reflectron time-of-flight mass analyzer~~ToF MS~~. The ATOFMS aerodynamic sizing was calibrated by standard polystyrene latex spheres (PSL) with different sizes (d = 151, 199, 269, 350, 499, and 799 nm, Duke Scientific Corp., USA). Mass calibration of the ATOFMS instrument was conducted with the standard solution (Ba, K, Pb, Na, Li, V in HNO_3).

During the winter campaign, ATOFMS detected 4,495,233 particles containing both size and chemical information, accounting

for 49% of all sized particles. Single particle mass spectrometers identify the peak at m/z −111 in the negative ion mode as HMS (Neubauer et al., 1997; Whiteaker and Prather, 2003; Dall'Osto et al., 2009~~; Neubauer et al., 1997~~). To eliminate interferences, HMS-containing particles were screened with a relatively high threshold: the peak area at m/z =111 in the negative ion mode should be greater than 2% of the total integrated area of the single particle negative ion mass spectrum (Whiteaker and Prather, 2003).

2.3 Offline sample collection and ion chromatography analysis

PM$_{2.5}$ samples were collected on 47 mm quartz filters at a flow rate of 15.4 L min^{-1} for 23.5 hours every day ~~in 2015 and 2016~~. Here, we analyzed ~~some~~ 36 and 33 samples ~~during haze episodes~~ in ~~four seasons~~the winter ~~in~~ of 2015 and ~~winter of~~ 2016, respectively. In the winter of 2016, we also collected 3 and 5 PM$_{2.5}$ samples on 90 mm quartz filters at a flow rate of 100 L min^{-1} in the ~~daytime~~ day- and nighttime, respectively. The filters were baked in a Muffle furnace at 550 °C for 4 h ~~and~~, put in the cassettes, and packed using aluminum foil prior to sampling, and all samples were stored at −20 °C before analysis. A quarter of each 47 mm filter or 3.14 cm^2 punch from each 90 mm filter was extracted twice with 5 mL 0.1% HCHO solution, ultrasonic agitation ~~oscillation~~ for 20 min in an ice water bath and then filtered through the 0.45 μm membrane syringe filter. Two extracts were combined for ion chromatography analysis. We found that HMS slowly converted to sulfate during conventional sample preparation (i.e. water extraction), leading to HMS underestimation and sulfate overestimation, ~~and~~ whereas extraction with 0.1% HCHO solution can counteract the HMS decomposition (Fig. S2a, b).

A Dionex Integrion HPIC Ion Chromatography system with AS11-HC analytical column and AG11-HC guard column (Dionex Corp., CA, US), typical columns used in previous studies during winter haze~~s~~ in Beijing (Cao et al., 2014), was used for the anion analysis. The separation of HMS and sulfate depends on ion chromatography conditions (i.e., column and eluent). We found the separation of HMS and sulfate peak was not ~~good~~ complete under conventional condition~~s~~ (eluent: 30 mM KOH, flow rate: 1.5 mL min^{-1}) (Fig. S2c). Here, we used an eluent of 11 mM KOH (pH≈12) with a flow rate 1.5 mL min^{-1}, and successfully distinguished HMS from sulfate (Fig. S2d). In addition, Moch et al. (2018) and Dovrou et al. (2019) found that the AS22 column could not fully separate HMS and sulfate, while AS12A was able to successfully separate HMS and sulfate ~~(Moch et al., 2018; Dovrou et al., 2019). Actually,~~ HMS dissociates into SO$_3^{2-}$ and HCHO rapidly in the eluent due to the short characteristic time for HMS dissociation at pH 12, and the HMS concentration is measured in the form of sulfite in ion chromatography (Fig. S2e) (Dasgupta, 1982). Thus, the ion chromatography method cannot distinguish HMS from sulfite directly. Previous studies indicated that the concentration of sulfite in atmospheric aerosols was much lower than that of HMS (Dixon and Aasen, 1999; Dabek-Zlotorzynska et al., 2002). In order to distinguish between sulfite and HMS, a second analysis was performed using dilute nitric acid (pH≈3) to extract samples. In the second analysis, sulfite is oxidized to sulfate, while HMS is stable. We tested some samples collected during severe winter haze~~s~~ in Beijing, and found that the influence of sulfite on HMS measurement was negligible (Fig. S2f). The method detection limit was 0.02 mg L^{-1} for SO$_3^{2-}$, equal to 0.03 mg L^{-1} for HMS. The blank quartz filter was analyzed as control. We also tested the accuracy (through recovery analysis) and precision (through repetitive analysis) of the method on HMS analysis. The recovery of blank and sample was 95.6% and 112.5%,

130   respectively. The relative standard deviation (RSD) of triple repetitive analysis of the sample (average: 3.17 mg L^{-1}) was 4.7%.

2.4 Supplementary data and analysis

Online measurements of gaseous pollutants, particulate matter, and meteorological parameters were conducted on the roof of School of Economics and Management, approximately 20 m above ground level and 100 m away from the ATOFMS observation site, on the campus of Tsinghua University as described in previous works (Zheng et al., 2015b; Xu et al., 2017~~;~~

135 ~~Zheng et al., 2015b~~). In brief, hourly mass concentrations of $PM_{2.5}$ and PM_1 were monitored based on the β-ray absorption method by using two dichotomous monitors (PM-712 and PM-714; Kimoto Electric Co., Ltd., Japan). The hourly concentrations of carbonaceous species including organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ in 2015 winter were monitored by APC-710 (Kimoto Electric Co., Ltd., Japan). The hourly OC and EC concentrations in $PM_{2.5}$ in 2016 winter were measured by a Sunset Model 4 Semi-Continuous Carbon Analyzer (Beaverton, OR, USA). We adopted a factor of 1.6 to

140   convert the OC mass into OM mass (Xing et al., 2013; Zhang et al., 2017). The hourly concentrations of gaseous pollutants including SO_2, CO, and O_3 were monitored with MCSAM-13 system (Kimoto Electric, Ltd., Japan). The hourly meteorological parameters including temperature and relative humidity (RH) were simultaneously monitored with an automatic meteorological observation instrument (Milos 520, VAISALA Inc., Finland).

Online concentrations of water-soluble ions in $PM_{2.5}$ and inorganic gases were measured by ~~the~~ a Monitor for AeRosols and

145 ~~Gases~~ GAses (MARGA, Metrohm Ltd., Switzerland) in 2016 winter at the Chinese Research Academy of Environmental Sciences, about 9 kilometers from Tsinghua University. We calculated the aerosol water content and pH with the ISORROPIA-II thermodynamic equilibrium model (Fountoukis and Nenes, 2007). Briefly, we adopted the forward mode constrained by gas (HNO_3, HCl, and NH_3) + aerosol (SO_4^{2-}, NO_3^-, Cl^-, K^+, Ca^{2+}, Na^+, Mg^{2+}, NH_4^+) measurements, and assumed the aerosol phase state to be metastable (Hennigan et al., 2015). The model inputs were taken from the MARGA measurements.

150   Online HCHO measurement was conducted in 2015 winter at the Chinese Academy of Meteorological Sciences, about 6 kilometers from Tsinghua University. ~~The~~Ambient HCHO was measured by an Aero-Laser GmbH HCHO analyzer (model AL4021) based on the Hantzsch reaction, as described in ~~the~~ previous work (Song et al., 2019). The Hantzsch reagents were prepared every 3 days and stored in a refrigerator. This analyzer was calibrated with a 1 μM HCHO standard solution every 2 to 3 days. The detection limit is 150 ppt in the field, and the accuracy and precision are ±15% or 150 ppt and ±10% or 150 ppt,

155   respectively (Hak et al., 2005).

The anthropogenic emission inventory data of HCHO was derived from the Multi-resolution Emission Inventory of China (MEIC) model framework (available at http://www.meicmodel.org/), as described in detail ~~by~~ in earlier papers (Li et al., 2019b). Briefly, the emissions were calculated based on a technology-based methodology using updated activity data from the MEIC model framework and a collection of state-of-the-art emission factors and source profiles. The uncertainty of volatile organic

160   compounds (VOCs) emission inventory in MEIC was estimated to be ±68% (Cheng et al., 2019).

3 Results and discussion

3.1 Identification of HMS in atmospheric particles

Our field measurements with ATOFMS showed that HMS was ubiquitous in aerosols from Beijing during winter. We found that 76% of particles contained the peak at $m/z =111$ in the negative ion mode, and screened HMS-containing particles (the relative peak area at $m/z =111$ in the negative ion mode greater than 2%, Fig. 1) accounted for 9% of the total particles. It should be noted that KCl_2^- and methyl sulfate ($CH_3SO_4^-$) could also contribute to the peak at $m/z =111$ in the negative ion mode. According to the natural isotopic distribution, the contribution of KCl_2^- was found to be insignificant. The peak area ratio of $m/z =111$ to $m/z =113$ in the negative ion mode in all screened particles was 18.7, which was consistent with the natural isotopic distribution of HMS (18.7) and much larger than that of KCl_2^- (4.8). Also, the peak area ratio of $m/z =109$ to $m/z =111$ in the negative ion mode in all screened particles was 0.03, which was much smaller than that of KCl_2^- (1.4). Considering the moderate aerosol pH (4–5; see Sect. 3.3) in Beijing winter haze and the tendency of $m/z =111$ in the negative ion mode to exist in supermicrometer particles (see Sect. 3.2) in this study, the peak at $m/z =111$ in the negative ion mode unlikely corresponds to methyl sulfate since methyl sulfate formation requires relatively high acidic conditions (Lee, 2003) and organosulfates tend to exist in submicrometer particles (Hatch et al., 2011). Therefore, the peak at $m/z =111$ in the negative ion mode in ambient particles can safely be assigned to HMS. Ambient particles in Beijing during winter contained a large amount of ammonium relative to sodium, and the ammonium was more common than sodium in HMS-containing particles (Fig. S3), indicating that the matrix effects on HMS detection due to counterions was not significant, because ammonium promotes the presence of the HMS marker peak in the negative ion spectrum (Neubauer et al., 1997; Whiteaker and Prather, 2003). The mass spectrum of HMS-containing particles observed in this study is similar to previous studies (Whiteaker and Prather, 2003; Dall'Osto et al., 2009; Song et al., 2019). In general, the positive mass spectra are characterized by the presence of ammonium (m/z 18 NH_4^+), elemental carbon (m/z 12 C^+, 36 C_3^+, 48 C_4^+, and 60 C_5^+), and organic carbon (m/z 27 $C_2H_3^+$, 37 C_3H^+, 39 $C_3H_3^+$, and 43 $C_2H_3O^+$), whilst the peaks at m/z 46 (NO_2^-), 62 (NO_3^-), 80 (SO_3^-), 81 (HSO_3^-), and 97 (HSO_4^-) are common in the negative mass spectra.

3.2 Quantification of HMS in atmospheric particles

Based on the optimized ion chromatography method, we determined the HMS concentration and its contribution to haze pollution in winter. We found that the HMS concentration was appreciable in humid haze conditions, but low in clean and dry haze conditions (Fig. S4). The HMS concentration exhibited similar periodic variation to that of $PM_{2.5}$ and sulfate concentration in winter, and was consistent with the variation of RH. With the deterioration of winter haze in 2015, i.e., from clean ($PM_{2.5} \leq 75$ µg m^{-3}, 10 days), polluted ($75 < PM_{2.5} \leq 150$ µg m^{-3}, 12 days) to heavily polluted ($PM_{2.5} > 150$ µg m^{-3}, 14 days), the HMS concentration increased rapidly (Fig. 2a). Also, the molar ratio of HMS to sulfate increased from 0 (clean), 0.02 (polluted), to 0.06 (heavily polluted). During the HMS increase process,

RH, SO$_2$, and ~~the~~ HCHO concentration ~~increases~~increased, while ~~the~~ O$_3$ concentration ~~declines~~declined (Fig. 2b, c). HMS tends to exist in supermicrometer particles. During the HMS events, the ratio of PM$_{1-2.5}$ to PM$_{2.5}$ was generally greater than 0.4, indicating ~~the~~ a large contribution of supermicrometer aerosols. The size distribution of HMS-containing particles displayed a mode at larger sizes compared with the total particle size distribution, and the percentage of HMS-containing particles increased with particle size and remained relatively constant when the diameter is greater than 1 μm (Fig. 2d), indicating the predominance of HMS in large_r_ particles.

Field measurements in Beijing in winter 2016 ~~also~~ showed _a_ similar HMS evolution _as that of winter 2015_~~pattern~~, i.e., high HMS concentrations usually occurred in humid haze conditions with high concentrations of precursors, high RH, and weak photochemical activity (Fig. S5 and S6), but HMS concentrations were higher than in winter 2015. During severe winter haze~~s~~ (PM$_{2.5}$ > 150 μg m^{-3}), _the concentrations of HMS, PM$_{2.5}$, OM, and sulfate were 4 μg m^{-3} (0.7–9.6 μg m^{-3}), 224 μg m^{-3} (160–379 μg m^{-3}), 83 μg m^{-3} (45–121 μg m^{-3}), 45 μg m^{-3} (23–108 μg m^{-3}) and 7 μg m^{-3} (0.4–18.5 μg m^{-3}), 237 μg m^{-3} (154–339 μg m^{-3}), 97 μg m^{-3} (65–147 μg m^{-3}), 36 μg m^{-3} (15–66 μg m^{-3}) in 2015 and 2016, respectively. The_ HMS accounted for 1.5% (0.4–4%) of PM$_{2.5}$ mass in 2015, and this contribution increased to 2.7% (0.3–6%) in 2016 (Fig. S7). Correspondingly, the contribution of HMS to estimated OM increased from 4.4% (0.9–11%) in 2015 to 7.6% (1.4–15%) in 2016. The increase of HMS from winter 2015 to winter 2016 was consistent with the increasing HCHO concentration. Instead, the concentrations of SO$_2$ during severe winter haze~~s~~ decreased significantly due to the strict control measures, resulting in a decrease of sulfate. Accordingly, the molar ratio of HMS to sulfate increased significantly from winter 2015 to winter 2016. Considering the conversion of HMS to sulfate in conventional ion chromatography analysis, the observed sulfate concentrations during severe winter haze~~s~~ ~~can~~could be overestimated by 6.4% (3–15%) in 2015, and the ratio increased to 15% (2.5–36%) in 2016.

3.3 Factors influencing HMS formation

HMS is formed in the aqueous phase, such as cloud (Moch et al., 2018), fog (Munger et al., 1986), and aerosol water (Song et al., 2019). We find that HMS is present in aerosols regardless of the presence of cloud/fog (Fig. S8a, b), and HMS concentrations show a good correlation ($r = 0.92$, P < 0.01) with aerosol water content (Fig. S8b), indicating that aerosol water serves as a medium for HMS formation. In some HMS events, cloud/fog processes exist (Fig. S8a, b) and may contribute together with heterogeneous processes in aerosol water to the formation of HMS. Our results indicate that high concentrations of precursors (i.e., SO$_2$ and HCHO) coupled with appropriate conditions (i.e., low oxidants, low temperature, high RH, and moderately acid_ic_ pH) in severe winter haze~~s~~ in the NCP facilitate the heterogeneous HMS formation.

Low oxidants and low temperature during winter haze facilitate the HMS formation. ~~The~~S(IV) oxidation reactions ~~are major competitions~~compete with HMS formation (Pandis and Seinfeld, 1989). The low O$_3$ concentration and low solar radiation during HMS events (Fig. S4 and S5) indicate the weak photochemical activity. Previous measurements also showed that OH radical and H$_2$O$_2$ concentrations were low in winter, especially during severe winter haze~~s~~ (_Zhang et al., 2012;_ Tan et al., 2018; ~~Zhang et al., 2012;~~Ye et al., 2018). Low temperature increases the solubility of gas (Sander, 2015), whereas _it_ decreases the reaction rate constant for HMS production (Boyce and Hoffmann, 1984). According to the kinetics calculation (Song et al.,

2019), the increase of gas solubility in water at low temperature is greater than the decrease of the reaction rate constant, leading to higher HMS formation rate in winter hazes. Once formed, HMS is relatively stable due to the self-acidification and resistance to oxidation by O_3, H_2O_2, and O_2 (Dasgupta et al., 1980; Hoigne et al., 1985; Kok et al., 1986; Munger et al., 1986; Dasgupta et al., 1980).

230   High RH is a key factor driving fast HMS formation in winter hazes. The HMS concentration increases slowly under low RH, whereas it increases rapidly under high RH (Fig. S9). Similarly, the aerosol water content exhibits an exponential increase with RH (Fig. S10), providing abundant reaction interfaces for HMS formation. The HMS concentration started to increase significantly with the enhancement in RH when the RH > 60%, coinciding with the reported deliquesce RH of particles in Beijing winter (Liu et al., 2017b). With the increase of RH, the atmospheric sulfur distribution shifts toward the particle phase

235   and more particulate sulfur exists in the form of HMS (Fig. 3). The molar ratio of HMS to sulfate also started to increase rapidly at the RH ~60%, and high values usually occurred under severe winter hazes with high $PM_{2.5}$ and HMS concentrations. Moderately acidic pH in Beijing winter hazes favors the HMS formation. Previous studies indicated that both HMS formation and decomposition rate increased rapidly with pH, thereby high HMS concentrations were usually observed in moderate pH conditions, since low pH retards the formation of HMS, while high pH is not suitable for its preservation (Munger et al., 1986).

240   The calculations based on the ISORROPIA-II thermodynamic equilibrium model constrained by in situ gas and aerosol measurements showed an average pH value of 4.5 (from 4 to 5) for aerosol water under severe winter hazes in 2016, which agreed reasonably with previous studies in the NCP (Liu et al., 2017a; Song et al., 2018; Ding et al., 2019; Ge et al., 2019; Li et al., 2019a) and was higher than those in the United States and Europe (Bougiatioti et al., 2016; Weber et al., 2016). Under such conditions, the HMS formation is favored, whereas the decomposition of HMS is negligible, thereby resulting in the

245   observed high HMS concentrations during severe winter hazes.

3.4 Implications for haze chemistry and control strategies

Our findings reveal the significant contribution of HMS to severe winter hazes. We propose a more comprehensive conceptual model of heterogeneous sulfur chemistry in NCP haze events, including traditional sulfate formation, and HMS formation under high HCHO concentrations, low oxidant levels, low temperature, high RH, and moderate pH (Fig. 4a). With the

250   deterioration of winter haze, the atmospheric oxidation capacity decreases associated with the weak photochemistry photochemical activity, while heterogeneous HMS chemistry is enhanced, resulting in the increase of HMS concentration and the ratio of HMS to sulfate (Fig. 4b). Adding heterogeneous HMS chemistry into the model could improve the simulation of OM. In addition, the presence of HMS could lead to sulfate overestimation in conventional measurements, such as ion chromatography and aerosol mass spectrometry (Song et al., 2019). This can partly explain the discrepancy between sulfate

255   simulation and observation during severe NCP winter hazes. Furthermore, HMS can be used as a tracer for heterogeneous chemistry and moderate pH during typical winter haze pollution.

Our results suggest that the reduction in HCHO concentration can help to mitigate severe winter haze pollution in the NCP. Previous studies show that HCHO is an important source of RO_x (OH+HO_2+RO_2) radicals and ozone (Niu et al., 2016; Tan et

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al., 2018; Li et al., 2019b; Niu et al., 2016), and has high toxicity as a Group 1 human carcinogen (Niu et al., 2016),); here in this study, we further demonstrate its significant contribution to particulate matter in winter. Since the implementation of 'Air Pollution Prevention and Control Action Plan' in 2013, SO_2 concentrations during winter hazes in Beijing have decreased significantly due to the implementation of desulfurization measures and controls on emission activities (Zheng et al., 2015b; Zheng et al., 2018), resulting in the decrease of sulfate, while HCHO concentrations show an increasing trend (Fig. S7), leading to the increased importance of HMS in winter haze. HCHO comes from primary emissions and secondary formation (Chen et al., 2014; Sheng et al., 2018). Therefore, the cooperative emission reduction in primary HCHO, which mainly comes from residential solid fuel (biofuel and coal) combustion and transportation (Fig. S11) (Li et al., 2019b), and VOCs (e.g., alkenes, aromatics, and alkanes) related to secondary HCHO formation, should be considered in the future pollutant control strategies in the NCP. Furthermore, the HMS chemistry and related control strategies can be applicable to other regions with high SO_2 and HCHO concentrations, such as India (De Smedt et al., 2015; Li et al., 2017).

4 Conclusion

Combining field measurements and laboratory experiments, we show the ubiquity of HMS in aerosols and the quantification of the large amounts of HMS in $PM_{2.5}$ in Beijing during winter, and elucidate the heterogeneous HMS chemistry in winter haze. High concentrations of precursors (SO_2 and HCHO), low oxidant levels, low temperature, high RH, and moderately acidic pH during severe winter hazes facilitate the heterogeneous formation of HMS, which could account for up to 15% of OM in winter haze and lead to up to 36% overestimates of sulfate. The HMS concentration and the molar ratio of HMS to sulfate increased with the deterioration of winter haze, as well as from winter 2015 to winter 2016 with the growth of HCHO concentration. Our results reveal the significant contribution of HMS to severe winter hazes, which help to improve the prediction of OM and sulfate, and suggest that the reduction in HCHO can help to mitigate severe winter haze pollution.

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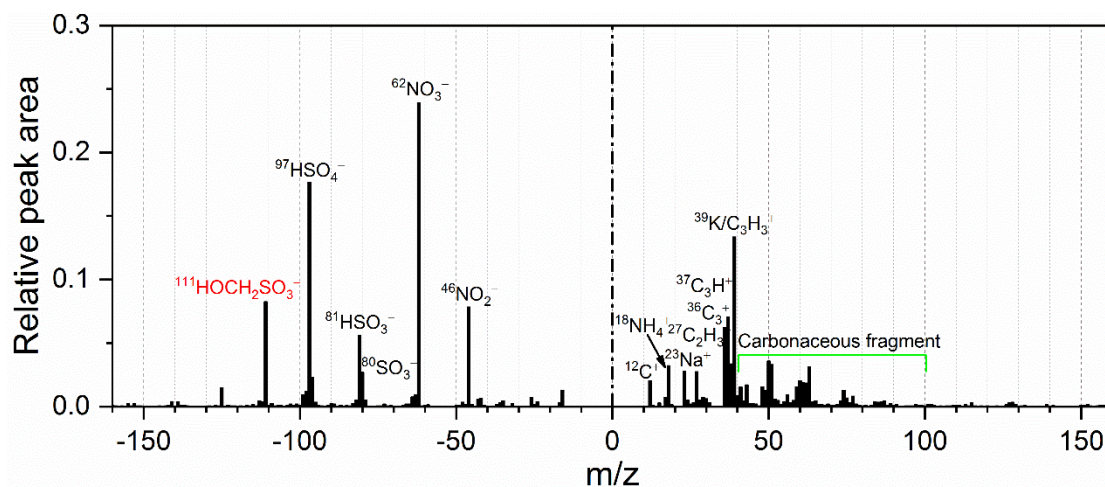
Figure 1. Presence of HMS in single particle mass spectra during winter in Beijing. The peak at m/z =111 <u>in the negative ion mode</u> is attributed to HMS ($HOCH_2SO_3^-$). The peaks at m/z =80 (SO_3^-), =81 (HSO_3^-), =97 (HSO_4^-), =46 (NO_2^-), and =62 (NO_3^-) are also common in the negative ion spectrum, indicating the presence of sulfur species and nitrate. In the positive mass spectra, inorganic ions (m/z 18 NH_4^+, 23 Na^+, and 39 K^+), elemental carbon (m/z 12 C^+, 36 C_3^+, and 48 C_4^+), and organic carbon (m/z 27 $C_2H_3^+$, 37 C_3H^+, 39 $C_3H_3^+$, and 43 $C_2H_3O^+$) are present.
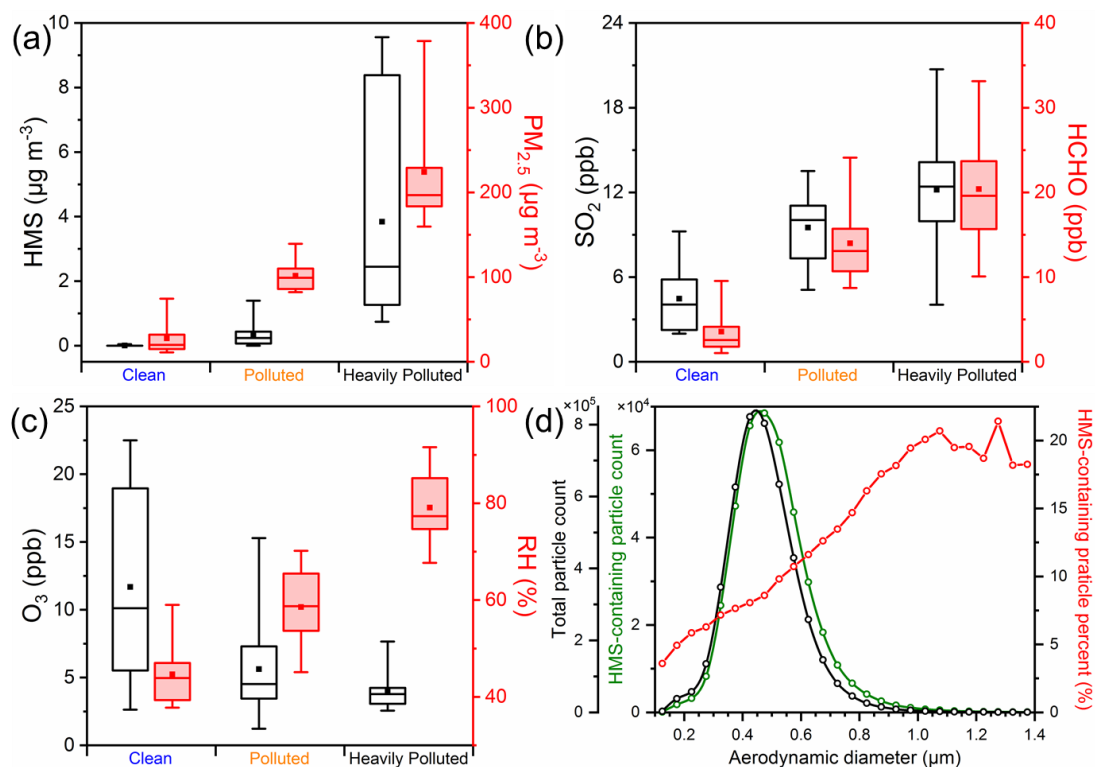
Figure 2. Evolution of HMS in Beijing winter of 2015. **(a-c)** Concentrations of HMS, $PM_{2.5}$, SO_2, HCHO, and O_3, and RH at

24

different pollution levels from 26 November 2015 to 8 January 2016. In the box-whisker plots, the whiskers, boxes, and points indicate the 95th, 75th, 50th, 25th, 5th percentiles and mean values, respectively. **(d)** Size distribution of HMS-containing particles from 21 December 2015 to 8 January 2016.
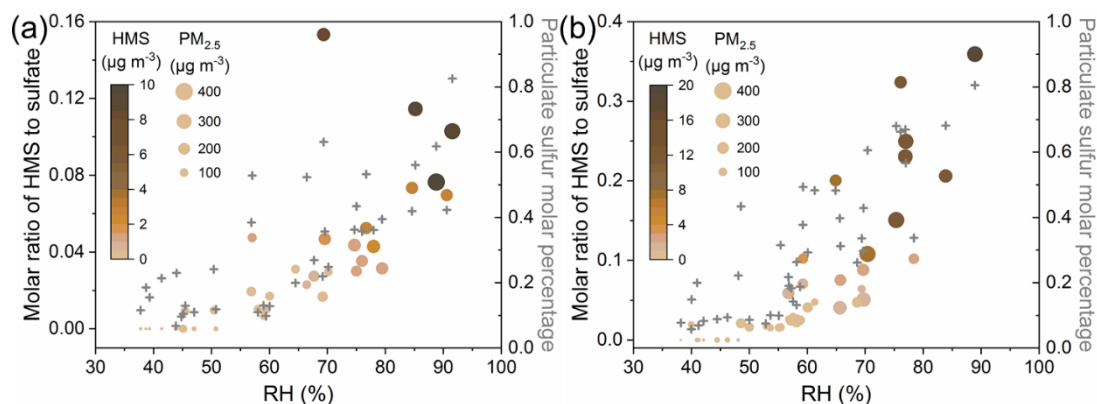
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Figure 3. Evolution of sulfur distribution with the increase of RH in the winter of **(a)** 2015 and **(b)** 2016. ~~(a) Relationship between the molar ratio of HMS to sulfate, particulate sulfur molar percentage, and RH in winter 2015.~~ The_solid circles represent the molar ratio of HMS to sulfate, with colored by the HMS concentrations, and ~~the sizes of the circles are scaled to~~sized by the PM$_{2.5}$ ~~mass~~ concentrations. The gray crosses represent the particulate sulfur molar percentage. Particulate sulfur molar percentage $= \frac{n(\text{SO}_4^{2-})+n(\text{HMS})}{n(\text{SO}_4^{2-})+n(\text{HMS})+n(\text{SO}_2)}$. ~~(b) Relationship between the molar ratio of HMS to sulfate, particulate sulfur molar percentage, and RH in winter 2016.~~
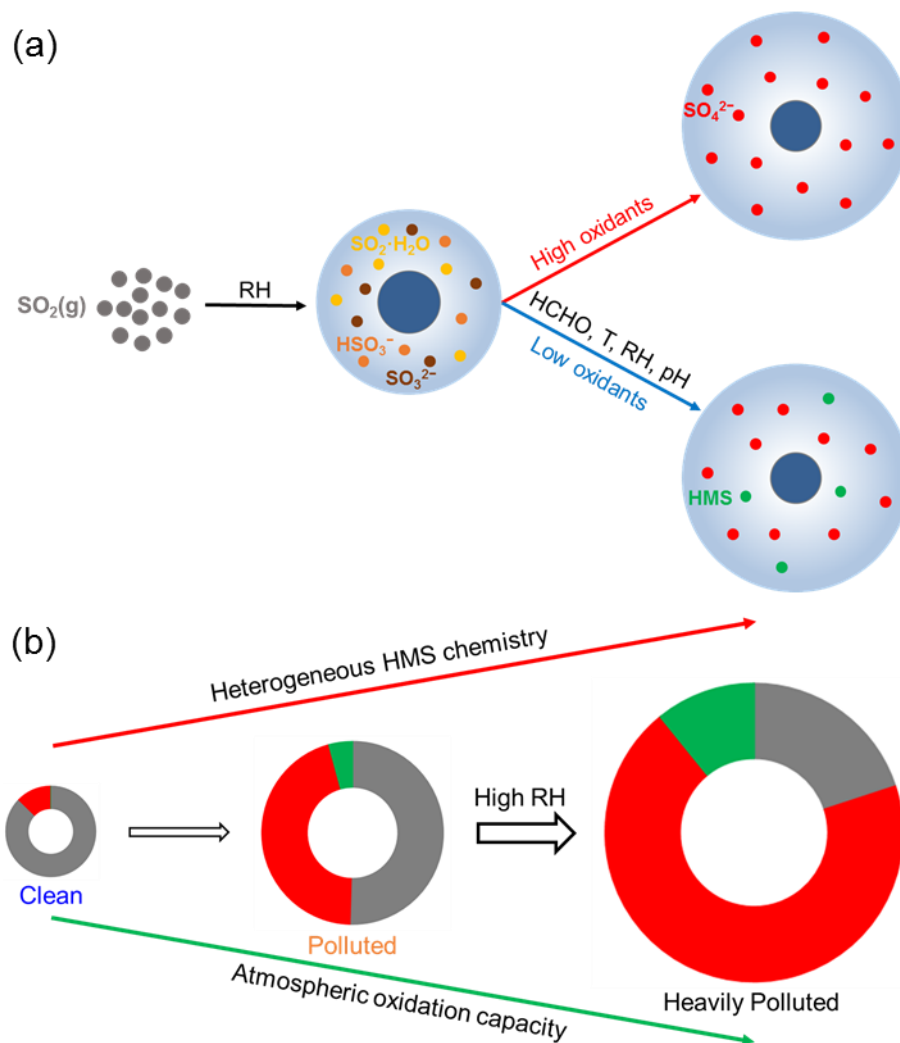
Figure 4. Schematic of the heterogeneous sulfur chemistry. **(a)** Oxidation and addition reaction pathways of dissolved SO_2 in aerosol water under different atmospheric conditions. **(b)** Evolution of sulfur-containing species during winter haze deterioration in the NCP. With the increase of RH and decrease of atmospheric oxidation capacity under NCP winter hazes, the atmospheric sulfur distribution shifts toward the particle phase and more particulate sulfur exists in the form of HMS. The gray, red, and green colors represent SO_2, SO_4^{2-} and HMS, respectively.

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Supplement of

Contribution of hydroxymethanesulfonate (HMS) to severe winter haze in the North China Plain

Tao Ma et al.

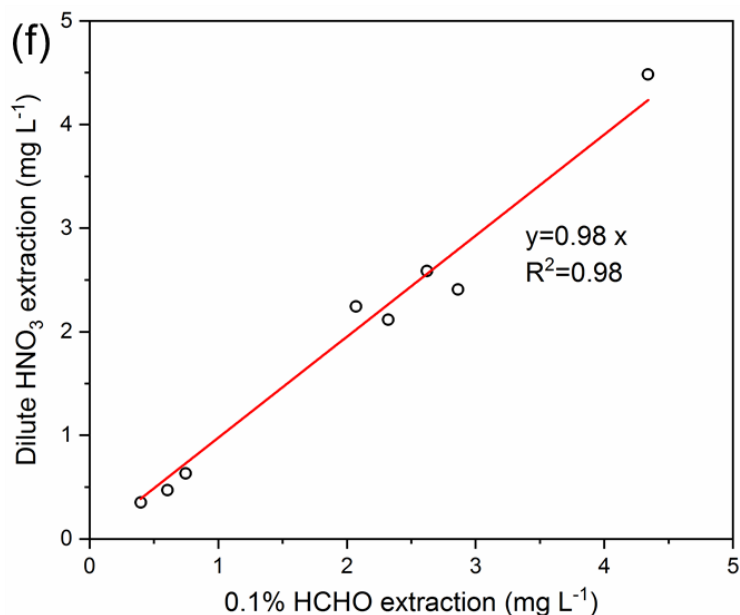*Correspondence to:* Fengkui Duan (duanfk@mail.tsinghua.edu.cn) and Kebin He (hekb@tsinghua.edu.cn)
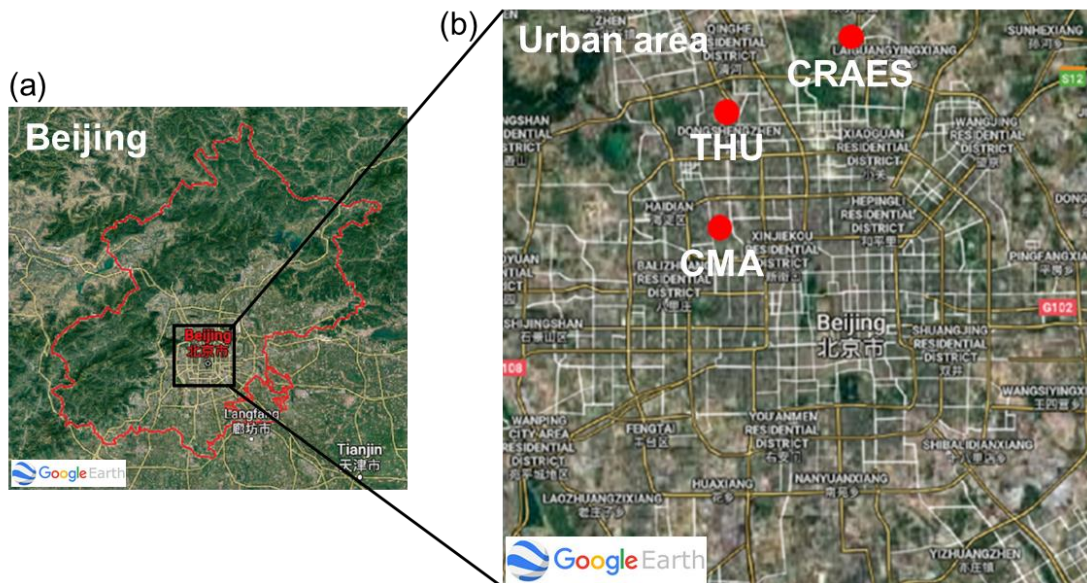
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Figure S1. Location of observational sites in urban Beijing. **(a)** Map of Beijing. **(b)** Observational sites in the urban area of Beijing. The THU, CMA, and CRAES sites represent the Tsinghua University (40.00° N, 116.34° E), the Chinese Academy of Meteorological Sciences (39.95° N, 116.33° E), and the Chinese Research Academy of Environmental Sciences (40.05° N, 116.42° E), respectively.

(a)

Water extraction — 19.0 mg/L, 1.29 mg/L; 1 - HMS - 16.733, 2 - Sulfate - 19.267

0.1% HCHO extraction — 18.9 mg/L, 1.41 mg/L; 1 - HMS - 16.737, 2 - Sulfate - 19.277

505

29

(b)

(c)

2 - Sulfate - 4.230

1 - HMS - 3.913

(d)

10 ppm standard solution

F⁻

Cl⁻

NO₂⁻

Br⁻ NO₃⁻

HMS SO₄²⁻

(e)

Na$_2$SO$_3$ (water solution)

1 - Sulfite - 17.097

2 - Sulfate - 19.807

NaHMS (water solution)

1 - Sulfite - 17.037

2 - Sulfate - 19.760

NaHMS (0.1% HCHO solution)

1 - Sulfite - 16.973

2 - Sulfate - 19.697

(f)

y=0.98 x
R^2=0.98

Dilute HNO_3 extraction (mg L^{-1})
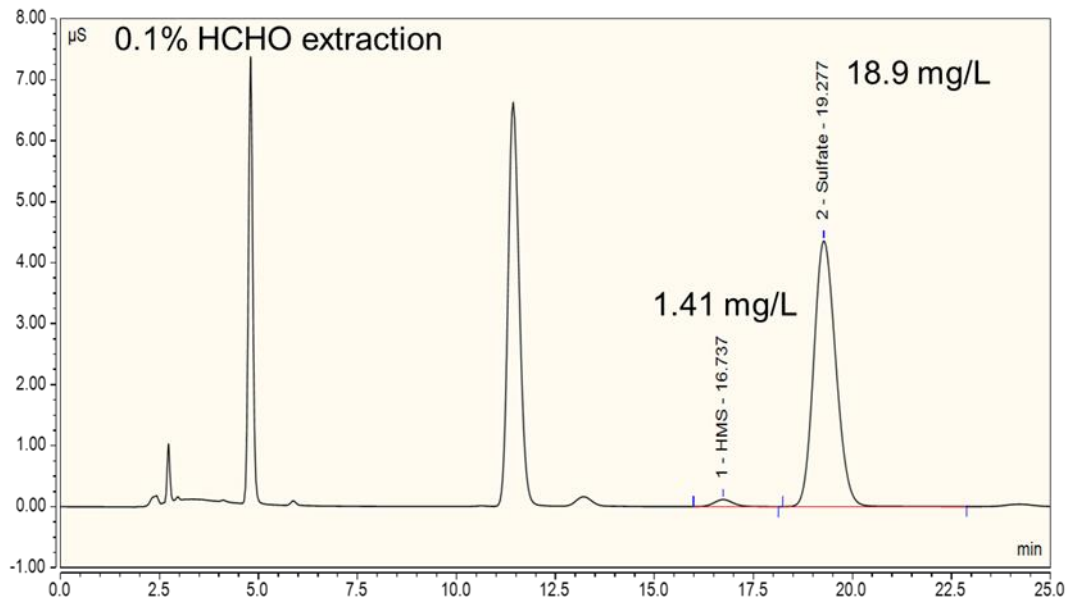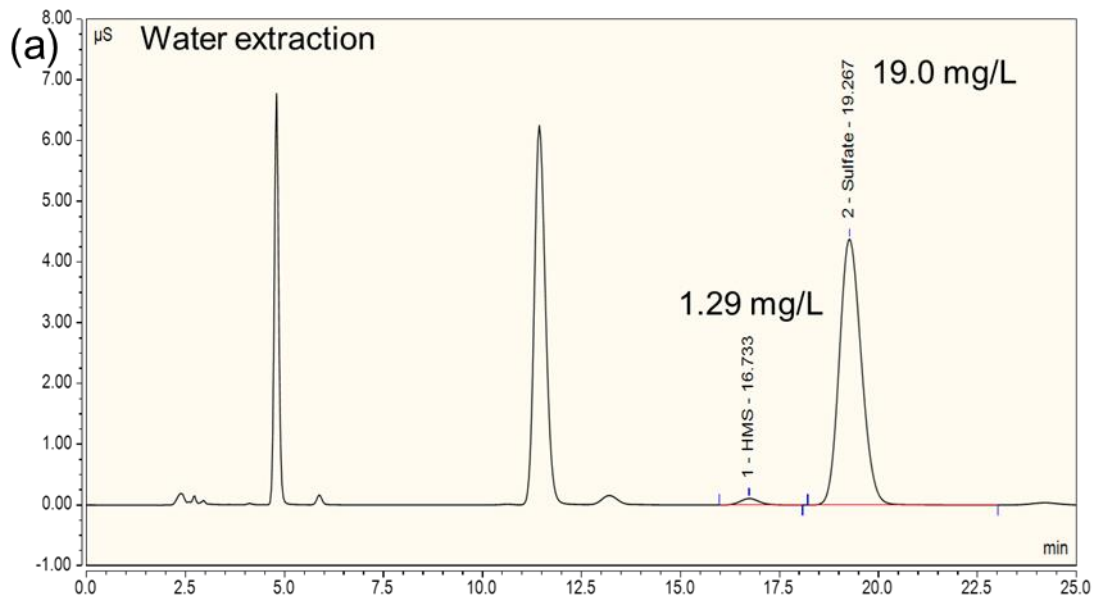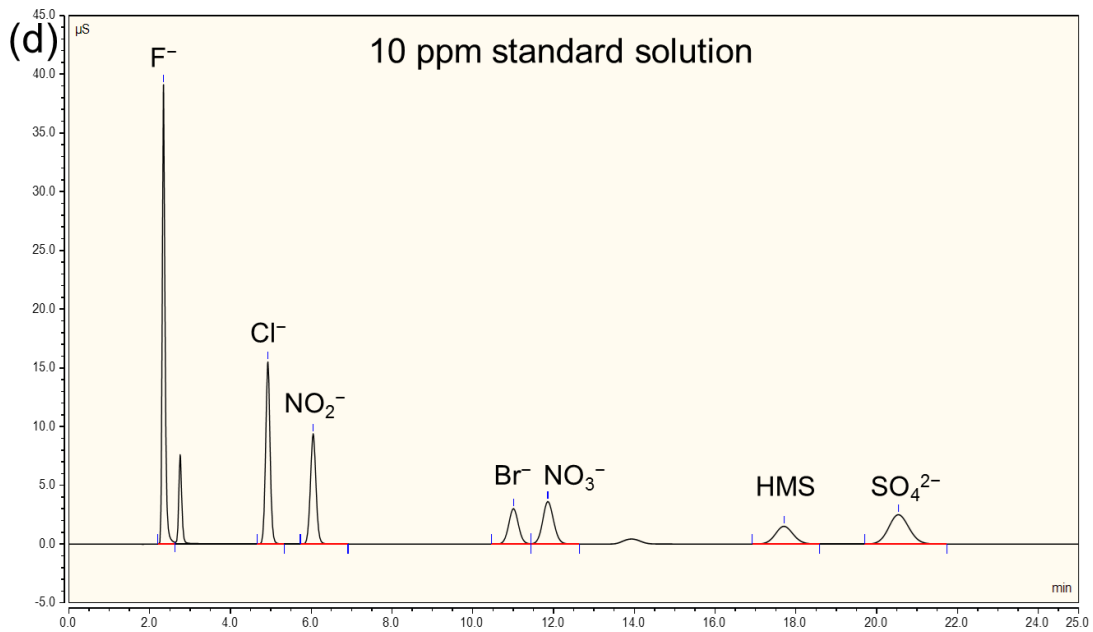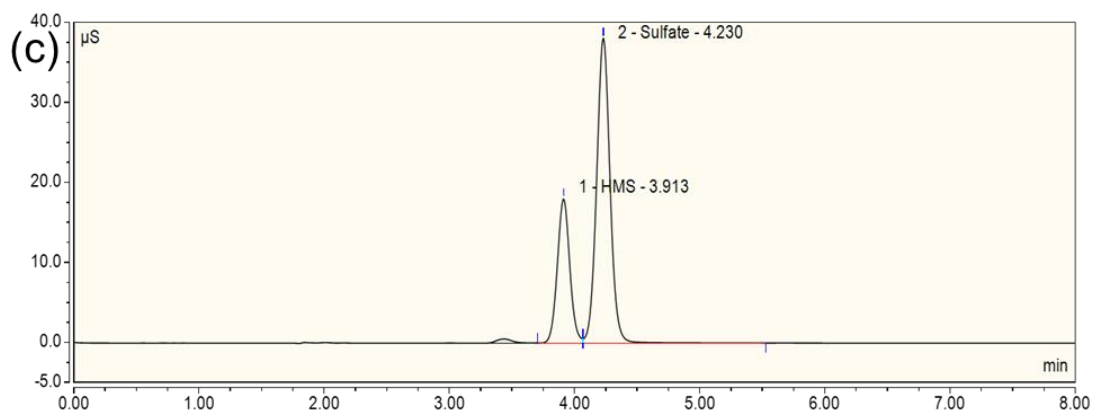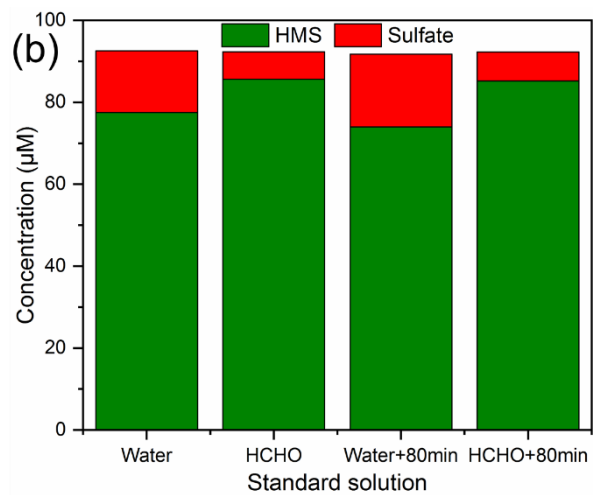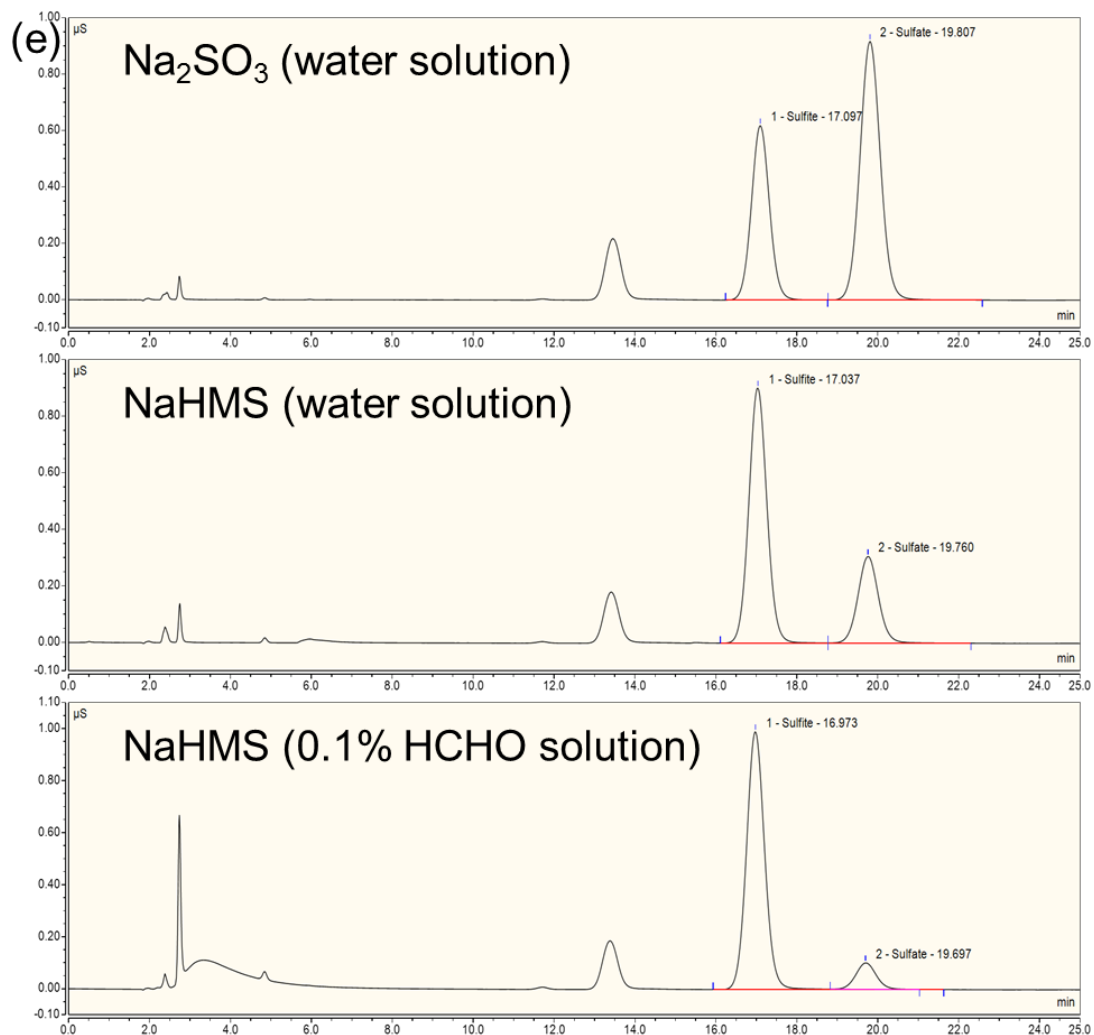
0.1% HCHO extraction (mg L^{-1})

510

Figure S2. HMS quantification by ion chromatography. **(a)** Comparison of sample ion chromatography spectrum after water extraction and 0.1% HCHO extraction. The ion chromatography is conducted immediately after sample extraction. **(b)** Evolution of HMS standard solution (purity: 97%) over time in water extraction and 0.1% HCHO extraction. **(c)** Separation of HMS and sulfate in AS11-HC column

515 with 30 mM KOH eluent. **(d)** Ion chromatogram spectrum of a 10 ppm mixed standard solution in the AS11-HC column with 11 mM KOH eluent. **(e)** Ion chromatography spectrum of standard Na_2SO_3, NaHMS, and NaHMS+0.1% HCHO solution. The retention time of Na_2SO_3 (purity: ≥98%), NaHMS (purity: 97%), and NaHMS+0.1% HCHO samples are same. **(f)** Comparison between HMS concentration in dilute nitric acid (pH≈3) extraction and total S(IV) concentration in 0.1% HCHO extraction in $PM_{2.5}$

520 samples. The concentrations in both extractions are sulfite-equivalent concentration.

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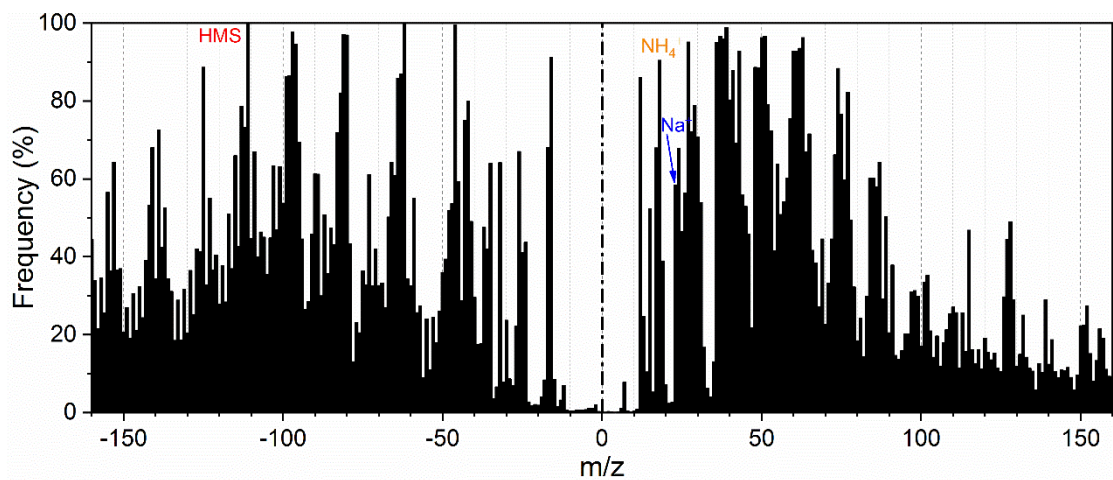
Figure S3. Positive and negative digital histograms of HMS-containing particles. The digital histogram represents the frequency of individual particles present at each *m/z*.
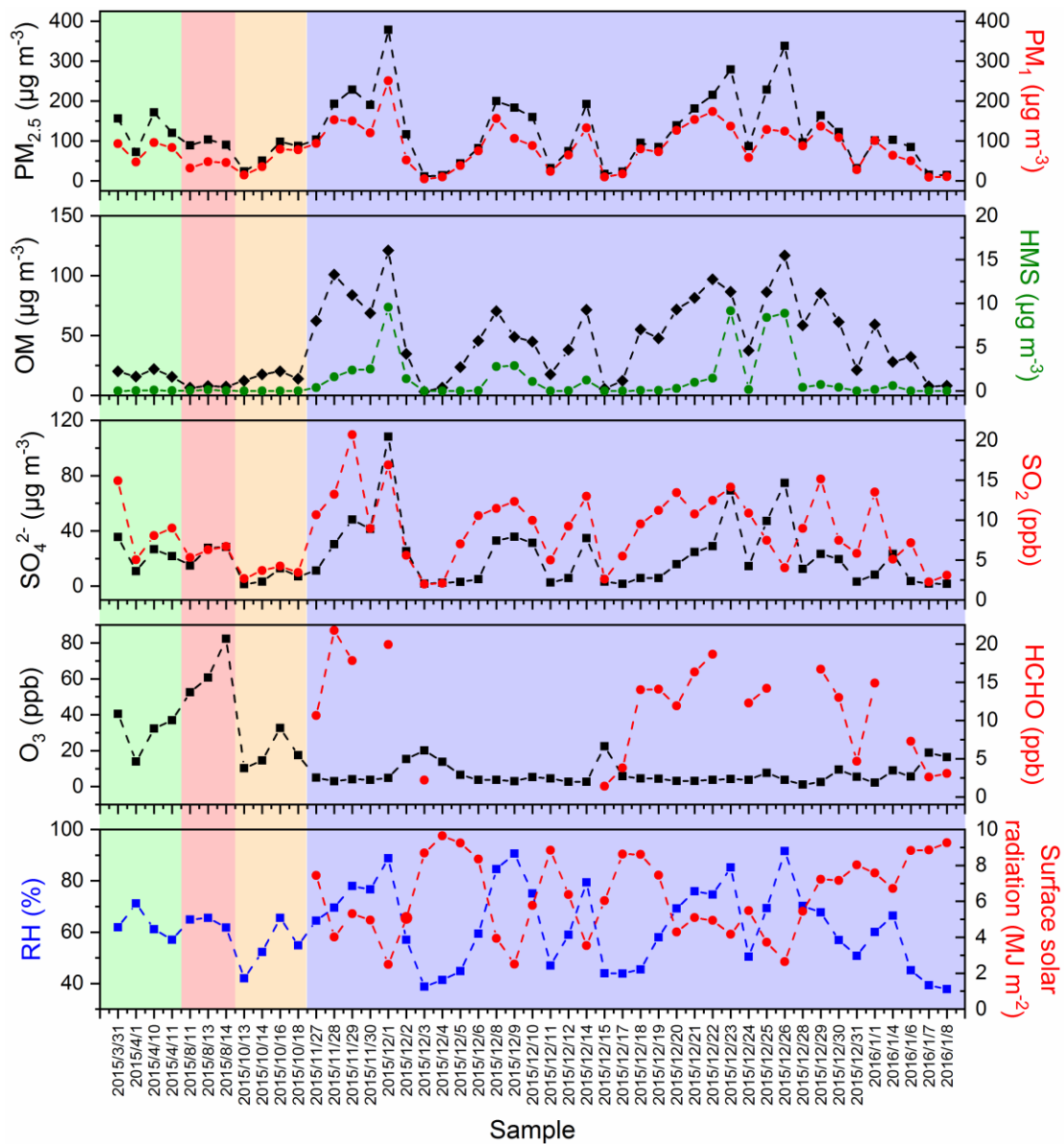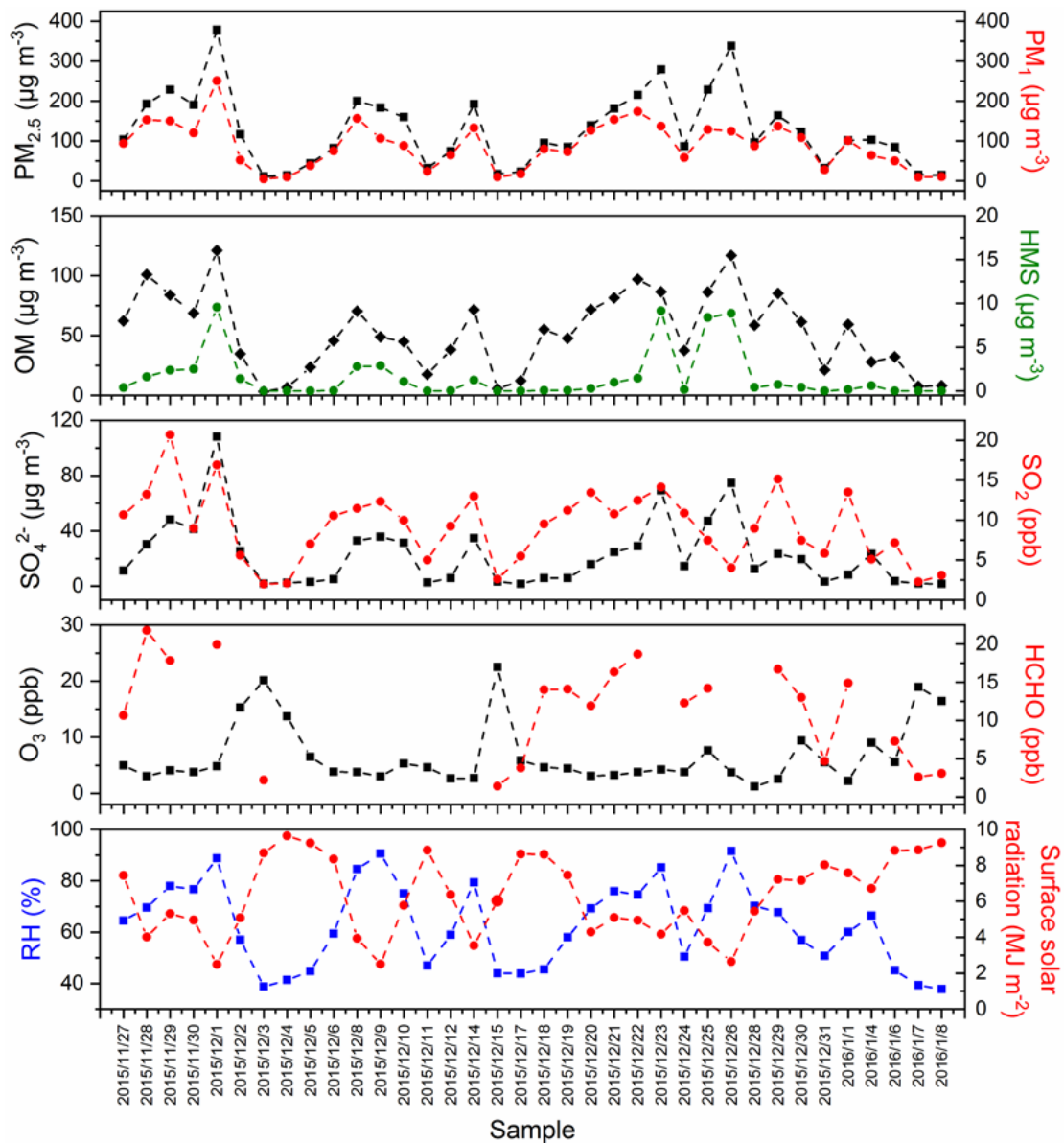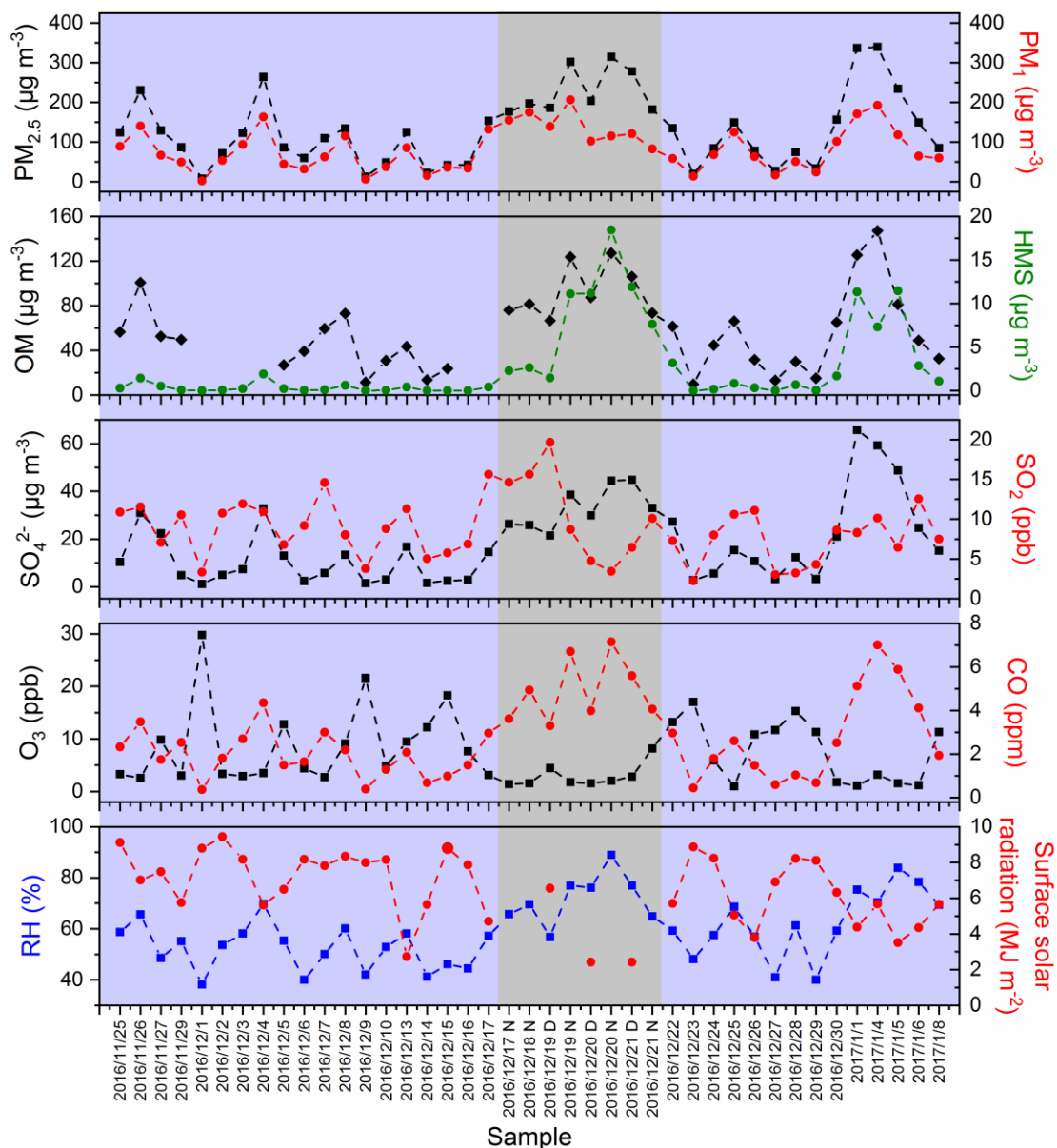
Figure S4. Characteristics of offline samples in <u>winter</u> 2015. Variation of $PM_{2.5}$, PM_1, organic matter (OM), HMS, SO_4^{2-}, SO_2, O_3, HCHO, relative humidity (RH)<u>,</u> and total surface solar radiation in ~~different seasons of~~<u>winter</u> 2015. OM is estimated as 1.6 times of OC. ~~The green, pink, yellow and blue shades represent daily samples of spring, summer, autumn, and winter, respectively.~~ SO_4^{2-} and HMS concentrations are derived from offline $PM_{2.5}$ samples measured by the optimized ion chromatography method, while other parameters are averages of online hourly data during sampling periods.

35

Figure S5. Characteristics of offline samples in winter 2016. Variation of $PM_{2.5}$, PM_1, organic matter (OM), HMS, SO_4^{2-}, SO_2, O_3, CO, relative humidity (RH), and total surface solar radiation in winter 2016. OM is estimated as 1.6 times of OC. The blue shade represents daily samples, and the gray shade represents half-day samples, where D and N correspond to samples collected during daytime and nighttime, respectively. SO_4^{2-} and HMS concentrations are derived from offline $PM_{2.5}$ samples measured by the optimized ion chromatography method, while other parameters are averages of online hourly data during sampling periods.
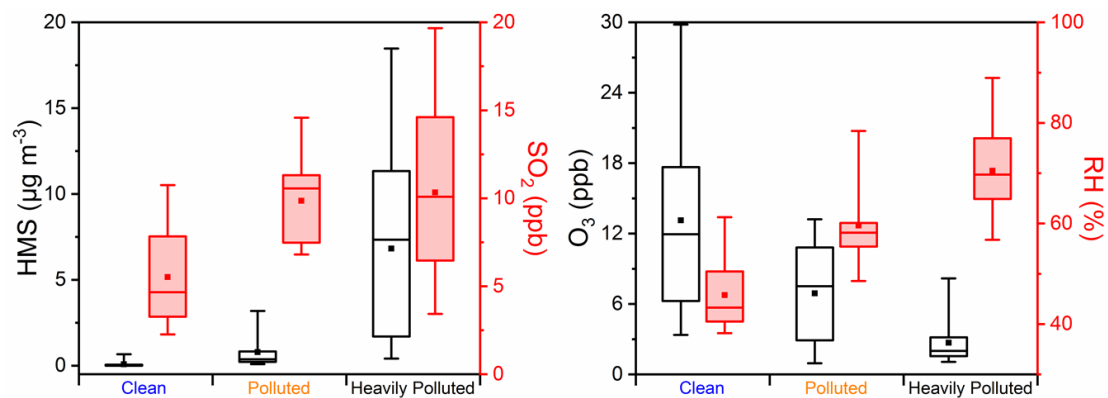
Figure S6. Evolution of HMS in Beijing winter of 2016. HMS, SO_2, O_3, and relative humidity (RH) at different pollution levels from 24 November 2016 to 8 January 2017.

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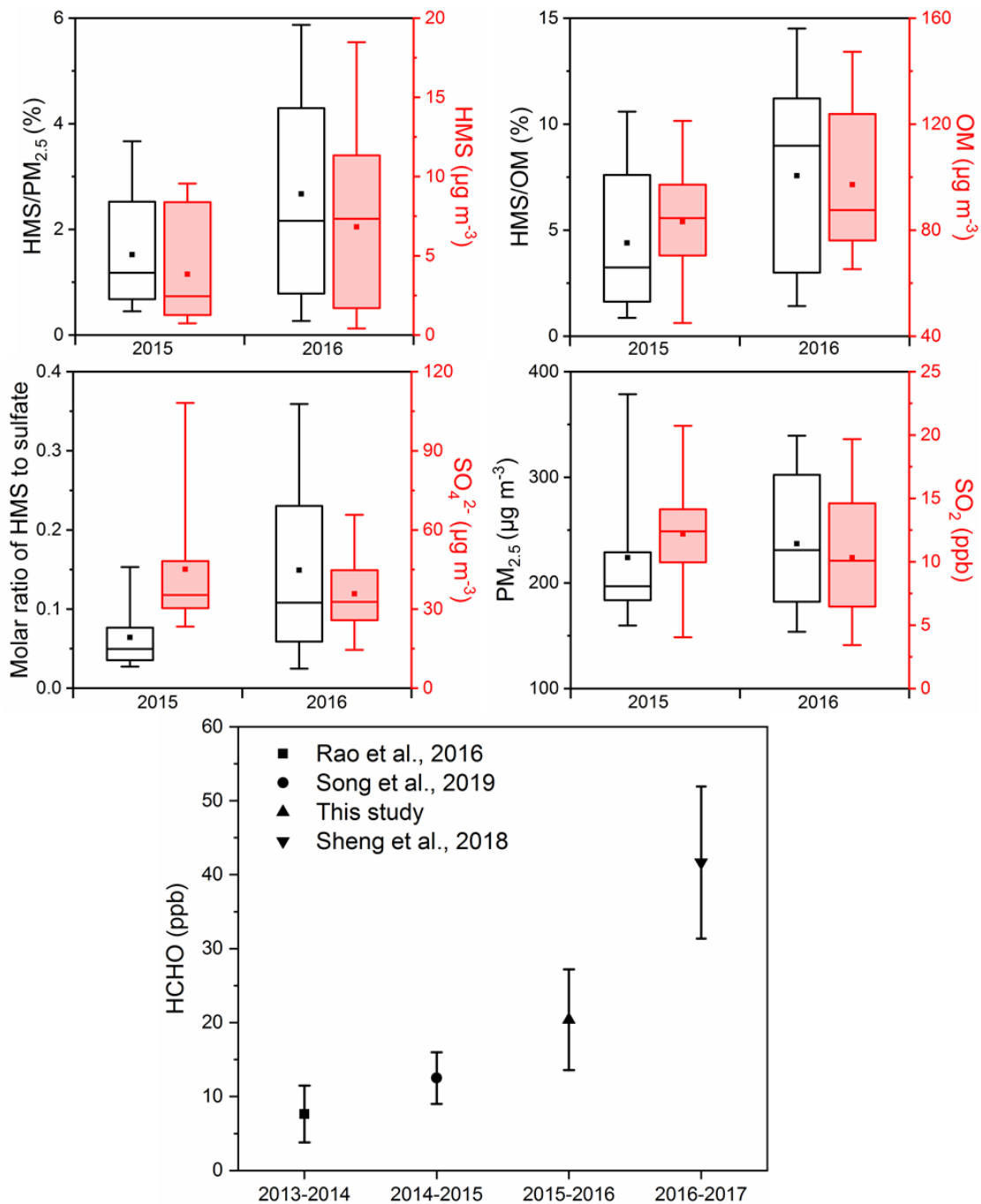
Figure S7. Change of haze characteristics in Beijing winter from 2015 to 2016. Variation of HMS/PM$_{2.5}$, HMS, HMS/OM, OM, the molar ratio of HMS to sulfate, SO$_4^{2-}$, PM$_{2.5}$, and SO$_2$ in Beijing winter from 2015 to 2016. OM is estimated as 1.6 times of OC. Variations in HCHO levels during winter hazes in

Beijing during 2013–2017. The HCHO concentrations in 2013–2014, 2014–2015, and 2016–2017 winter are derived from the work by Rao et al. (Rao et al., 2016), Song et al. (Song et al., 2019), and Sheng et al. (Sheng et al., 2018), respectively.
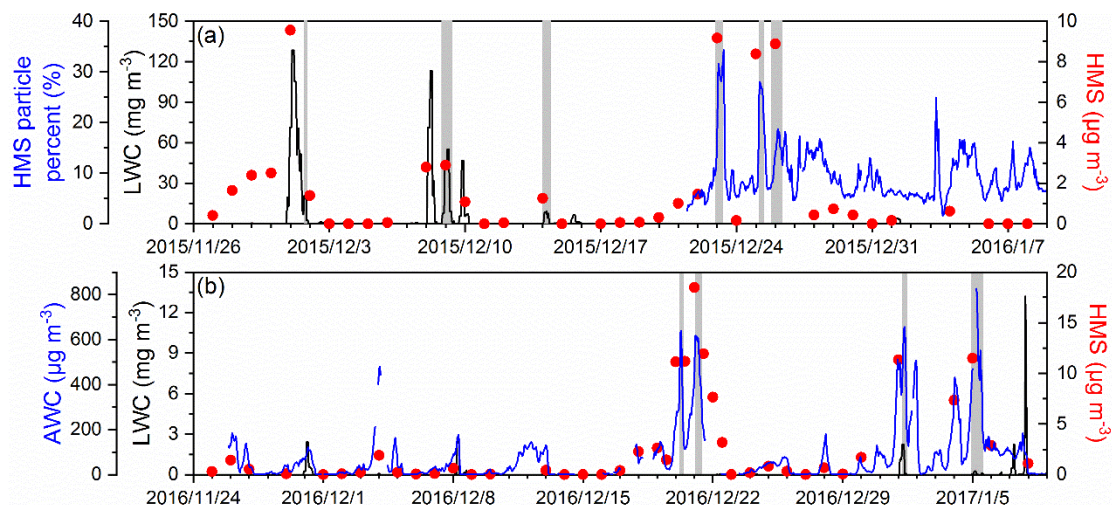

Figure S8. Relationship between HMS events and cloud/fog/aerosol water in Beijing winter. **(a)** Time series of HMS concentration, HMS-containing particle percentage, and cloud/fog liquid water content (LWC) in winter 2015. LWC is obtained from the MERRA-2 (Modern-Era Retrospective analysis for Research and Applications, Version 2) reanalysis meteorology (Gelaro et al., 2017). The average LWC below the planetary boundary layer height over the Beijing area is calculated and shown. The gray shades represent the possible presence of fog events (RH > 90%). **(b)** Time series of HMS concentration, aerosol water content (AWC), and ~~cloud/fog liquid water content (~~LWC~~)~~ in winter 2016.
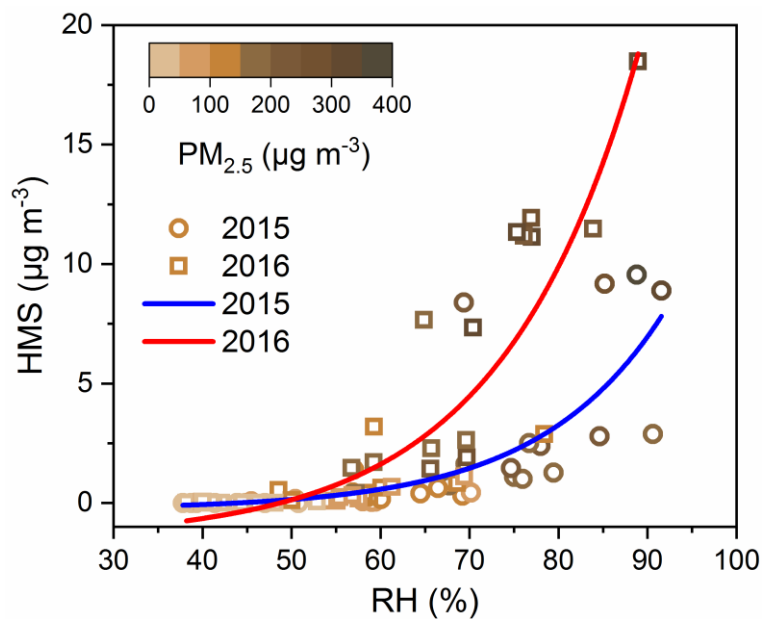
Figure S9. Effects of RH on HMS formation. Correlation between RH and HMS concentration in the winter of 2015 and 2016. The markers represent HMS concentrations and are colored by the $PM_{2.5}$ concentrations. The blue and red curve represents the exponential fitting between RH and HMS concentration in 2015 and 2016, i.e., $y = -0.27 + 1.2 \times 10^{-2} e^{0.072x}$ ($R^2 = 0.56$) and $y = -1.51 + 6.5 \times 10^{-2} e^{0.065x}$ ($R^2 = 0.78$), respectively.
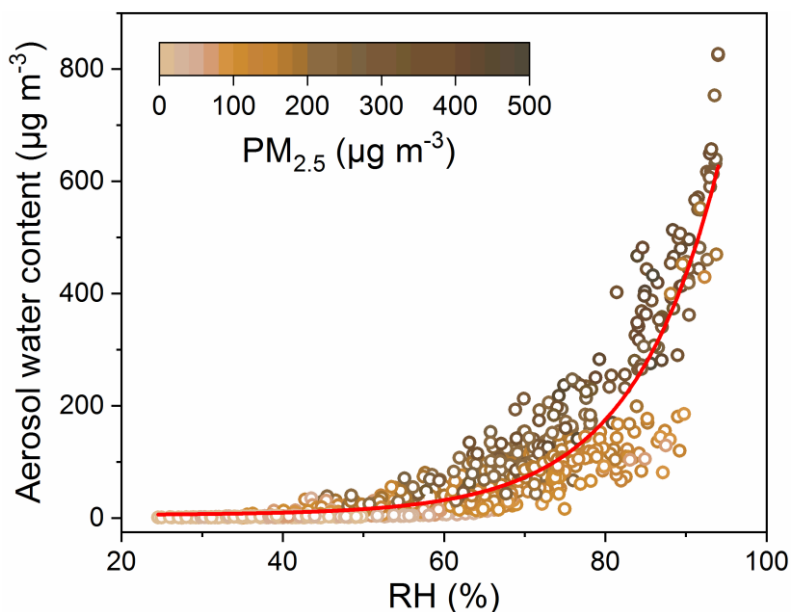
Figure S10. Relationship between RH and aerosol water content in Beijing in winter 2016. The markers represent aerosol water content and are colored by the $PM_{2.5}$ concentrations. The red curve represents the exponential fitting between RH and aerosol water content, i.e., $y = 5.5 + 0.1e^{0.09x}$ ($R^2 = 0.85$).
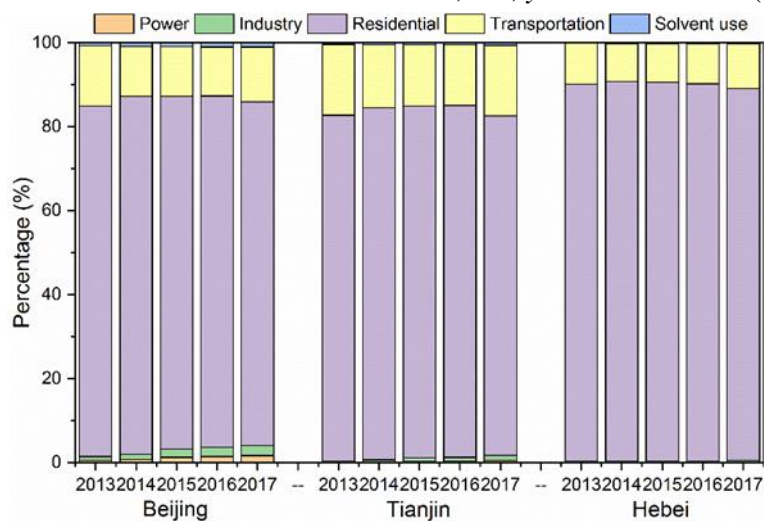
Figure S11. Emission percentages of HCHO across source sectors in winter (January, February, and December) from 2013 to 2017 in Beijing-Tianjin-Hebei.

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