

# The potential overlooked importance of hydroxymethanesulfonate in ambient particulate matter

7/18/19

Pictures taken in Beijing during summer 2016



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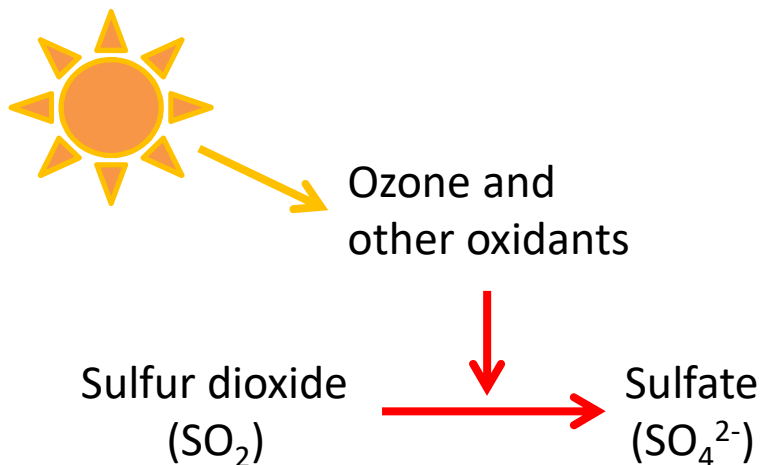
**Jonathan M. Moch**

# Outline

- Hydroxymethanesulfonate (HMS) chemistry
  - Initial motivation: significance for China
  - HMS through the 1980s
- Measurement challenges
- The global picture of HMS
- Conclusions

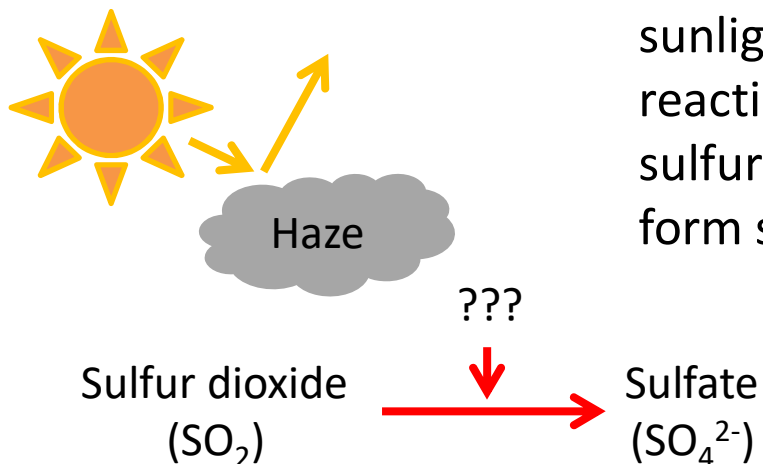
# One paradox: sulfur oxidation is depressed during haze

Haze free conditions:

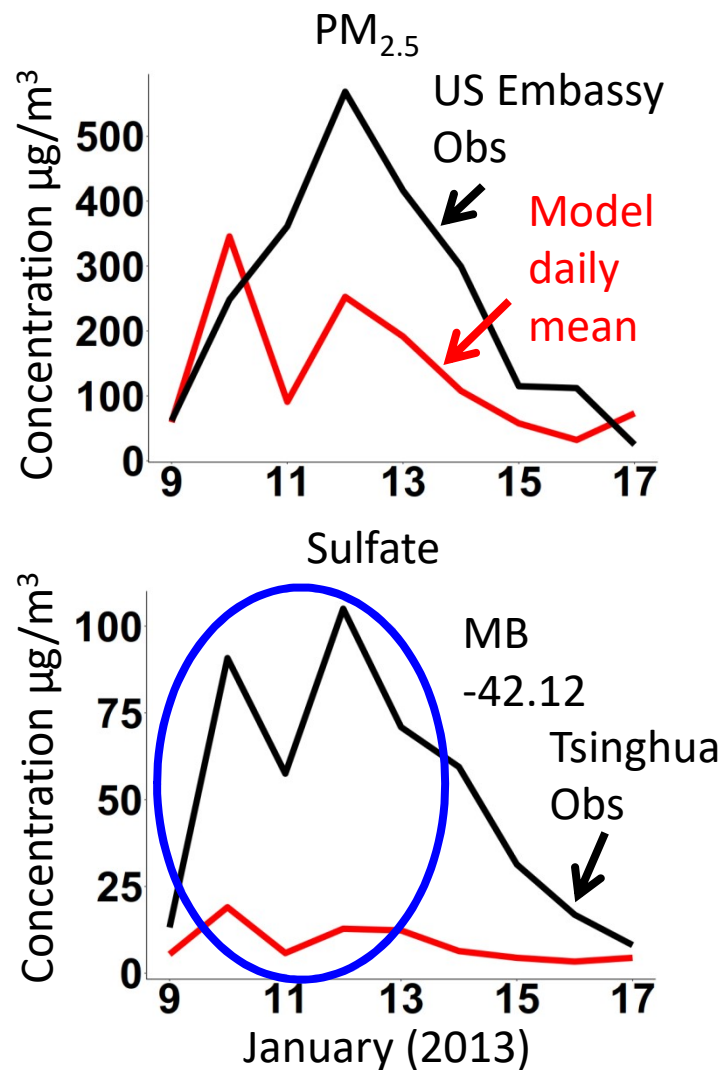


Atmospheric chemistry models cannot reproduce severe Beijing haze, with one major factor being sulfate underestimates.

Haze conditions:

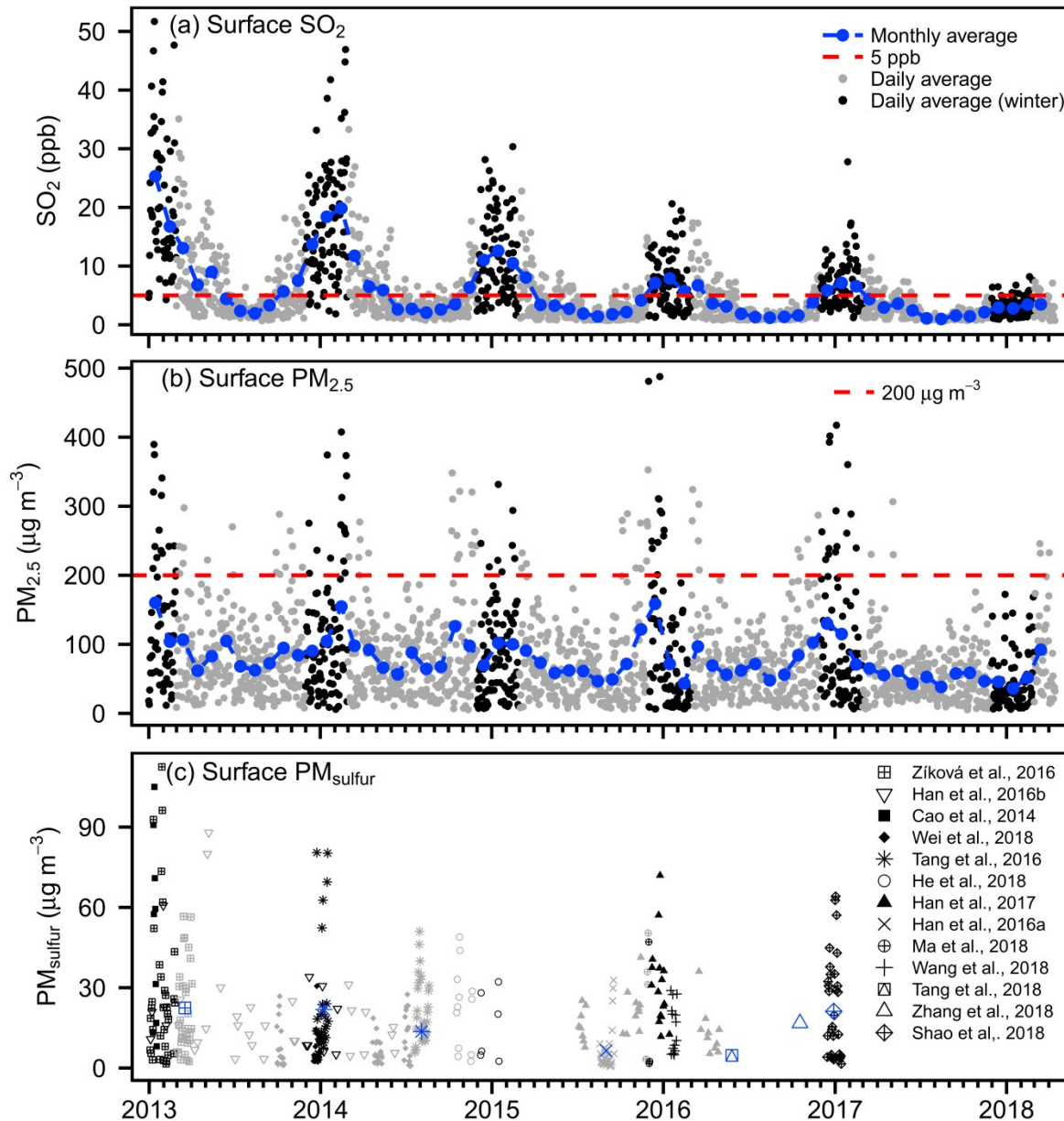


Since there is low sunlight, what is reacting with sulfur dioxide to form sulfate?



# Another issue: extreme haze seems disconnected from SO<sub>2</sub>

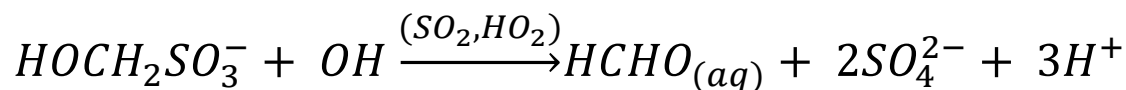
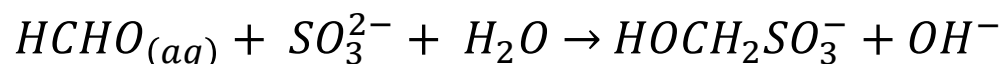
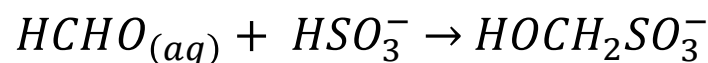
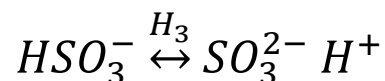
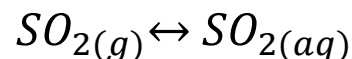
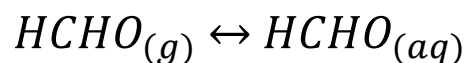
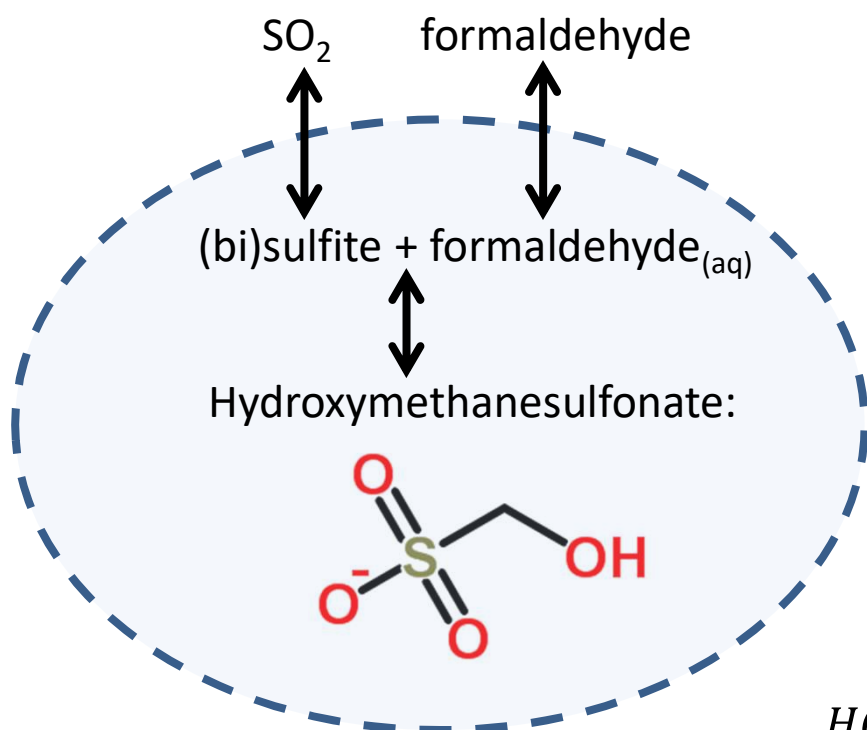
Surface observations of SO<sub>2</sub>, PM<sub>2.5</sub>, and PM<sub>sulfur</sub> in Beijing



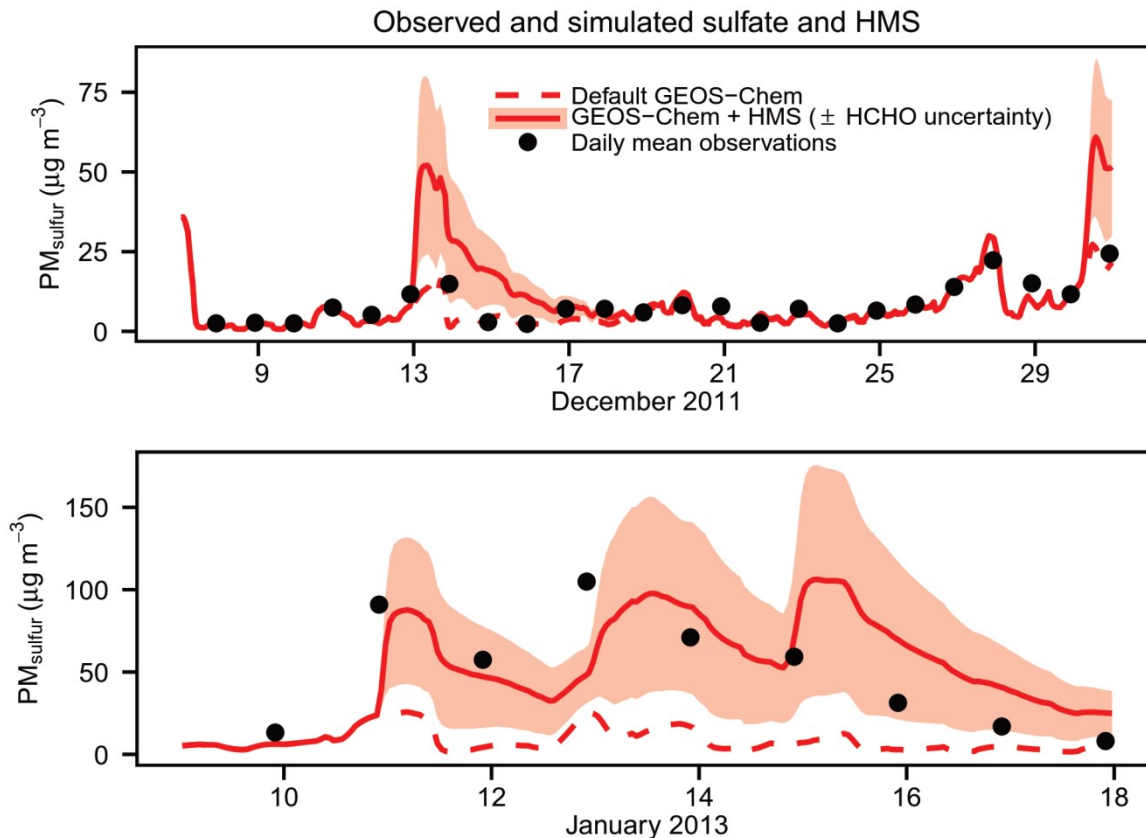
- SO<sub>2</sub> has decreased consistently since 2013.
- The number of winter extreme haze days was consistent except for 2017-2018.
- The winter of 2017-2018 was the first time when SO<sub>2</sub> fell below HCHO and would have controlled HMS formation.
- HMS can explain high particulate sulfur in dim conditions with low oxidants.

# An overview of HMS chemistry

- Sulfite and bisulfite react with dissolved formaldehyde to form hydroxymethanesulfonate (HMS) in clouds and fogs.



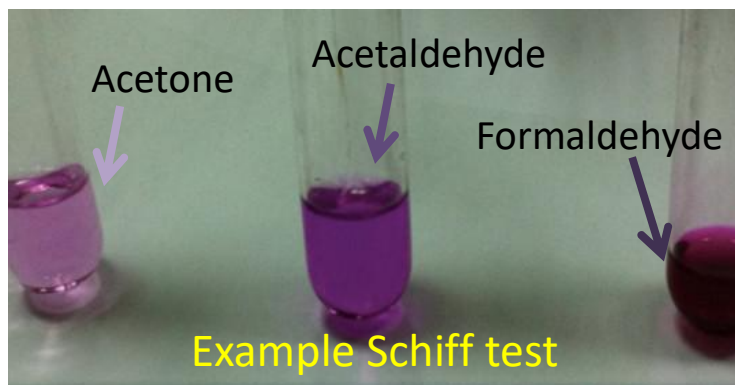
## Previous work found HMS could explain a large part of 'missing' $\text{SO}_4^{2-}$



- GEOS-Chem underestimates sulfur PM in January 2013 but does ok in December 2011.
- Dim winter conditions mean too little oxidant to produce sulfate.
- Adding HMS can improve match with observations in January 2013 without making too much of a mess of December 2011.
- A key difference between the two time periods is the presence and timing of low clouds.



# Sulfur-aldehyde chemistry was first examined in the 1860s



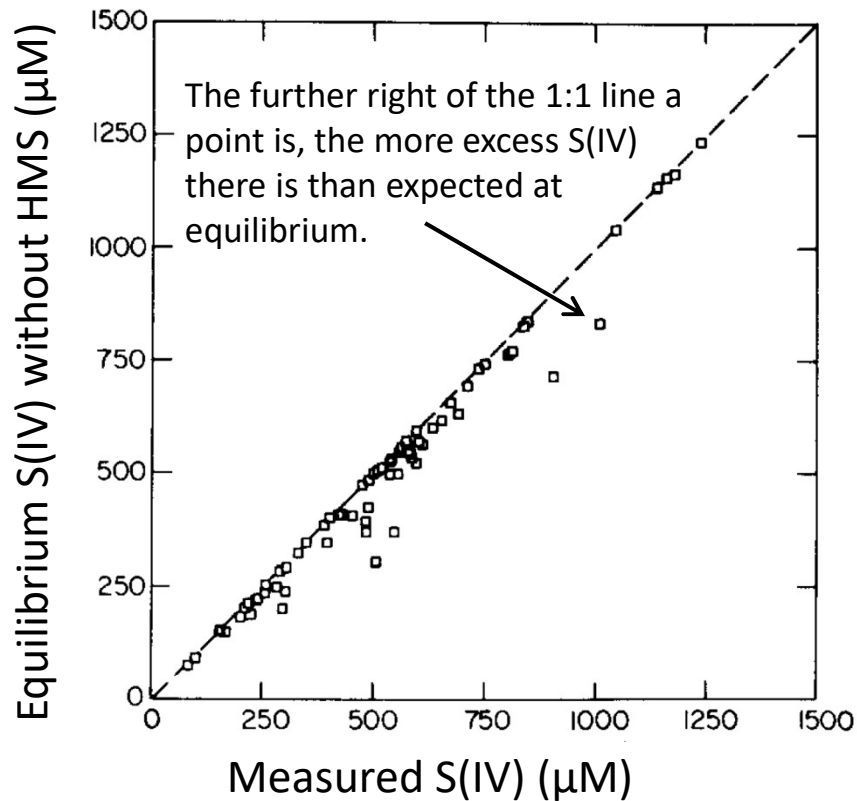
- Hugo Schiff developed the Schiff test in 1866 for the detection of aldehydes.
  - In the test a bisulfite is added to a fuchsin dye solution, draining the color and forming a sulfonic acid.
  - Addition of aldehydes returns the color due to the formation of sulfur-aldimine adducts.
- Dasgupta et al. (1980) built on this for a simplified test based on HMS for the determination of atmospheric  $\text{SO}_2$ .



Hugo Schiff (1834-1915)

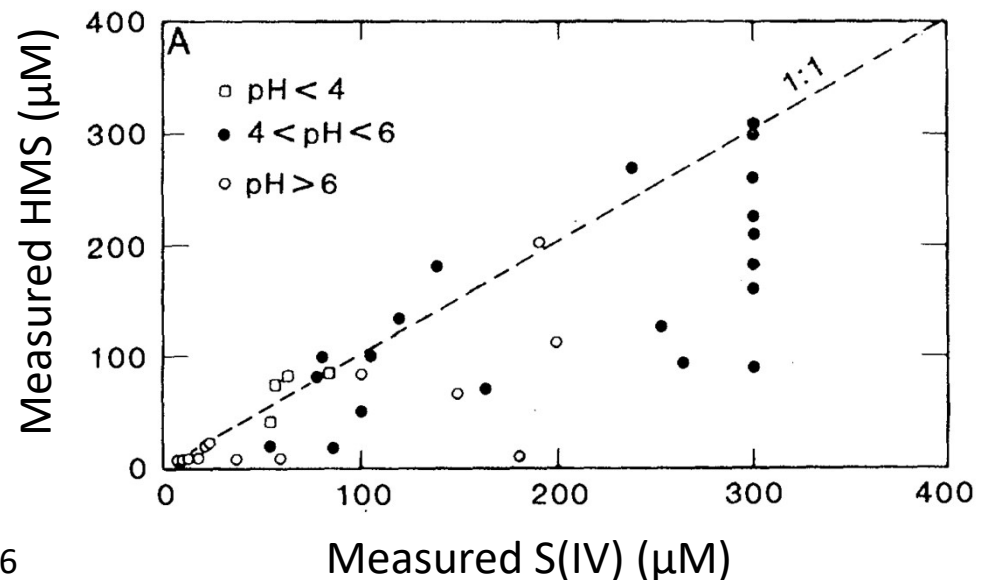
# In the 1980s HMS was used to explain deviations from equilibrium

## S(IV) in Bakersfield 1983 fog water



- S(IV) in Bakersfield, CA fog water samples were found to have more S(IV) than could be explained from  $\text{SO}_2 - \text{HSO}_3^- - \text{SO}_3^{2-}$  equilibrium.
- Including HMS in equilibrium calculations could mostly resolve this discrepancy.
- Follow up specialized measurements showed HMS as a significant fraction of S(IV).

## S(IV) and HMS in Bakersfield fog water ('84-'85)

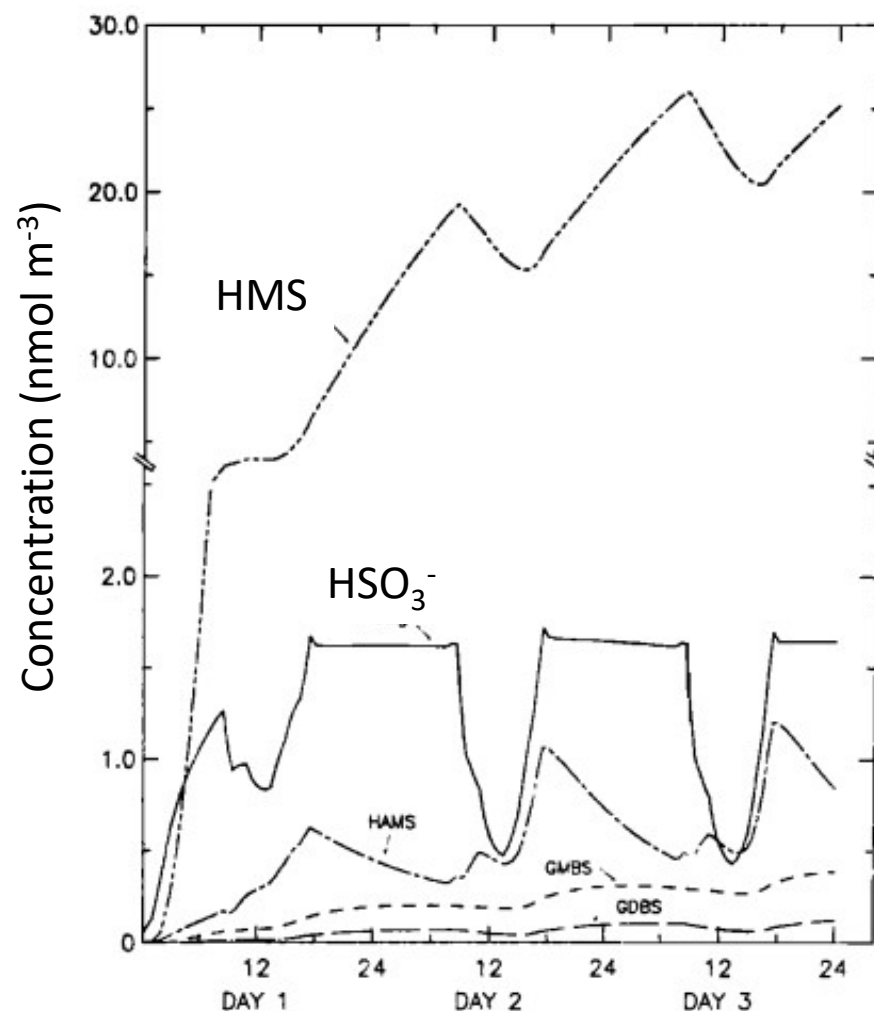




# HMS chemistry has been mostly ignored since the late 1980s

- HMS was included in some early atmospheric chemistry models.
- HMS was also detected in aerosol particles in the early 1990s.
- Funding for cloud/fog and sulfur chemistry dried up with the passage of the 1990 Clean Air Act amendments.
- Difficulties measuring HMS in aerosol samples combined with a lack of representation in most models led HMS to be mostly ignored until very recently.

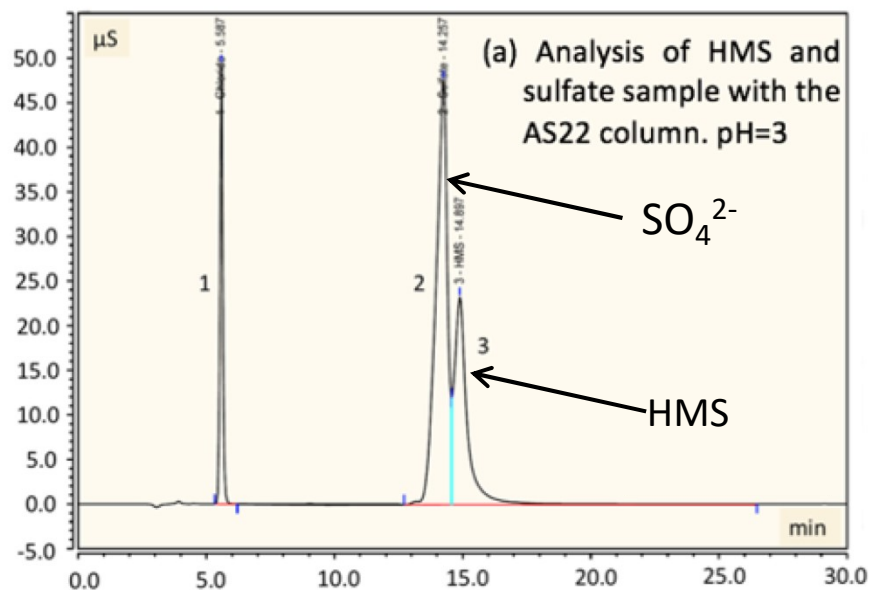
Simulated top of boundary layer S(IV)  
for winter in San Joaquin Valley, CA



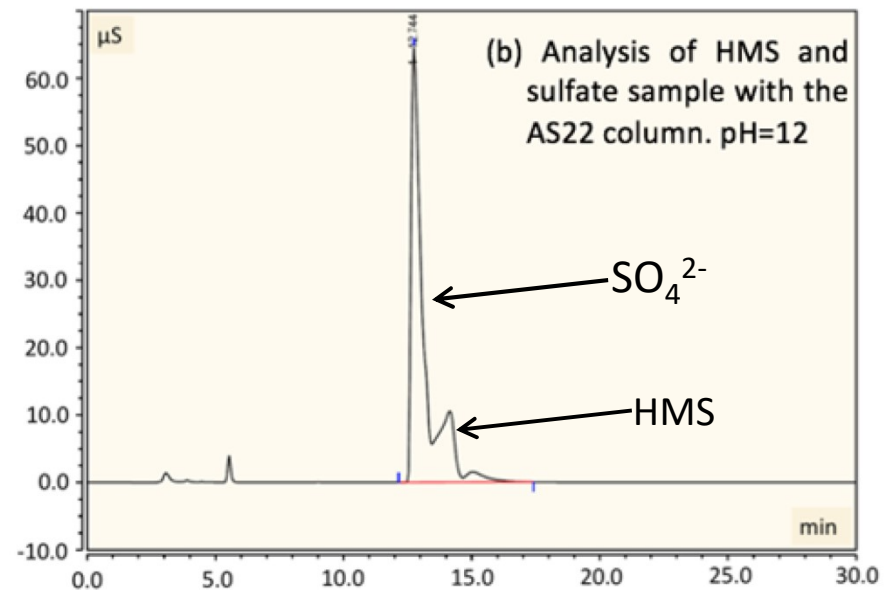
# HMS can be easily confused for $\text{SO}_4^{2-}$ in measurements: IC

- Ion chromatography 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  $\text{SO}_4^{2-}$  together and interpret it all as  $\text{SO}_4^{2-}$ .
- High pH, such as due to use of a KOH eluent, can also cause HMS to fall apart and potentially be oxidized to  $\text{SO}_4^{2-}$

HMS +  $\text{SO}_4^{2-}$  in AS22  
(can not separate)



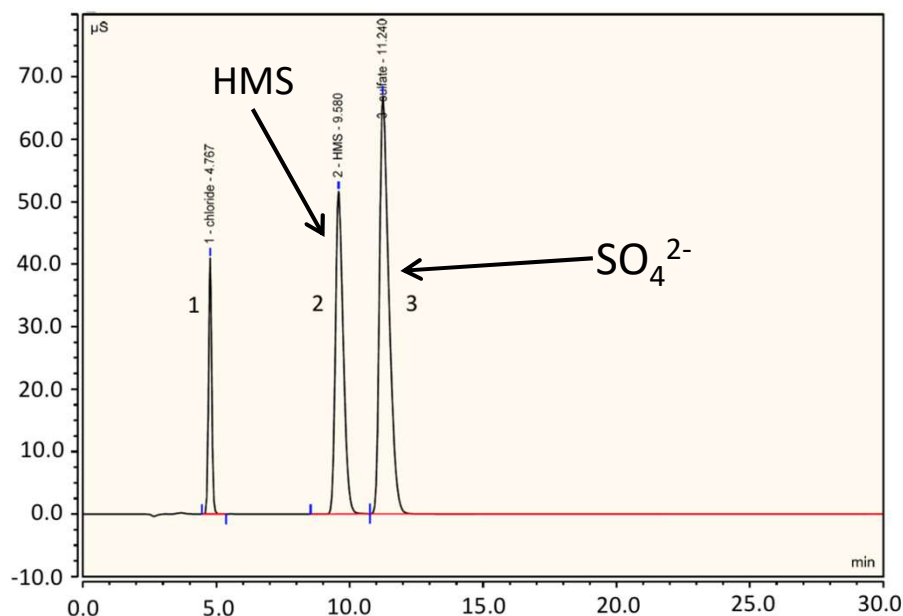
HMS +  $\text{SO}_4^{2-}$  in AS22  
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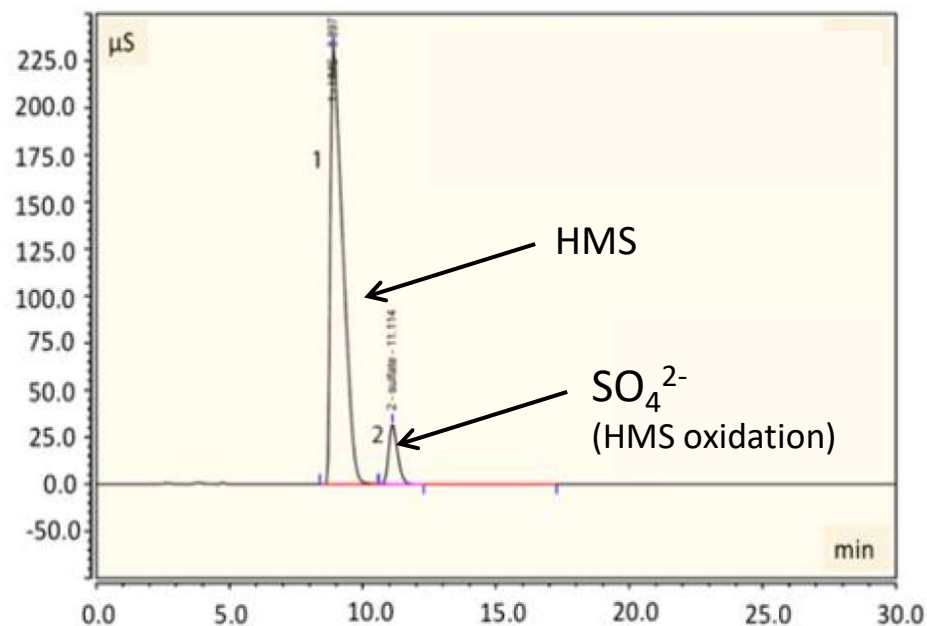
# HMS can be easily confused for $\text{SO}_4^{2-}$ in measurements: IC

- Use of an alkyl quaternary ammonium IC column (e.g. AS12a) can separate HMS and  $\text{SO}_4^{2-}$  when using a calcium-carbonate eluent.
- There is still the issue of HMS decomposition and oxidation at high sample pH.
- Use of a high pH eluent would likely further complicate separation of HMS and  $\text{SO}_4^{2-}$

HMS +  $\text{SO}_4^{2-}$  in AS12A at pH=3  
(can separate)

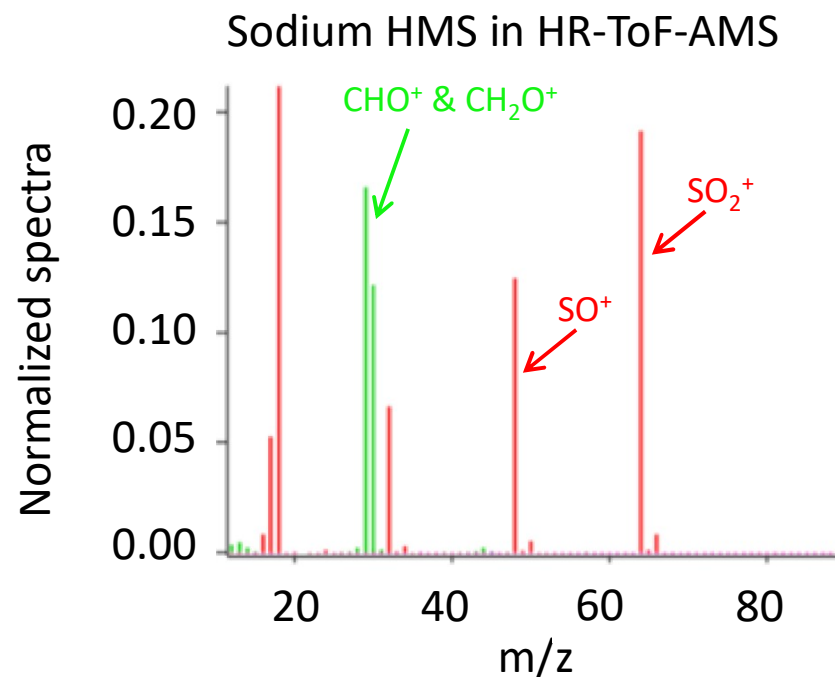
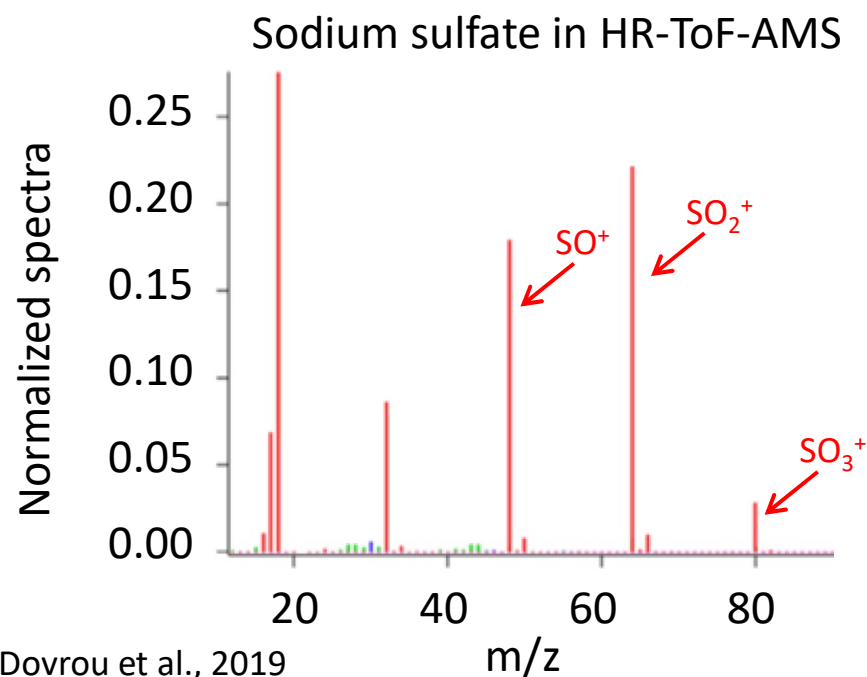


HMS in AS12A at pH=12  
(can separate)



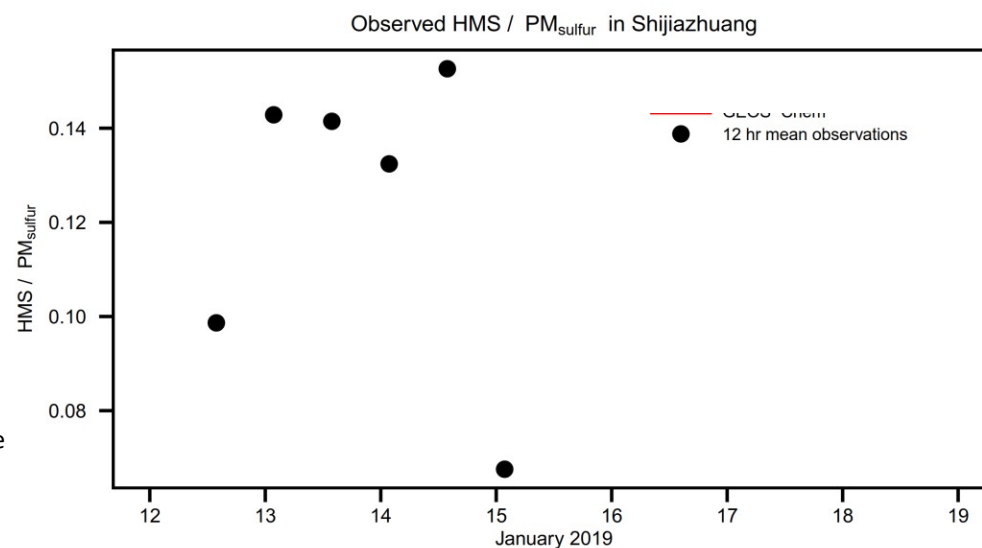
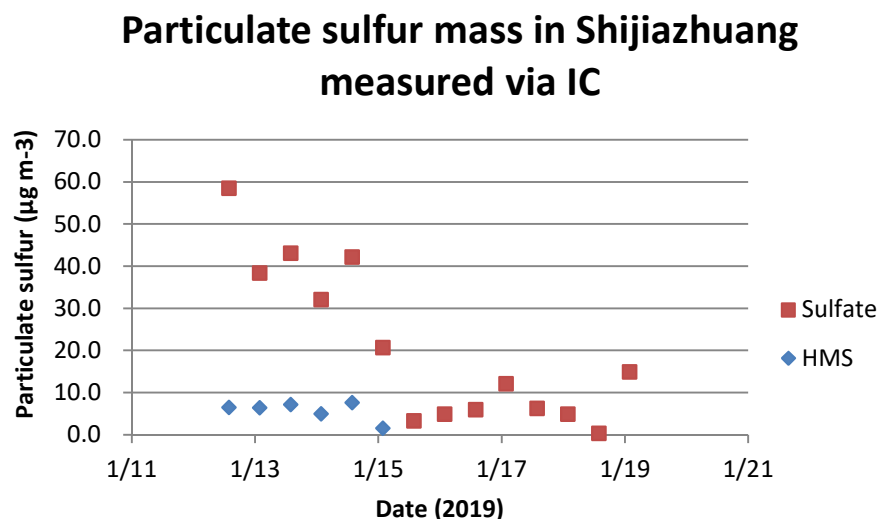
# HMS can be easily confused for $\text{SO}_4^{2-}$ in measurements: AMS

- 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  $\text{SO}_4^{2-}$ .
- 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.



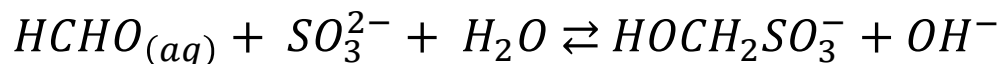
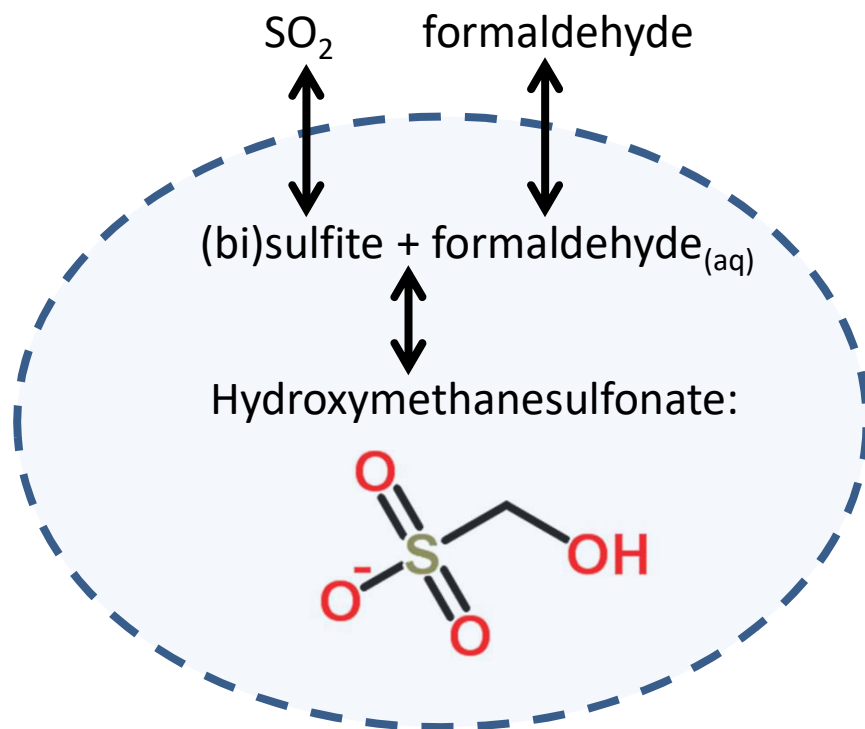
## HMS can be easily confused for $\text{SO}_4^{2-}$ in measurements: decomposition

- Recent measurements using the AS12A showed up to 15% of particulate sulfur mass as HMS.
- No HMS was detected upon reanalysis of the same samples after being stored in a freezer for about 3 months.
- HMS may decay in filters sent in the mail or if significant time has elapsed before samples are analyzed.
- HMS may also decay during analysis if a high pH eluent is used.



Shijiazhuang is a city of 10 million people 165 miles southwest of Beijing

# HMS decomposition before analysis may lead to additional $\text{SO}_4^{2-}$



- In aqueous media, HMS is constantly decaying and forming given HCHO and  $\text{SO}_2$ .
- Given constant  $\text{SO}_2$  and HCHO, HMS formation is always much greater than HMS decomposition.
- If HMS decomposition occurs in a low HCHO environment, HCHO may outgas from the particle before HMS reforms.
- Sulfite released into the particle may be oxidized to sulfate.

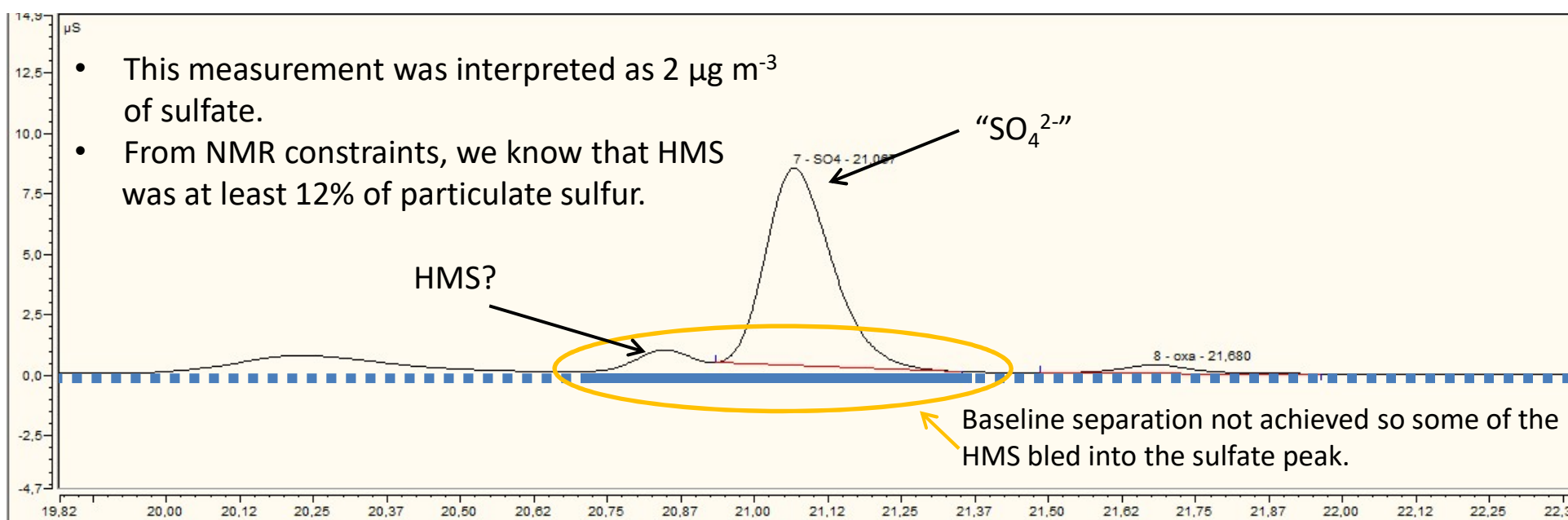
Aerosol or cloud pH	HMS lifetime
3	~ 2 years
4	Months
5	~Week
6	~1 day
7	~2 hours



# How might HMS have been overlooked in observations?

- Measurements of HMS and sulfate have been carried out in the Po Valley, Italy
  - HMS was measured via NMR.
    - First the sample was stored for  $\sim 1$  year and then dried, likely leading to HMS decomposition.
  - Total particulate sulfur was measured via IC.

Chromatogram for Bologna, Italy from Feb 18, 2014

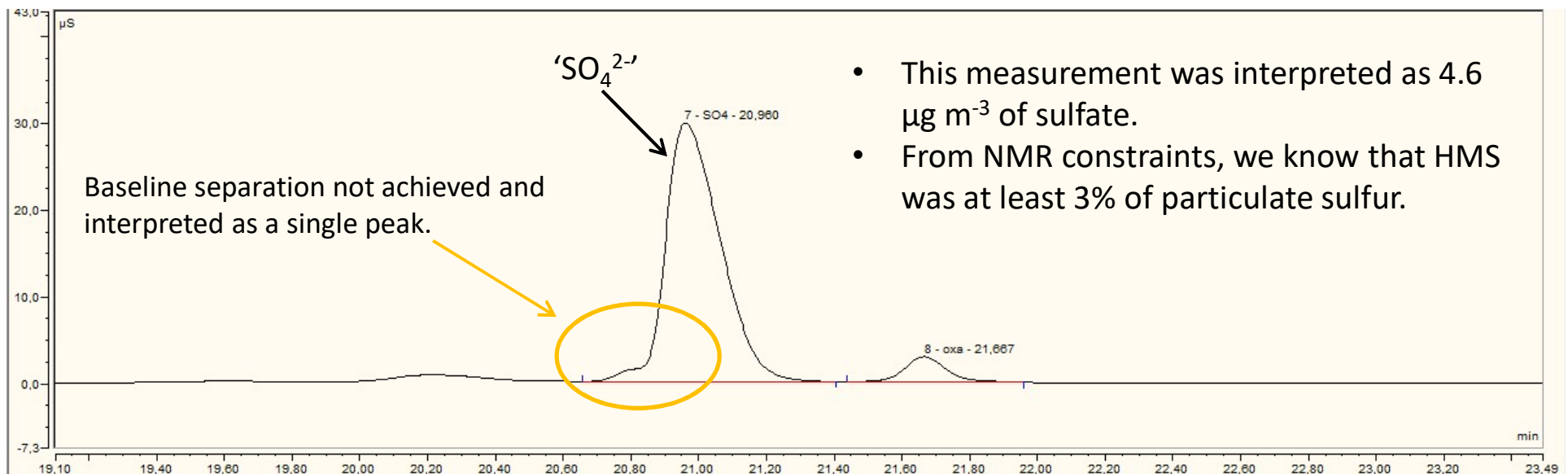


Data provided courtesy of Stefano Decesari and Marco Paglione, National Research Council Italy (unpublished)

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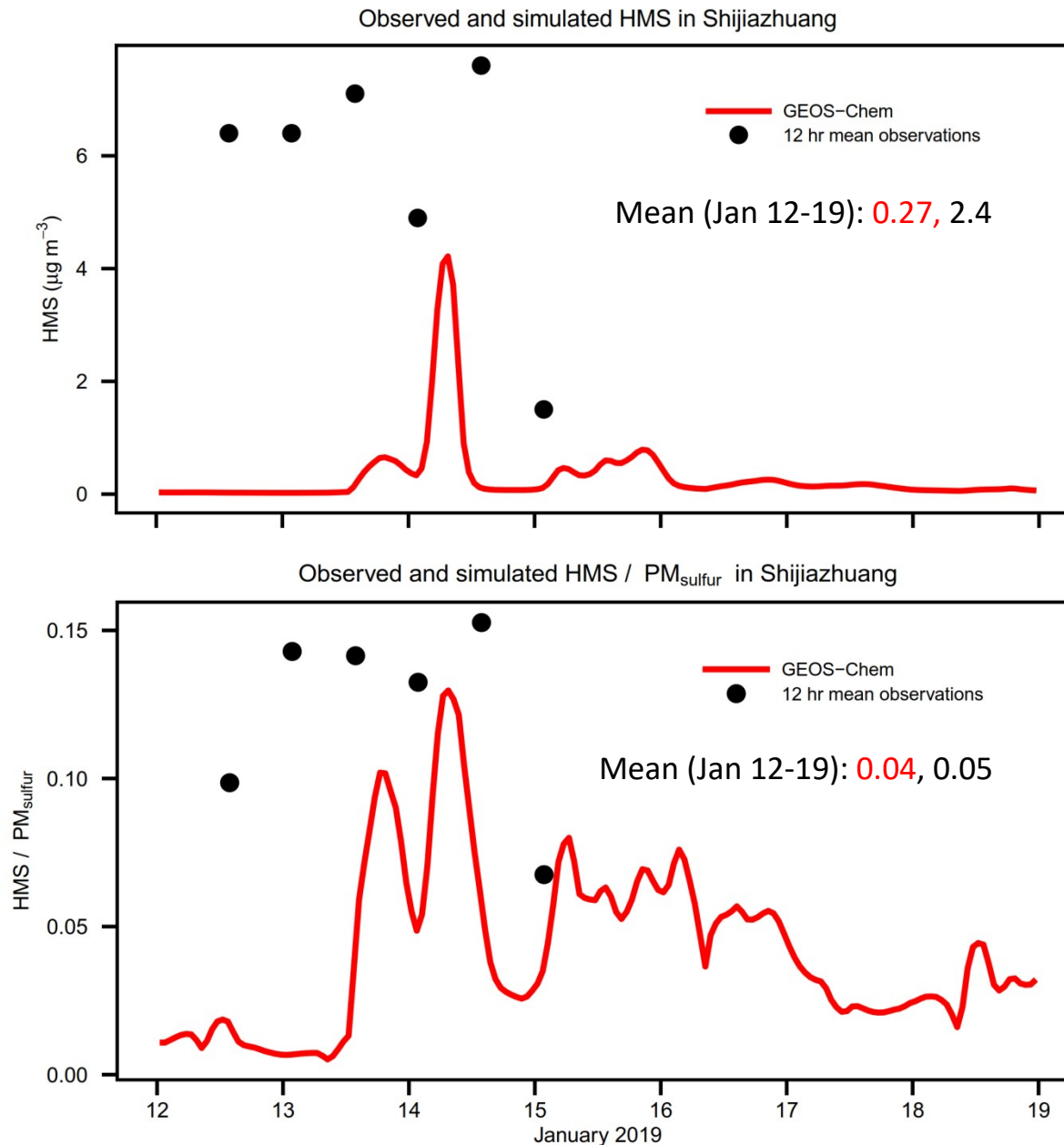
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Chromatogram for Bologna, Italy from Feb 17, 2014



Data provided courtesy of Stefano Decesari and Marco Paglione, National Research Council Italy (unpublished)

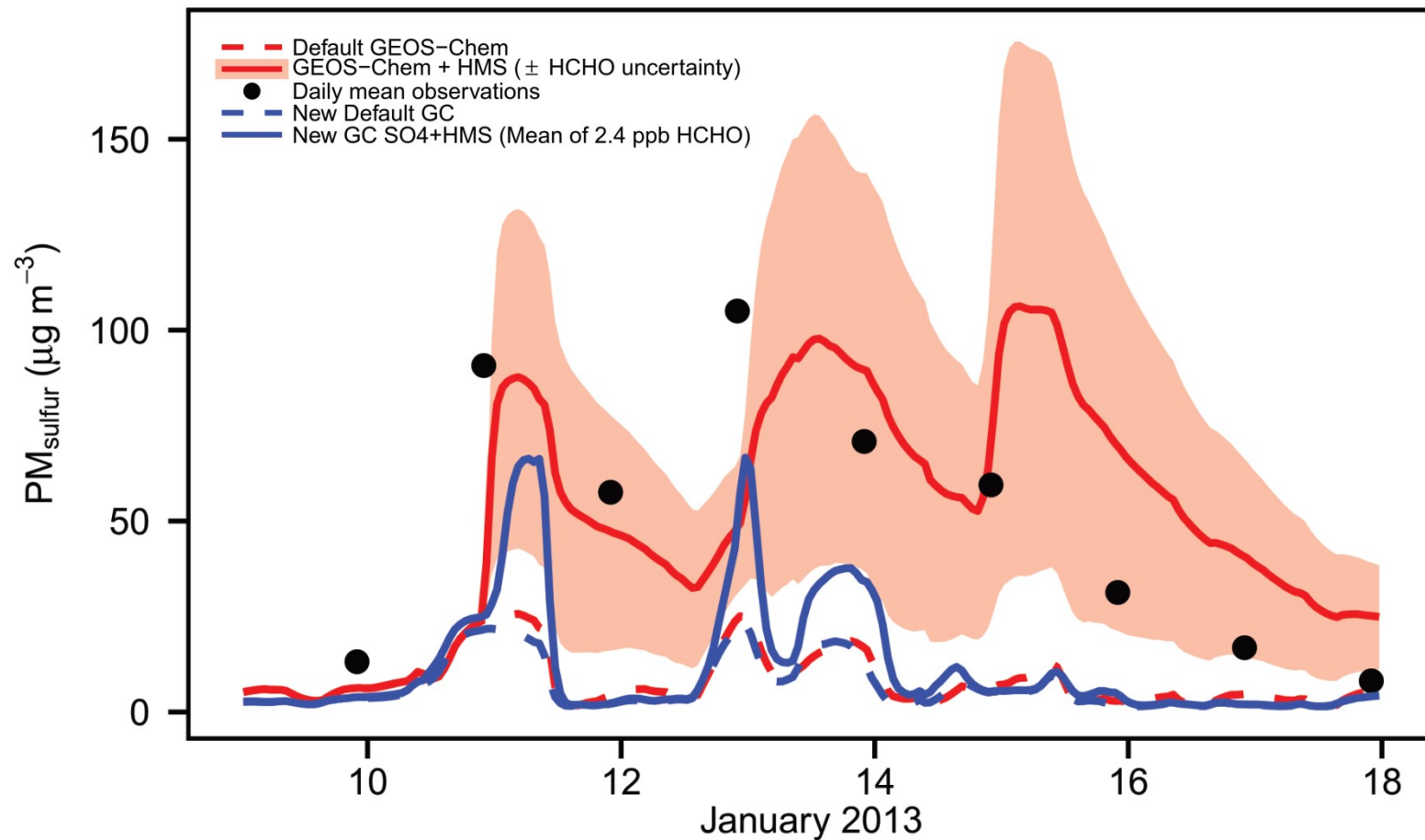
# HMS in GEOS-Chem: Underestimates in China



- GEOS-Chem underestimates HMS and  $\text{SO}_4^{2-}$  during the non-cloudy periods, indicating uncertainty due to clouds.
- Low values of modelled HCHO, compared to observations may also be a factor.
- GEOS-Chem underestimates HMS as a fraction of particulate sulfur.

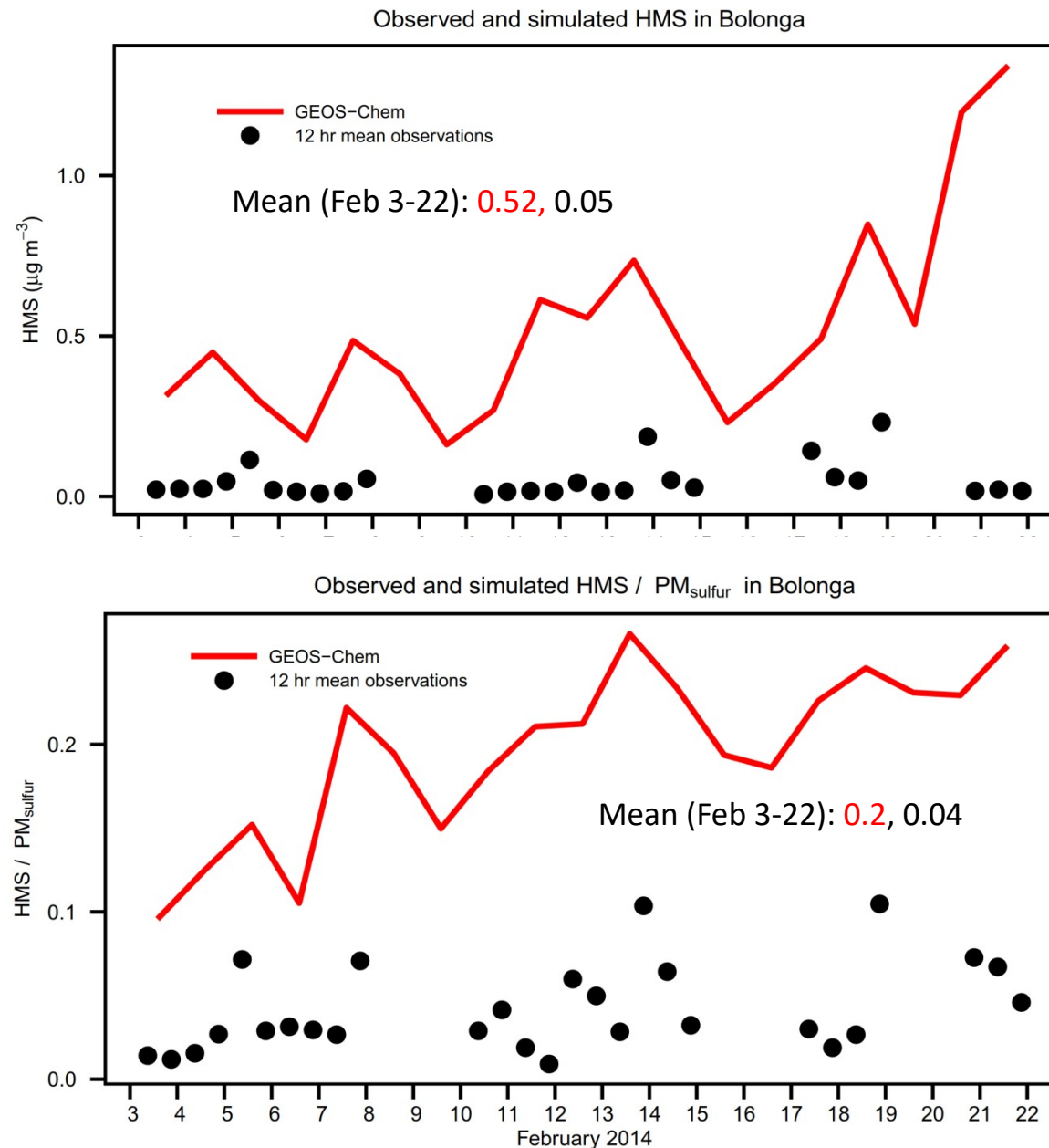
Measurements provided by Zirui Liu,  
CAS (unpublished)

# HMS in GEOS-Chem: Revisiting January 2013 Beijing



- Particulate sulfur is underestimated compared to observations.
- HMS may be underestimated over Beijing in GEOS-Chem due to low values of modelled HCHO, compared to observations.
- Even with inadequate HCHO, HMS is >50% of particulate sulfur during peak simulated haze.

# HMS in GEOS-Chem: Overestimate in Bologna or decomposed HMS?

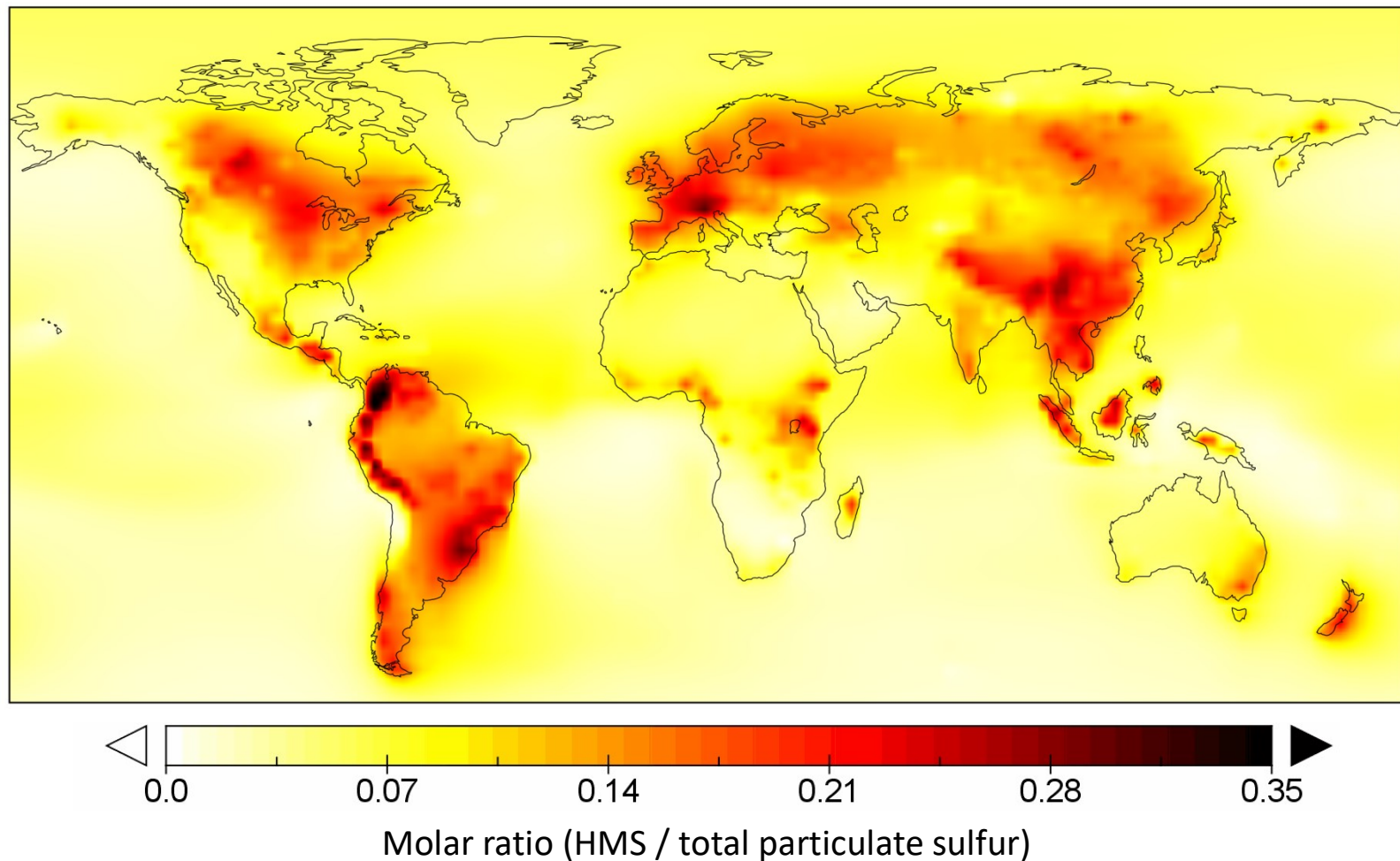


- NMR measurements of HMS serve as a lower limit on HMS.
- IC measurements give total particulate sulfur.
- GEOS-Chem  $\text{SO}_4^{2-}$  is greater than total particulate sulfur measurements, indicating uncertainty due to clouds.
- GEOS-Chem overestimates HMS compared to NMR observations likely due to:
  - HMS decomposition prior to analysis
  - Uncertainty in clouds

Measurements provided by Stefano Decesari and Marco Paglione, National Research Council Italy (unpublished)

HMS may be an important fraction of particulate sulfur in many areas

Annual Mean fraction of HMS in total particulate sulfur  
(2013- 2018)

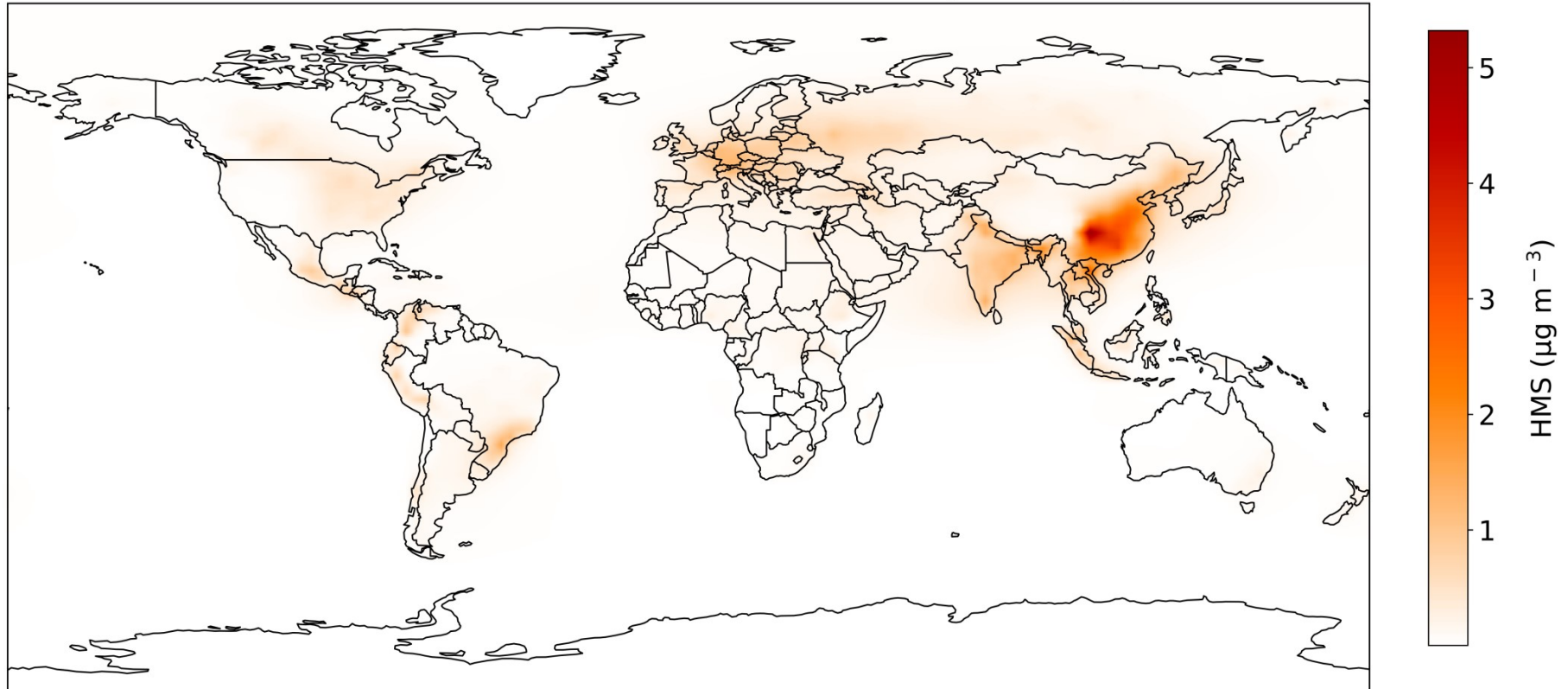


- HMS may be >20% of annual mean particulate sulfur in many polluted areas.



# Highest annual mean HMS is in Sichuan basin

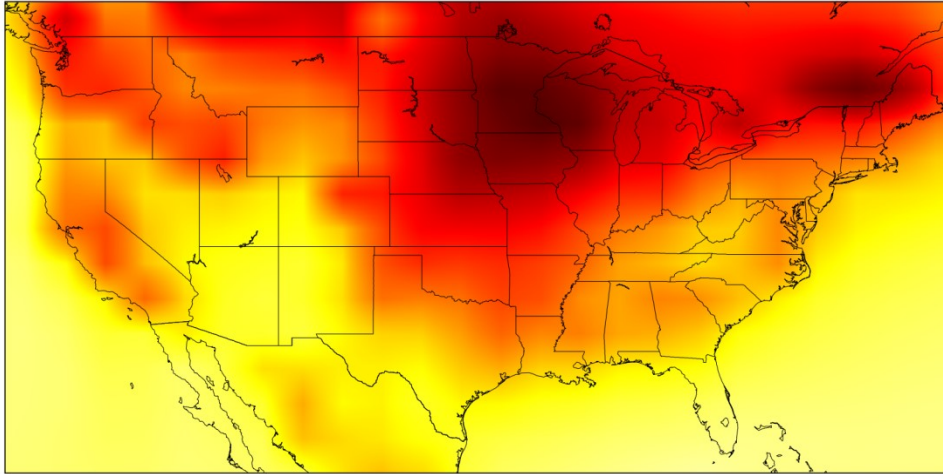
Annual mean concentration of HMS in aerosol (2013-2018)



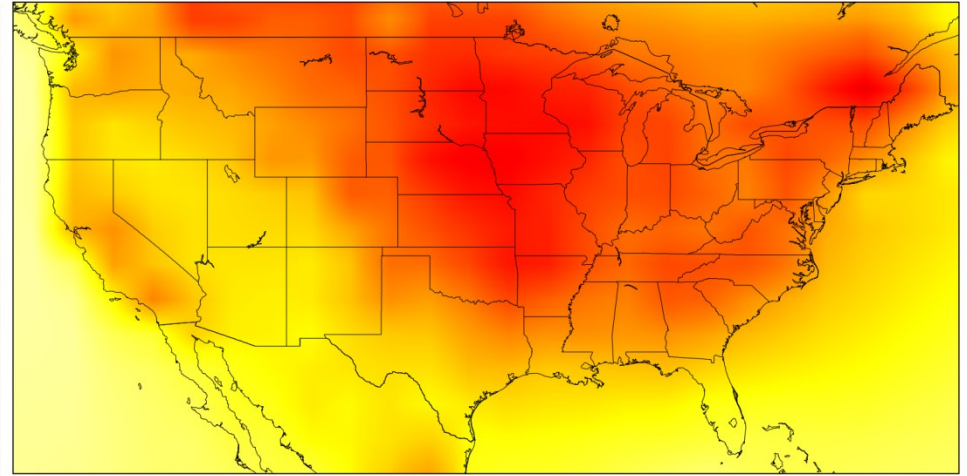
In addition to China, HMS is important in central Europe, India, Southeast Asia, and parts of North and South America.

# HMS in the United States: Large seasonal variability

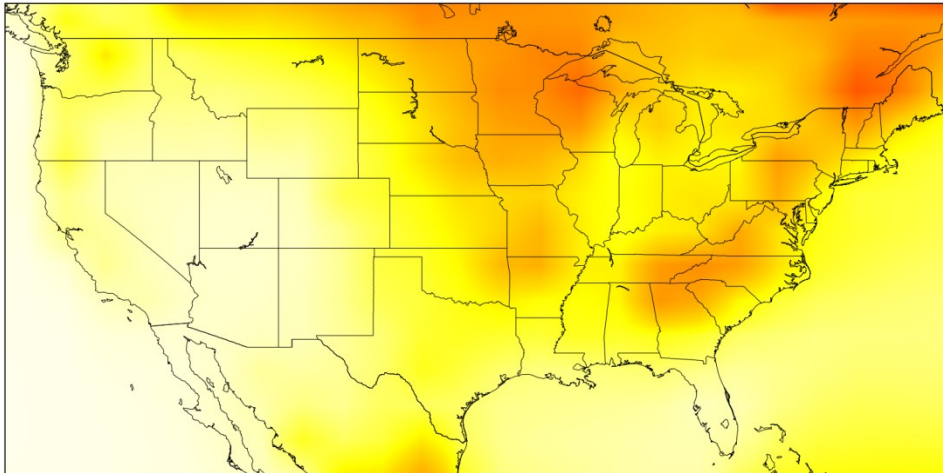
DJF (2013-2018)



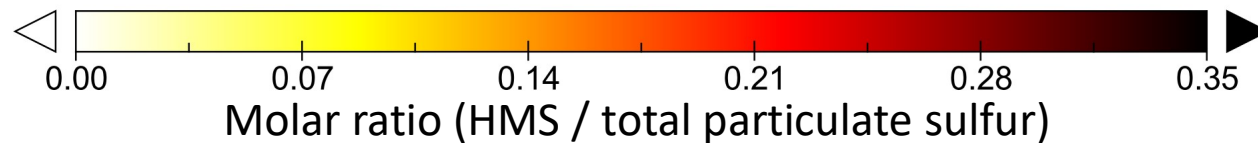
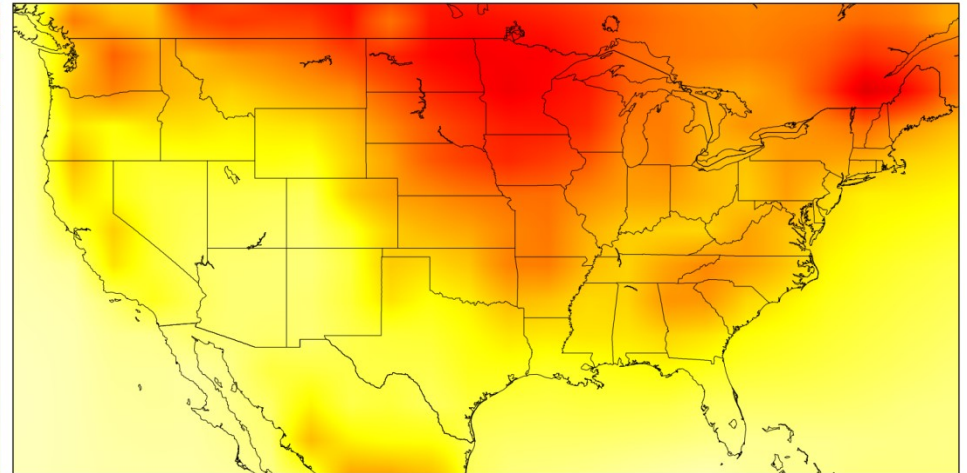
MAM (2013-2018)



JJA (2013-2018)

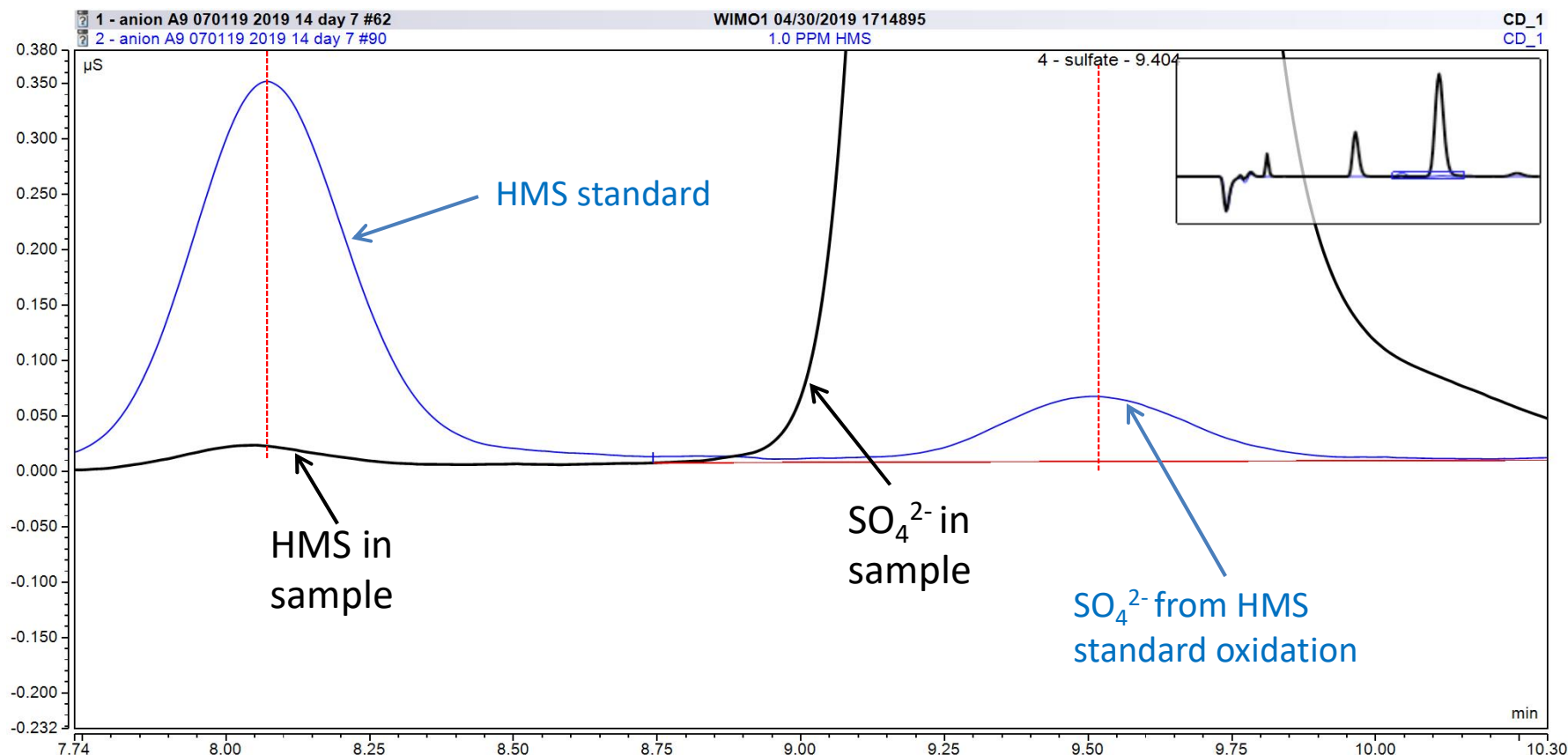


SON (2013-2018)



# How can we detect HMS in previous IMPROVE measurements?

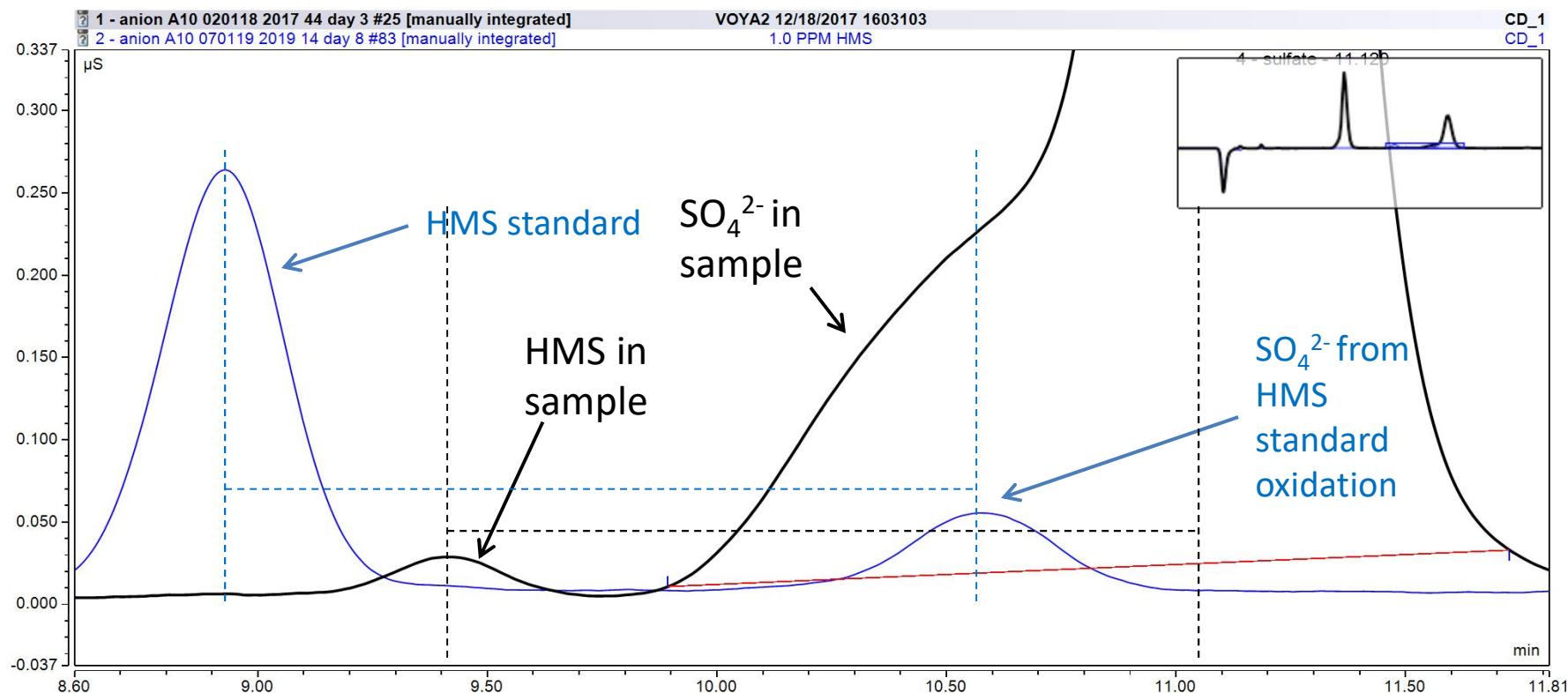
## IMPROVE chromatogram for Wichita Mountains, OK (04/30/19)



- Samples are stored for a month or two before analysis, which would lead to significant HMS decomposition and likely oxidation to sulfate.
- HMS can be identified and quantified by comparing sample peaks with a standard analyzed right before sample analysis.

# How can we detect HMS in previous IMPROVE measurements?

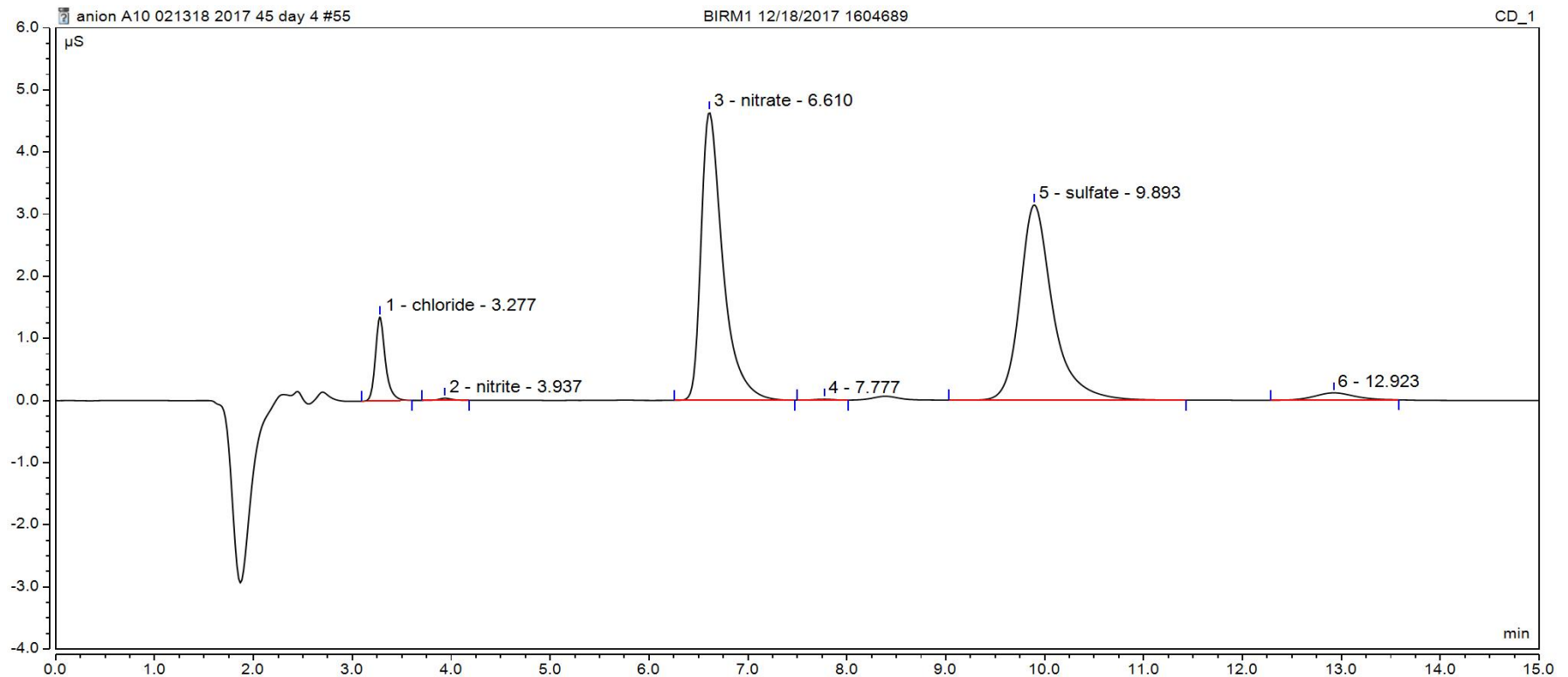
## IMPROVE chromatogram for Voyageurs National Park, MN (12/18/17)



- Samples are stored for a month or two before analysis, which would lead to significant HMS decomposition and likely oxidation to sulfate.
- HMS can be identified in previous samples by looking for peaks appearing the same distance prior to sulfate as in the standard.

# How can HMS be overlooked in IMPROVE?

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

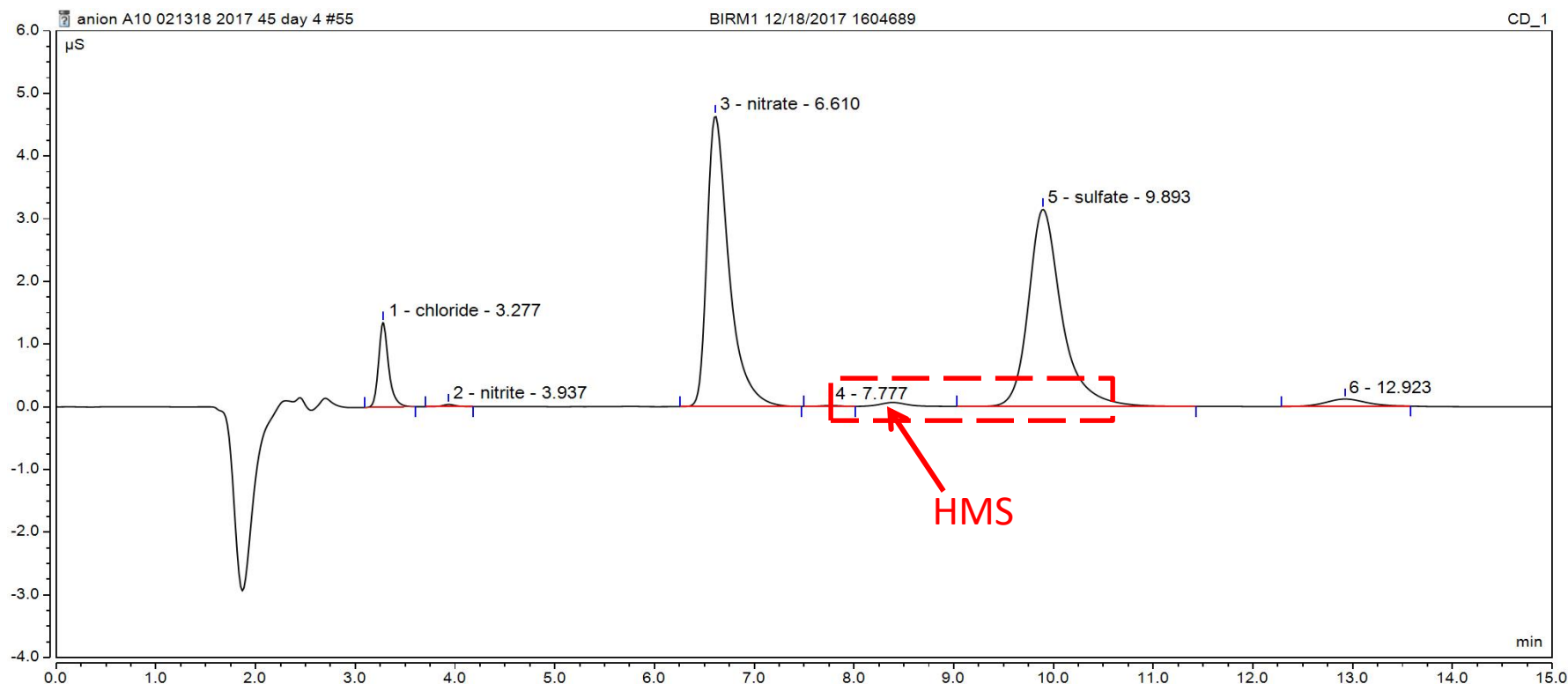


- The chromatogram analysis program is set to automatically integrate peaks corresponding to nitrate and sulfate for the anions.
- Chromatograms are also checked by eye for anomalies that could affect the sulfate and nitrate quantification.



# How can HMS be overlooked in IMPROVE?

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

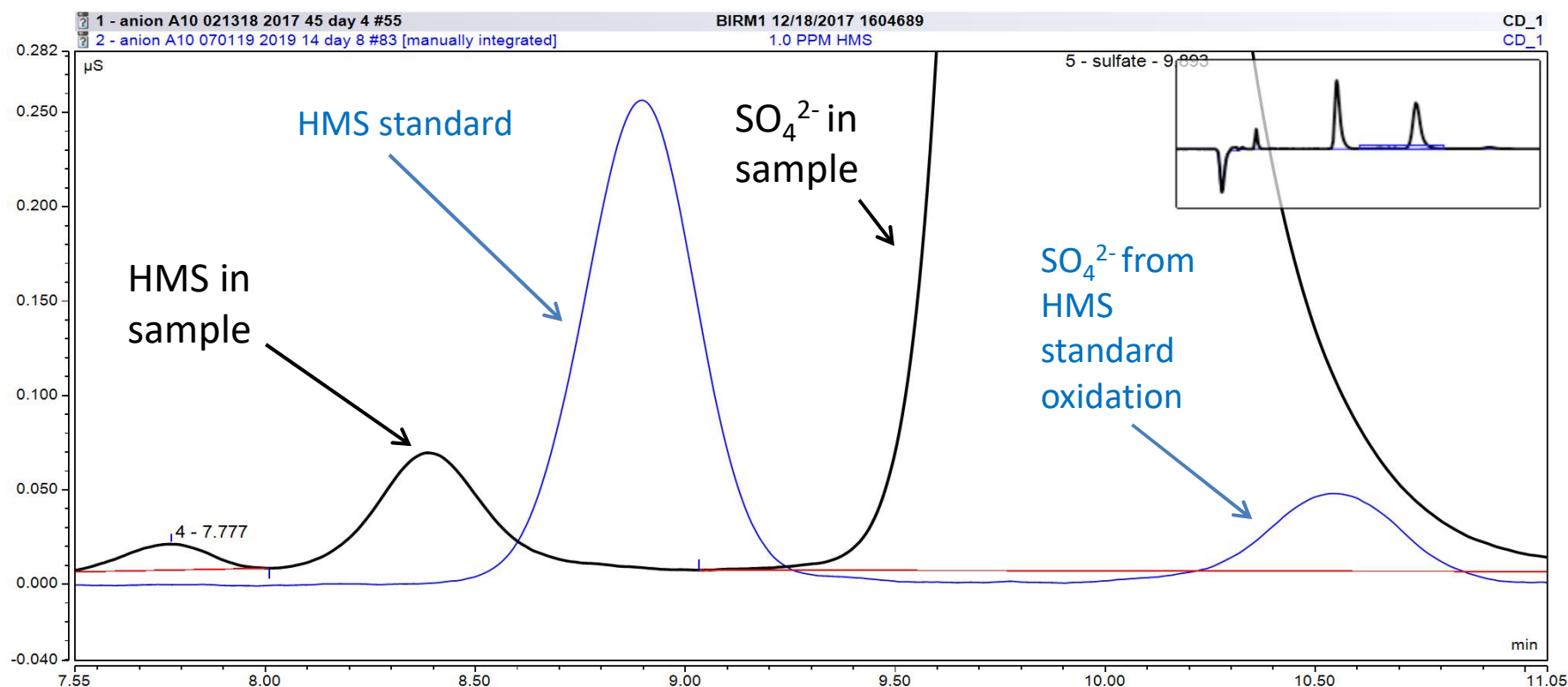


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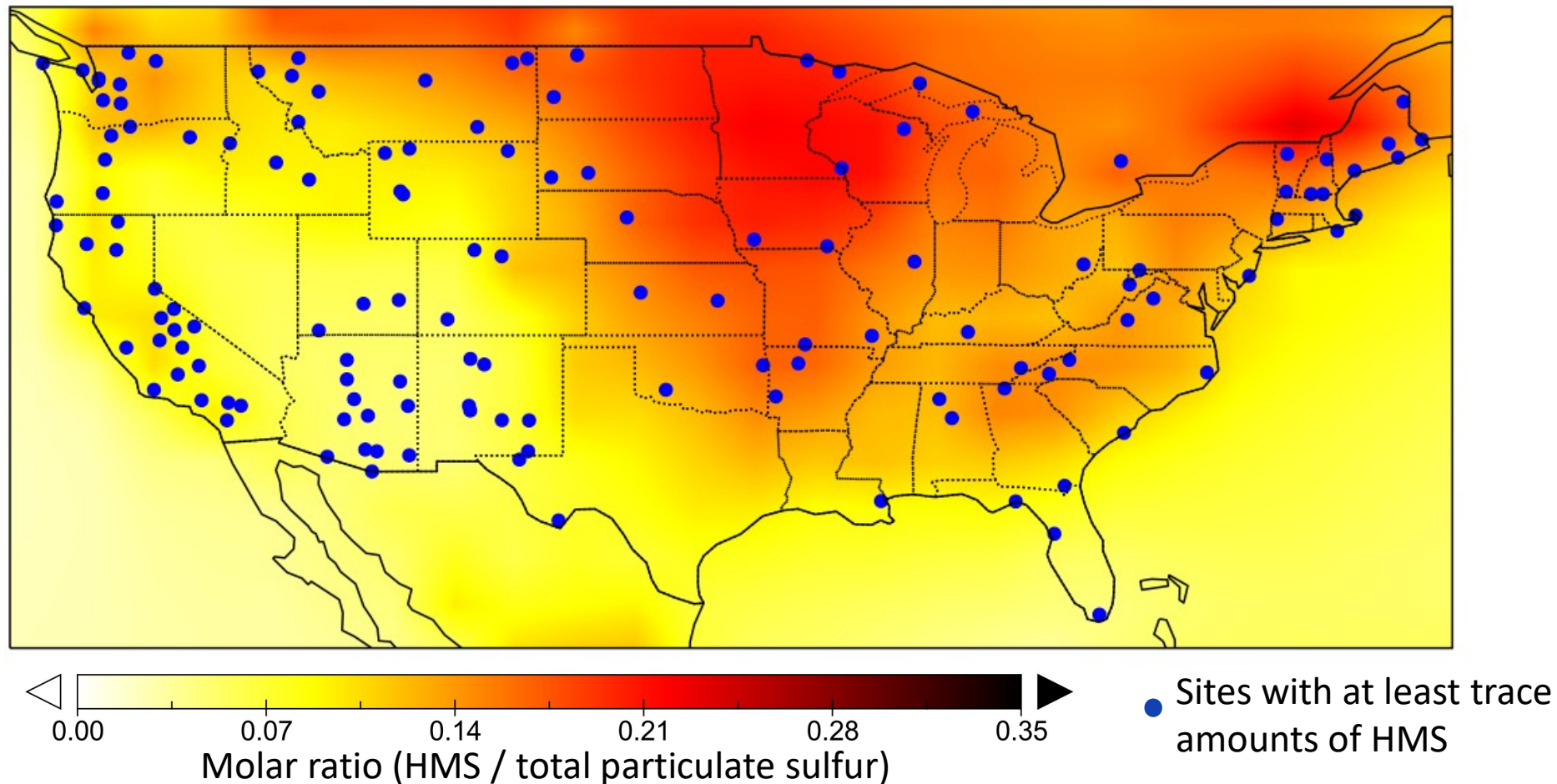
## IMPROVE chromatogram for Birmingham, AL (12/18/17)



- The HMS peak is readily visible if you zoom in on the chromatogram, but this is not typically done.
- Until recently it was also uncertain what these peaks prior to sulfate were from.

# Ubiquitous evidence of trace amounts of HMS in IMPROVE chromatograms

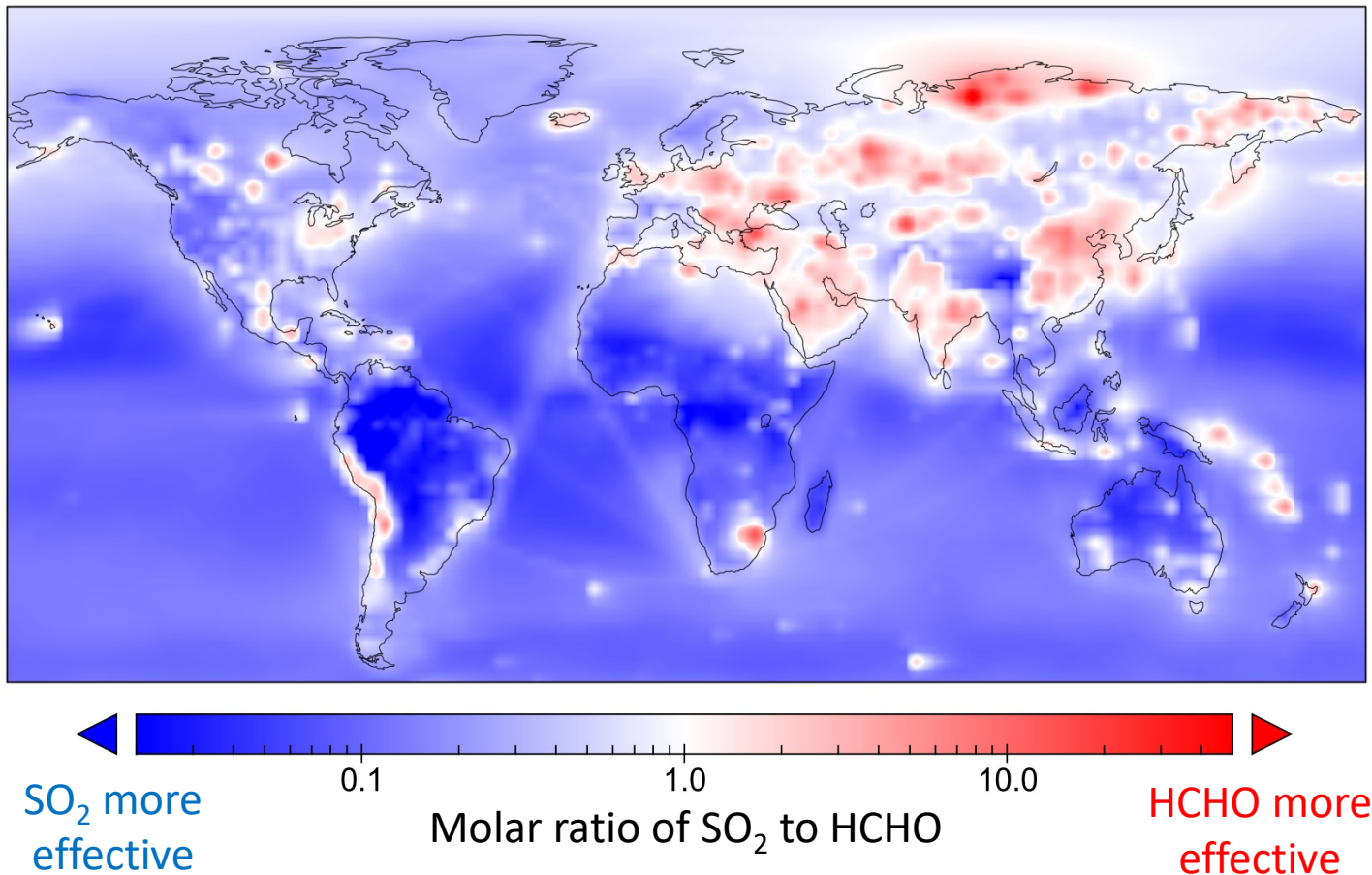
Annual mean (2013-2017) HMS fraction of particulate sulfur in the United States  
and IMPROVE locations from 2017 where HMS has been detected



- At least trace amounts of HMS are detected at 139 of the 158 IMPROVE sites
- Of the 7085 chromatograms examined, 1888 (26.7%) had contained evidence of HMS

# Implications: are HCHO reductions an effective way to reduce PM?

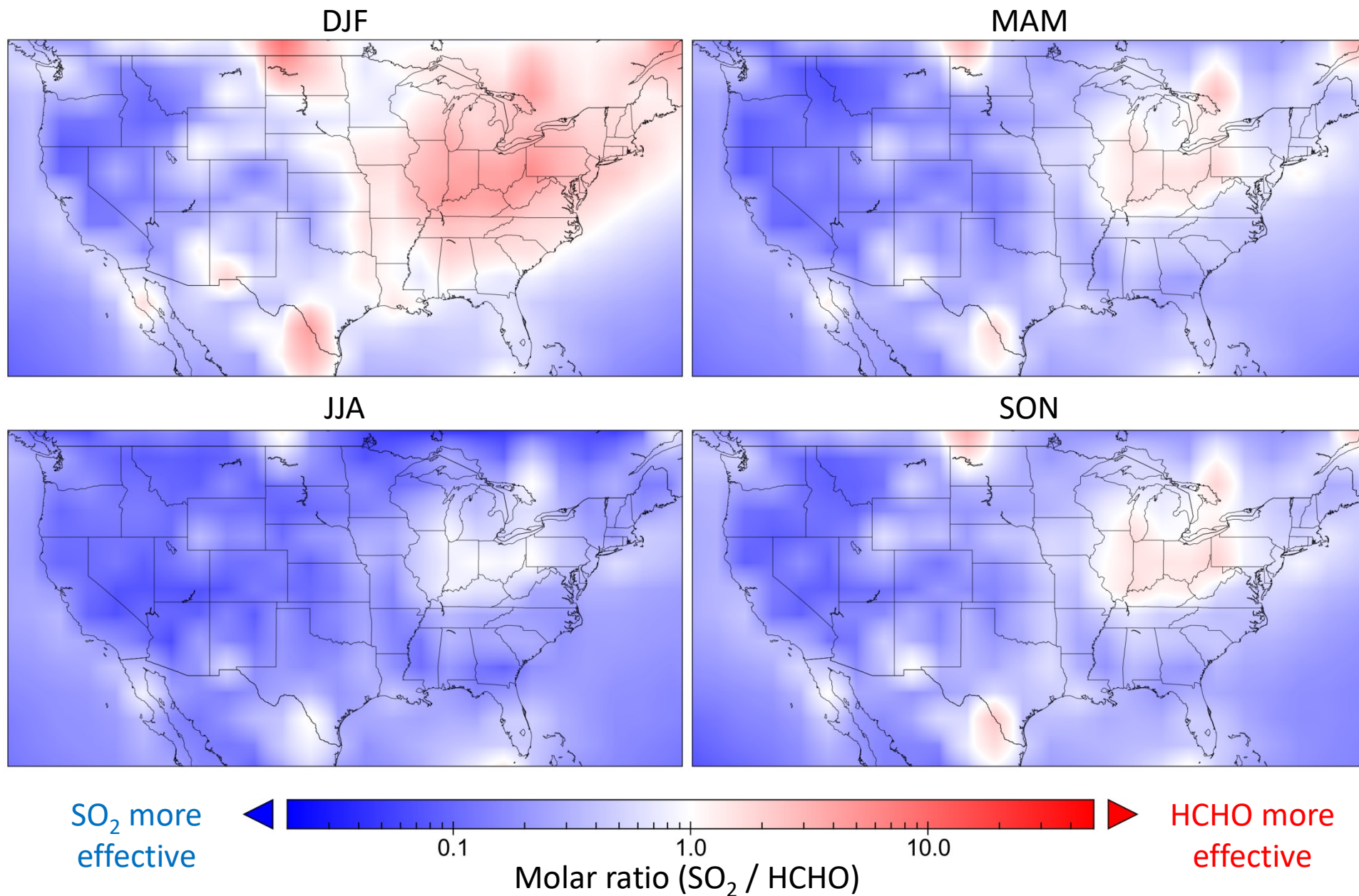
Limiting reactant for HMS formation



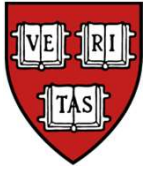
- HMS requires HCHO and  $\text{SO}_2$  to react in a 1:1 ratio.
- Because the reaction is slow, the lower concentration reactant can control the reaction.
- In some areas where  $\text{SO}_2 \gg \text{HCHO}$  or  $\text{HCHO} \gg \text{SO}_2$ , reducing the reactant in excess may have little effect on HMS production (e.g. the Beijing experience).



## Seasonal effectiveness of HCHO versus SO<sub>2</sub> reductions for the US (2013-2018)



# Thank you



## Harvard:

- Jonathan Moch; Loretta Mickley; Daniel Jacob; Eleni Dovrou; Frank Keutsch; Bill Munger



## Tsinghua University:

- Jingkun Jiang; Meng Li; Yuan Cheng; Xiaohui Qiao; Qiang Zhang



## Chinese Academy of Sciences:

- Zirui Liu



## National Research Council, Italy:

- Stefano Decesari, Marco Paglione



## Research Triangle Institute:

- Tracy Dombek

## Conclusions:

- HMS may be a significant fraction of particulate sulfur in many regions.
- In the United States, HMS is simulated to be most significant in the Midwest during wintertime.
- There is abundant evidence of HMS in IMPROVE aerosol samples that was previously overlooked.
- Whether HMS is controlled by  $\text{SO}_2$  or  $\text{HCHO}$  varies by region and season.
- 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.