Hydroxymethane sulfonate as a possible explanation for observed high levels of particulate sulfur during severe winter haze episodes in Beijing, China.

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1. Motivation

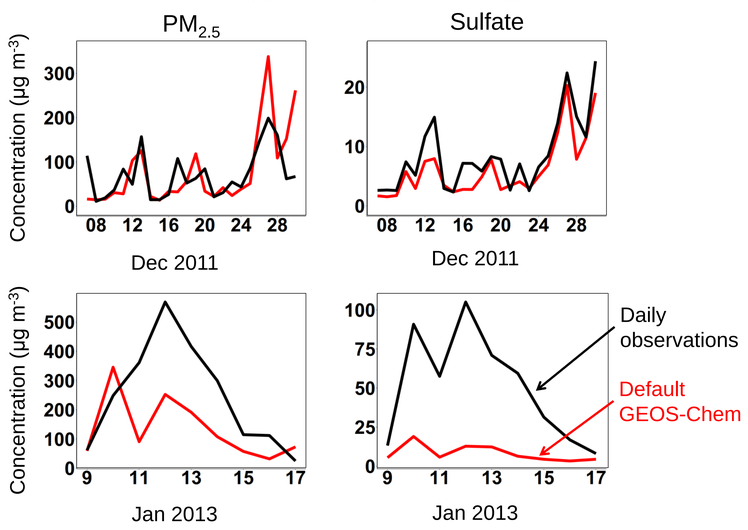
Air pollution in China is a severe public health problem. Mean wintertime $PM_{2.5}$ has slightly increased since 2008 according to US Embassy measurements, and extreme pollution events frequently show large enhancements in particulate sulfur (Wang et al., 2014). All of this is despite policies enacted by the Chinese government, including a successful reduced sulfur dioxide (SO_2) emissions (Krotkov et al., 2016).

View of Beijing during a haze day (~120 μg m^{-3} $PM_{2.5}$) and a non-haze day (~20 μg m^{-3} $PM_{2.5}$).

2. CTMs have trouble explaining extremely high particulate sulfur

Oxidant levels are typically low in winter due to low sun angles and heavy haze. Chemical transport models thus can have difficulty generating sufficient sulfate to match the observed enhancements in particulate sulfur.

Simulation of two Beijing pollution episodes using GEOS-Chem



Time series of observed and simulated daily mean $PM_{2.5}$ and sulfate for December 2011 and January 2013 in Beijing for GEOS-Chem v11 using the MEIC emissions inventory for China and MERRA2 meteorology.

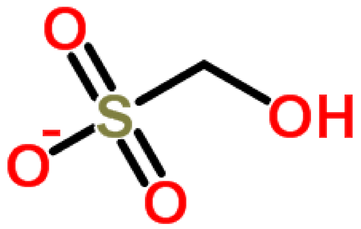
- Dec 2011: little model bias – e.g., mean bias of -2.26 μg m^{-3} for sulfate.
- Jan 2013: large model bias – e.g., mean bias of -42.1 μg m^{-3} for sulfate.

3. 1-D model setup

- We develop a 1-D model for Beijing cloud and aerosol chemistry, eddy diffusion, and entrainment in the boundary layer .
- We track HMS, SO_2, and HCHO, and estimate HCHO and SO_2 emissions by calculating the monthly mean emissions required to maintain specified, mean surface concentrations of HCHO and SO_2.
- Cloud liquid water content and other meteorological parameters are taken from MERRA2. The CERES satellite product is used to check MERRA2.

4. Hydroxymethane sulfonate forms in clouds and could be interpreted as sulfate in measurements

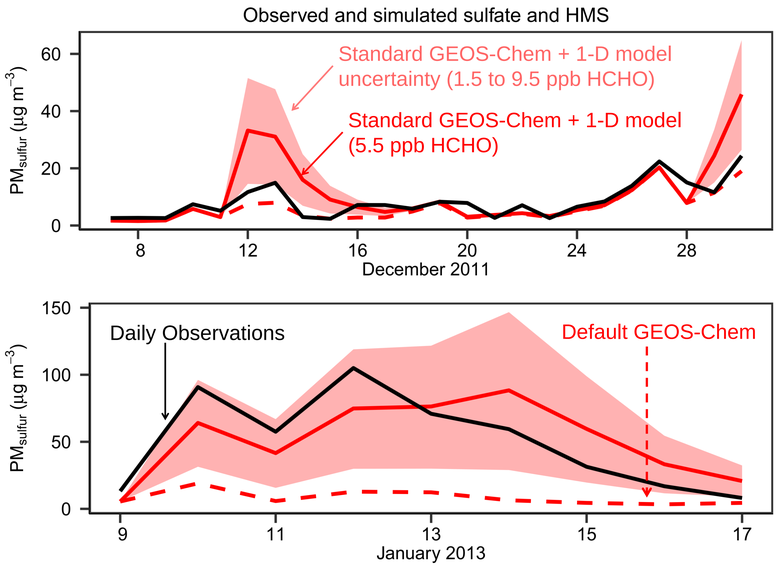
Conditions promoting Hydroxymethane sulfonate (HMS, $HOCH_2SO_3^-$) formation:
- Presence of clouds or fog
- High SO_2 and HCHO
- Cold temperatures
- Low concentrations of oxidants



$$SO_{2(g)} \leftrightarrow SO_{2(aq)}$$
$$SO_{2(aq)} \leftrightarrow HSO_3^- + H^+$$
$$HSO_3^- \leftrightarrow SO_3^{2-} H^+$$
$$HCHO_{(g)} \leftrightarrow HCHO_{(aq)}$$
$$HCHO_{(aq)} + HSO_3^- \rightarrow HOCH_2SO_3^-$$
$$HCHO_{(aq)} + SO_3^{2-} + H_2O \rightarrow HOCH_2SO_3^- + OH^-$$
$$HOCH_2SO_3^- + OH^- \rightarrow SO_3^{2-} + HCHO_{(aq)} + H_2O$$

- 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 could be confused for sulfate in both ion chromatography and in AMS or single-particle measurements.

5. Adding HMS chemistry improves match with observed particulate sulfur

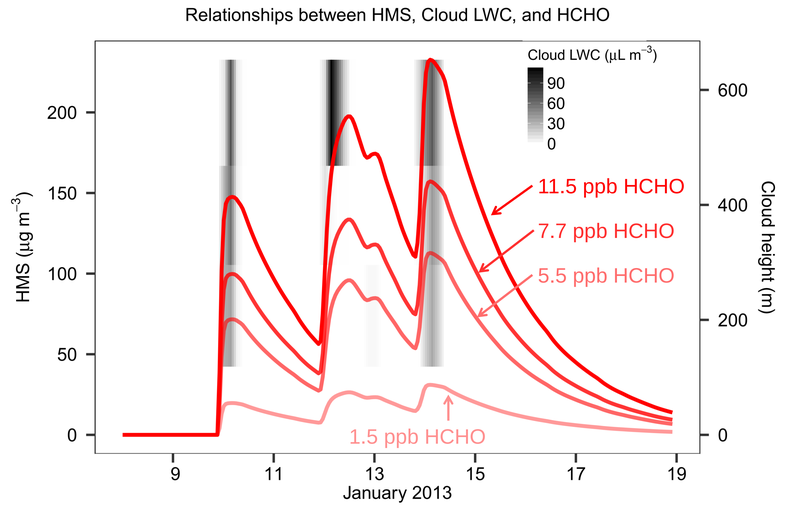


Time series of observed and simulated daily mean PM_{sulfur} for December 2011 and January 2013 in Beijing.

Specified conditions are:
- Cloud pH of 5
- Monthly mean concentrations of 50 ppb SO_2 and 5.5±3.9 ppb HCHO

Mean bias between observation and GEOS-Chem + 1-D model for particulate sulfur are much smaller than in GEOS-Chem, especially for Jan 2013.
- Jan 2013: small mean bias of 1.5 μg m^{-3} for particulate sulfur.

6. HMS levels in the 1-D model are controlled by ambient HCHO and clouds



In the 1-D model, HMS is primarily determined by the timing of low clouds and the amount of HCHO present at the onset of cloudiness

- HCHO is the limiting reactant.
- Key threshold: whether or not the lifetime of HCHO is less than the lifetime of the low clouds (~8-15 hours).

At the onset of cloudiness, the bulk of HMS is formed and is transported to the surface within a few hours. Further HMS production is limited by HCHO flux into the cloud, which is small compared to the HCHO already consumed. After the clouds disappear, HMS levels fall as entrainment of fresh air occurs.

HMS sensitivity to other parameters:
- Cloud pH no longer matters above ~4.5.
- SO_2 affects HMS only at concentrations less than HCHO.

7. Conclusions

- HMS provides a potential explanation for high particulate sulfur observed during winter haze events in Beijing.
- Production of HMS in our model is controlled by available HCHO in the presence of low clouds.

9. References

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