Hydroxymethane sulfonate in extreme haze: Initial results from GEOS-Chem

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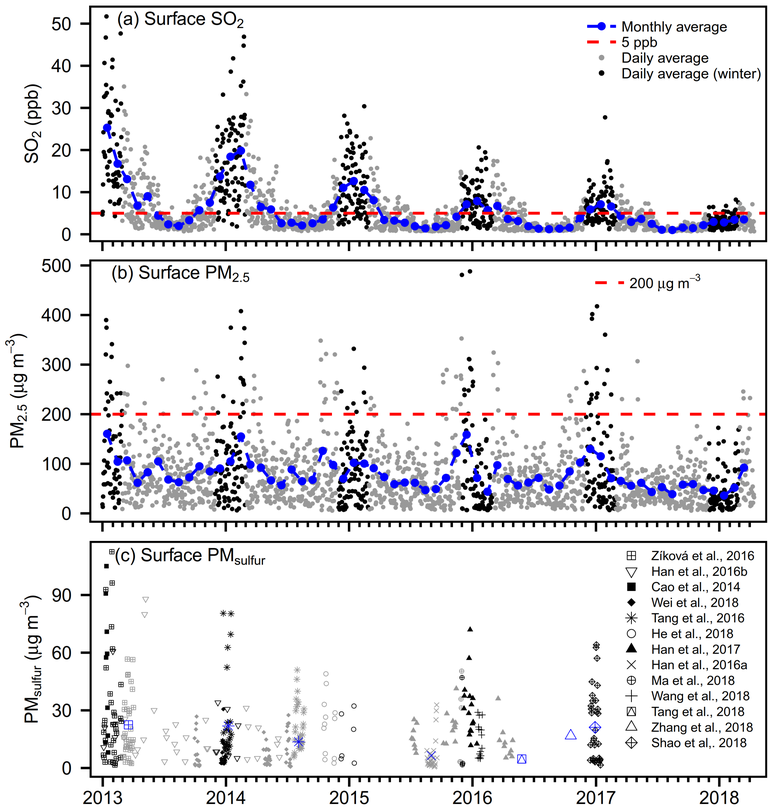
1. Motivation

Air pollution in China is a severe public health problem. In Beijing, the number of winter days with extreme particulate pollution ($PM_{2.5}$ > 200 μg m^{-3}) remained roughly constant between 2013 and 2017 despite significant reductions in SO_2. One possible reason for this discrepancy is that a large portion of what was previously assumed to sulfate in measurements from extreme haze is actually a molecule called hydroxymethane sulfonate (HMS). HMS chemistry is dependent on both HCHO and on SO_2, but in the Beijing area would have been controlled by HCHO until the winter of 2017-2018.

Surface observations of SO_2, $PM_{2.5}$, and PM_{sulfur} in Beijing



Previous work also showed that (Moch et al., 2018):

- Adding a 1-D model of HMS chemistry to GEOS-Chem could explain a large portion of particulate sulfur that was otherwise missing during extreme winter haze.
- Typical ion chromatography measurement systems can easily misinterpret HMS as sulfate.
- HMS chemistry is typically limited by HCHO as long as SO_2 concentrations are in excess

2. GEOS-Chem simulation setup

- We implemented the sulfur-formaldehyde chemistry described in Section 3 into GEOS-Chem.
- We also set a cloud pH floor of 5 for the North China Plain area in order to bring simulated cloud pH closer to observations from the Beijing area.
- We used MERRA2 (2012-2016) for a global 2x2.5º simulation to look at the global significance of HMS chemistry and a nested 0.5x0.625º simulation to look at HMS across China in more detail.
- TMI catalyzed SO_2 oxidation was examined as a sensitivity test.

3. Hydroxymethane sulfonate forms in clouds and can easily be misinterpreted as sulfate in measurements

Conditions promoting hydroxymethane sulfonate (HMS, $HOCH_2SO_3^-$) formation:

- Presence of clouds or fog
- High SO_2 and HCHO
- Cold temperatures
- Low concentrations of oxidants

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

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

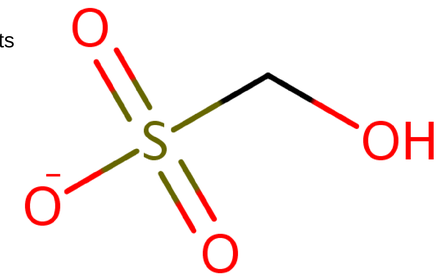
$$HSO_3^- \rightleftarrows SO_3^{2-} H^+$$

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

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

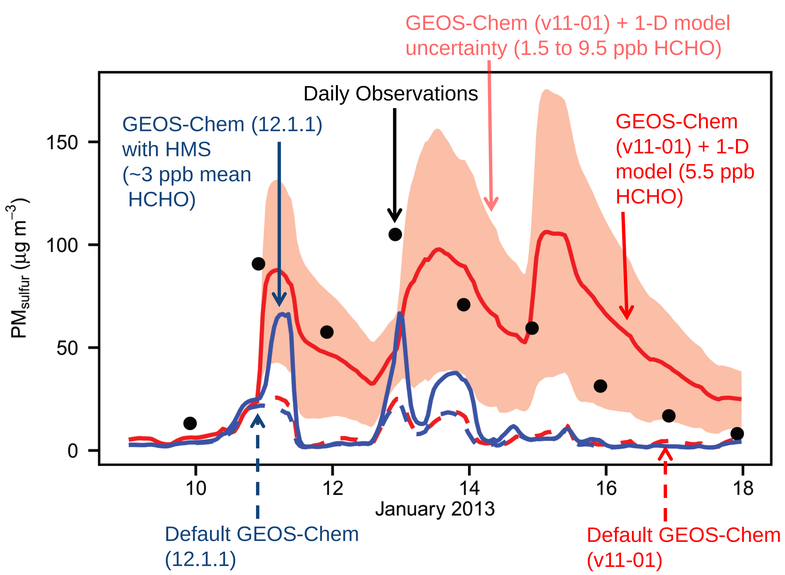
$$HCHO_{(aq)} + SO_3^{2-} + H_2O \rightarrow HOCH_2SO_3^- + OH^-$$

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



- HMS has a lifetime on the order of months to days for the pH range ~4-6
- HMS has been directly observed in clouds and aerosol.
- HMS can be easily confused for sulfate in both ion chromatography and in AMS or single-particle measurements.

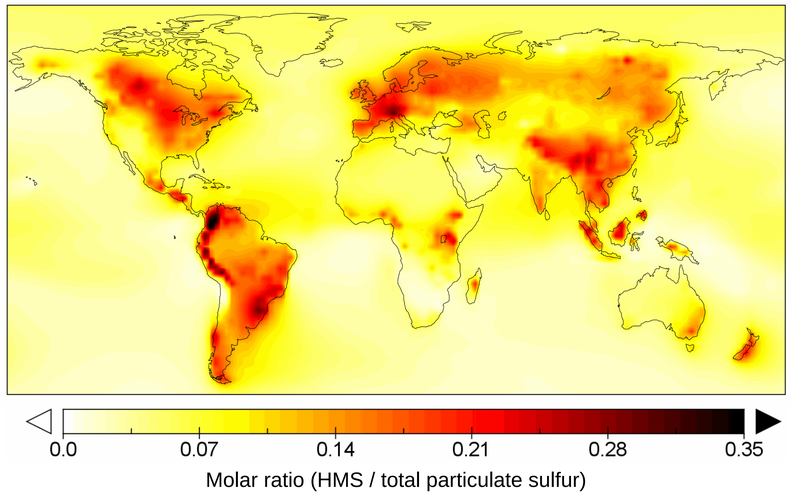
4. HMS in GEOS-Chem can be roughly equal to sulfate during extreme haze in Beijing



- HMS may be underestimated over Beijing in GEOS-Chem due to low values of modelled HCHO, compared to observations.
- GEOS-Chem also may not capture mixing of HCHO into cloudy layers at the top of the PBL.
- Even with inadequate HCHO, HMS is >50% of particulate sulfur during peak simulated haze.

5. HMS may be a significant fraction of annual mean particulate sulfur in many regions

Annual Mean fraction of HMS in total particulate sulfur (07/2012-06/2016)

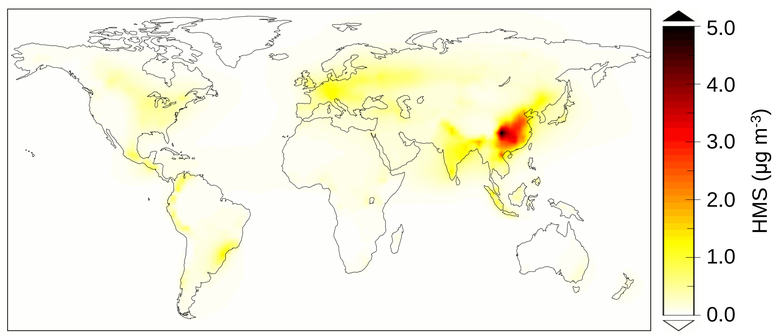


HMS may be an significant fraction of annual average particulate sulfur in multiple areas across the globe such as:

- Central Europe (Po Valley)
- Southeast Asia
- South America (e.g. Andes)
- Central Canada
- China

Because HMS has no gas phase source, it makes up an even larger fraction of particulate sulfur during hazy days.

Annual Mean HMS (07/2012-06/2016)



High annual mean HMS levels are simulated in the Sichuan Basin.

6. Preliminary conclusions

- Despite possible underestimates of HCHO over Beijing, HMS is nevertheless a significant fraction of particulate sulfur during haze episodes (>50%).
- In addition to China, HMS may be important in places like India, Europe, Southeast Asia, and South America.

7. References

1. Moch et al., 2018, “Contribution of hydroxymethane sulfonate to ambient particulate matter: A potential explanation for high particulate sulfur during severe winter haze in Beijing.” GRL.

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