

RESEARCH LETTER

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Key Points:

- Chemistry models have been unable to explain high levels of observed particulate sulfur, usually interpreted as sulfate, during Beijing winter haze events
- Typical measurement systems for ambient particulates easily misinterpret hydroxymethane sulfonate (HMS) as sulfate
- HMS may comprise a large portion of particulate sulfur during extreme haze, implying that HCHO, rather than SO<sub>2</sub>, would be a limiting factor for such events

Supporting Information:

- Supporting Information S1
- Data Set S1

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# Contribution of Hydroxymethane Sulfonate to Ambient Particulate Matter: A Potential Explanation for High Particulate Sulfur During Severe Winter Haze in Beijing

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**Abstract** PM<sub>2.5</sub> during severe winter haze in Beijing, China, has reached levels as high as 880 μg/m<sup>3</sup>, with sulfur compounds contributing significantly to PM<sub>2.5</sub> composition. This sulfur has been traditionally assumed to be sulfate, although atmospheric chemistry models are unable to account for such large sulfate enhancements under dim winter conditions. Using a 1-D model, we show that well-characterized but previously overlooked chemistry of aqueous-phase HCHO and S(IV) in cloud droplets to form a S(IV)-HCHO adduct, hydroxymethane sulfonate, may explain high particulate sulfur in wintertime Beijing. We also demonstrate in the laboratory that methods of ion chromatography typically used to measure ambient particulates easily misinterpret hydroxymethane sulfonate as sulfate. Our findings suggest that HCHO and not SO<sub>2</sub> has been the limiting factor in many haze events in Beijing and that to reduce severe winter pollution in this region, policymakers may need to address HCHO sources such as transportation.

**Plain Language Summary** Air pollution in Beijing is especially severe in winter, when concentrations of tiny particles in the air can reach concentrations over 20 times greater than the safe level recommended by the World Health Organization. In these severe pollution episodes, observations show that a large portion of the particles is made up of sulfur. Scientists have assumed that this sulfur is in the form of sulfate; however, computer simulations of air pollution chemistry have been unable to explain such high sulfate concentrations. We show with a simple computer simulation that a large portion of the sulfur in these haze episodes may, instead of sulfate, actually be a molecule called hydroxymethane sulfonate, which is formed by a chemical reaction in cloud droplets of dissolved formaldehyde with dissolved sulfur dioxide. We also show in laboratory experiments that the machines typically used for determining the chemical composition of particles easily misinterpret hydroxymethane sulfonate as sulfate. Importantly, the chemistry that produces hydroxymethane sulfonate is usually limited by formaldehyde, implying that reductions in sulfur dioxide would be ineffective at reducing severe haze. Instead, focusing future emissions reductions on formaldehyde emissions may be an effective way to curtail severe winter haze in the Beijing area.

## 1. Introduction

Air pollution in China imposes a significant burden on human health and welfare, with over 1 million deaths per year attributed to high levels of fine particles (PM<sub>2.5</sub>, particulate matter with diameter less than 2.5 μm; Cohen et al., 2017). Beijing and the surrounding area of the North China Plain (NCP) frequently experience episodes of severe winter haze when PM<sub>2.5</sub> levels exceed 200 μg/m<sup>3</sup> (e.g., Rao et al., 2016; Y. Wang et al., 2014; Zheng et al., 2015). Measurements made during these haze episodes often show large enhancements in particulate sulfur compounds, which have been interpreted as sulfate (Wang et al., 2012; Y. Wang et al., 2014; Wang et al., 2016). Due to low oxidant conditions, however, chemical transport models relying on

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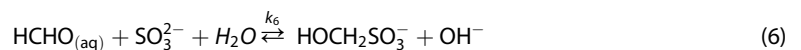
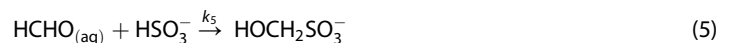
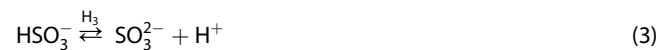
conventional photochemical oxidation pathways for sulfur dioxide (SO<sub>2</sub>) often cannot reproduce the enhanced particulate sulfur seen during these haze events (Cheng, Zheng, et al., 2016; Y. Wang et al., 2014; Wang et al., 2016; Zhang et al., 2015).

Here we propose that enhanced particulate sulfur in some winter haze events may follow from the aqueous phase reaction of sulfite or bisulfite with formaldehyde (HCHO) to form the adduct hydroxymethane sulfonate (HMS; Boyce & Hoffmann, 1984; Kok et al., 1986; Kovacs et al., 2005; Olson & Hoffmann, 1986). Indeed it would be challenging to show that HMS is not present under conditions typical of wintertime Beijing. We also demonstrate in the laboratory that commonly used measurement techniques easily misinterpret HMS as sulfate.

During severe winter haze events in the NCP, PM<sub>2.5</sub> concentrations climb rapidly within the span of a few hours (Ji et al., 2014). Meteorological conditions common to these events include low surface wind speeds and a shallow planetary boundary layer, which limit ventilation of pollutants (Ji et al., 2014; Quan et al., 2014; H. Wang et al., 2014; X. J. Zhao et al., 2013). In addition, levels of relative humidity tend to be high (60%–90%; Ji et al., 2014; Quan et al., 2014; Zheng et al., 2015). Aerosol optical depths during these events are typically in excess of 1 and thus strongly attenuate incoming solar radiation (Bi et al., 2014; Li et al., 2013), which is already low during wintertime.

SO<sub>2</sub> oxidation in the troposphere mainly occurs via OH in the gas phase and via H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> in the aqueous phase. Replenishment of these oxidants depends in large part on the availability of sunlight (Alexander et al., 2009; Quan et al., 2014; Wang et al., 2016), but both observations and modeling studies reveal especially low levels of O<sub>3</sub> and other oxidants during winter haze events in the NCP (Ji et al., 2014; Quan et al., 2014; Zheng et al., 2015). Traditional chemical schemes in models relying on SO<sub>2</sub> oxidation to form sulfate thus consistently underestimate particulate sulfur during severe haze events, with models showing mean biases of –40 to –50 μg/m<sup>3</sup> (Gao et al., 2016; Y. Wang et al., 2014; Zhang et al., 2015). Models also underestimate the relative contribution of particulate sulfur to total PM<sub>2.5</sub> during haze events: observations show particulate sulfur comprising ~20%–30% of total dry PM<sub>2.5</sub> mass, while models predict contributions of just ~4%–15% (Gao et al., 2016; Y. Wang et al., 2014). Several chemical mechanisms have been suggested to address this shortfall—for example, aqueous phase oxidation of SO<sub>2</sub> by NO<sub>2</sub> (Cheng, Zheng, et al., 2016; Wang et al., 2016), but some of these appear problematic (supporting information S1).

An alternative pathway that may explain the high particulate sulfur observed during winter haze events is the reaction of dissolved bisulfite (HSO<sub>3</sub><sup>–</sup>) and sulfite (SO<sub>3</sub><sup>2–</sup>) with HCHO to form HMS (Boyce & Hoffmann, 1984; Kok et al., 1986; Kovacs et al., 2005; Munger et al., 1983; Olson & Hoffmann, 1986). In this pathway, which does not require oxidative conditions, dissolved SO<sub>2</sub> dissociates to form bisulfite and sulfite, which then combine with dissolved formaldehyde to form HMS (HOCH<sub>2</sub>SO<sub>3</sub><sup>–</sup>):



HMS formation is known to occur in fog and cloud water, especially under conditions of high SO<sub>2</sub> and HCHO, cold temperatures, and low concentrations of oxidants that would typically compete with HMS formation (Munger et al., 1983, 1986). Such conditions are often present during severe haze episodes in winter in Beijing (Ji et al., 2014; Rao et al., 2016), as we describe below. HMS would also form in aerosol water; however, since aerosol liquid water content is usually multiple orders of magnitude less than

cloud liquid water content, formation of HMS in aerosol water should be insignificant as long as clouds occasionally appear. The high levels of HCHO necessary for HMS formation have been observed in Beijing in winter (Y. Zhang et al., 2014; Rao et al., 2016). For example, mean HCHO in winter 2014 was  $5.51 \pm 3.90$  ppb, with peak concentrations of 14–17 ppb (Rao et al., 2016). The high level of wintertime HCHO in Beijing, which occurs under conditions of low photochemical activity, has been attributed largely to primary anthropogenic emissions (Chen et al., 2016; Rao et al., 2016). Especially important is the transportation sector, which is estimated to account for ~62% of HCHO emissions in the Beijing area (Li et al., 2017). Wintertime concentrations of  $\text{SO}_2$  in Beijing are also high, at ~50 ppb  $\text{SO}_2$  (Jiang et al., 2015; Rao et al., 2016; Y. Wang et al., 2014).

HMS formation also requires moderate cloud pH in the range of ~4–6 (Munger et al., 1984, 1986; Olson & Hoffmann, 1986). Measurements from fog/low cloud water in Beijing showed a pH of 5.2–6.2 between 1999 and 2006 (Jiang et al., 2009). More recent observations infer an aerosol pH of ~4–5 during haze events (Guo et al., 2017; Liu et al., 2017; Song et al., 2018), which implies a somewhat higher pH in cloud droplets due to ion exchange between cloud and aerosol during cloud processing (Ervens, 2015; Liu et al., 2017). In addition, precipitation in Beijing reveals pH values of ~5.5–6 (Huo et al., 2010; Tang et al., 2005; Zhu et al., 2016). These observations together suggest that cloud pH in Beijing likely occurs in the 5–6 range.

Chemical loss of HMS occurs primarily by reaction with aqueous OH radical and with aqueous  $\text{OH}^-$  (Munger et al., 1986; Olson & Fessenden, 1992). Concentrations of OH radical are expected to be low during winter haze events due to diminished sunlight, implying that primary chemical loss of HMS is via  $\text{OH}^-$ , which, like HMS production, is dependent on pH (equation (6)). Assuming that reaction with  $\text{OH}^-$  is the only sink yields an HMS lifetime of about 1 month at pH 4, about a week at pH 5, and a few hours at pH 6 (Munger et al., 1986). This result suggests that HMS is stable in the aerosol phase after cloud droplets have evaporated, given an aerosol pH of ~4.5 (Guo et al., 2017; Liu et al., 2017). With high levels of ammonia common in Beijing (Guo et al., 2017), HMS in the particle phase could exist as a salt with  $\text{NH}_4^+$  as the counter ion. Dust could also provide counter ions for an HMS salt (Zhang et al., 2015).

Given the observed high levels of HCHO and  $\text{SO}_2$ , HMS should be formed during Beijing winter haze conditions when clouds top the boundary layer. That HMS has not to date been reported may be because HMS, which is in the form of S(IV), has been misinterpreted in measurements as sulfate (S(VI)). In ion chromatography, columns typically have trouble separating HMS and sulfite (Dixon & Aasen, 1999) and separating sulfite and sulfate (Cao et al., 2014; Cheng, He, et al., 2016; Wang et al., 2005). In the most commonly employed types of aerosol mass spectroscopy, aerosol particles are first evaporated thermally with lasers or other methods, which can result in the decomposition of molecules such as HMS. Subsequent ionization can result in fragmentation so that observation of the parent component is extremely challenging. Thus, especially for common AMS and single-particle methods of measuring aerosol, only sulfur-containing fragments are typically identified. Not properly accounting for the fragmentation of HMS could lead to its misidentification (Neubauer et al., 1996; Whiteaker & Prather, 2003).

In this work, we first construct a simple 1-D model with well-known chemical reactions to determine whether HMS may help explain the high concentrations of particulate sulfur observed during severe winter haze. We simulate two time periods characterized by haze and for which we have speciated measurements of  $\text{PM}_{2.5}$ : December 2011 and January 2013. We also explore the factors that control HMS production by analyzing the model timescales for different processes and conducting a series of sensitivity tests with the model. Our use of a simple model allows us to bypass the uncertainties in emissions and transport inherent in 3-D chemistry models and to focus on HMS production.

## 2. Data and Methods

We develop a simple 1-D model for tracking cloud and aerosol chemistry in Beijing, following the approach of Jacob et al. (1989). We focus on 7–31 December 2011 and 9–17 January 2013, due to the availability of speciated  $\text{PM}_{2.5}$  observations at these times (Cao et al., 2014; Cheng, He, et al., 2016; Y. Wang et al., 2014). The model spans the boundary layer (~700 m), with four vertical layers and eddy-driven diffusion allowing transport between layers. Fresh air mixes into the top layer, and chemical production and loss occurs in each layer in the presence of cloud water. We track three chemical species in the gas, aerosol, and cloud phase—HMS,

SO<sub>2</sub>, and HCHO. Details on the setup of the 1-D model are described in the supporting information (sections S2 and S3).

Cloud pH and gas-phase concentrations of HCHO and SO<sub>2</sub> are constrained in the model using measurements. For the base case scenario, we specify HCHO concentrations at 5.5 ppb, based on surface observations in winter 2014 (Rao et al., 2016). We also specify SO<sub>2</sub> at 50 ppb, based on observations in January 2013 (Y. Wang et al., 2014). We select cloud pH value of 5 for the base case, based on the constraints described in section 1 (Jiang et al., 2009; Liu et al., 2017; Zhu et al., 2016). By varying pH and HCHO and SO<sub>2</sub> concentrations in a series of simulations, we test the sensitivity of HMS formation to these three parameters. To validate model results, we use daily mean measurements of particulate sulfur. These measurements, taken by ion chromatography at Tsinghua University in Beijing, were made during December 2011 (Cheng, He, et al., 2016) and January 2013 (Cao et al., 2014; Y. Wang et al., 2014). To track trends in Beijing pollution, we also use observations of total PM<sub>2.5</sub> and SO<sub>2</sub> spanning January 2013 to April 2018 from a network of 12 monitoring stations throughout the city (Jiang et al., 2015).

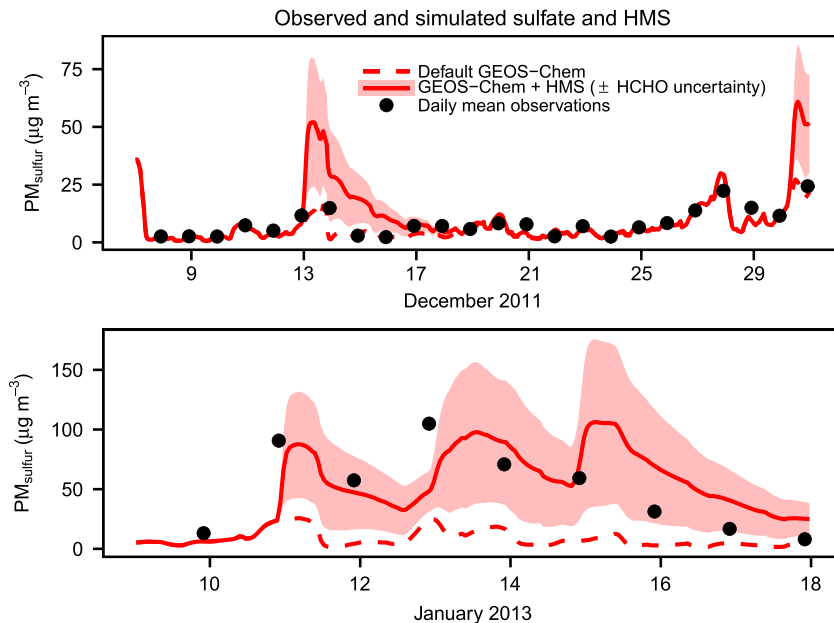
To simulate conditions for the two haze periods without HMS chemistry, we use the GEOS-Chem chemical transport model version 11-01 (Alexander et al., 2012; Park et al., 2004) driven by MERRA-2 meteorology (Gelaro et al., 2017) with the Multi-resolution Emission Inventory for China (MEIC; Li et al., 2017), as described in section S4.

In support of our model simulations, we conduct laboratory experiments to test whether typical ion chromatography techniques can, in fact, distinguish between HMS and sulfate. We prepare solutions with varying levels of HMS, sulfate, and sulfite and use two different ion chromatography systems (section S5).

### 3. Results

Observations of particulate sulfur during December 2011 reveal both clean and polluted periods, with daily mean particulate sulfur ranging from ~2 to 24  $\mu\text{g}/\text{m}^3$  with a mean of 8.5  $\mu\text{g}/\text{m}^3$  (Figure 1). By comparing the observations to the sulfate concentrations simulated by GEOS-Chem, we can estimate the amount of particulate sulfur that needs to be explained by HMS production or by some other mechanism. We find that GEOS-Chem produces a good match with observed particulate sulfur in this month, with a daily mean bias of  $-2.0 \mu\text{g}/\text{m}^3$ . In the base case 1-D model, HMS is near zero for most of the month except for the cloudy periods (13–17 December and 30 December), when it averages 13  $\mu\text{g}/\text{m}^3$ . During these intervals, cloud liquid water content averages  $\sim 30 \mu\text{L}/\text{m}^3$ , initiating HMS production. Figure 1 shows what we call *total particulate sulfur*: the sum of the GEOS-Chem sulfate and HMS from the 1-D model. To approximate how HMS may be interpreted in the observations, which assume that all particulate sulfur is sulfate, we treat HMS here as having the same molecular weight as sulfate. The daily mean bias of total particulate sulfur with observations over the December 2011 observation period is  $+2.1 \mu\text{g}/\text{m}^3$  ( $-0.88$  to  $+5.0 \mu\text{g}/\text{m}^3$ ). However, adding HMS to GEOS-Chem sulfate reduces the modeled match with observations during the first and last episodes, with daily biases during these cloudy periods ranging from  $+1.58$  to  $+23.8 \mu\text{g}/\text{m}^3$ . The biases likely arise from uncertainty in HCHO and in clouds (section S3). On 27 December, HMS is near zero and the peak in total particulate sulfur matches the peak in GEOS-Chem sulfate.

A different picture emerges for January 2013. January 2013 was cloudier than December 2011, with peaks in MERRA-2 low cloud liquid water path ranging from 33 to 116  $\text{g}/\text{m}^2$ , compared to a peak of just 34.2  $\text{g}/\text{m}^2$  for December 2011 (Figure S1). The time series of observed particulate sulfur for this month shows a mostly polluted period with particulate sulfur ranging from ~8 to 105  $\mu\text{g}/\text{m}^3$ , with a mean of 50  $\mu\text{g}/\text{m}^3$ . There are peaks in daily mean total particulate sulfur of 90.8  $\mu\text{g}/\text{m}^3$  on 10 January and 105.0  $\mu\text{g}/\text{m}^3$  on 12 January (Figure 1). Mean particulate sulfur is significantly higher for January 2013 than for December 2011. GEOS-Chem cannot capture either the variability or the large observed values ( $>30 \mu\text{g}/\text{m}^3$ ) of particulate sulfur for January 2013. The daily mean bias between the GEOS-Chem and surface observations is  $-42.1 \mu\text{g}/\text{m}^3$ . Adding the time series of HMS calculated with the 1-D model to the GEOS-Chem sulfate greatly improves the model match with observations. Simulated total particulate sulfur for January 2013 has a daily mean bias against observations of just  $-0.01 \mu\text{g}/\text{m}^3$  ( $-30.5$  to  $+29.9 \mu\text{g}/\text{m}^3$ ). Peaks in daily mean total particulate sulfur in the model are  $\sim 66$ – $90 \mu\text{g}/\text{m}^3$  ( $\sim 27$  to  $150 \mu\text{g}/\text{m}^3$ ), compared to  $\sim 6$ – $12 \mu\text{g}/\text{m}^3$  of sulfate in GEOS-Chem.



**Figure 1.** Time series of observed and simulated PM components for December 2011 and January 2013 in Beijing. The black points represent daily mean observed particulate sulfur concentrations measured at Tsinghua University, centered at 10 p.m. local time, or midway between the start and end times of the daily filter measurements (Cao et al., 2014). The red dashed line indicates hourly sulfate concentrations from GEOS-Chem, and the solid red line represents the hourly sum of GEOS-Chem sulfate and HMS concentrations generated by the 1-D model of HMS chemistry for a cloud pH of 5, and monthly mean concentrations of 50 ppb SO<sub>2</sub> and 5.5 ppb HCHO as boundary conditions for deriving implied emissions to approximate January 2013 conditions. Red shading denotes the range of HMS values derived from simulations using the observed uncertainty range for winter mean HCHO in 2014 in Beijing (Rao et al., 2016). Scale in y axes differs between the two panels.

Peaks in hourly mean total particulate sulfur in the model are  $\sim 87\text{--}106\ \mu\text{g}/\text{m}^3$  ( $\sim 36$  to  $176\ \mu\text{g}/\text{m}^3$ ), compared to  $\sim 9\text{--}26\ \mu\text{g}/\text{m}^3$  of sulfate in GEOS-Chem.

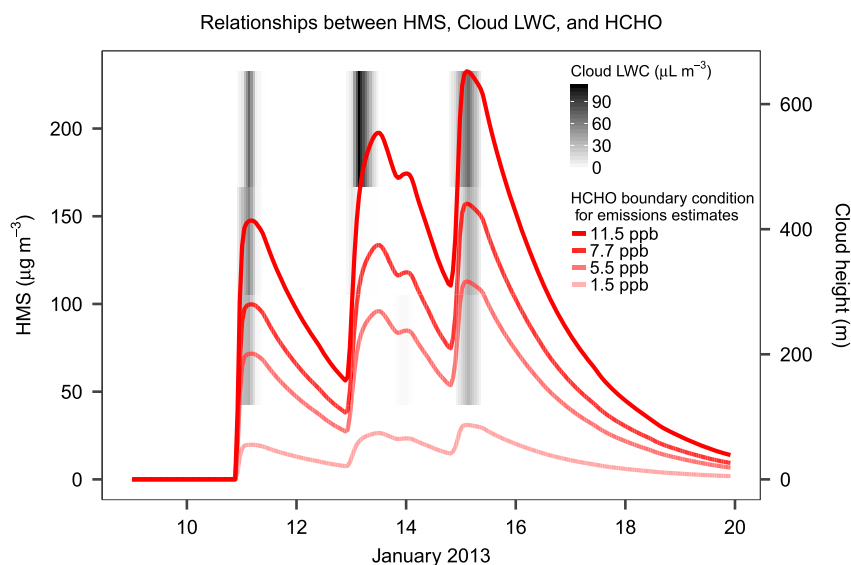
Further supporting our hypothesis regarding HMS, laboratory experiments show that HMS and sulfate cannot be well separated by typical ion chromatography columns (section S5 and Figure S2).

### 3.1. Factors Controlling HMS Production

To explain the factors controlling HMS production, we consider the timescales of the processes involved and identify the rate-limiting factors and reactants. Reactions (5)–(6) have a 1:1 ratio for aqueous-phase reactants HCHO and SO<sub>2</sub>, so these reactions will deplete atmospheric HCHO at the same rate as SO<sub>2</sub>. Because HCHO concentrations in wintertime Beijing are an order of magnitude less than SO<sub>2</sub>, HCHO in the presence of clouds is depleted long before SO<sub>2</sub>, making HCHO the limiting reactant; emissions are not fast enough to replenish HCHO concentrations. In other words, if we assume that the HCHO lifetime is less than the cloud lifetime, then the availability of atmospheric HCHO is what controls HMS production.

The timescale for eddy diffusion from the surface to model layers 2–3 ( $\sim 200\text{--}400$  m) is  $\sim 2$  hr, while the duration of low clouds in MERRA-2 for December 2011 and January 2013 ranges between 7.5 and 15 hr. For conditions in the 1-D model base case at pH  $\sim 5$ , HCHO has a lifetime against conversion to HMS of  $< 1$  hr, signifying that HCHO is effectively titrated within the cloud on timescales faster than boundary layer mixing and that increases in cloud pH would not affect total HMS. Since HCHO is limiting, changes in SO<sub>2</sub> should have little effect on HMS concentrations as long as SO<sub>2</sub> is in excess of HCHO, which is confirmed by sensitivity tests with the 1-D model (section S6 and Figure S3). Similarly, we find that increasing the modeled cloud pH above 4.5 has little effect on HMS yield (section S6 and Figure S3).

Once HCHO in the cloud is consumed, further HMS production is limited by eddy diffusion of HCHO from the surface. During December 2011 and January 2013, the interval between cloud events is on the order of days,



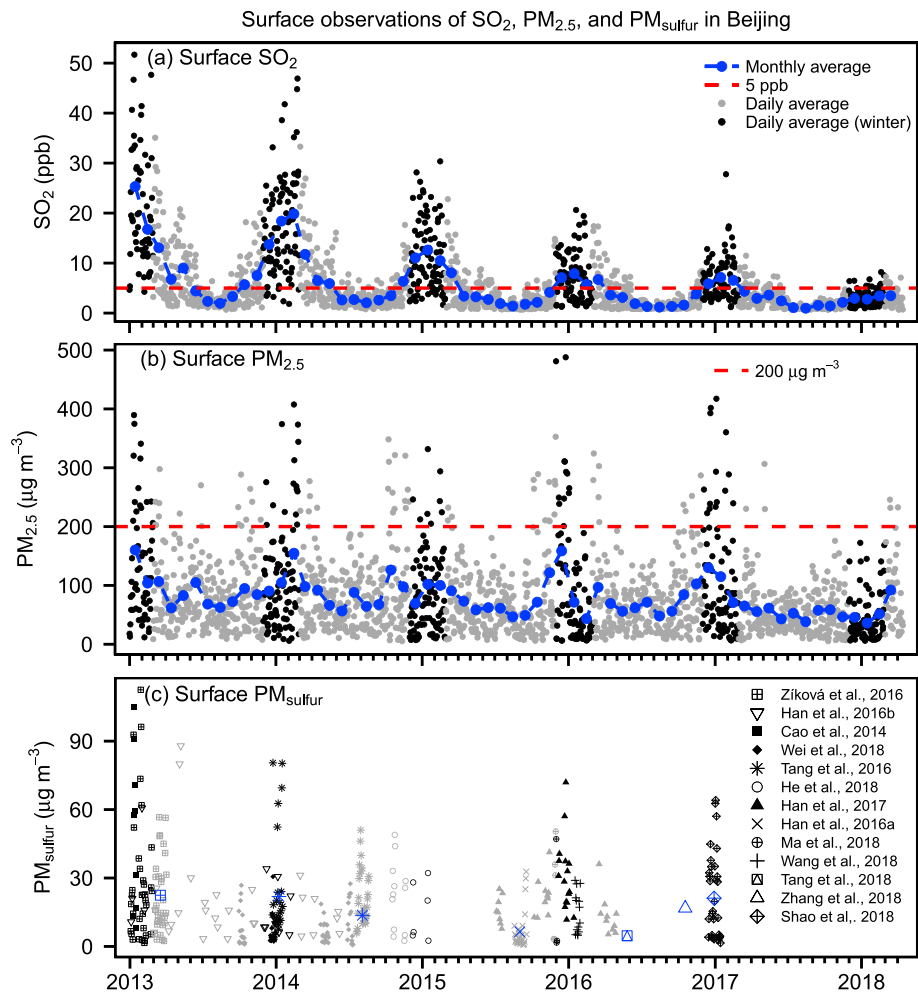
**Figure 2.** Effect of varying the mean surface HCHO concentration on modeled HMS production during January 2013 in Beijing. Red curves represent the time series of hourly surface HMS concentrations, with increasing darkness denoting increasing estimates of the mean HCHO surface concentrations during this time period, from 1.5 to 11.5 ppb. Black shading represents hourly average cloud liquid water content (LWC) in each layer from MERRA-2, with darker colors indicating greater LWC.

allowing HCHO to build up before the onset of cloudiness. HCHO prior to the onset of clouds is controlled in the model by a ventilation timescale of  $\sim 1\text{--}2$  days, and so its accumulated mass is generally much greater than that of HCHO entering the cloudy layer via eddy diffusion during the lifetime of the cloud, which is just  $\sim 7\text{--}15$  hr. As HCHO is depleted in clouds, surface HCHO continues to be taken up by the cloudy layer, driving down gas-phase concentrations. Figure S4 shows a sample time series of simulated HCHO for one set of assumptions.

Figure 2 shows the effect of varying the HCHO emissions in the model on HMS production; it also reveals the relationship between the onset of clouds and the timing of the HMS peaks, a key difference between December 2011 and January 2013 (Figure S1). Here we fix cloud pH at 5 and the  $\text{SO}_2$  surface boundary concentrations at 50 ppb for deriving emissions. We vary mean HCHO concentrations used in deriving the HCHO emissions from 1.5 to 11.5 ppb, within the range observed by Rao et al. (2016) for January and February 2014 in Beijing. The resulting HCHO emissions for January 2013 range from  $2.1 \times 10^{-11}$  to  $1.6 \times 10^{-10}$   $\text{kg m}^{-2} \text{s}^{-1}$ . The corresponding estimate in the MEIC inventory falls at the low end of this range at  $2.3 \times 10^{-11}$   $\text{kg m}^{-2} \text{s}^{-1}$  (Li et al., 2017). Figure 2 shows surface HMS concentrations rising rapidly over the course of 3–5 hr after cloud onset, as HCHO in the cloudy layer is converted to HMS. Continued HMS production occurs more slowly for the duration of the cloud, limited by eddy diffusion of HCHO into the cloudy layer, which has a timescale of 2 hr.

These rapid increases in HMS match the rapid increase in total  $\text{PM}_{2.5}$  observed during the January 2013 haze event (Ji et al., 2014). In the model 1 ppb of gas-phase HCHO yields  $\sim 5$   $\mu\text{g}/\text{m}^3$  of HMS. Thus, HMS peaks seen in the base case in Figure 1 require  $\sim 10\text{--}15$  ppb of available HCHO; such values of HCHO have been observed in wintertime Beijing, with average levels of  $\sim 5.5$  ppb (Rao et al., 2016). After 14–30 hr, the clouds completely disappear, and the HMS concentrations slowly fall as fresh air is mixed into the boundary layer. The magnitudes of the HMS peaks in the model roughly scale with the mean HCHO used in deriving HCHO emissions; for mean HCHO concentrations of 5.5 ppb, surface hourly HMS concentrations in the model peak at  $\sim 71\text{--}112$   $\mu\text{g}/\text{m}^3$ .

Observations of surface  $\text{SO}_2$  and total  $\text{PM}_{2.5}$  in Beijing during 2013–2018 also support our HMS hypothesis (Figure 3). Seasonal mean  $\text{SO}_2$  concentrations have decreased significantly in winter by 18 ppb in this time-frame, with values below  $\sim 5$  ppb in winter 2017–2018. In contrast, the number of extreme pollution days, defined as days with daily mean  $\text{PM}_{2.5} > 200$   $\mu\text{g}/\text{m}^3$ , reveals no significant trend over 2013 to 2018. Except



**Figure 3.** Time series of observed surface SO<sub>2</sub> and PM<sub>2.5</sub> concentrations in Beijing, averaged across 12 monitoring stations (Jiang et al., 2015), and of PM<sub>sulfur</sub> across 13 separate field studies using ion chromatography. Blue points indicate monthly means, while black points are daily means in winter and gray the daily means for other seasons. The horizontal dashed line in panel (a) corresponds to 5 ppb SO<sub>2</sub>, an estimate of the SO<sub>2</sub> concentration below which SO<sub>2</sub> becomes the limiting reactant for HMS production in winter by dropping below typical HCHO levels. In panel (b), the dashed line represents 200 µg/m<sup>3</sup>, which we define as the threshold for extreme haze. In panel (c), each shape corresponds to an individual field study.

for winter 2017–2018, each winter had 8–15 extreme pollution days. We hypothesize that concentrations of SO<sub>2</sub> may have fallen below those of HCHO in winter 2017–2018, limiting HMS production for the first time in this time series. Field studies from 2015–2016 and 2016–2017 winters also show high levels of particulate sulfur during haze, as much as 60 µg/m<sup>3</sup>, despite significant SO<sub>2</sub> reductions since 2013 (Figure 3).

#### 4. Discussion and Conclusion

Here we demonstrate that particulate sulfur in wintertime Beijing may occur as an S(IV)-HCHO adduct, hydroxymethane sulfonate (HMS), formed by reaction of aqueous-phase HCHO and S(IV) in cloud droplets. Indeed, it would be challenging to show that HMS is not produced during episodes of low cloud cover in winter, given typical levels of HCHO and SO<sub>2</sub> in Beijing. High levels of ambient ammonia likely allow HMS to persist as a salt with NH<sub>4</sub><sup>+</sup> as the counter ion. We find that modeled HMS, when added to GEOS-Chem sulfate, can successfully capture the magnitude of the observed severe haze of January 2013, when particulate sulfur, defined as the sum of HMS and sulfate, frequently exceeded 50 µg/m<sup>3</sup> and total PM<sub>2.5</sub> approached 900 µg/m<sup>3</sup>. (To facilitate comparison with existing observations, which have been interpreted as sulfate,

we treat HMS as having the same molecular weight as sulfate.) Previous studies have assumed that particulate sulfur during this episode was mainly composed of sulfate, but we show that typical measurement systems easily misinterpret HMS as sulfate.

We identify HCHO emissions and the onset of low cloud cover as key factors controlling HMS production in winter haze. We further show that HMS formation is relatively insensitive to SO<sub>2</sub> concentrations so long as SO<sub>2</sub> is in excess of HCHO; it is also insensitive to cloud pH at levels above 4.5. Our work stands in contrast to previous studies that have used novel sulfur oxidation mechanisms to explain high levels of observed particulate sulfur (Cheng, Zheng, et al., 2016; Wang et al., 2016). Biases in total particulate sulfur in our model likely arise from uncertainties in the timing of cloud events (section S3), liquid water content, and/or HCHO emissions. In the 1-D model, HMS chemistry leads to episodes of HCHO depletion. Such transient depletions do show up in observations for winter 2014, but not concurrently with large increases in PM<sub>2.5</sub> (Rao et al., 2016). We hypothesize that factors unaccounted for in the model—for example, spatial heterogeneity in clouds (Gautam & Singh, 2018), horizontal transport, or feedbacks between haze and boundary layer height (Ding et al., 2016; Li et al., 2010)—could slow the depletion of surface HCHO such that the clouds disappear before significant drawdown of surface HCHO. This issue could be further investigated with a 3-D chemical transport model. To further confirm the mechanism proposed here, HMS could be explicitly measured in Beijing haze by ion chromatography using columns designed to separate S(IV) and S(VI), with the addition of H<sub>2</sub>O<sub>2</sub> to oxidize sulfite in the sample prior to analysis (Dixon & Aasen, 1999). HMS could also be measured with a mass spectrometry system if the effects of evaporation/ionization on HMS can be properly accounted for (Whiteaker & Prather, 2003).

The dependence of HMS production on a cloud topped boundary layer implies that HMS chemistry is episodic. The role of HCHO in HMS production may help explain the continued occurrence of winter haze events despite observed reductions in SO<sub>2</sub>. The SO<sub>2</sub> column declined more than 50% over the NCP area between 2005 and 2015 (Krotkov et al., 2016), and surface observations show wintertime SO<sub>2</sub> decreasing by ~18 ppb since 2013. Although such reductions in SO<sub>2</sub> would reduce PM<sub>2.5</sub> under some circumstances, our results imply that SO<sub>2</sub> concentrations in Beijing in winter were typically too far in excess of HCHO for these emissions cuts to have an effect on HMS. We hypothesize that unless ambient SO<sub>2</sub> drops below ~5 ppb, policies such as the shutting of coal plants in the Beijing area and adoption of stricter SO<sub>2</sub> emissions controls (Schreifels et al., 2012; Y. Zhao et al., 2013) would be ineffective against severe haze. Policymakers may need instead to focus on quantifying and reducing sources of HCHO, such as from gasoline and diesel engines (Li et al., 2014). It is of interest that the winter of 2017–2018 marks the first time since at least the winter of 2012–2013 in which monthly average SO<sub>2</sub> in Beijing dropped below this 5 ppb threshold. This winter is also the first in which daily mean PM<sub>2.5</sub> never exceeded 200 µg/m<sup>3</sup>.

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