Global Importance of Hydroxymethanesulfonate in Ambient Particulate Matter: Implications for Air Quality

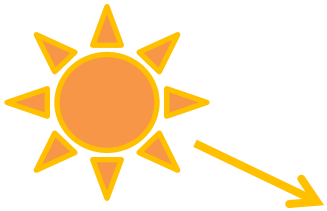
10/28/20

ROBERT & PATRICIA SWITZER FOUNDATION

Jonathan M. Moch, Dovrou, E., Mickley, L.J., Keutsch, F.N., Liu, Z., Wang, Y.,Dombek, T.L., Kuwata, M., Budisulistiorini, S.H., Yang, L., Decesari, S., Paglione, M., Alexander, B., Shao, J., Munger, J.W., Jacob, D.J.

Given low oxidation rates, high burden of $PM_{2.5}$ is a puzzle

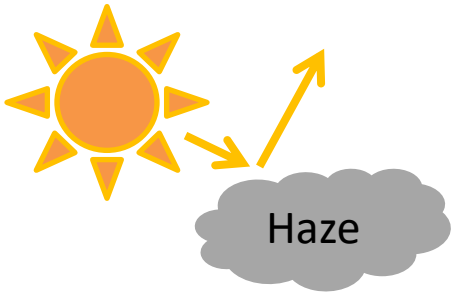
Haze free conditions:



Ozone and other oxidants

Sulfur dioxide (SO_2) → Sulfate (SO_4^{2-})

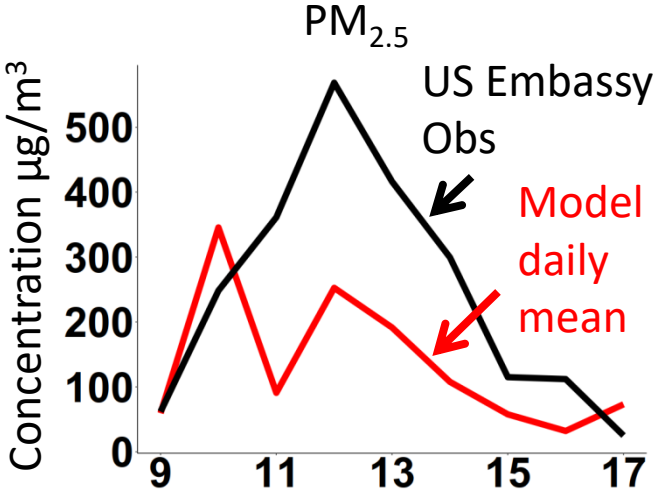
Haze conditions:

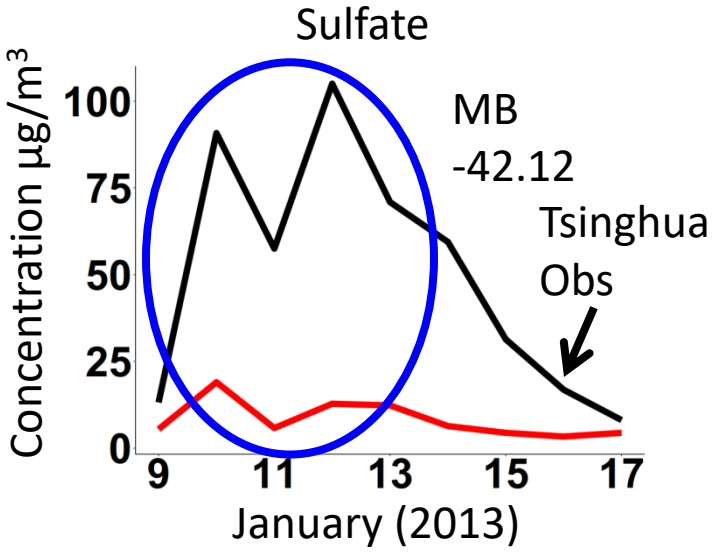


??? → Sulfur dioxide (SO_2) → Sulfate (SO_4^{2-})

Since there is low sunlight, what is reacting with sulfur dioxide to form sulfate?

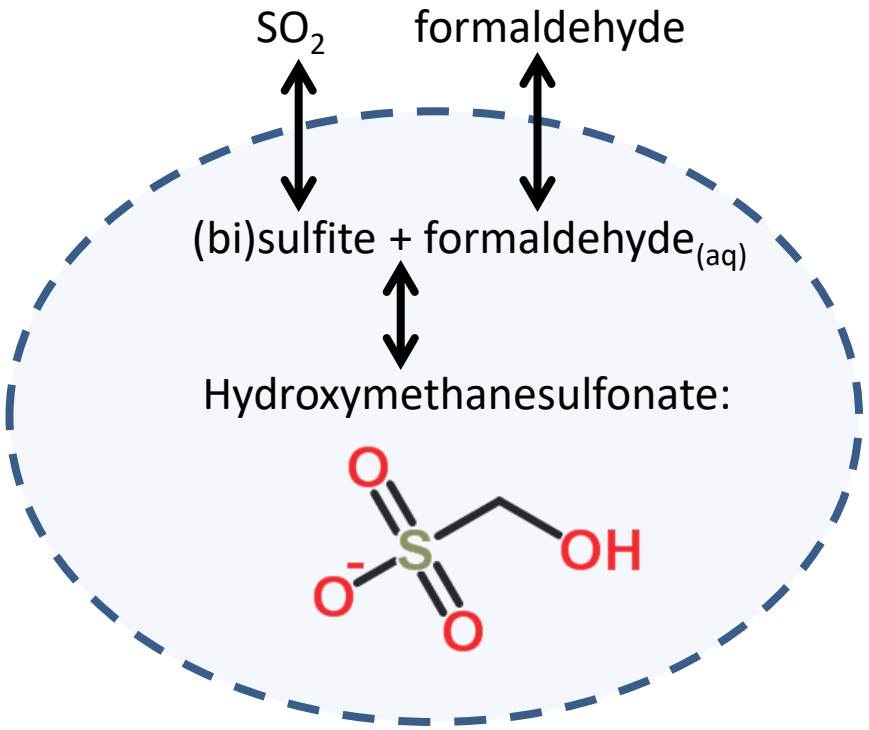
Atmospheric chemistry models cannot reproduce severe Beijing haze, with one major factor being sulfate underestimates.





HMS chemistry may explain paradox of high sulfur PM even as SO_2 declines

- Sulfite (HO_3^-) and bisulfite (SO_3^{2-}) react with dissolved formaldehyde (HCHO) to form HMS in clouds and fogs.



$$HCHO_{(g)} \leftrightarrow HCHO_{(aq)}$$

$$SO_{2(g)} \leftrightarrow SO_{2(aq)}$$

$$SO_{2(aq)} \leftrightarrow HSO_3^- + H^+$$

$$HSO_3^- \overset{H_3}{\leftrightarrow} SO_3^{2-}\ H^+$$

$$\boldsymbol{HCHO_{(aq)} + HSO_3^- \rightarrow HOCH_2SO_3^-}$$

$$\boldsymbol{HCHO_{(aq)} + SO_3^{2-} + H_2O \rightarrow HOCH_2SO_3^- + OH^-}$$

$$HOCH_2SO_3^- + OH^- \rightarrow SO_3^{2-} + HCHO_{(aq)} + H_2O$$

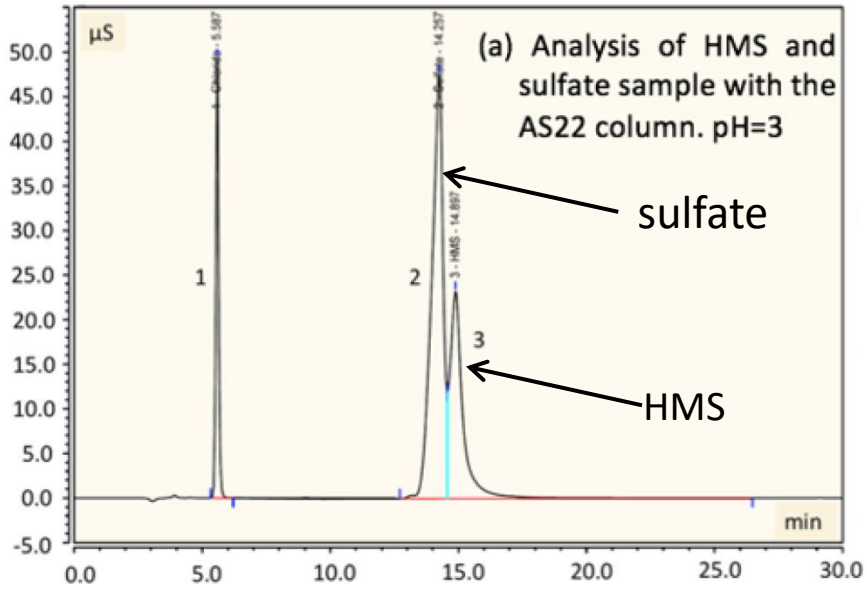
$$HOCH_2SO_3^- + OH \xrightarrow{(SO_2, HO_2)} HCHO_{(aq)} + 2SO_4^{2-} + 3H^+$$

Munger et al., 1983;
Olson and Hoffman, 1986;
Olson and Fessenden, 1992

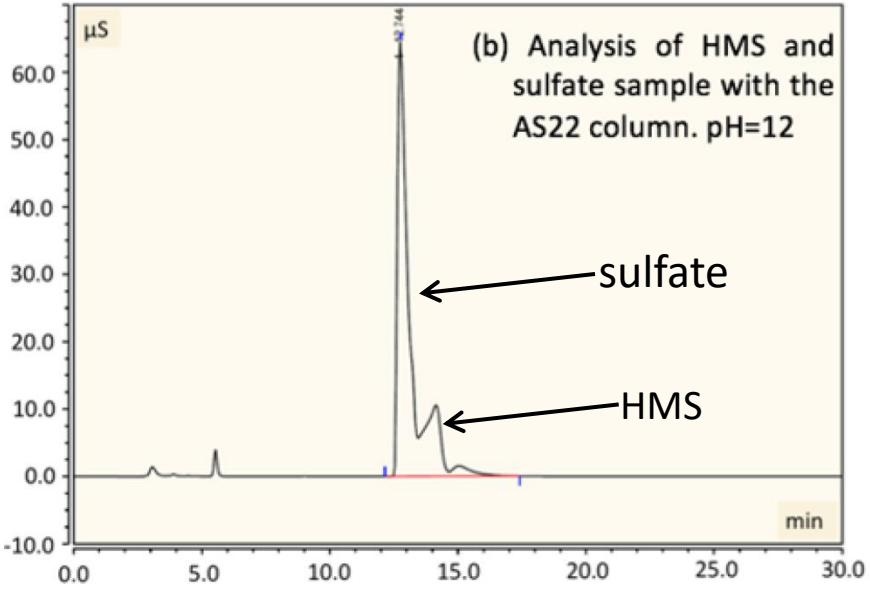
HMS can be easily confused for sulfate in measurements

- Ion chromatography (IC) works by separating ions according to their affinity to different ion exchangers.
  - Peaks in the chromatogram are integrated to get concentrations.
- For standard IC measurements (e.g. AS22), automated systems often lump HMS and sulfate together and interpret it all as sulfate.
- High pH, such as due to use of a KOH eluent, can also cause HMS to decompose and potentially be oxidized to sulfate.

HMS + sulfate in AS22
(can not separate)



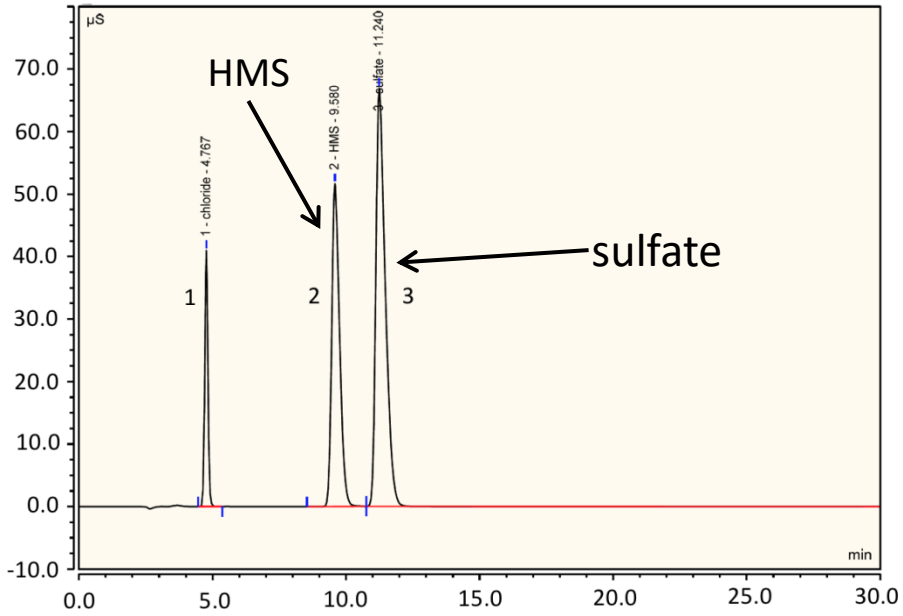
HMS + sulfate in AS22
(can not separate)



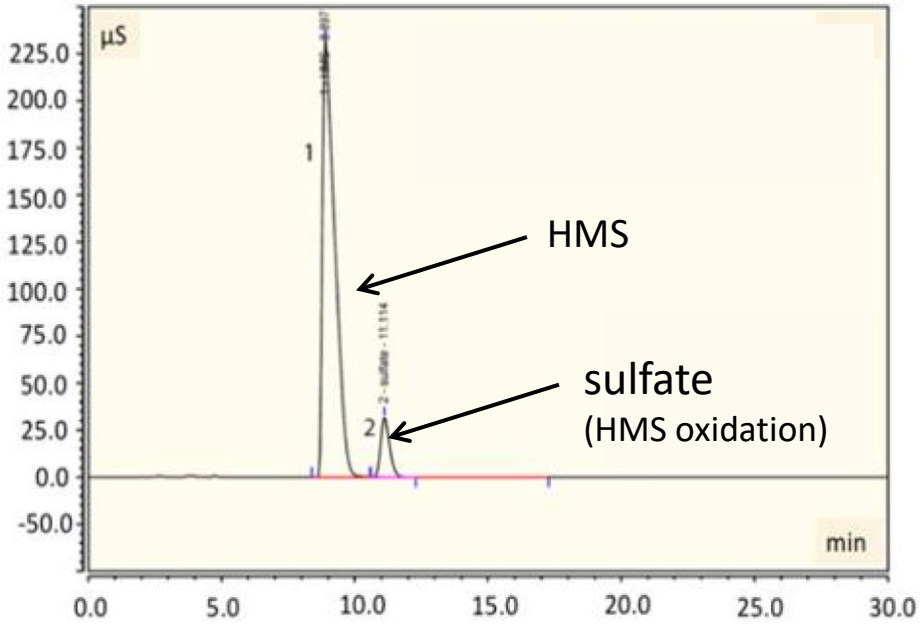
Some IC column types can separate HMS and sulfate

- Use of an alkyl quaternary ammonium IC column and a calcium-carbonate eluent can separate HMS and sulfate.
- HMS may decompose over time – e.g., via oxidation to sulfate during sample storage and preparation.
- Use of a high pH eluent would likely further complicate separation of HMS and sulfate.

HMS + sulfate in AS12A at pH=3
(can separate)



HMS in AS12A at pH=12
(can separate)

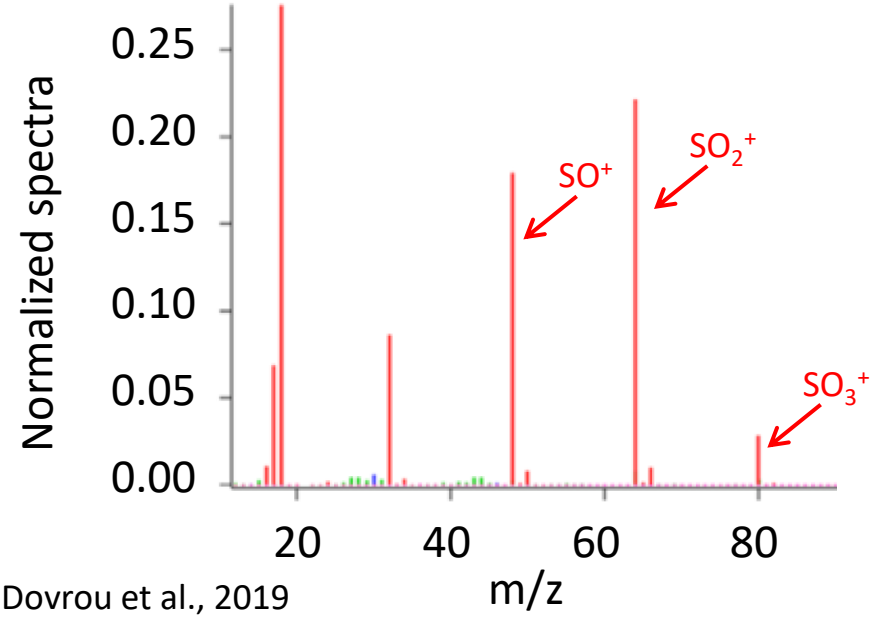


Moch et al., 2018; Dovrou et al., 2019

HMS can be easily confused for SO_4^{2-} in measurements: AMS

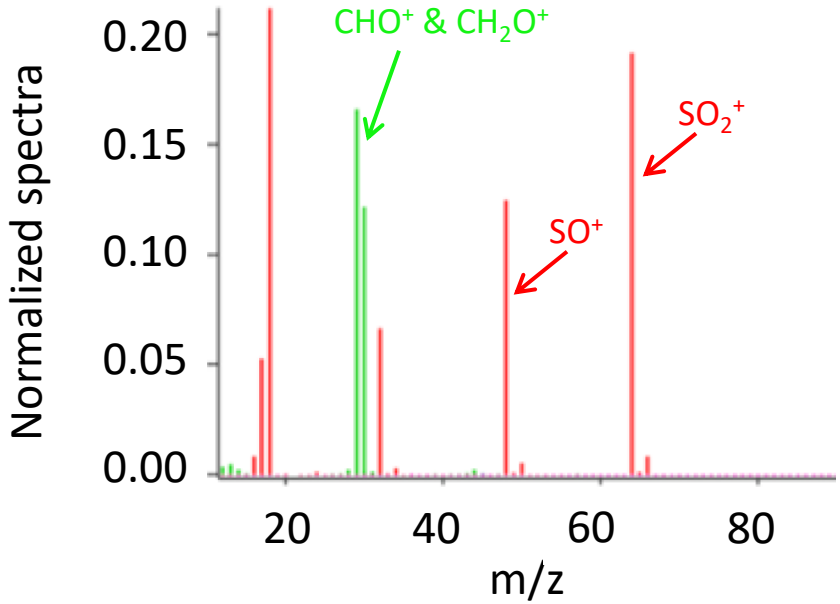
- Aerosol mass spectrometers work by fragmenting aerosols into ions which are separated by the mass to charge ratio with the intensity of the peaks used for quantification.
- For AMS, usually sulfur containing fragments are identified and assumed to be all from sulfate.
- HMS fragmentation patterns overlap with sulfate and make distinguishing the two difficult.
- Organic ions from HMS are common to many organic species.
- Because HMS has no unique identifiable fragments quantifying it in complex mixtures is extremely difficult.

Sodium sulfate in HR-ToF-AMS

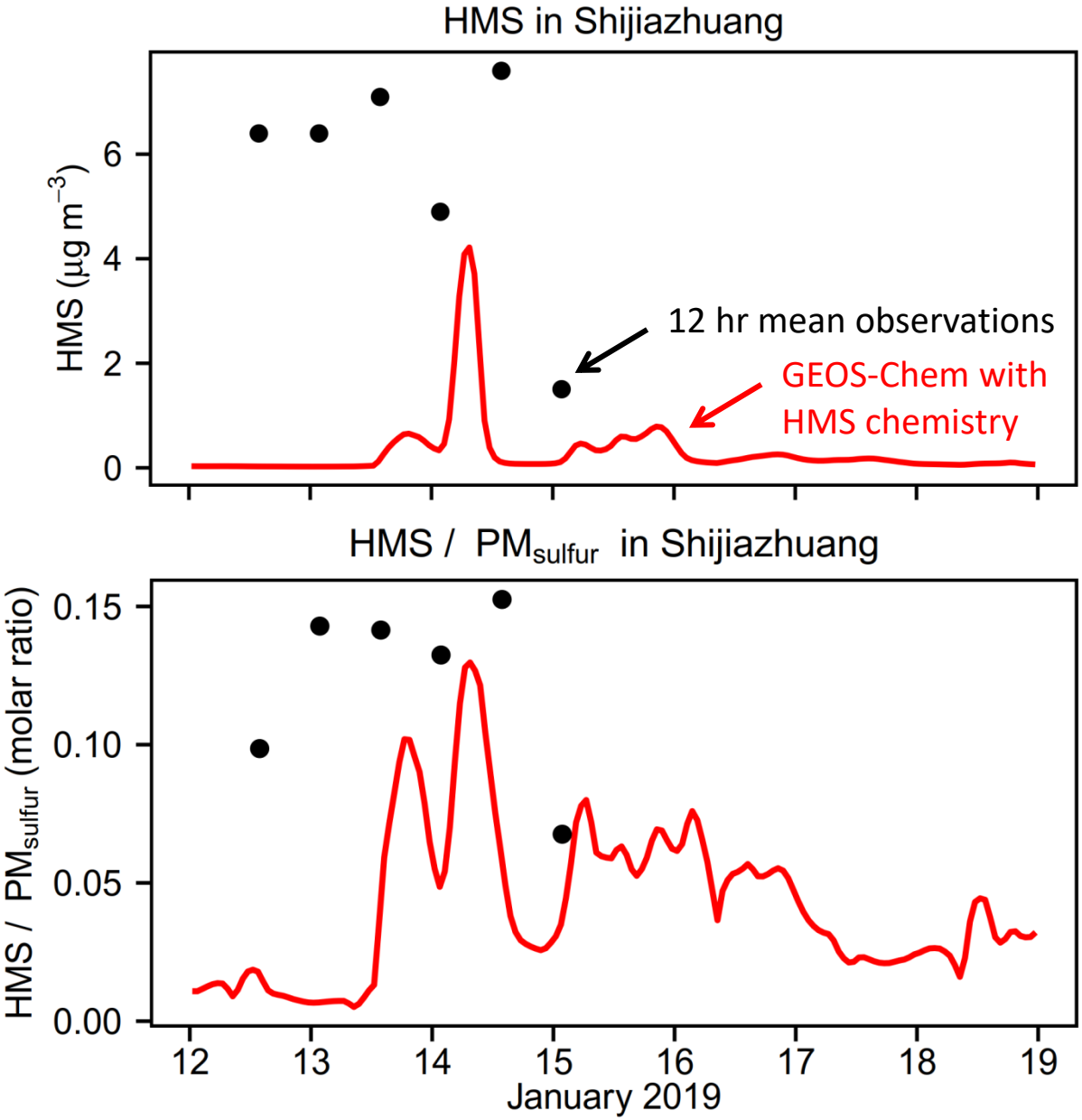


Dovrou et al., 2019

Sodium HMS in HR-ToF-AMS

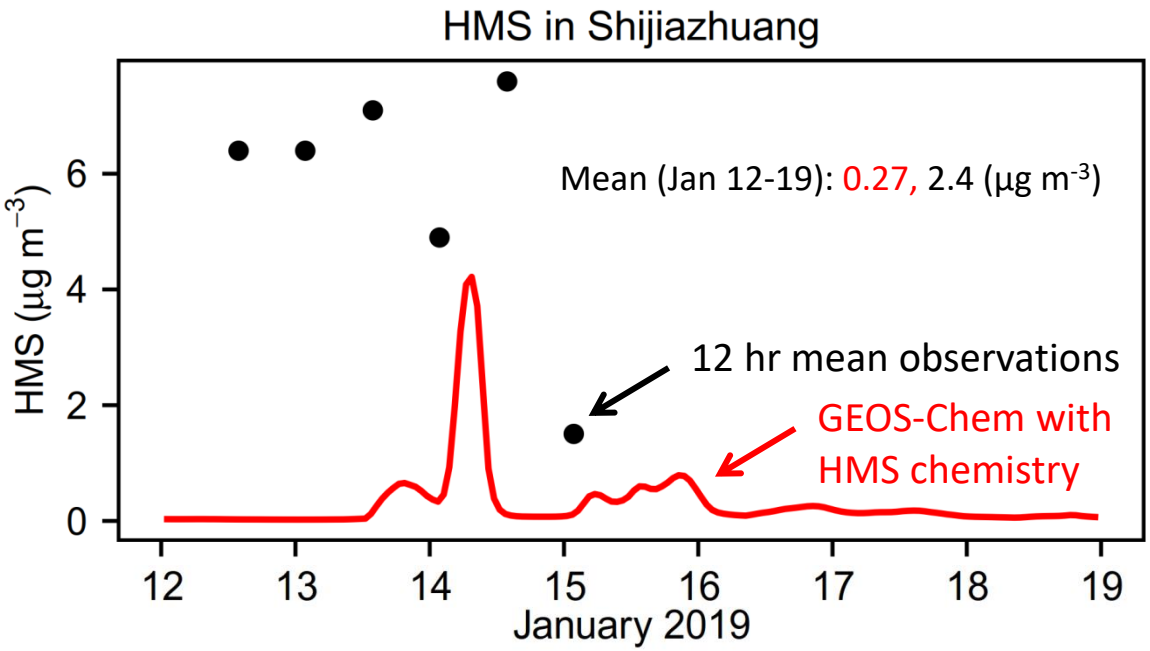


New observations show large values of HMS in Shijiazhaung in winter 2019



- New measurements from Shijiazhuang, China, show large concentrations of HMS when using an IC system capable of differentiating HMS and sulfate.
- GEOS-Chem underestimates HMS and sulfate during the non-cloudy periods, indicating uncertainty due to clouds.
- Low values of modelled HCHO, compared to observations may also be a factor.
- Modeled contribution of HMS to particulate sulfate is close to that observed.

Potential problem of HMS decomposition

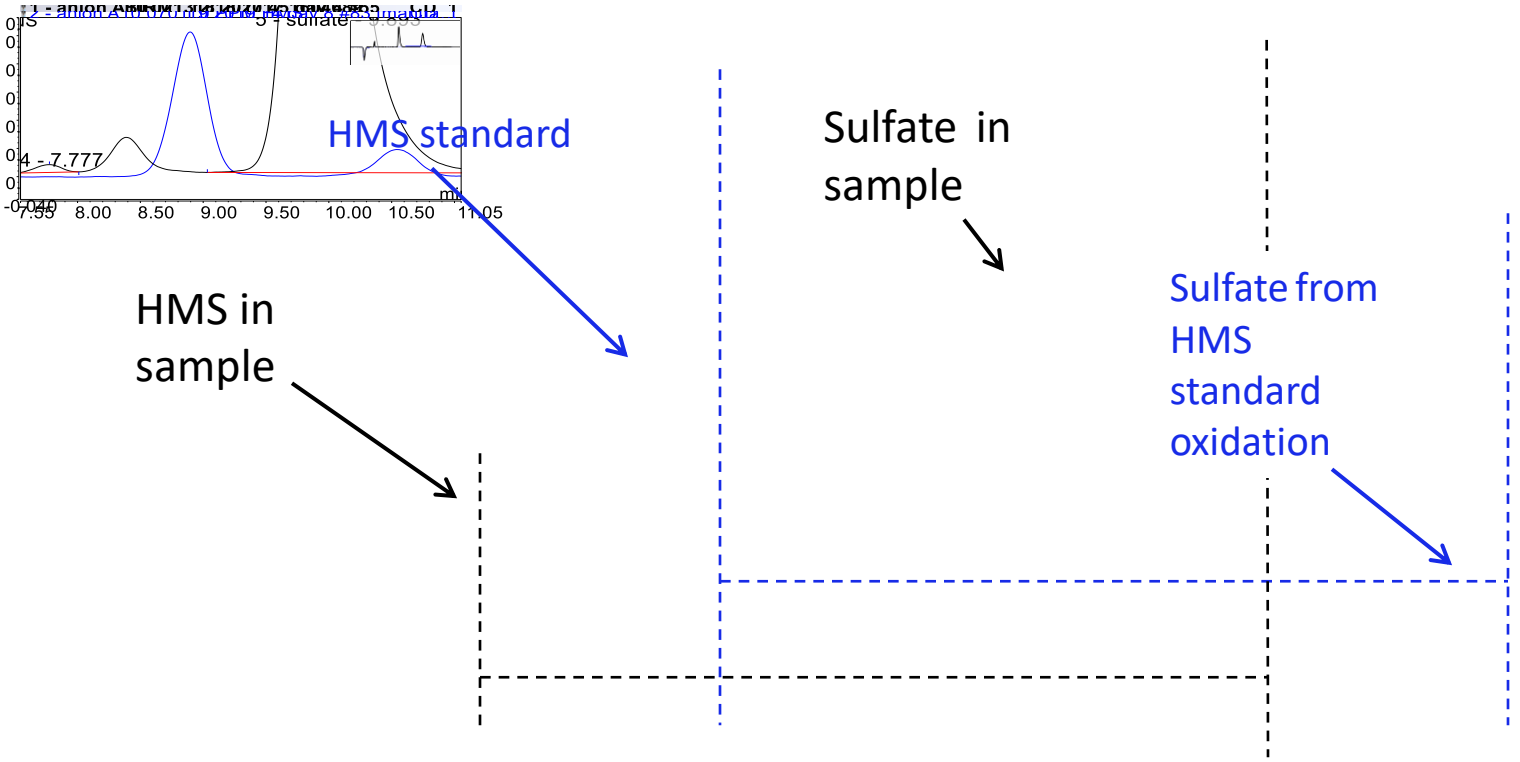


Aerosol or cloud pH	HMS lifetime
3	~ 2 years
4	Months
5	~Week
6	~1 day
7	~2 hours

- Only trace levels of HMS were detected upon reanalysis of the Shijiazhuang samples after 4 months of storage in a freezer.
- Decomposed HMS may outgasses from particles as SO_2 and HCHO or be oxidized to sulfate.

We identify traces of HMS in old IMPROVE measurements

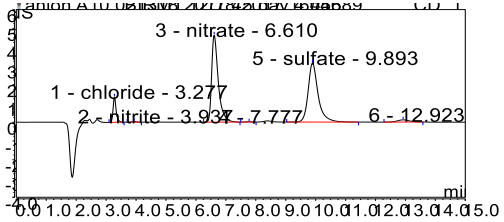
IMPROVE chromatogram for Birmingham, AL (12/18/17)



- IMPROVE is an EPA run network of PM monitoring across the US.
- Samples are stored for a month or two before analysis, which could lead to significant HMS decomposition and oxidation to sulfate.
- The small peaks seen here as similar to what was seen with the Shijiazhaung samples after 4 months of storage.

We are able to identify HMS in previous IMPROVE measurements

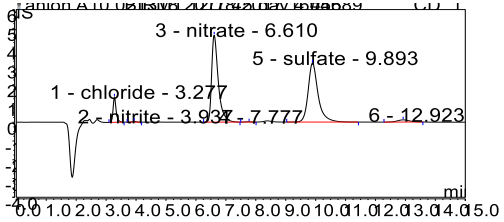
IMPROVE chromatogram for Birmingham, AL (12/18/17)

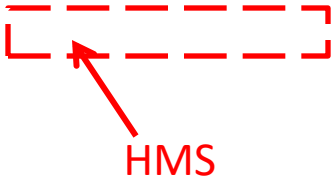


- The chromatogram analysis program is set to automatically integrate peaks corresponding to nitrate and sulfate for the anions.
- Chromatograms are also checked by eye for anomalies that could affect the sulfate and nitrate quantification.

We are able to identify HMS in previous IMPROVE measurements

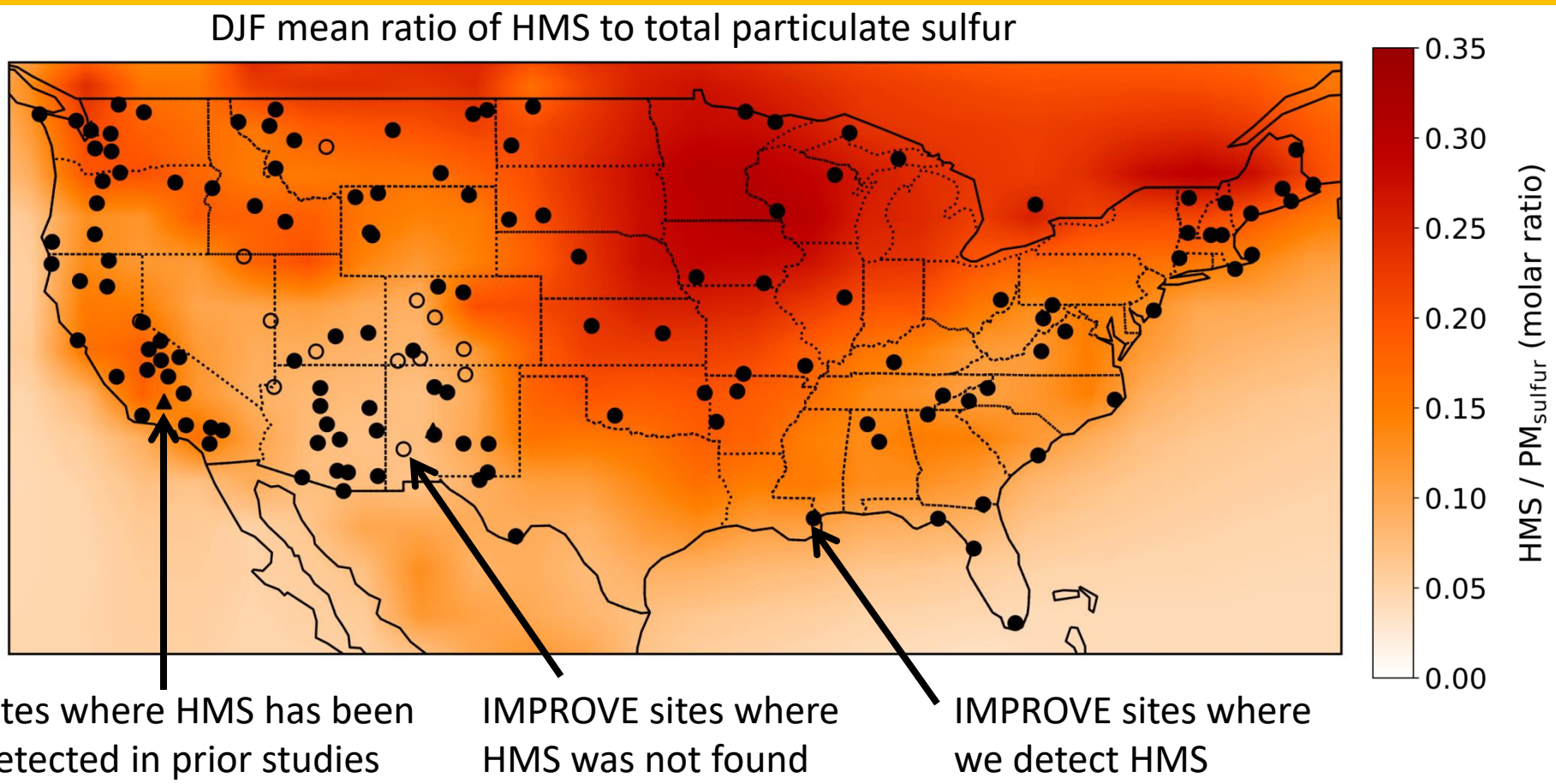
IMPROVE chromatogram for Birmingham, AL (12/18/17)





- The HMS peak is readily visible if you zoom in on the chromatogram, but this is not typically done.

IMPROVE observations and GEOS-Chem suggest an ubiquitous presence of HMS



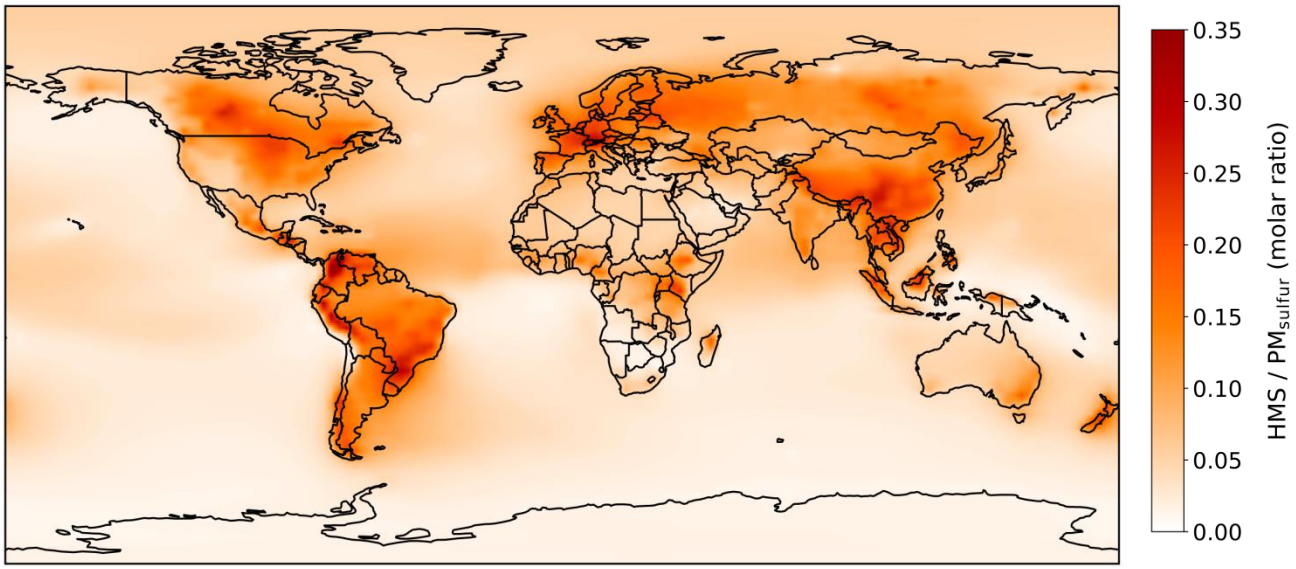
- We find evidence of HMS at 139 of the 158 IMPROVE sites worldwide.
- GEOS-Chem simulates > 25% of particulate sulfur as HMS for many regions.
- Wet deposition is the major sink of HMS, responsible for nearly 80% of HMS removal.

Conclusions

- New and reanalyzed observations suggest a ubiquitous global presence of HMS in particulate matter
- GEOS-Chem simulations suggest HMS may comprise over 25% of particulate sulfur in many polluted regions
- HMS is difficult to measure and may have been overlooked in previous observations or have been interpreted as sulfate.
- Specialized ion chromatography methods may be able to quantify HMS, especially if the sample is analyzed quickly after collection.

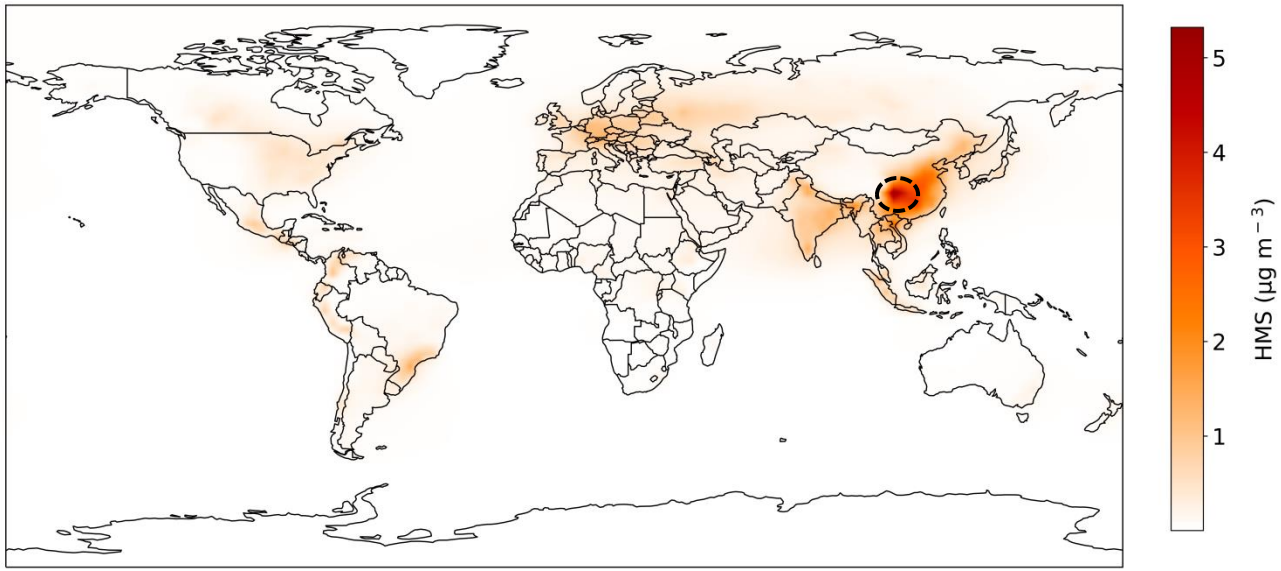
Extra: GEOS-Chem suggests an ubiquitous global presence of HMS

Annual mean ratio of HMS to total particulate sulfur (2013-2016)



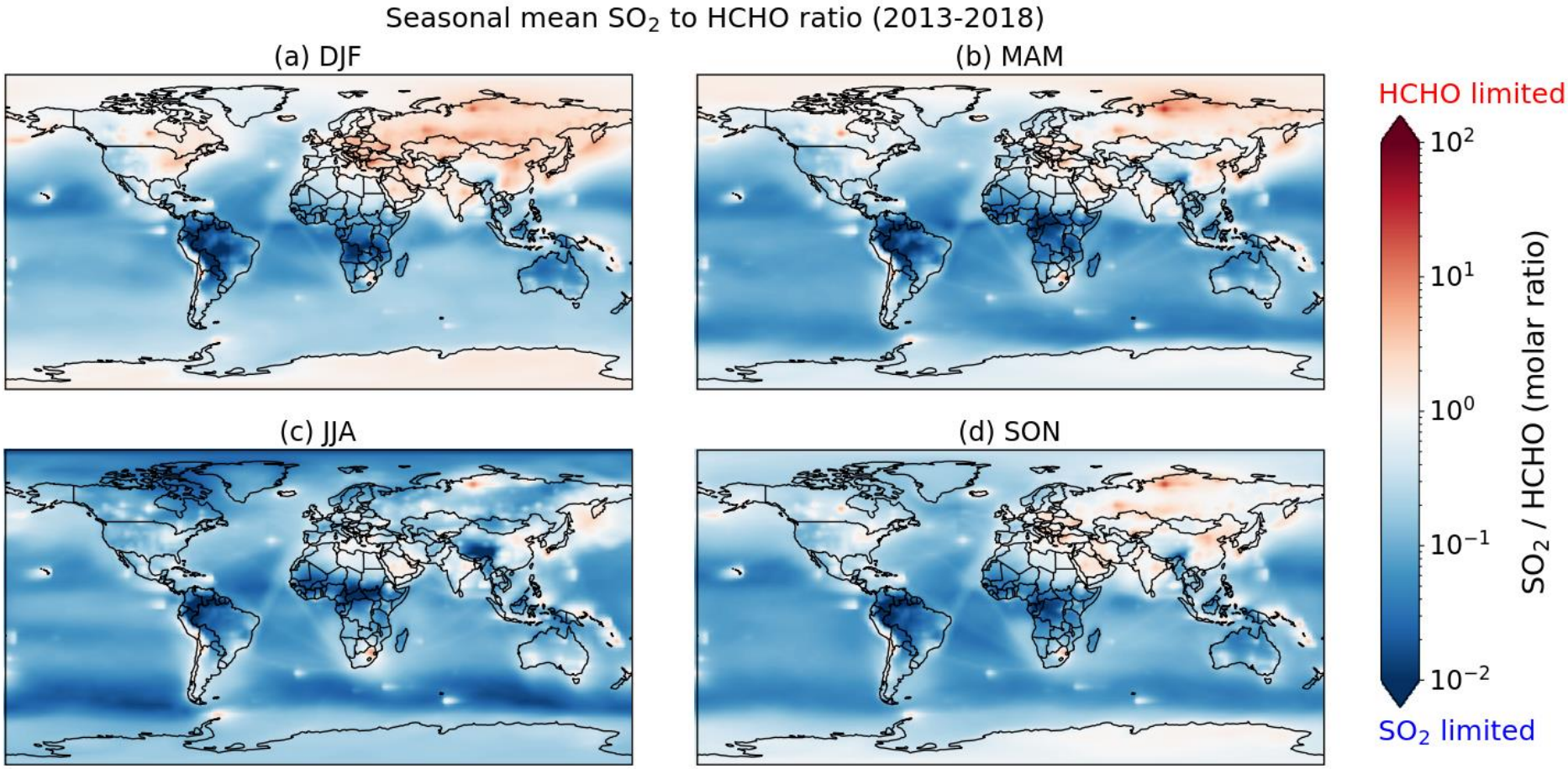
- Over land, the global mean fraction of HMS in particulate sulfur is ~10% in surface air over 2013-2018.
- For many regions, the model yields seasonal HMS fractions of 25% or more of particulate sulfur.

Annual mean concentration of HMS in aerosol (2013-2016)



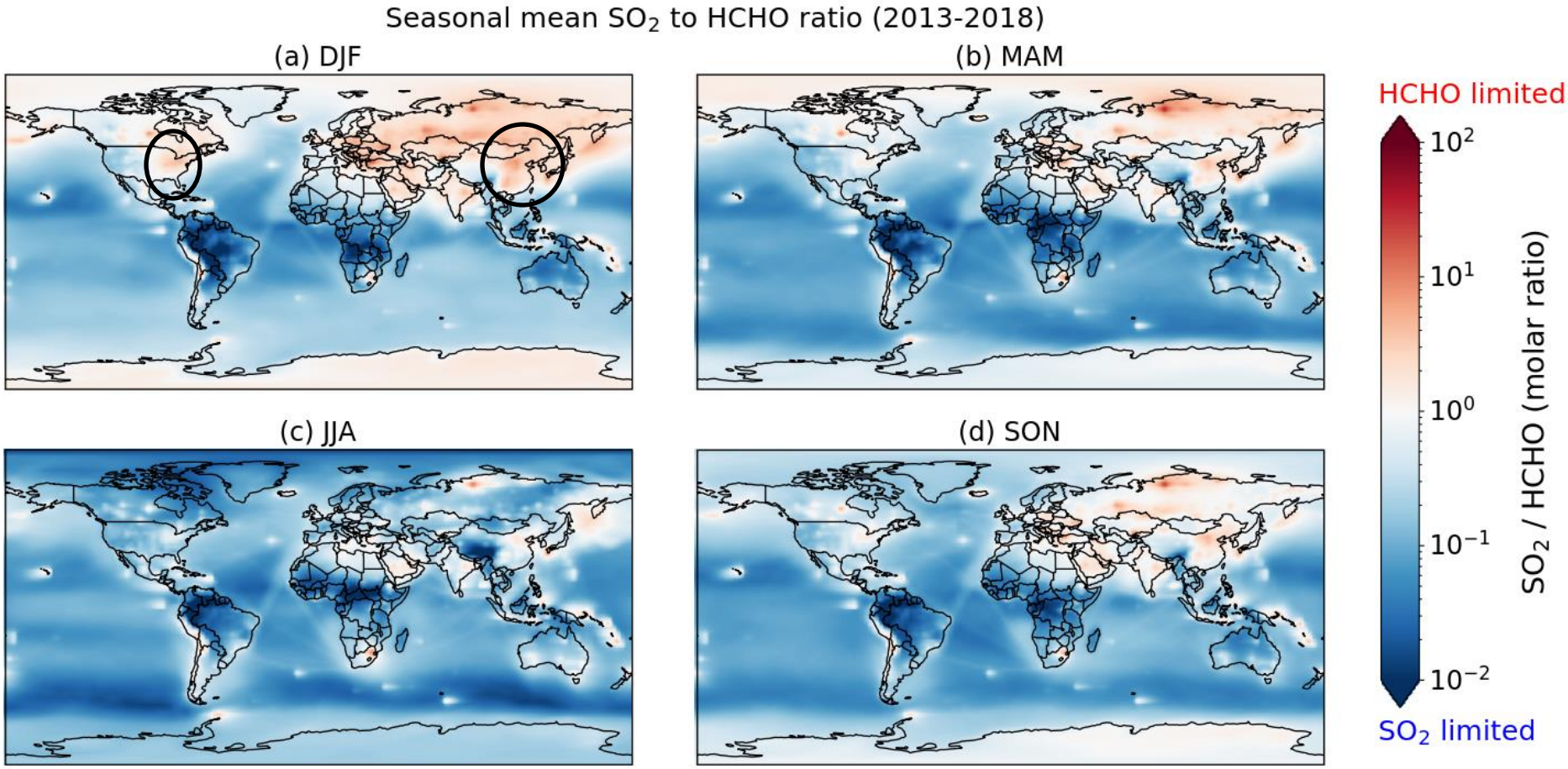
- Annual mean simulated HMS mass is highest in China, specifically in the Sichuan Basin region.

Extra: Implications of HMS for air quality control strategies



- In regions where SO_2 > HCHO, HCHO will likely be the limiting reactant for HMS formation.
- In regions where HCHO controls HMS formation and HMS makes up a large fraction of particulate sulfur, SO_2 reductions could be less effective at controlling PM.

Extra: Implications of HMS for air quality control strategies



- In regions where SO_2 > HCHO, HCHO will likely be the limiting reactant for HMS formation.
- In regions where HCHO controls HMS formation and HMS makes up a large fraction of particulate sulfur, SO_2 reductions could be less effective at controlling PM.