Modeling $PM_{2.5}$ Sulfate (SO_4^{2-}) and Hydroxymethanesulfonate (HMS) in Fairbanks, Alaska, during the ALPACA field campaign

United States Environmental Protection Agency

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Fairbanks has high wintertime $PM_{2.5}$

Fairbanks is a serious nonattainment area for the 24-hr $PM_{2.5}$ NAAQS

- High local emissions coupled with poor dispersion and strong temperature inversions lead to build-up at the surface
- $PM_{2.5}$ during episodes consists mostly of organic carbon and **SO_4^{2-}**

The Fairbanks Alaskan Layered Pollution and Chemical Analysis (ALPACA) winter air quality study was undertaken in early 2022

- Designed to better understand what processes/sources/chemistry lead to high PM concentrations in an extremely cold and dark environment
- Extensive suite of meteorological and chemical measurements collected in and around Fairbanks in combination with pre- and post- campaign modeling

Models underestimate SO_4^{2-} under cold, dark conditions

Major SO_2 oxidation reaction pathways are unable to capture high SO_4^{2-} observations during periods of low photochemical activity

- Fairbanks moderate SIP: Avg SO_4^{2-} obs (mod) = 6.2 (2.1) μgm^{-3}

Potential reasons for this model observation discrepancy:

- Heterogeneous sulfur chemistry in/on aerosol is not included in most models
- Typically minor reactions in clouds may be important depending on pH, oxidant levels
- Misidentification of other sulfur species (e.g., HMS) as sulfate

CMAQ particulate sulfur chemistry updates

Aerosol: reactive uptake

$$ASO_4\ production\ rate = k \times [SO_2\ or\ reactant]$$

$$k = \left(\frac{r}{D_g} + \frac{4}{v\gamma}\right)^{-1} A$$

$$\gamma = \left(\frac{1}{\alpha} + \frac{v}{4H^*RT\sqrt{D_a k_{chem}}}\frac{1}{f_r}\right)^{-1}$$

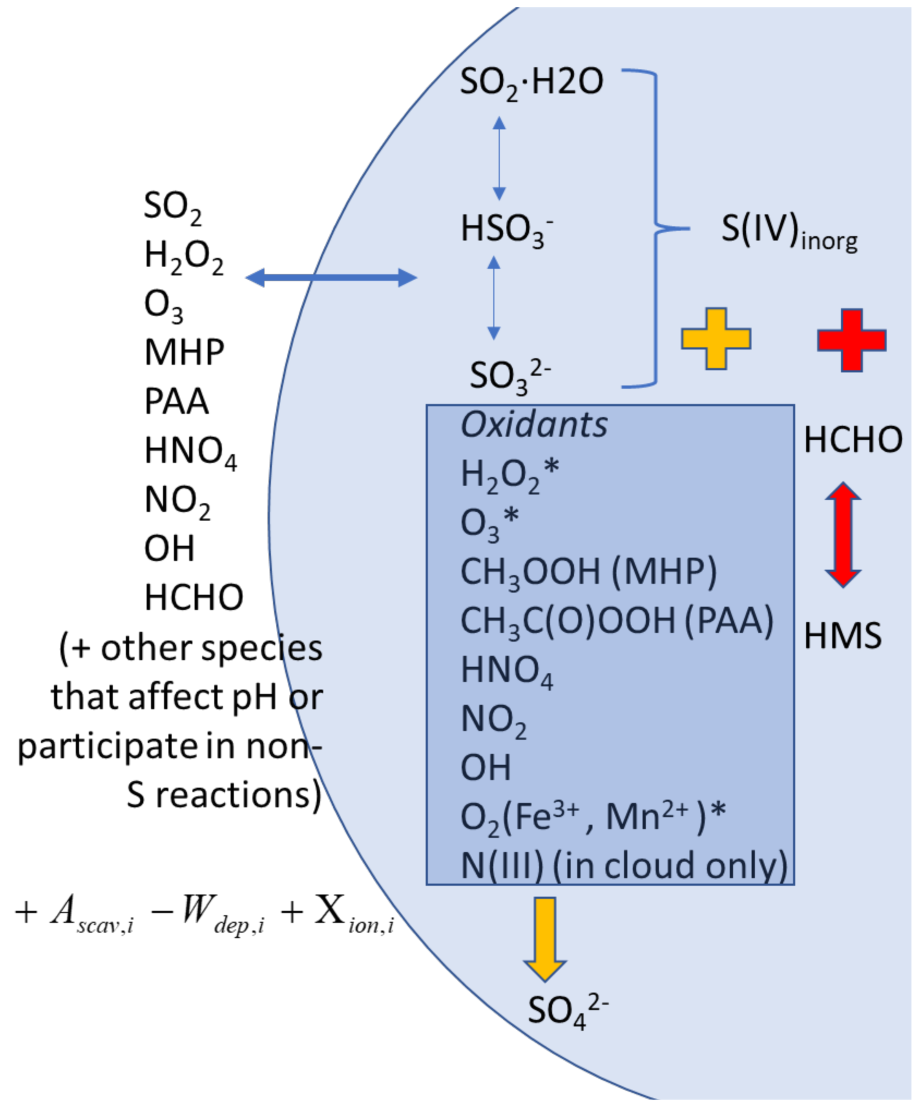
Cloud/fog: KMTv2 (kinetic mass transfer)

$$k_{mt} = \left(\frac{r^2}{3D_g} + \frac{4r}{3v\alpha}\right)^{-1}$$

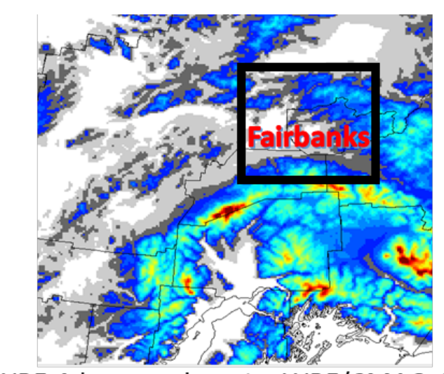
$$\frac{dC_{g,i}}{dt} = -k_{mt,i} w_L C_{g,i} + \frac{k_{mt,i}}{H_i RT} C_{aq,i}$$

$$\frac{dC_{aq,i}}{dt} = k_{mt,i} w_L C_{g,i} - \frac{k_{mt,i}}{H_i RT} C_{aq,i} + Q_i R_{aq,i} + A_{scav,i} - W_{dep,i} + X_{ion,i}$$

$$\frac{dC_{aero,i}}{dt} = -A_{scav,i}$$

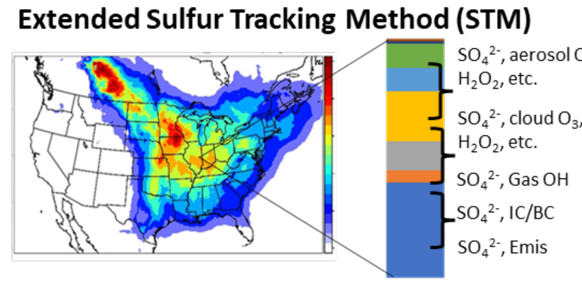


WRF/SMOKE/CMAQ modeling platform for ALPACA



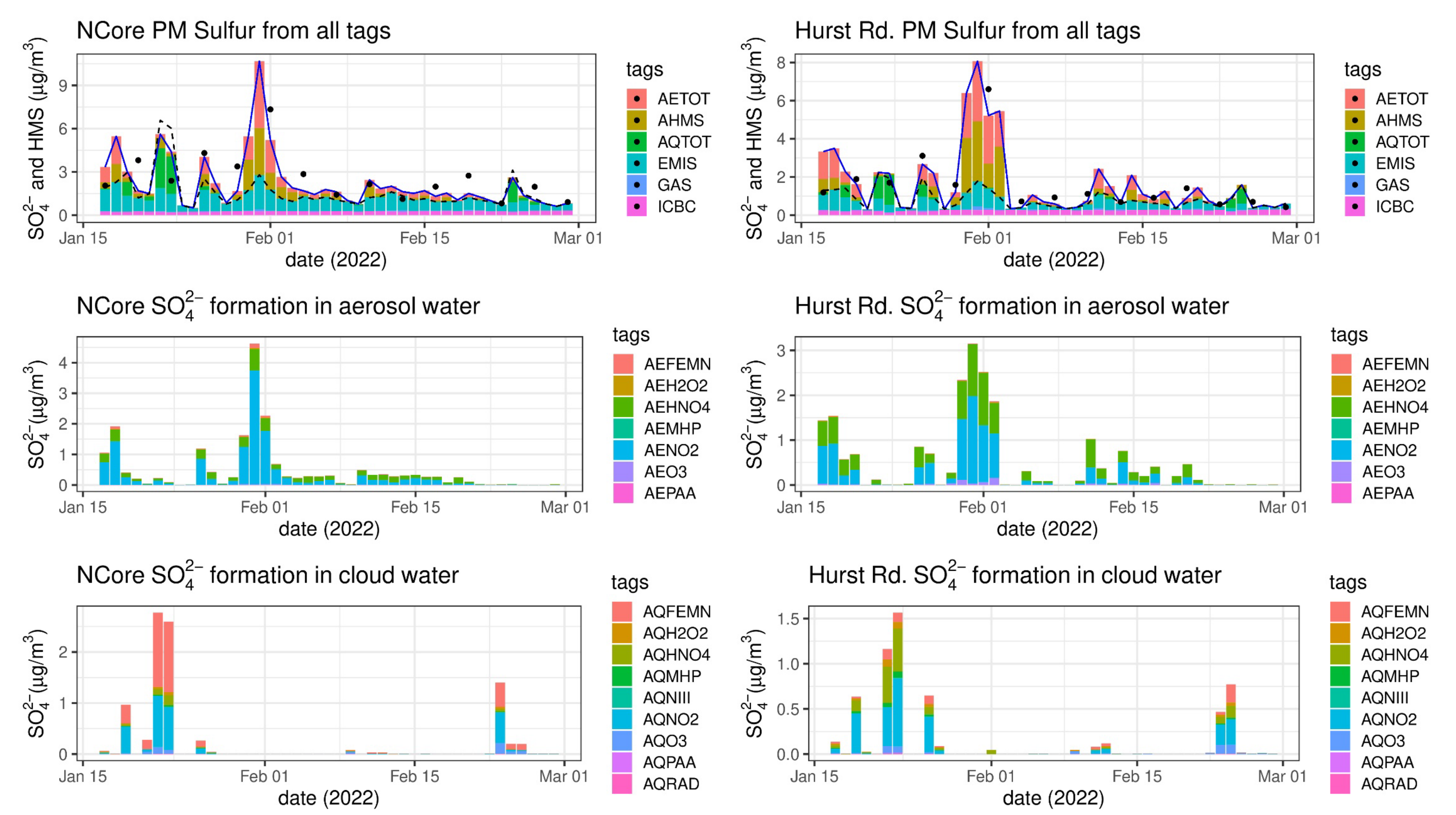
WRF 4-km res. domain, WRF/CMAQ 1.33-km res. domain centered over Fairbanks

Extended Sulfur Tracking Method (STM)



Domain	1.33-km horiz. resolution, 199x199 cells, 38 vert. layers
Meteorology	MCIP-processed WRFv4.1.1 meteorology; WRF model configuration optimized for ALPACA, leveraging rich dataset collected during the field study (Gilliam et al., 2023)
Emissions	Sector-separated CMAQ-ready emissions for Jan-Feb 2022 generated with SMOKE. 2022 gridded space heating inventory, 2019 inventories and surrogates for onroad, airports, nonroad, and other area sectors, and 2020 inputs for point sources provided by ADEC. Point sources are updated with ALPACA operations information when available (provided by S. Arnold (U. of Leeds)).
IC/BCs	2016 hemispheric CMAQ seasonal average
Simulations	Jan 2 - Feb 28, 2022
Base	Standard CMAQ configuration with STM
Hetchem	KMT cloud chemistry and heterogeneous chemistry updates with extended STM

Sulfur-tracking for modeled PM Sulfur vs. observed SO_4^{2-}



There are two AQS PM speciation sites in the Fairbanks area: NCore (downtown Fairbanks) and Hurst Road (North Pole). Here we show modeled SO_4^{2-} (or SO_4^{2-} + HMS) and routine measurements. Observations provided by ADEC.

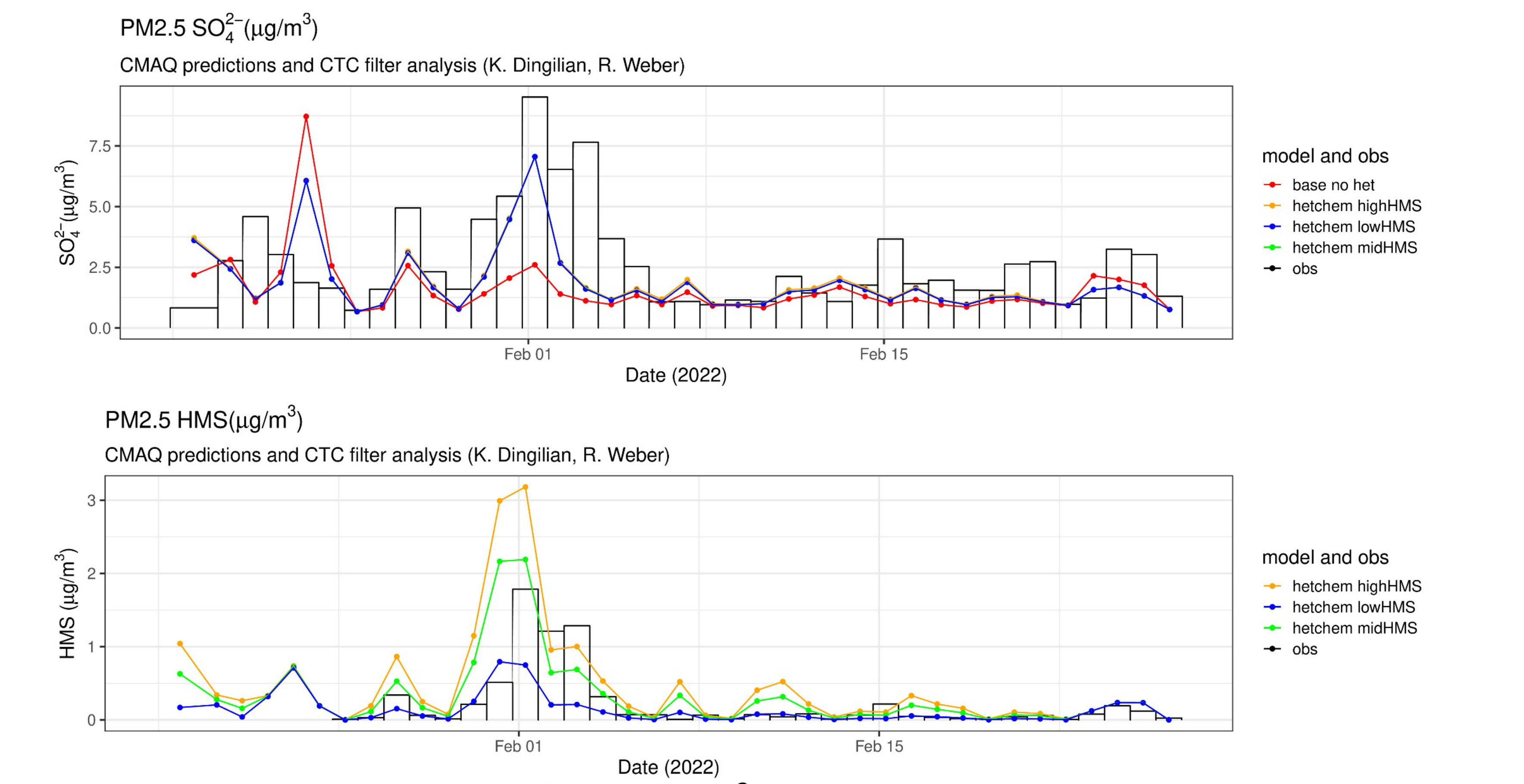
First row: model/obs SO_4^{2-} and HMS at NCore (left) and Hurst Road (right). The bars represent model SO_4^{2-} + HMS broken down by process, the points represent SO_4^{2-} observations, and the dashed line represents the SO_4^{2-} predicted by the base model without multiphase sulfur chemistry updates.

Middle row: SO_4^{2-} formed in aerosol water separated by oxidation reaction.

Bottom row: SO_4^{2-} formed in cloud water separated by oxidation reaction.

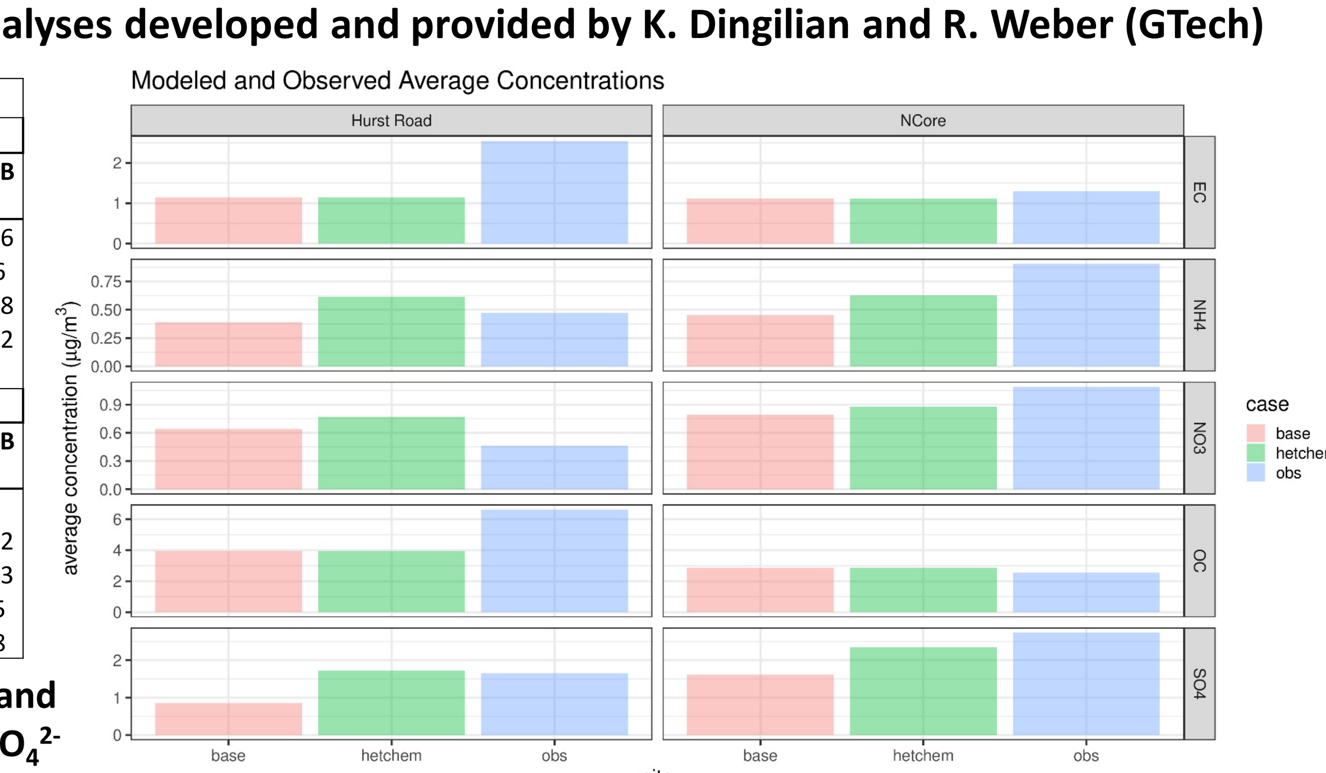
Tags: AETOT = secondary SO_4^{2-} formed in aerosol water, AHMS = HMS formed in aerosol and cloud water, AQTOT = secondary SO_4^{2-} formed in cloud water, EMIS = primary SO_4^{2-} emissions, GAS = secondary SO_4^{2-} formed in the gas phase, and ICBC = SO_4^{2-} from initial/boundary conditions.

SO_4^{2-} and HMS in downtown Fairbanks



Comparison of modeled and observed SO_4^{2-} (top) and HMS (bottom) in downtown Fairbanks. Modeled HMS is shown for high and low HMS production rates (Song et al., 2021) as well as their average. Filter analyses developed and provided by K. Dingilian and R. Weber (GTech)

Base case			Hetchem		
NCore					
Spcs	NME (%)	NMB (%)	Spcs	NME (%)	NMB (%)
SO4	58.9	-38.8	***SO4***	38.1	-15.6
OC	45.1	13.6	***OC***	45.0	13.6
EC	40.2	-11.9	***EC***	40.1	-11.8
NH4	70.5	-46.5	***NH4***	56.5	-26.2
NO3	35.1	-17.6	***NO3***	34.2	-8.3
Hurst Road					
Spcs	NME (%)	NMB (%)	Spcs	NME (%)	NMB (%)
SO4	50.7	-47.7	***SO4***	30.9	-8.1
OC	54.8	-45.3	***OC***	54.7	-45.2
EC	60.3	-57.4	***EC***	60.2	-57.3
NH4	46.7	-18.7	***NH4***	39.7	23.5
NO3	58.3	27.6	***NO3***	79.3	55.8



Average Base, Hetchem, and obs EC, $NH4^+$, NO_3^-, OC, SO_4^{2-}

Summary

- CMAQ was updated with heterogeneous sulfur chemistry in aerosol water, including the production and loss of HMS, which may sometimes be misidentified as sulfate during routine PM composition analysis
- The update improves model-obs comparisons of sulfate for the ALPACA period, and model HMS compares well with measurements in magnitude and timing
- Multiphase (cloud/fog/aerosol) sulfur chemistry is a significant contributor to modeled $PM_{2.5}$ sulfur in Fairbanks where the cold, dark conditions dampen the existing secondary sulfate pathways in the standard configuration of CMAQ
  - The production of HMS and sulfate from S(IV) reactions with HCHO, NO_2, HNO_4, and O_2 (Fe^{3+}, Mn^{2+} catalyzed) are predicted to be most impactful here