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$_2$) production. HMS has a lifetime on the order of months to days for the pH range ~3-4.5. We track HMS, SO$_2$, and HCHO, and estimate HCHO and SO$_2$ levels in the 1-2 days. The CERES satellite product is used to check MERRA2. The small mean bias of 1.5 ppb HCHO and sulfate for particulate sulfur. HMS sensitivity to other parameters:

- Cloud pH no longer matters above ~4.5.
- SO$_2$ affects HMS only at concentrations less than HCHO.

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.

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$_2$SO$_3$) formation:

- Presence of clouds or fog
- High SO$_2$ and HCHO
- Cold temperatures
- Low concentrations of oxidants

\[ \text{SO}_2 (g) \leftrightarrow \text{SO}^2 (aq) \]
\[ \text{SO}^2 (aq) \leftrightarrow \text{HSO}^{-} + \text{H}^+ \]
\[ \text{HSO}^{-} \leftrightarrow \text{SO}^2^{-} + \text{H}^+ \]
\[ \text{HCHO} (g) \leftrightarrow \text{HCHO} (aq) \]
\[ \text{HCHO} (aq) + \text{SO}^2^{-} \rightarrow \text{HOCH}_2\text{SO}^3^{-} \]
\[ \text{HCHO} (aq) + \text{SO}^2^{-} + \text{H}_2\text{O} \rightarrow \text{HOCH}_2\text{SO}^3^{-} + \text{OH}^{-} \]
\[ \text{HOCH}_2\text{SO}^3^{-} + \text{OH}^{-} \rightarrow \text{SO}^2^{-} + \text{HCHO} (aq) + \text{H}_2\text{O} \]

- 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 sulfate

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

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.

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.

8. References

3. www.macmodel.org

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