



Possible heterogeneous chemistry of hydroxymethanesulfonate (HMS) in northern China winter haze

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Abstract. The chemical mechanisms responsible for rapid sulfate production, an important driver of winter haze formation in northern China, remain unclear. Here, we propose a potentially important heterogeneous hydroxymethanesulfonate (HMS) chemical mechanism. Through analyzing field measurements with aerosol mass spectrometry, we show evidence for a possible significant existence in haze aerosols of organosulfur primarily as HMS, misidentified as sulfate in previous observations. We estimate that HMS can account for up to about one-third of the sulfate concentrations unexplained by current air quality models. Heterogeneous production of HMS by SO₂ and formaldehyde is favored under northern China winter haze conditions due to high aerosol water content, moderately acidic pH values, high gaseous precursor levels, and low temperature. These anal-

yses identify an unappreciated importance of formaldehyde in secondary aerosol formation and call for more research on sources and on the chemistry of formaldehyde in northern China winter.

1 Introduction

Severe haze episodes occur frequently in Beijing and throughout the North China Plain (NCP), especially in winter, posing substantial threats to public health (Ding et al., 2016; Fu and Chen, 2017; Gao et al., 2017). High concentrations of fine particles and reduced visibility are associated with stagnant meteorological conditions, i.e., shallow boundary layers, weak winds, and high relative humidity (RH)

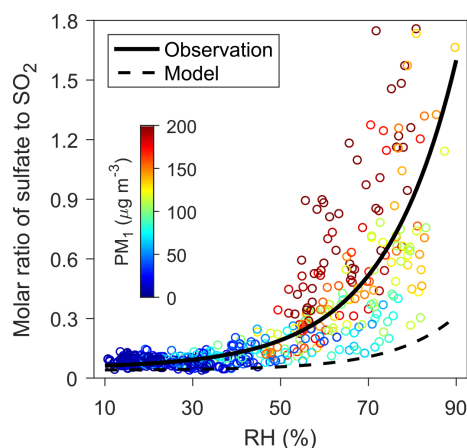


Figure 1. Relationship between sulfate / SO_2 molar ratio and RH. The circles indicate hourly observations during the 2014 winter in urban Beijing and are colored according to the observed PM_{10} (particles with diameter less than $1\text{ }\mu\text{m}$) concentrations. The solid and dashed curves represent, respectively, the exponential fitting between the observed and modeled sulfate / SO_2 ratios and the observed RH, i.e., $y = 0.05 + 7 \times 10^{-3} e^{0.06x}$ ($R^2 = 0.6$) and $y = 0.04 + 5 \times 10^{-4} e^{0.07x}$ ($R^2 = 0.3$). Sulfate concentrations are obtained from HR-AMS PM_{10} measurements, and the corresponding model results are from WRF-Chem simulations.

(Wang et al., 2014a; Cai et al., 2017; Tie et al., 2017). The rapid formation of particulate sulfate is considered one of the key drivers of haze pollution for several reasons: sulfate is an important component of fine particles; it facilitates the partitioning of gaseous ammonia into the particle phase; and it enhances aerosol water uptake, changing the optical and chemical properties of aerosols (Guo et al., 2014; Huang et al., 2014). Sulfate is also known to impact climate and acid deposition (Charlson et al., 1992; Xie et al., 2015).

Most of the sulfate is of secondary origin, formed by the oxidation of anthropogenic SO_2 (He et al., 2018). The exponential relationship between RH and the molar ratios of sulfate relative to SO_2 , as observed during the 2014 winter in Beijing (Fig. 1; see Sect. 2) and in many previous studies (Sun et al., 2013; Zheng et al., 2015b; Wang et al., 2016), imply that heterogeneous chemistry (processes involving both gas and aerosol phases) plays an important role in the production of sulfate. Indeed, air quality model simulations fail to capture the rapid increase in sulfate from clean to hazy periods when considering only the oxidation of SO_2 in the gas phase and in cloud/fog water, suggesting missing heterogeneous sources of sulfate (Wang et al., 2014b; Zheng et al., 2015a; Li et al., 2017a) (Fig. 1). Adding an apparent RH-dependent heterogeneous uptake for SO_2 on aerosols greatly reduces the negative bias in the modeled sulfate concentrations (see Sect. 2) (Wang et al., 2014b; Zheng et al., 2015a).

Several heterogeneous reaction pathways have been proposed (He et al., 2014; Cheng et al., 2016; Wang et al., 2016; Li et al., 2017a; Hung et al., 2018; Qin et al., 2018; Yu et

al., 2018), including the oxidation of SO_2 in aerosol water (by NO_2 , transition-metal-catalyzed O_2 , or H_2O_2) and on aerosol surfaces (by NO_2 and/or O_2). Their relative importance for sulfate production in winter haze, however, is unknown due to uncertainties in relevant reaction rates and estimates for aerosol water pH values (most reaction pathways are pH-dependent) (Guo et al., 2017b; Liu et al., 2017a; Li et al., 2018b; Wang et al., 2018; Zhao et al., 2018). For example, Wang et al. (2016, 2018) found in laboratory experiments that the rate for the oxidation of SO_2 by NO_2 strongly depended on the types of seed particles. In another example, Cheng et al. (2016) suggested that reactions of SO_2 with NO_2 in aerosol water could be the source of missing sulfate given the neutralized feature of haze aerosols (with a pH value of about 6 estimated with the ISORROPIA-II thermodynamic equilibrium model). Guo et al. (2017b) argued that the ISORROPIA-II calculation in Cheng et al. (2016) overestimated aerosol water pH and that transition-metal-catalyzed O_2 instead of NO_2 was the key oxidant of SO_2 .

Therefore, solution to the missing-sulfate problem (discrepancy between observations and model results) in northern China winter haze remains challenging and controversial. The term sulfate in the atmospheric chemistry literature commonly refers to inorganic sulfate species. In addition to inorganic sulfate, organosulfur compounds (OSs) have also been demonstrated to be present in atmospheric aerosols, including organosulfates (ROSO_3^-), sulfones ($\text{RSO}_2\text{R}'$), and sulfonates (RSO_3^-) such as methanesulfonate (CH_3SO_3^- , the deprotonated anion of methanesulfonic acid, MSA) and hydroxyalkylsulfonates ($\text{RCH}(\text{OH})\text{SO}_3^-$) (Eatough and Hansen, 1984; Dixon and Aasen, 1999; Surratt et al., 2008; Tolocka and Turpin, 2012; Sorooshian et al., 2015). OS may have been misidentified as inorganic sulfate in previous ambient measurements, thus leading to a positive observational bias (as described later). The formation of OS is typically not included in air quality model simulations and thus can partly explain the missing-sulfate problem if concentrations of these species are appreciable. However, OS concentrations in northern China winter haze aerosols have rarely been reported, and their formation mechanisms are also unknown.

In this study, we interpreted measurement data collected by a high-resolution time-of-flight aerosol mass spectrometer (HR-AMS) and a single-particle aerosol mass spectrometer (SPAMS) in Beijing winter. We demonstrated the possible presence of OS in haze aerosols and discussed the potential of different OS species. Hydroxymethanesulfonate (HMS, $\text{CH}_2(\text{OH})\text{SO}_3^-$) was found to likely be the primary OS component. We found that heterogeneous production rate of HMS through the reaction of formaldehyde (HCHO) and SO_2 was fast enough to account for the identified OS by HR-AMS. Furthermore, we hypothesized that HMS might lead to additional sulfate production through a mechanism involving aqueous hydroxyl radicals (OH). Finally, we discussed the implications of this heterogeneous HMS chemical mecha-

nism for the missing-sulfate problem and also future research needs.

2 Methods

2.1 Field measurements

Aerosol and gaseous pollutants were measured in urban Beijing during winter 2014 (mid-November to mid-December) (Fig. S1 in the Supplement). Chemical composition of non-refractory PM_{10} was measured by a HR-AMS (Aerodyne Research, Inc., USA). Individual particles (0.2–2 μm) were detected by a SPAMS (Hexin Analytical Instrument Co., China). The gas and aerosol collector ion chromatography (GAC-IC) system determined the concentrations of semi-volatile gases (HNO_3 , NH_3 , and HCl), and commercial analyzers were used to measure black carbon (AE33, Magee Scientific, USA), gaseous HCHO (AL4021, Aero-Laser GmbH, Germany), and SO_2 and O_3 (Thermo Fisher Scientific Inc., USA). Meteorological data were also recorded. Details are provided below and in Table S1 in the Supplement.

2.2 HR-AMS measurements

Particles were vaporized by impaction on a heated surface (600 °C), and the resulting vapors were ionized by an electron impact ionization source (70 eV) (DeCarlo et al., 2006; Sun et al., 2016). The positive fragment ions generated were detected then using time-of-flight mass spectrometry. The HR-AMS switched every 5 min between the mass-sensitive V mode (mass resolution of ~ 2000) and the high-resolution W mode (mass resolution of ~ 4500). A default collection efficiency of 0.5 was assumed (Middlebrook et al., 2012); because the mass fraction of ammonium nitrate was below 40 %, the aerosol particles were moderately acidic (Song et al., 2018), and a silica gel dryer was used to reduce RH in the sampling line. The ionization efficiency calibrations were performed using pure ammonium nitrate particles following Jayne et al. (2000), and the default relative ionization efficiencies (RIEs), except for ammonium that was calibrated by ammonium nitrate, were applied to all the chemical species for mass quantifications. It is noted that the calibrated RIE values of sulfate later in 2017 and 2018 ranged from 1.22 to 1.39 (unpublished data), implying a possible overestimation of sulfate mass concentrations by 2 %–14 %. Mass concentrations of chemical components (ammonium, sulfate, nitrate, chloride, and organics) and inorganic and organic sulfur-containing fragment ions (H_ySO_x^+ and $\text{C}_x\text{H}_y\text{O}_z\text{S}^+$) were quantified with the standard data analysis software packages (Sueper et al., 2018). These sulfur-containing ions were well separated from adjacent peaks in the observed mass spectra and thus quantified with high confidence (examples in Fig. S2). The uncertainty quantification of chemical species followed Bahreini et al. (2009) (details in Sect. S1 in the Supplement).

2.2.1 SPAMS measurements

The SPAMS (Li et al., 2011) was based on the same principle as the ATOFMS (aerosol time-of-flight mass spectrometer) designed by Prather et al. (1994). Ambient aerosol particles were introduced and focused into a narrow beam using an aerodynamic lens. Particles passed through two continuous 532 nm Nd:YAG lasers with velocities determined on the basis of observed traveling times. The individual particles were ionized using a 266 nm Nd:YAG laser, and both positive and negative ions were generated and detected by bipolar time-of-flight mass spectrometry. The Computational Continuation Core software framework based on MATLAB (The MathWorks, Inc., USA) was used to analyze these ions. The negative ion peak at $m/z -111$ has been assigned to HMS ($\text{CH}_2(\text{OH})\text{SO}_3^-$) with no significant interference from other species in previous laboratory and field studies (Lee et al., 2003; Whiteaker and Prather, 2003; Dall'Osto et al., 2009; Zhang et al., 2012). HMS-containing particles were identified by the presence of a peak at $m/z -111$ with the absolute and relative peak areas greater than 50 % and 0.5 %, respectively. The negative ion peaks at $m/z -155$, -187 , -199 , and -215 were also analyzed in order to detect individual organosulfate species. This technique has been employed to measure individual organosulfates in different regions around the world (Hatch et al., 2011a; Wang et al., 2017).

2.2.2 HCHO measurements

The AL4021 analyzer is based on the Hantzsch reaction (HCHO reacts with acetylacetone and ammonia in aqueous solution to form α - α' -dimethyl- β - β' -diacetyl-pyridine which is excited at 400 nm and fluoresces at 510 nm). The Hantzsch reagents were prepared every 3 days and were kept cool in a refrigerator. A Teflon filter was installed at the sampling inlet to remove particles from the air. This analyzer was calibrated with 1 μM HCHO standard solution every 2 to 3 days during the field measurements. The measurement uncertainty is ~ 20 %, and the detection limit is ~ 0.15 ppb (Hak et al., 2005).

2.2.3 GAC-IC measurements

Three semi-volatile gases (NH_3 , HNO_3 , and HCl) were measured with a time resolution of 30 min. The instrument was modified based on the Steam Jet Aerosol Collector (Khlystov et al., 1995) in order to better apply to the heavily polluted conditions in China (Dong et al., 2012). Gases were absorbed in a wet annular denuder and quantified by ion chromatography analyzers. Intercomparison experiments with filter sampling and other online methods showed that the relative uncertainties in GAC-IC were within ± 20 % for major species (Song et al., 2018).

2.3 Approaches to estimating OS and methanesulfonate with HR-AMS

OSs are primarily fragmented into separate organic ions ($C_xH_yO_z^+$) and inorganic sulfur-containing ions ($H_ySO_x^+$) with minimal organic sulfur-containing ions ($C_xH_yO_zS^+$), due to the low thermal stability of OS and thermal vaporization and electron ionization of HR-AMS (Farmer et al., 2010; Huang et al., 2015; Hu et al., 2017a). The sulfate concentrations obtained by the standard HR-AMS data analysis are contributed not only by inorganic sulfate but also by OS. $(NH_4)_2SO_4$ is considered the dominant inorganic sulfate species in northern China winter haze aerosols due to the relatively high NH_3 levels and the resulting moderate particle acidity (Song et al., 2018). The presence of OS and its contribution to the HR-AMS sulfate (considered as the total sulfate) may be detectable using ratios between different $H_ySO_x^+$, due to different fragmentation patterns of $(NH_4)_2SO_4$ and OS (Hu et al., 2017a). For example, the major $H_ySO_x^+$ from $(NH_4)_2SO_4$ includes S^+ , SO^+ , SO_2^+ , SO_3^+ , HSO_3^+ , and $H_2SO_4^+$, while some of these (SO_3^+ , HSO_3^+ , and $H_2SO_4^+$) are not generated by HMS (Ge et al., 2012; Gilardoni et al., 2016). We observed in Beijing winter that the six ratios of $SO^+/H_ySO_x^+$ and $SO_2^+/H_ySO_x^+$ ($H_ySO_x^+$ refers to SO_3^+ , HSO_3^+ , and $H_2SO_4^+$) were highly correlated with each other ($r > 0.9$, $P < 0.001$) and that all of these ratios significantly increased with RH and PM_{10} concentrations (Figs. 2a, b and S3). From the clean and dry conditions (average $PM_{10} = 10 \mu g m^{-3}$ and RH = 20 %) to the haze (polluted and humid) conditions (average $PM_{10} = 160 \mu g m^{-3}$ and RH = 70 %), these ion ratios increased by approximately 25 %–41 %. During clean and dry periods, the observed ratios agreed well with values from pure $(NH_4)_2SO_4$ calibrations (Ge et al., 2012; Gilardoni et al., 2016; Hu et al., 2017a), supporting the dominance of $(NH_4)_2SO_4$ over other sulfur-containing compounds. The variations in $SO^+/H_ySO_x^+$ and $SO_2^+/H_ySO_x^+$ were unlikely to be due to changes in the acidity of haze aerosols (a pH of about 4 to about 5 in both clean and haze conditions) (Song et al., 2018), and no clear relationship was found between these fragment ratios and the fraction of ammonium nitrate in haze aerosols (Chen et al., 2018). Examples are given in Fig. S4.

The enhancements of $SO^+/H_ySO_x^+$ and $SO_2^+/H_ySO_x^+$ under haze conditions may suggest the presence of additional sulfur compounds, which should either not generate SO_3^+ , HSO_3^+ , and $H_2SO_4^+$ ions or have higher ratios of $SO^+/H_ySO_x^+$ and $SO_2^+/H_ySO_x^+$ relative to $(NH_4)_2SO_4$. Since several types of OS (e.g., organosulfates and HMS) satisfy this requirement, the observed HR-AMS mass spectra of inorganic sulfur-containing ions cannot be used to quantify the speciation of OS but may allow an estimate of sulfate-equivalent OS concentration (C_{OS} , $\mu g m^{-3}$):

$$C_{OS} = M_{SO_4^{2-}} \left[\frac{SO_{obs}^+ - \overline{R_{cd,SO^+/H_ySO_x^+}} \cdot H_ySO_{x,obs}^+}{M_{SO^+}} + \frac{SO_{2,obs}^+ - \overline{R_{cd,SO_2^+/H_ySO_x^+}} \cdot H_ySO_{x,obs}^+}{M_{SO_2^+}} \right], \quad (1)$$

where SO_{obs}^+ , $SO_{2,obs}^+$, and $H_ySO_{x,obs}^+$ ($SO_{3,obs}^+$, $HSO_{3,obs}^+$, and $H_2SO_{4,obs}^+$) are concentrations of the observed inorganic sulfur-containing ions, M_{SO^+} , $M_{SO_2^+}$, and $M_{SO_4^{2-}}$ are molar masses, and $\overline{R_{cd,SO^+/H_ySO_x^+}}$ and $\overline{R_{cd,SO_2^+/H_ySO_x^+}}$ indicate the average ratios of the two corresponding ions observed during the clean and dry periods. $\overline{R_{cd,SO^+/H_ySO_x^+}} \cdot H_ySO_{x,obs}^+$ is considered to be the concentration of SO^+ attributable to inorganic sulfate, and its difference to SO_{obs}^+ represents the contribution of OS. The same applies to $\overline{R_{cd,SO_2^+/H_ySO_x^+}} \cdot H_ySO_{x,obs}^+$. This approach results in a conservative estimate of C_{OS} because (1) it is assumed that OS do not generate SO_3^+ , HSO_3^+ , and $H_2SO_4^+$ ions and (2) several minor ions (e.g., S^+ and $^{33}SO_2^+$) generated by OS fragmentation are not taken into account (Hu et al., 2017b). The uncertainty quantification of C_{OS} is provided in Sect. S1.

The organic sulfur-containing ions $CH_3SO_2^+$ and $CH_2SO_2^+$ were used as the signature fragments of methanesulfonate (Ge et al., 2012). In our field measurements, an excellent linear correlation ($r = 0.98$, $P < 0.001$) was observed between these two ions, and the average ratio of $CH_3SO_2^+$ to $CH_2SO_2^+$ (2.9 ± 0.1) was consistent with the value of 2.9 ± 0.3 from the HR-AMS mass spectrum of pure MSA particles found in previous studies (Ge et al., 2012; Huang et al., 2015, 2017), confirming the presence of methanesulfonate in haze aerosols (Fig. S5). We estimated the levels of methanesulfonate using the observed $CH_3SO_2^+$ and its fraction in the total signal intensity of MSA standards identified in Huang et al. (2017).

2.4 WRF-Chem air quality model simulation

The Weather Research and Forecasting model coupled with Chemistry (WRF-Chem; version 3.5.1) (Grell et al., 2005) was adopted to simulate concentrations of particulate sulfate and gas-phase HCHO during the 2014 winter (November–December). Two nested domains were configured to cover East Asia, and model results from the inner domain focused on northern China with a horizontal resolution of about 27 km were used for analysis. The meteorological initial and boundary conditions were obtained from the NCEP FNL (Final) Operational Global Analysis (NCEP, 2000), and temperature, moisture, and wind fields were nudged to constrain the accuracy of the simulated meteorology. The chemical initial and boundary conditions were provided from MOZART-4 global model simulations of trace gases and aerosols (Emmons et al., 2010). The Lin microphysics scheme (Lin et

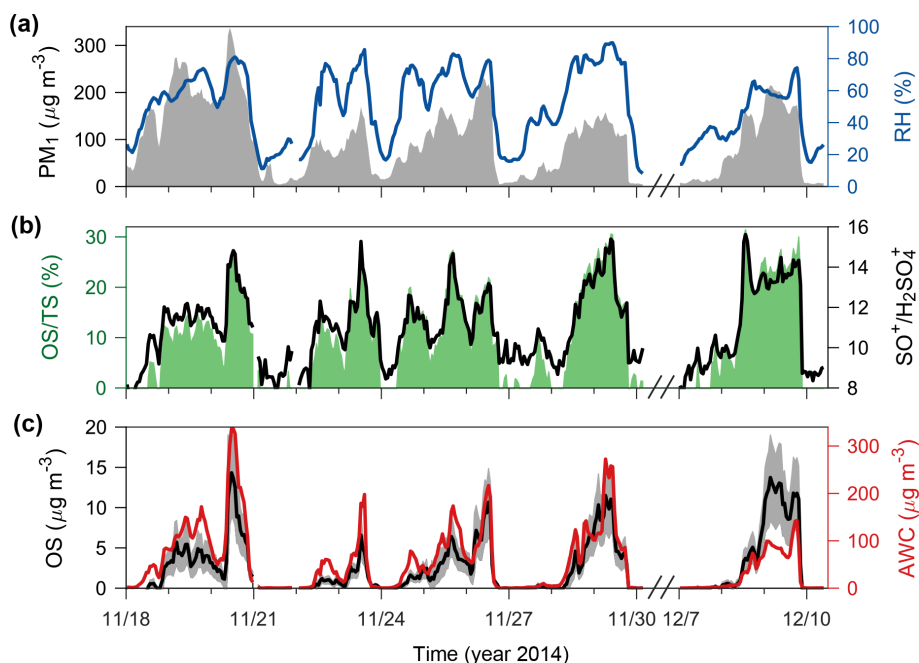
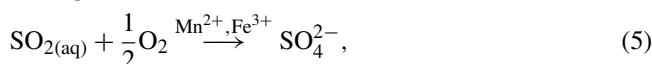
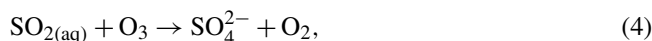
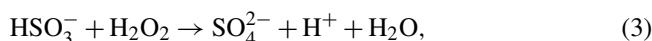
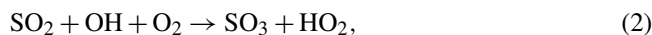


Figure 2. Possible presence of OS in Beijing winter haze aerosols. (a) PM_{10} concentrations (left, gray-shaded area) and RH (right, blue line). (b) Contributions of OS to TS (left, green-shaded area) and ratios of SO^+ to H_2SO_4^+ (right, black line). The ratios between the other inorganic sulfur-containing ions are given in Fig. S3. (c) Sulfate-equivalent OS concentrations (left, black line) and AWC (right, red line). The gray-shaded area in (c) indicates the 1σ uncertainty range of OS concentrations (on average $\sim 40\%$ during haze periods).

al., 1983), Rapid Radiative Transfer Model (Mlawer et al., 1997), Goddard shortwave radiation scheme (Kim and Wang, 2011), Noah Land Surface Model (Chen and Dudhia, 2001), and YSU planetary boundary layer scheme (Hong et al., 2006) were used for the calculations of cloud microphysics, longwave radiation, shortwave radiation, land surface, and boundary layer processes, respectively. The Carbon Bond Mechanism version Z (CBM-Z) (Zaveri and Peters, 1999) gas-phase chemical mechanism coupled with the thermodynamic module MOSAIC (Model for Simulating Aerosol Interactions and Chemistry) (Zaveri et al., 2008) was applied to simulate gas-phase reactions and aerosol processes.

Anthropogenic emissions were obtained from the MIX inventory (Li et al., 2017b) for five sectors, namely power generation, industry, residential, transportation, and agriculture, including the emissions of SO_2 , NO_x , CO, non-methane volatile organic compounds (NMVOCs), NH_3 , and primary inorganic and organic particulate matters. In addition, biogenic emissions were estimated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006), and open biomass burning emissions were taken from the Global Fire Emissions Database version 4 (GFEDv4) (Randerson et al., 2017). In the WRF-Chem model, sulfate was formed by the oxidation of SO_2 both in the gas phase (initiated by OH) and in cloud/fog water (by dissolved H_2O_2 , O_3 , and transition-metal-catalyzed O_2)

(Pandis and Seinfeld, 1989):



where $\text{SO}_{2(\text{aq})}$ represents the sum of $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , and SO_3^{2-} . We conducted two model simulations: (1) a BASE scenario with normal settings and (2) a $5 \times \text{EMIS}$ scenario in which primary HCHO emissions from the transportation sector were elevated by a factor of 5. This is because, as described in Sect. 3, the BASE scenario significantly underestimated ambient HCHO concentrations. It remains unclear whether primary or secondary sources of HCHO are responsible for its high wintertime levels. Jobson and colleagues have recently suggested that HCHO emissions during motor vehicle cold starts, especially in cold winter, are significantly underestimated in current inventories (Jobson et al., 2017). Accordingly, a $5 \times \text{EMIS}$ scenario with increasing primary HCHO emissions from transportation was conducted, which greatly reduces the negative biases in the modeled HCHO and thus was used to calculate the formation rate of HMS.

2.5 Apparent heterogeneous sulfate production rate

An apparent heterogeneous uptake of SO₂ on aerosols has been shown to be able to compensate for the missing sulfate (ΔSO_4^{2-}) in current air quality models during northern China winter haze episodes (Wang et al., 2014b; Zheng et al., 2015a; Li et al., 2018b). The heterogeneous sulfate production rate, P_Δ , was parameterized with an uptake coefficient γ (the fraction of gas–aerosol collisions resulting in chemical reaction) (Jacob, 2000):

$$P_\Delta = (R_p/D_g + 4/v\gamma)^{-1} S_p [\text{SO}_{2(g)}] M_{\text{SO}_4^{2-}}, \quad (6)$$

where R_p is the average aerosol droplet radius taken as 0.15 μm following Cheng et al. (2016), D_g is the gas-phase diffusion coefficient of SO₂, v is the average molecular speed of SO₂, S_p is the aerosol surface area per unit volume of air, and $[\text{SO}_{2(g)}]$ is the gas-phase concentration. γ is 2×10^{-5} when $\text{RH} \leq 50\%$ and increases linearly from 2×10^{-5} to 5×10^{-5} when $50\% < \text{RH} \leq 100\%$ (Zheng et al., 2015a), consistent with other laboratory and model studies (Wang et al., 2016; Li et al., 2017a). The heterogeneous reaction rate required to produce the identified OS (P_{OS}) can be expressed as

$$P_{\text{OS}} = (C_{\text{OS}}/\Delta\text{SO}_4^{2-}) \cdot P_\Delta. \quad (7)$$

2.6 ISORROPIA-II thermodynamic equilibrium model calculation

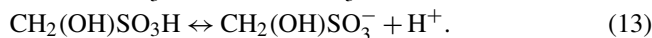
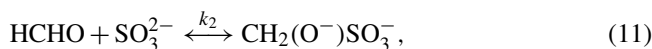
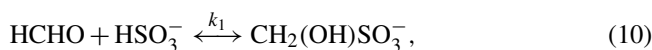
We estimated aerosol water content (AWC), aerosol water pH, and ionic strength with the ISORROPIA-II inorganic model (Fountoukis and Nenes, 2007) and also considered the contribution of carbonaceous species. Detailed calculations were given in our recent study (Song et al., 2018). Briefly, ISORROPIA-II predicts the phase partitioning of an $\text{NH}_4^+ \text{-K}^+ \text{-Ca}^{2+} \text{-Na}^+ \text{-Mg}^{2+} \text{-SO}_4^{2-} \text{-NO}_3^- \text{-Cl}^- \text{-H}_2\text{O}$ aerosol and semi-volatile gases (HNO₃, NH₃, and HCl), and can be used in either forward mode (the total (gas + aerosol) concentration of each species is fixed) or reverse mode (the aerosol concentration of each species is fixed). The forward-mode results were adopted in this study, since the reverse-mode calculations of pH are sensitive to aerosol composition measurement errors and should be avoided. The model inputs were taken from the HR-AMS (bulk PM₁ composition) and GAC-IC (semi-volatile gas) measurements except for crustal species that were estimated based on their levels in PM_{2.5} and typical size distributions (Song et al., 2018). The inorganic aerosol phase state was assumed to be metastable, meaning that the aqueous solution does not crystallize but remains supersaturated when the RH is below the deliquescence RH, although aerosols may reside in a stable state, meaning that the aqueous solution crystallizes once saturation is exceeded (Rood et al., 1989). The assumed phase state led to a small difference in pH (< 0.01 units on average) and an average $\sim 20\%$ difference in AWC (Song et al., 2018) and

thus did not affect the major conclusions of this study. The AWC modeled by ISORROPIA-II has been shown to be in good agreement with those based on ambient measurements in northern China (Wu et al., 2018). The validity of pH calculations was supported by the reasonable agreement between the predicted and observed gas-particle partitioning of semi-volatile species (Song et al., 2018).

The aerosol water associated with carbonaceous species was estimated with the hygroscopicity parameter κ (Cheng et al., 2016). κ values of 0.06 and 0.04 were used for organics and black carbon, respectively (Song et al., 2018). The contribution of carbonaceous species to AWC was found to be small ($\sim 10\%$), leading to a minor effect on pH (~ 0.05 unit). The ionic strength of aerosol water was estimated using the predicted aerosol composition and AWC (Herrmann, 2003). The uncertainty in pH was estimated with a Monte Carlo approach accounting for measurement errors in the model inputs including gas and aerosol species and meteorological parameters. The 95 % confidence interval for calculated pH values was 4.1 to 5.5, very similar to the pH range found in previous northern China winter haze studies (Song et al., 2018).

2.7 Kinetics and thermodynamics of HMS heterogeneous production

The chemical mechanism for HMS production can be expressed as (Boyce and Hoffmann, 1984)



CH₂(OH)SO₃H (hydroxymethanesulfonic acid, HMSA) dissociates twice to form CH₂(OH)SO₃[−] and CH₂(O[−])SO₃[−] with the dissociation constants $pK_{a1} < 0$ and $pK_{a2} \sim 12$, respectively, and thus, in the pH range of this study, the adduct existed as CH₂(OH)SO₃[−]. The acid catalysis of HMS production was significant only at pH < 1 and thus irrelevant in the present context (Olson and Hoffmann, 1989). It is noted that CH₂(OH)SO₃[−] may form salts by the neutralization reaction with ammonium or other cations (e.g., Na⁺, K⁺, and Ca²⁺) and undergo precipitation when the ambient RH becomes lower than the efflorescence RH value.

The production of HMS in aerosol water was not found to be limited by the mass transfer processes and hydration of HCHO (Sect. S2). The rate for the heterogeneous production of HMS, P_{HMS} (in sulfate-equivalent $\mu\text{g m}^{-3} \text{h}^{-1}$), was

calculated as

$$P_{\text{HMS}} = (k_1\alpha_1 + k_2\alpha_2) \cdot [\text{SO}_{2(\text{aq})}] \cdot [\text{HCHO}_{(\text{aq})}] \cdot \text{AWC} \cdot M_{\text{SO}_4^{2-}}, \quad (14)$$

where k_1 and k_2 were, respectively, the forward rate constants for Eqs. (10) and (11), $[\text{SO}_{2(\text{aq})}]$ (defined as the sum of $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , and SO_3^{2-}) and $[\text{HCHO}_{(\text{aq})}]$ was aqueous-phase concentrations estimated with their gas-phase levels and Henry's law constants. α_1 and α_2 represented the fractions of HSO_3^- and SO_3^{2-} in $\text{SO}_{2(\text{aq})}$, respectively, and both were functions of pH. The production of HMS was reversible and the equilibrium constant K_{eq} could be expressed as

$$K_{\text{eq}} = [\text{HMS}_{(\text{aq})}] / ([\text{HMS}_{(\text{aq})}][\text{SO}_{2(\text{aq})}]), \quad (15)$$

where $[\text{HMS}_{(\text{aq})}]$ was the aqueous-phase concentration of HMS. Because the time to reach the equilibrium under winter haze conditions was typically greater than that for haze formation, the precursors and HMS were usually not equilibrated (Sect. S3). The relevant physical and chemical properties of SO_2 , HCHO, and HMS are summarized in Tables S2 and S3.

3 Results and discussion

3.1 The presence of OS in Beijing winter haze aerosols

The standard HR-AMS data analysis usually does not distinguish OS from inorganic sulfate, since OSs are fragmented primarily into separate organic ions and inorganic sulfur-containing ions (Hu et al., 2017a). Using the distinct fragmentation patterns of inorganic sulfur-containing ions in the observed HR-AMS mass spectra, we derived a conservative estimate of total OS concentrations (expressed in sulfate-equivalent $\mu\text{g m}^{-3}$) in PM_{10} (particles with an aerodynamic diameter below $1 \mu\text{m}$), as described in Sect. 2. During several winter haze periods (defined as $\text{PM}_{10} > 100 \mu\text{g m}^{-3}$), OSs were estimated to contribute significantly to the total sulfate (TS) identified by the standard HR-AMS data analysis, with an average OS/TS ratio of $17\% \pm 7\%$ and a maximum ratio of 31 % (Fig. 2a–b). Thus, previously reported sulfate concentrations in Beijing winter haze aerosols from HR-AMS measurements may have been biased high due to the presence of OS.

A good positive correlation ($r = 0.82$, $P < 0.001$) was found between OS and the AWC (Fig. 2c) estimated on the basis of the ISORROPIA-II thermodynamic equilibrium model constrained using in situ gas and aerosol compositional and meteorological measurements (see Sect. 2), suggesting that aerosol water serves as a medium enabling the production of OS. It has been shown that PM_{10} is in the liquid phase state during Beijing winter haze periods (Liu et al., 2017b). In contrast, OSs were unrelated to the presence or absence of cloud/fog events (Fig. S6), indicating

that the identified OSs were less likely formed by local cloud/fog processing (Moch et al., 2018). Although our interpretation of the HR-AMS fragmentation of inorganic sulfur-containing ions cannot directly determine the speciation of OS (organosulfates, sulfones, methanesulfonate, and hydroxyalkylsulfonates), we suggest, through the following analyses, that HMS may be the major OS species in Beijing winter haze aerosols.

3.2 Methanesulfonate, sulfones, and organosulfates are likely minor OS species

The contribution of methanesulfonate to OS was only 2 %–8 % estimated using CH_3SO_2^+ as the characteristic fragment in the HR-AMS mass spectra (see Sect. 2 and Fig. S5) (Huang et al., 2017). Its estimated concentrations were comparable to those from a previous study (Yuan et al., 2004). The methanesulfonate in Beijing winter is likely formed by the oxidation of dimethyl sulfite or dimethyl sulfoxide emitted from waste disposal (Yuan et al., 2004). Aerosol water has been suggested to play important roles in the formation of methanesulfonate and its condensation onto particles (Barnes et al., 2006; Gaston et al., 2010).

The formation of bis-hydroxymethyl sulfone ($\text{C}_2\text{H}_6\text{SO}_4$), the only sulfone that has been identified in ambient aerosols, is inhibited by atmospheric water and is thus unlikely to be important in winter haze (Eatough and Hansen, 1984). Organosulfates, formed through reactions of gaseous organics (e.g., epoxides and aldehydes) and particulate inorganic sulfate, also seem to represent minor contributions to OS based on the following evidence. The most common organosulfates identified previously in ambient aerosols, such as glycolic acid sulfate ($\text{C}_2\text{H}_3\text{SO}_6^-$), 2-methylglyceric acid sulfate ($\text{C}_4\text{H}_7\text{SO}_7^-$), isoprene epoxydiols sulfate ($\text{C}_5\text{H}_{11}\text{SO}_7^-$), and benzyl (or methyl phenyl) sulfate ($\text{C}_7\text{H}_7\text{SO}_4^-$) (Froyd et al., 2010; Hatch et al., 2011a; Ma et al., 2014), were not detected by SPAMS measurements taken in Beijing winter. The production of organosulfates is enhanced by increased aerosol acidity (Surratt et al., 2010; Hatch et al., 2011b; Riva et al., 2016), whereas the relatively high pH values of about 4 to about 5 for winter haze aerosols in northern China may represent a limiting factor (Song et al., 2018).

3.3 HMS is likely the major OS species

Since the only known source of HMS ($\text{CH}_2(\text{OH})\text{SO}_3^-$) is the nucleophilic addition of HSO_3^- and SO_3^{2-} to HCHO in aqueous solutions (Boyce and Hoffmann, 1984) (Fig. 3a; see Sect. 2), the dominance of HMS in OS can explain the excellent correlation found between OS and AWC (Fig. 2c). The other hydroxyalkylsulfonate species are estimated to be less important than HMS, according to the laboratory experimental data from Hoffmann and colleagues (Olson and Hoff-

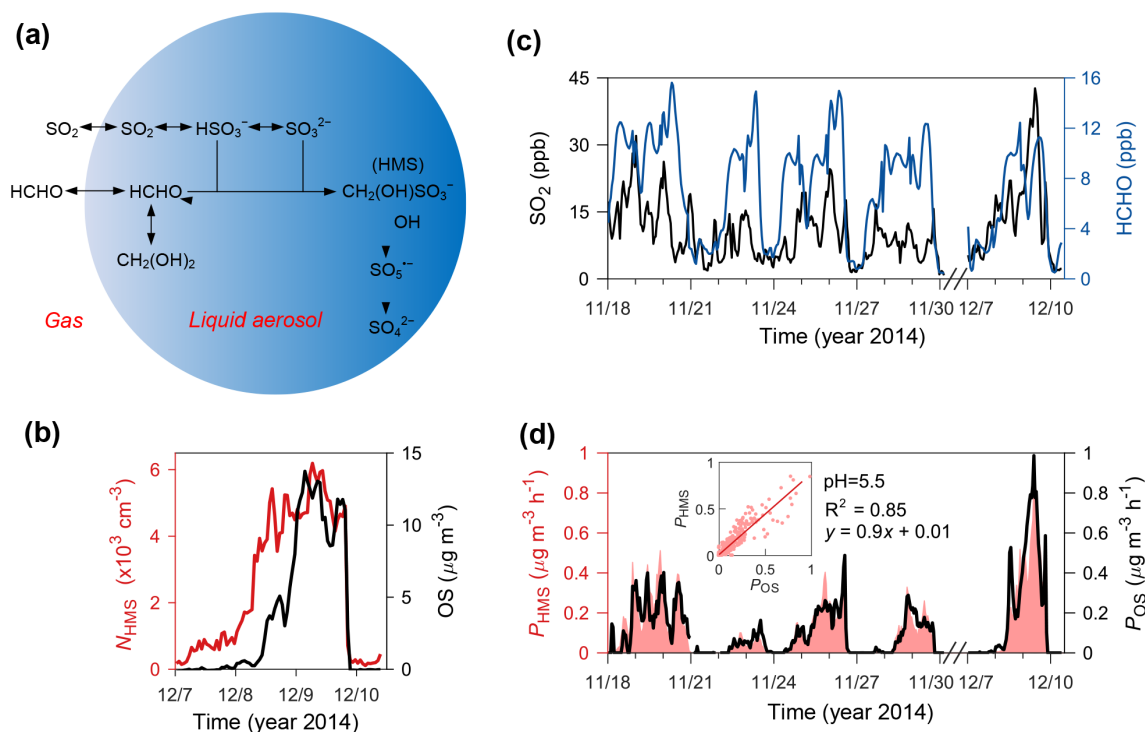


Figure 3. Production and existence of HMS in Beijing winter haze aerosols. **(a)** Schematic of heterogeneous HMS chemistry in northern China winter haze. **(b)** N_{HMS} (left, red line) and OS concentrations (right, black line). N_{HMS} was only available for a haze episode in December 2014 due to instrumentation constraints. **(c)** Gas-phase concentrations of observed SO_2 (left, black line) and modeled HCHO (right, blue line). **(d)** P_{HMS} (left, pink-shaded area) and P_{OS} (right, black line). The pink-shaded area shows the uncertainty in P_{HMS} due to the estimated range of pH (4.1–5.5). The inserted figure indicates the linear correlation of P_{HMS} and P_{OS} at a pH of 5.5.

mann, 1989) and the abundance of different aldehydes in the atmosphere (Sect. S3).

Mass concentrations of HMS have been observed to be low, on the order of $0.01 \mu\text{g m}^{-3}$, during several field campaigns in the United States, Germany, and Japan (Dixon and Aasen, 1999; Suzuki et al., 2001; Scheinhardt et al., 2014). However, the heterogeneous production of HMS can be fast during winter haze periods in northern China because of a moderately acidic pH of aerosol water, high AWC, high precursor (SO_2 and HCHO) concentrations, and low temperature. First, laboratory experiments have indicated that HMS production rates increase rapidly with pH, responding mainly to the dependence of SO_3^{2-} (a more efficient nucleophile than HSO_3^-) on pH (Boyce and Hoffmann, 1984; Kok et al., 1986). Values of aerosol water pH of about 4 to 5 obtained during the NCP winter haze events (Song et al., 2018) are 2 to 3 units higher than typically found in North America and Europe (Guo et al., 2017a), implying a factor of $> 10^4$ enhancement in HMS production rates. Second, the AWC during winter haze periods (on the order of $100 \mu\text{g m}^{-3}$) is among the highest in the world (Nguyen et al., 2016), providing a reactor to facilitate aqueous reactions. Third, concentrations of both precursor gases are relatively high. Gaseous HCHO has been measured to be about 6 ppb on average in

Beijing winter and increases on haze days (Rao et al., 2016). Although emissions of SO_2 have rapidly declined, especially since the implementation of the National Air Pollution Prevention and Control Action Plan in 2013, its concentrations in the NCP remain much higher than in many other parts of the world (Shao et al., 2018). Last, low temperature in winter increases the solubility of precursor gases in water (Sander, 2015) and thus enhances HMS production rates. The reaction rate constants for HMS production decrease at low temperature but to a lesser extent (Boyce and Hoffmann, 1984).

In order to evaluate whether HMS production was fast enough to account for the identified OS, we calculated the rate for HMS production in aerosol water (P_{HMS}) and compared this with the apparent heterogeneous reaction rate that would be required to produce the identified OS (P_{OS}). As described in Sect. 2, P_{HMS} calculations involved concentrations of gaseous SO_2 and HCHO (Fig. 3c), Henry's law constants, AWC and pH (95 % confidence interval: 4.1–5.5), and reaction rate constants from laboratory experiments. HCHO concentrations simulated by the WRF-Chem air quality model ($5 \times \text{EMIS}$ scenario; see Sect. 2) were used because its measurements were available only in December. The modeled HCHO was well correlated with its measured values ($r = 0.8$, $P < 0.001$) but was biased low by $\sim 20\%$ (Fig. 4). P_{HMS}

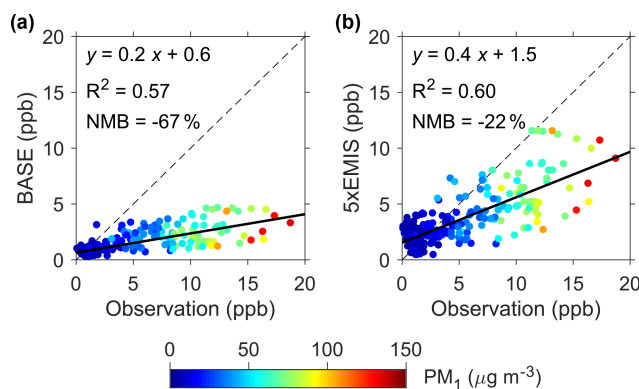


Figure 4. Comparison of modeled and observed HCHO concentrations. (a) BASE scenario. (b) $5 \times$ EMIS scenario. The dots are colored according to PM_{10} concentrations. Model results from WRF-Chem are shown.

was most sensitive to particle acidity and increased rapidly with pH, becoming comparable to P_{OS} when using the upper limit of pH (5.5) (Fig. 3d). P_{HMS} calculated here was expected to be conservative. Henry's law constants and kinetic data were obtained in relatively dilute solutions, while aerosol water constitutes a concentrated electrolyte solution. The high ionic strength of aerosol water (~ 11 M during haze periods) may strongly increase formaldehyde solubility (Toda et al., 2014) and may further enhance kinetic rates for HMS production (Sect. S4). Gaseous HCHO concentrations used in the calculations were also biased low. It is very likely that the actual P_{HMS} was comparable to P_{OS} at a pH below 5.5, within the uncertainty range of the calculated aerosol water pH. Note that the production of HMS was a minor sink of HCHO because the corresponding lifetime of ~ 4 days was greater than that of photolysis and oxidation by OH (~ 1 day in Beijing winter).

Our field measurements with SPAMS confirmed the existence of HMS in winter haze aerosols (Fig. 3b). Individual particles containing HMS were identified by the characteristic mass-to-charge ratio $m/z -111$ ($\text{CH}_2(\text{OH})\text{SO}_3^-$) in the SPAMS mass spectra (Whiteaker and Prather, 2003). The observed number concentration of HMS-containing particles (N_{HMS}) was closely correlated with AWC ($r = 0.86$, $P < 0.001$), supporting the production of HMS in aerosol droplets. A good relationship was also found between N_{HMS} and the identified OS from HR-AMS (Fig. 3b). Although the SPAMS data showed a significant percentage ($\sim 10\%$ during haze periods) of HMS-containing particles in the total particle counts, a quantitative estimate of HMS mass concentration is not available here because HMS may be fragmented into smaller ions, such as HSO_3^- and SO_3^- , depending on the counterions in particles (i.e., matrix effects) (Neubauer et al., 1997; Whiteaker and Prather, 2003). These ions coexist with the HMS peak in the SPAMS mass spectra (Fig. S7).

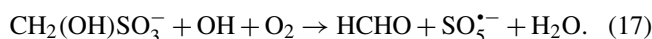
3.4 Implications of heterogeneous HMS chemistry

We have shown above in Beijing winter haze aerosols that a significant fraction of the missing sulfate based on HR-AMS measurements may be attributed to OSs, which likely exist primarily as HMS and are misidentified as inorganic sulfate by the standard HR-AMS data analysis. If HMS is assumed to represent the only OS compound, we estimated that it may account for about one-third of the missing sulfate in Beijing winter haze aerosols (Fig. S8). Interestingly, HMS would also likely be misidentified as inorganic sulfate (SO_4^{2-}) with typical ion chromatography (IC) analysis, another common method used to determine aerosol chemical compositions. In fact, nearly all of the particulate sulfate measurements in northern China winter haze have been made using these two techniques (He et al., 2014, 2018; Cheng et al., 2016; Wang et al., 2016; Li et al., 2017a). For anion detection in IC, the pH of the carrier fluid (known as eluent, a solution of KOH, NaOH, NaHCO_3 , etc.) is usually greater than 9 (Wang et al., 2005; Cao et al., 2012; Liu et al., 2016; Han et al., 2017). HMS is unstable under such an alkaline environment and dissociates rapidly into SO_3^{2-} and HCHO (Seinfeld and Pandis, 2016):



The characteristic time for HMS dissociation at $\text{pH} > 9$ is less than 1 min (Seinfeld and Pandis, 2016), much less than the retention time of SO_4^{2-} . The product SO_3^{2-} can be rapidly oxidized to SO_4^{2-} by oxidants (e.g., O_3 and H_2O_2) either generated or dissolved in aqueous extracts.

As described in Sect. 2.6, HMS should exist as the $\text{CH}_2(\text{OH})\text{SO}_3^-$ anion in wet aerosols and may form salts with ammonium or other cations when aerosol particles dry out. A possible fate of HMS is to be oxidized by aqueous OH radicals producing peroxy sulfate radicals ($\text{SO}_5^{\bullet-}$) (HMS is resistant to H_2O_2 and O_3) (Olson and Fessenden, 1992):



$\text{SO}_5^{\bullet-}$ is an intermediate in the free-radical chain reactions oxidizing SO_2 to SO_4^{2-} , and for each attack of OH on HMS, multiple SO_4^{2-} ions are produced (Fig. S9). Importantly, an HCHO molecule is released by Eq. (17), suggesting that this reaction pathway does not result in net consumption of HCHO and that HMS serves as a temporary reservoir of tetravalent sulfur. We speculate from the diurnal patterns of HMS production rates (P_{HMS}) and the identified OS concentrations that the oxidation of HMS by OH is likely to occur during daytime (Tan et al., 2018) (Fig. S9). But the rate of Eq. (17) should be relatively slow when compared with that of Eqs. (10)–(11) because a significant level of HMS is expected to reside in the haze aerosol particles. A quantitative rate estimation for this pathway, however, is difficult because aqueous OH is short-lived and it can be derived as a result of uptake from the gas phase or be generated or scavenged in the condensed phase (Jacob, 1986; Ervens et al., 2014).

3.5 Future research needs

This study points to a potentially important role of heterogeneous HMS chemistry in explaining the missing-sulfate problem during Beijing winter haze episodes. HMS has also been suggested to promote new particle formation by stabilizing sulfuric acid clusters (Li et al., 2018a). Although our field measurements and data interpretation focus on Beijing, this chemical mechanism should be important throughout the NCP because winter haze pollution is regional, as indicated by the distribution of SO_2 and HCHO (Fig. S10). Different from many other proposed pathways for sulfate production, HMS chemistry has a characteristic reaction product. More accurate quantification of HMS (e.g., using capillary electrophoresis and ion pairing chromatography; Munger et al., 1986; Scheinhardt et al., 2014) in future field studies is essential to improve our understanding of this mechanism. In addition, three-dimensional chemical transport model studies should be conducted to further explore the HMS formation pathways and the associated uncertainties (e.g., pH values). The modeling simulations may also demonstrate whether significant amounts of HMS can be formed in cloud droplets before being transported to the ground level (Eck et al., 2012; Li et al., 2014). This study reveals the unappreciated role of HCHO in Chinese haze through forming the complex HMS with SO_2 , and it should be noted that HCHO also serves as a critical source of HO_x ($\text{OH} + \text{HO}_2$) radicals by photolysis (Rao et al., 2016) and as a carcinogen (Zhu et al., 2017). In spite of its importance, our knowledge of the sources and chemical processes of HCHO during northern China winter haze events remains limited. Further research should be conducted to elucidate HCHO sources in the northern China winter and to design targeted mitigation measures.

4 Summary

Combining field measurements and model calculations, we propose a potentially important chemical mechanism, heterogeneous HMS chemistry, for secondary aerosol formation during northern China winter haze episodes. This mechanism involves the production of HMS by HCHO and SO_2 in aerosol water, which is favored under northern China winter haze conditions due to several factors, including high aerosol water content, a moderately acidic pH, high gaseous precursor levels, and low temperature. More field, laboratory, and modeling studies are needed in order to elucidate this chemical mechanism and to better understand the emission sources and atmospheric chemical processes impacting HCHO under winter haze conditions.

Data availability. All data supporting this study are available in this article and its Supplement or from the corresponding authors upon request.

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/acp-19-1357-2019-supplement>.

Author contributions. SS, YS, and MBM designed and led the study. YS, WX, DRW, and JTJ contributed to HR-AMS measurement and data analysis. ML, ZZ, CC, YB, and YL collected and analyzed SPAMS measurement data. YW, WP, and XX performed HCHO measurements. MG, NL, YW, and SW provided air quality model results. YZ, LZ, JWM, and DJ contributed to data interpretation. SS wrote the paper with input from all co-authors.

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

Special issue statement. This article is part of the special issue “Multiphase chemistry of secondary aerosol formation under severe haze”. It is not associated with a conference.

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