Environmental Science & Technology

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Article

Aerosol Water Content Drives Changes in Hydroxymethanesulfonate in Beijing Winter from 2015 to 2021

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Cite This: *Environ. Sci. Technol.* 2025, 59, 13903−13911

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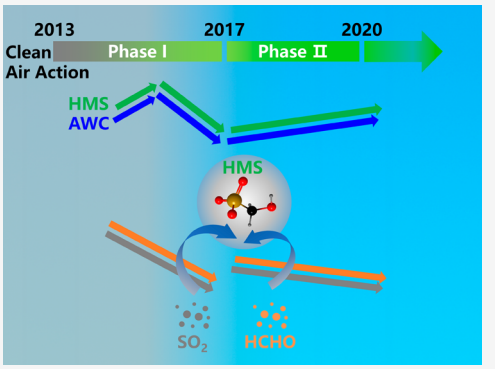
ABSTRACT: Hydroxymethanesulfonate (HMS) is an abundant secondary organosulfur aerosol during winter in the North China Plain, while the variation and affecting factors of HMS with implementing clean air actions remain unclear. Here, we conducted long-term field measurements in Beijing during the winter, including Phase I (2015−2017) and Phase II (2018−2021). Our results showed that HMS concentrations decreased significantly in Phase I, consistent with changes in $PM_{2.5}$, organic matter (OM), and sulfate, and showed an increasing trend in Phase II in contrast to the decreasing trend of $PM_{2.5}$, OM, and sulfate. In addition, HMS contributions to $PM_{2.5}$, OM, and particulate sulfur increased significantly during Phase II. HMS contributed up to 6% of $PM_{2.5}$ and 24% of OM during heavy pollution periods in 2019. Despite the continuous reduction in gaseous precursors, the changes in aerosol water content driven by relative humidity and total chemical composition concentrations were the main factors influencing the interannual changes in HMS concentrations from 2015 to 2021 winter. Our findings highlight the importance of HMS during clean air actions and indicate that adverse meteorological conditions may somewhat offset the impact of precursor emission reductions on secondary aerosol formation.



KEYWORDS: *hydroxymethanesulfonate, long-term variation, heterogeneous chemistry, aerosol water content*

1. INTRODUCTION

Hydroxymethanesulfonate (HMS) is a ubiquitous organosulfur compound in aerosols around the world,[1−9] formed from dissolved SO_2 and HCHO. Among them, the concentrations of HMS in particulate matter were higher in winter in northern China, which can be as high as 18.5 $\mu g\ m^{-3}$.[4,5,8] HMS contributed a substantial mass of organic matter (OM)[3,4] and could be misidentified as sulfate in conventional aerosol mass spectrometry (AMS) and ion chromatography (IC) measurements.[4,10] Besides, the reaction of HMS with hydroxyl (OH) radicals in the aqueous phase is a potential source of sulfate.[11−13]

Previous studies of HMS have focused on short-term periods. With the implementation of the Air Pollution Prevention and Control Action Plan from 2013 to 2017 and the Three-Year Action Plan on Defending the Blue Sky from 2018 to 2020, the concentrations of particulate matter have decreased significantly due to the changes in anthropogenic emissions and meteorological conditions,[14−16] while the variation trends of various chemical components are different.[17,18] Some studies have investigated long-term variations of sulfate, nitrate, and organic aerosols (OA) and their response to the changes in emissions and meteorology[17−19] and have found widespread decreases in inorganic and organic aerosol concentrations. However, the secondary OA (SOA) mass fractions in OA increased from 49% in 2013 to 61% in 2020.[20] As one of the typical SOA components, long-term changes in HMS during clean air actions are still poorly understood.

The factors affecting HMS formation are complex. The production medium of HMS in aerosols could be cloud water,[21] fog water,[5,6] and aerosol water.[4,22,23] The formation rate constant of HMS in high ionic strength aerosol water is several orders of magnitude higher than that in dilute cloud and fog water.[24] Considering the enhancement effect of the ionic strength on the HMS formation rate constant, the model simulation could better capture the variations of HMS.[9,22,25] HMS formation is highly dependent on pH, and the formation rate of HMS increases rapidly at higher pH values due to the increased dissociation of $SO_2{\cdot}H_2O$ into HSO_3^- and SO_3^{2-}.[26] The decomposition rate of HMS also increases rapidly with the increase of pH.[27,28] Field measurements have observed HMS in

Received: January 23, 2025
Revised: June 23, 2025
Accepted: June 25, 2025
Published: July 4, 2025

https://doi.org/10.1021/acs.est.5c01170
Environ. Sci. Technol. 2025, 59, 13903−13911

aerosols under moderate-pH conditions from 3 to 6.[4,5,8,29,30] Theoretically, high concentrations of gaseous precursors (SO_2 and HCHO), low atmospheric oxidizing capacity, low temperature, high water content, and moderately acid pH are favorable conditions for HMS formation and stability.[3,4,23,25,31] However, the main factors influencing the variation of HMS concentrations in the ambient atmosphere remain unclear.

In this study, we conducted winter field measurements of HMS and collocated instruments in Beijing from 2015 to 2021. We investigated the changes in HMS concentration and its importance during clean air actions. In addition, we analyzed the influence of gaseous precursors, atmospheric oxidants (e.g., O_3), relative humidity (RH), temperature (T), aerosol water content (AWC), and pH on the variation of the HMS concentration and identified the key influencing factors of HMS formation in ambient aerosols.

2. MATERIALS AND METHODS

2.1. Field Measurements. We conducted offline sampling of $PM_{2.5}$ based on a low-volume air sampler (AS250D, Kimoto Electric Co., Ltd., Japan) and a medium-volume air sampler (Laoying 2030, Qingdao, China) in Tsinghua University (40.00° N, 116.34° E) in winter (November after municipal central heating, December, and the following January and February) from 2015 to 2021. The detailed sampling information is provided in Table S1 in the Supporting Information (SI). Hourly average $PM_{2.5}$ mass concentrations were measured with a PM-712 (Kimoto Electric Co., Ltd., Japan). Hourly concentrations of organic carbon (OC) in $PM_{2.5}$ were measured with a particulate carbon analyzer (APC-710; Kimoto Electric, Ltd., Japan), and the OM concentration was estimated as 1.6 times OC. Hourly concentrations of SO_2 were obtained by an online monitoring instrument SA-731 (Kimoto Electric Co., Ltd., Japan). Online HCHO measurement was conducted at the Chinese Academy of Meteorological Sciences by an Aero-Laser GmbH HCHO analyzer (model AL4021) in winter 2015,[4] Peking University by an Aero-Laser GmbH HCHO analyzer (model AL4021) in winter 2017,[32] and the Institute of Atmospheric Physics, Chinese Academy of Sciences by a proton transfer reaction-time-of-flight/mass spectrometry (PTR-TOF 4000, Ionicon, Austria) instrument in winter 2021.[33] The average HCHO concentration in winter of 2018 and 2019 was obtained from previous studies.[32,33] Hourly average T and RH were monitored with an automatic meteorological observation instrument (Milos 520, VAISALA Inc., Finland).

2.2. HMS and Sulfate Quantification. The detailed analysis method of HMS and sulfate has been described in our previous study.[4,34] For HMS and sulfate quantitation, 90 mm diameter quartz filters and 47 mm diameter quartz filters were cut by a 2 cm diameter circular punch and a quarter, respectively. Then, the cut filters were ultrasonically extracted twice with 5 mL of a 0.1% HCHO solution for 20 min each time and then filtered through 0.45 μm membrane syringe filters. The 0.1% HCHO solution was used to prevent S(IV) loss during pretreatment. Two extracts were combined for subsequent analysis in a Dionex Integrion HPIC system. An AS11-HC analytical column and an AG11-HC guard column (Dionex Corp., CA) were used for the anion analysis. The eluent of 11 mM KOH with a flow rate of 1.5 mL min^{-1} was used for the complete separation of S(IV) (i.e., HMS and other S(IV) species) and the sulfate peak. Previous parallel experiments with H_2O_2 or HNO_3 solution to extract filter samples to isolate HMS from free S(IV) showed that free S(IV) had a negligible influence on the HMS measurement in Beijing winter.[4,5] The UHPLC-LTQ-Orbitrap mass spectrometry method to quantify HMS concentration showed high reproducibility and agreement with the results by IC in Beijing winter.[5] Therefore, the IC method is a feasible technique for quantifying HMS in Beijing winter. It should be noted that the IC method may not be able to assume that the peak is exclusively HMS when applied to other regions, such as Fairbanks winters.[35]

2.3. AWC and pH Calculations. AWC and pH values were calculated by the thermodynamic model ISORROPIA-II.[36−38] Input data were attained by the online gas and aerosol monitoring instrument MARGA (Metrohm Ltd., Switzerland) at an hourly resolution on the campus of Tsinghua University. We used the forward model constrained by the measurements of gases (HNO_3, HCl, and NH_3) and aerosols (SO_4^{2-}, NO_3^-, Cl^-, K^+, Ca^{2+}, Na^+, Mg^{2+}, and NH_4^+), and we assumed the aerosol phase state to be metastable. The calculation of pH is described in Text S1. Considering that aerosols are unlikely to be completely liquid at low RH, data with RH < 20% were excluded when calculating pH.[39] The simulated NH_3(g) and NH_4^+(p) were in good agreement with the observations (Figure S1), indicating good performance of the ISORROPIA-II model in this study.

2.4. Sensitivity of AWC. To explore the major influencing factors on the AWC, sensitivity tests were performed by ISORROPIA-II. RH, T, SO_4^{2-}, TNO_3 ($HNO_3 + NO_3^-$), TNH_3 ($NH_3 + NH_4^+$), and crustal ions ($Ca^{2+} + Mg^{2+}$) were selected as variables in the sensitivity analysis. The control variable method was applied to quantify the independent effects of specific parameters. Taking the effect of RH on AWC for example, RH is set as the actual observed series data, while all other input variables are fixed as the average values during the observation period to obtain the variations of AWC. The average value and variation range for each variable in different years are listed in Table S2. Relative standard deviation (RSD) was calculated to reflect the impact of variable variations on AWC. The higher the RSD, the greater the impact and vice versa.

2.5. Kinetics of HMS Heterogeneous Production. Based on kinetics, the HMS formation rate (P_{HMS}) in aerosol water is calculated as follows.[3]

$$P_{HMS} = \frac{k_1 K_{s1}[H^+] + k_2 K_{s1} K_{s2}}{[H^+]^2} H_{SO_2} P_{SO_2} H_{HCHO} P_{HCHO} AWC \cdot M_{HMS} \quad (1)$$

$$SO_2(g) + H_2O \rightleftharpoons SO_2 \cdot H_2O \quad (R1)$$

$$SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^- \quad (R2)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \quad (R3)$$

$$HCHO(g) \rightleftharpoons HCHO(aq) \quad (R4)$$

$$HCHO(aq) + HSO_3^- \rightleftharpoons HOCH_2SO_3^- \quad (R5)$$

$$HCHO(aq) + SO_3^{2-} \rightleftharpoons {}^-OCH_2SO_3^- \quad (R6)$$

Here, k_1 and k_2 are reaction rate constants for R5 and R6, respectively. K_{s1} and K_{s2} are acid dissociation constants for R2 and R3, respectively. H_{SO_2} and H_{HCHO} are Henry's law constants for SO_2 and HCHO, respectively. The above six parameters are temperature-related and need to be calculated according to the

https://doi.org/10.1021/acs.est.5c01170
Environ. Sci. Technol. 2025, 59, 13903−13911

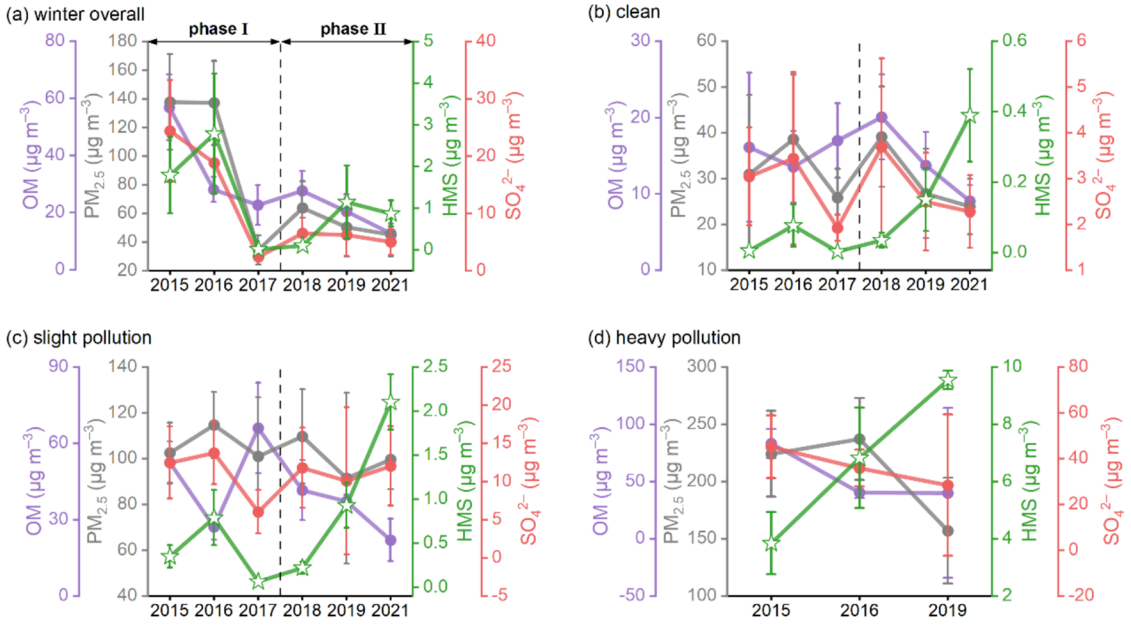


Figure 1. Variation of $PM_{2.5}$, OM, sulfate, and HMS mass concentrations in (a) overall winter, (b) clean periods, (c) slight pollution periods, and (d) heavy pollution periods from 2015 to 2021. The error bars represent the 95% confidence intervals of the mean.

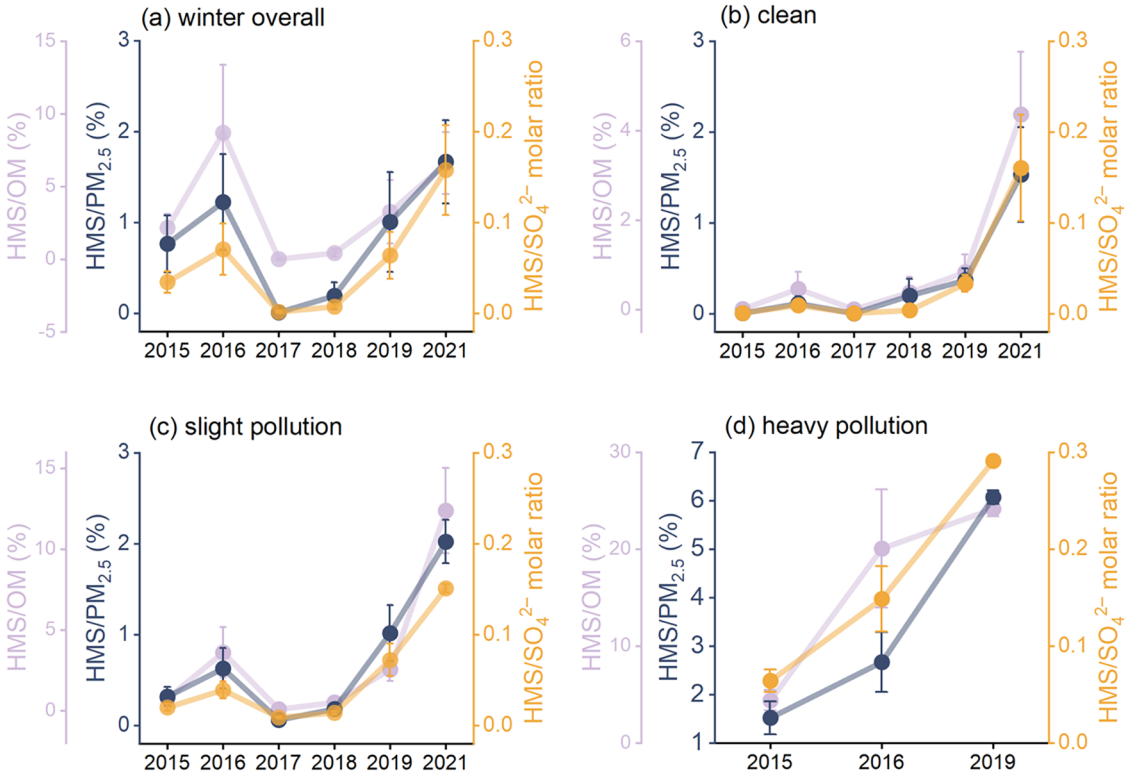


Figure 2. Variations of the $HMS/PM_{2.5}$ mass ratio, HMS/OM mass ratio, and HMS/sulfate molar ratio in (a) overall winter, (b) clean samples, (c) slight pollution samples, and (d) heavy pollution samples from 2015 to 2021. The error bars represent the 95% confidence intervals of the mean.

actual temperature. P_{SO_2} and P_{HCHO} are partial pressures for SO_2 and HCHO, respectively. AWC is the aerosol water content. M_{HMS} is the molar mass of the HMS.

3. RESULTS AND DISCUSSION

3.1. Long-Term Variations of $PM_{2.5}$, OM, Sulfate, and HMS Concentrations. Figure 1a shows the long-term variations of $PM_{2.5}$, OM, sulfate, and HMS in Beijing winter from 2015 to 2021. With the implementation of clean air actions, the mean concentrations of $PM_{2.5}$, OM, sulfate, and HMS in Beijing winter reduced by 67%, 78%, 79%, and 51%, respectively, from 2015 to 2021. The detailed variation trend is different during Phase I (2015−2017) and Phase II (2018−2021), corresponding to the implementation of the Air Pollution Prevention and Control Action Plan and the Three-Year Action Plan on Defending the Blue Sky, respectively. In Phase I, $PM_{2.5}$

https://doi.org/10.1021/acs.est.5c01170
Environ. Sci. Technol. 2025, 59, 13903−13911

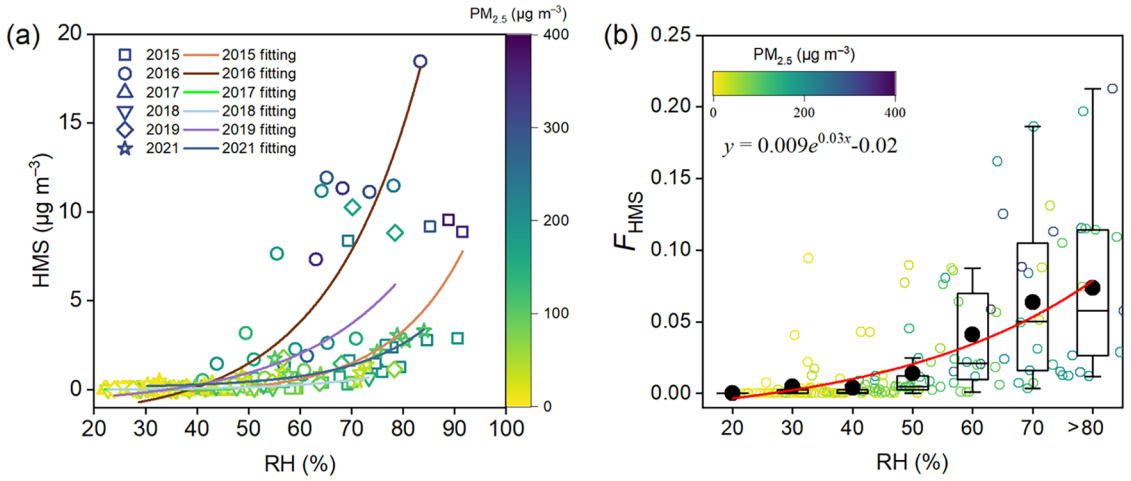


Figure 3. (a) Relationship between HMS concentration and RH in the winter of 2015−2021. The points are colored by $PM_{2.5}$ concentrations. (b) Relationship between F_{HMS} and RH colored by $PM_{2.5}$ concentrations. The data are binned according to RH (10% increment), and the median (middle horizontal line), mean (solid circles), 25th and 75th percentiles (lower and upper box), and 5th and 95th percentiles (lower and upper whiskers) are shown for each bin.

concentration dropped significantly from the high values in 2015 (137.8 ± 93.1 $\mu g\ m^{-3}$) and 2016 (137.2 ± 92.9 $\mu g\ m^{-3}$) to 34.4 $\pm$ 29.5 $\mu g\ m^{-3}$ in 2017. After entering Phase II, the $PM_{2.5}$ concentrations were in the low-value range and showed a slight downward trend year by year from 63.8 ± 39.5 $\mu g\ m^{-3}$ in 2018 to 45.1 ± 36.9 $\mu g\ m^{-3}$ in 2021. Geng et al. also reported an entire decreasing trend of $PM_{2.5}$ concentration during the 2013−2020 period and a slower $PM_{2.5}$ reduction rate during Phase II than during Phase I across China.[16] The reduction in OM and sulfate concentrations was mainly from Phase I, with a 60% and 90% reduction in 2017 compared to 2015, respectively. The rate of reduction slowed in Phase II, with a 54% and 23% reduction in 2021 compared to 2018. The variation of HMS was not consistent with that of $PM_{2.5}$, OM, and sulfate. The HMS concentration increased from 1.79 $\mu g\ m^{-3}$ in 2015 to 2.79 $\mu g\ m^{-3}$ in 2016 and then decreased to 0.01 $\mu g\ m^{-3}$ in 2017. Different from the declining trend of $PM_{2.5}$, OM, and sulfate concentrations in Phase II, HMS concentrations increased from 2018 to 2021.

The rising trend of HMS concentration in Phase II was more obvious under similar pollution levels. According to $PM_{2.5}$ concentration, we classified the air quality into clean periods ($PM_{2.5} \leq 75$ $\mu g\ m^{-3}$), slight pollution periods (75 $\mu g\ m^{-3} < PM_{2.5} \leq 150$ $\mu g\ m^{-3}$), and heavy pollution periods ($PM_{2.5} > 150$ $\mu g\ m^{-3}$). As shown in Figure S2, HMS concentrations increased with the deterioration of air quality, consistent with our previous study.[4] Therefore, the interannual downward trend of HMS from 2015 to 2021 was related to a reduction in the proportion of polluted samples (Figure S3). Figure 1b−d shows the interannual variation of $PM_{2.5}$, OM, sulfate, and HMS concentrations under three different pollution levels in Beijing winter. Under clean and slightly polluted conditions, $PM_{2.5}$, OM, and sulfate concentration showed a fluctuating variation, while HMS concentration showed a minor spike in 2016 and increased significantly in Phase II. In years with heavy pollution samples, HMS concentration also showed an upward trend from 2015 to 2019.

Figure 2 shows the interannual trend of the HMS contribution to $PM_{2.5}$, OM, and particulate sulfur. In general, the contributions of HMS to $PM_{2.5}$ and OM mass and HMS/sulfate molar ratios spiked in 2016 in Phase I and increased significantly in Phase II (Figure 2a). The interannual increase in the molar ratio of HMS to sulfate is consistent with the GEOS-Chem simulation,[22] indicating the increasing importance of HMS in particulate sulfur. In addition, the contribution of HMS to $PM_{2.5}$ and OM mass and the molar ratio of HMS to sulfate increased with the aggravation of pollution (Figure S2). The proportion of HMS in $PM_{2.5}$ and OM and the molar ratio of HMS to sulfate during clean, slight pollution, and heavy pollution periods (Figure 2b−d) showed interannual variation similar to that of HMS concentration. HMS contributed up to 6% of the $PM_{2.5}$ mass and 24% of the OM mass under heavy pollution conditions in 2019.

3.2. Drivers of Variation in HMS. The formation of HMS in Beijing winter was associated with heterogeneous processes. Referring to previous studies,[40] here, we proposed a parameter, F_{HMS} (eq 2), to evaluate the fraction of HMS in total sulfur. HMS concentrations and F_{HMS} increased slowly at low RH (<50%) and accelerated at high RH above 50% (Figure 3). The exponential relationship between RH and HMS concentration, F_{HMS}, and the molar ratio of HMS to SO_2 (Figure S4) suggests an important role of heterogeneous chemistry in HMS formation under wet conditions.[40,41] The rate of change in HMS with RH varied across years, with faster changes in the winter of 2016, 2019, and 2015. We further investigated the effects of cloud/fog events on HMS formation and found that the frequency of clouds and fogs in Beijing winter was low, and the correlation between cloud/fog liquid water content (LWC) and HMS concentration was insignificant (Figure S5, $P > 0.05$), suggesting that the cloud/fog process may be less important than aqueous aerosol processes for HMS production in Beijing winter. Recent studies have also indicated the critical role of aqueous aerosol chemistry in HMS formation in regions where cloud liquid water is scarce.[23]

$$F_{HMS} = \frac{n[HMS]}{n[HMS] + n[SO_4^{2-}] + n[SO_2]} \quad (2)$$

Here, $n[HMS]$, $n[SO_4^{2-}]$, and $n[SO_2]$ refer to the molar concentrations of HMS, SO_4^{2-}, and SO_2, respectively.

To identify the key parameters that affect the formation of HMS in ambient air, we investigated the correlation between HMS concentration and influencing factors in the winter from

https://doi.org/10.1021/acs.est.5c01170
Environ. Sci. Technol. 2025, 59, 13903−13911

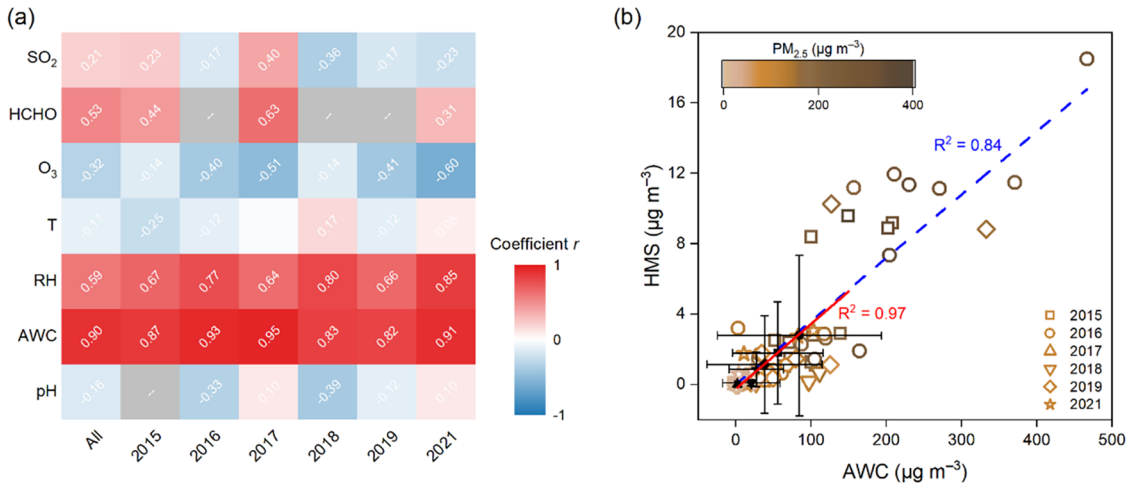


Figure 4. (a) Pearson *r* values for the correlations between HMS concentration and major influencing factors in the winter from 2015 to 2021. (b) Relationship between HMS concentration and AWC, colored by the $PM_{2.5}$ concentration. Solid black dots represent annual averages. The solid red line fits the annual mean, and the dashed blue line fits the sample data points.

2015 to 2021 (Figure 4a). Theoretically, high concentrations of precursors (SO_2 and HCHO), low oxidant levels, low temperature, high RH, and pH favor the HMS formation.[4,42−44] AWC and RH correlated strongly and positively (r = 0.59−0.95, P < 0.0001) with HMS concentration, consistent with previous studies,[4] indicating that aerosol water serves as a medium for the formation of HMS. High RH conditions were usually accompanied by rapid secondary chemical processes in Beijing haze.[40,41] Rural HMS at the Gucheng site was higher than that at the urban site Beijing due to the higher RH.[8] HMS concentration correlated well with HCHO concentration (r = 0.31−0.63, P < 0.05), while the relationship between HMS and SO_2 concentration was insignificant (P > 0.05), suggesting the importance of HCHO concentration on HMS formation.[21,35] HMS concentration showed a negative correlation with O_3 concentration (P < 0.05). Because HMS formation competes with S(IV) oxidation reactions, low oxidants may reduce the oxidation of S(IV) and facilitate the formation of HMS.[4,22,25] In addition, HMS could be oxidized by OH radicals to form sulfate,[12] and low oxidants were unfavorable for the heterogeneous oxidation of HMS.[22] The correlation between temperature, pH, and HMS concentration was insignificant (P > 0.05). From the perspective of daily changes in HMS concentration, AWC was the key factor affecting the concentration of HMS, followed by RH.

We further studied the interannual variation of the factors influencing HMS formation and found that AWC showed the best agreement with the interannual variation in HMS concentrations (Figure S6). The concentration of SO_2 in Beijing winter continued to decline from 9.7 ± 4.4 ppb in 2015 to 1.1 ± 0.3 ppb in 2021 (Figure S6b), consistent with the variation trend of SO_2 reported in northern China.[45] The reduction in SO_2 concentration was mainly attributed to the implementation of strict desulfurization measures in power plants and emission-intensive industrial sectors.[14] The interannual variation of HCHO also showed a downward trend (Figure S6c). The decrease in the concentration of precursors could not explain the increase in HMS concentration in Phase II mentioned above. O_3 concentration showed an interannual increasing trend (Figure S6b), which is unfavorable for HMS formation. The interannual variation trend of RH was almost consistent with that of the HMS concentration in Phase II (Figure S6d). The interannual variation trend of AWC (Figure S6e) agreed well with the trend in HMS concentration, while the variation trend of LWC and HMS concentrations was not consistent (Figure S6a). As shown in Figure 4b, the annual average HMS concentration correlated well with the AWC (R^2 = 0.97). The pH of aerosol in Beijing in winter fluctuated in the range of 4−5.5 (Figure S6e). Theoretically, high pH facilitated the formation of HMS, since high pH favored the dissociation of $SO_2{\cdot}H_2O$ into HSO_3^- and SO_3^{2-}.[3,31] Moderately acidic pH in Beijing winter haze favored the HMS formation and prevented the HMS decomposition.[3] In the real atmosphere, the interannual variation of the pH could not explain the observed variation of HMS concentrations. In addition, the calculated heterogeneous HMS formation rate (Figure S7) in 2015, 2017, and 2021 was consistent with the variation of HMS concentration, implying the importance of heterogeneous chemistry on HMS formation.

Figure S8 shows the effects of RH, T, total chemical compositions, SO_4^{2-}, TNO_3, TNH_3, and crustal ions on AWC through sensitivity analysis using the ISORROPIA-II model. In the sensitivity test, AWC showed an exponential relationship with RH (Figure S8a). Temperature exhibited an opposite trend to AWC (Figure S8b), indicating the inhibitory effect of temperature on AWC. The total concentration of chemical compositions showed a linear relationship with AWC (Figure S8c). Based on the RSD analysis in Table S3, RH and total concentration of chemical compositions were the two factors with higher RSD, reflecting their strong influence on AWC. We then studied the effect of individual chemical components on AWC (Figure S8d−g). AWC increased with the concentrations of SO_4^{2-}, TNO_3, and TNH_3, while crustal ions Ca^{2+} and Mg^{2+} showed a minor negative effect on AWC. The impact of SO_4^{2-} on AWC was significant in 2016, while the impact of TNO_3 and TNH_3 on AWC gradually increased and exceeded that of SO_4^{2-} since 2017. As the dominant ions in $PM_{2.5}$ shifted from sulfate to nitrate after 2017,[46] nitrate became the main driver of AWC increase.[47] The interannual variation of AWC was similar to that of RH and the total concentration of chemical compositions (Figure S6). In general, the driving factors affecting AWC variations in winter from 2015 to 2021 were the RH and total concentration of chemical compositions.

https://doi.org/10.1021/acs.est.5c01170
Environ. Sci. Technol. 2025, 59, 13903−13911

3.3. Atmospheric Implications. Our field measurements reveal the long-term variation of HMS in Beijing winter during clean air actions. HMS showed growing importance in Phase II in terms of concentration and contribution to $PM_{2.5}$, OM, and particulate sulfur. Primary emissions, secondary formation, and adverse meteorological conditions affected the formation of particulate matter.[41,48,49] During clean air actions, the significant reductions in anthropogenic emissions drove the improvement of air quality in China.[16] However, enhanced secondary formation accompanied by adverse meteorological conditions may exacerbate particulate matter pollution.[50] HMS can be used as a marker for secondary processing in the aqueous/heterogeneous phase.[23] Despite the decreases in precursors (SO_2 and HCHO), the growing importance of HMS indicates that secondary formation under adverse meteorological conditions may somewhat offset the impact of primary emission reductions on particulate matter mitigation.

This study demonstrates the important role of AWC in HMS formation in Beijing winter. Factors affecting HMS changes in the atmosphere are complex. Aerosol water is an important component of atmospheric aerosols, which serves as a medium that enables aqueous-phase reactions.[51] AWC is the key factor affecting HMS variation in Beijing winter, and RH and chemical components determine the AWC.[47] Experimental and model studies also confirmed that aerosol water plays an important role in HMS chemistry during haze in China.[22,24] Previous model results showed that atmospheric acidity was a critical factor in HMS variation.[22,31] Actually, the field measurements show that aerosol acidity during winter in the North China Plain is relatively stable, with pH values ranging from 4 to 5.[3,4,52,53] In this study, the fluctuating pH value in Beijing winter cannot explain the changes in HMS. In Alaska, low temperatures can play a role through a unique effect on pH that enables substantial HMS production.[23] In the future, more field, laboratory, and modeling research is needed to study the key factors influencing the formation of HMS in different regions of the world.[35]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.5c01170.

Details of aerosol pH calculation (Text S1); ISORROPIA-II validation (Figure S1); sampling information (Figure S3 and Table S1); AWC sensitivity test (Figure S8 and Tables S2 and S3); and additional figures on HMS and related parameters (Figures S2 and S4−S7) (PDF)

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https://doi.org/10.1021/acs.est.5c01170
Environ. Sci. Technol. 2025, 59, 13903−13911

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (22188102 and 22206098), National Key R & D Program of China (2022YFE0105500), special fund of State Key Laboratory of Regional Environment and Sustainability (24K13ESPCT), and Natural Science Foundation of Tianjin City (22JCYBJC01330).

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https://doi.org/10.1021/acs.est.5c01170
Environ. Sci. Technol. 2025, 59, 13903−13911