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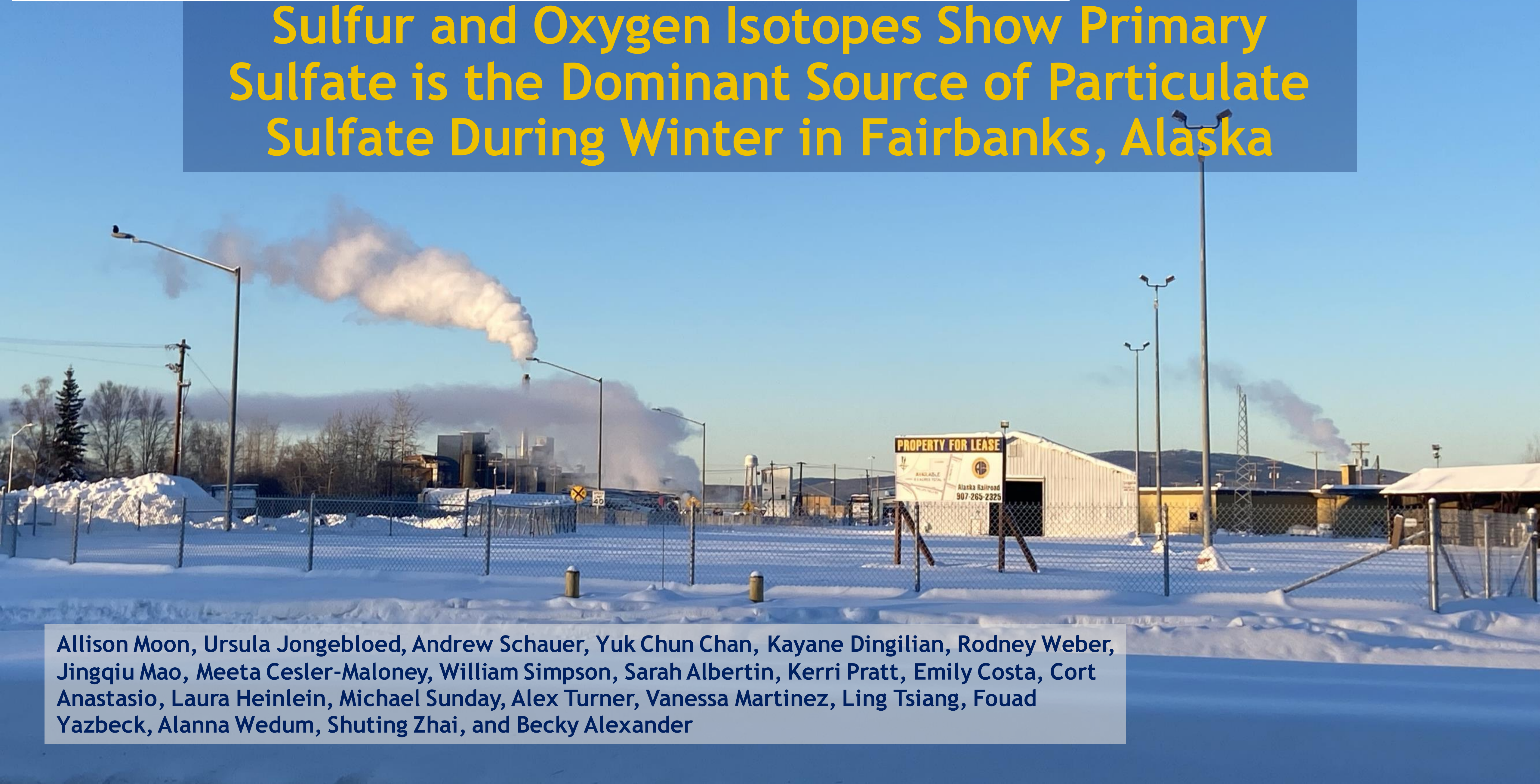
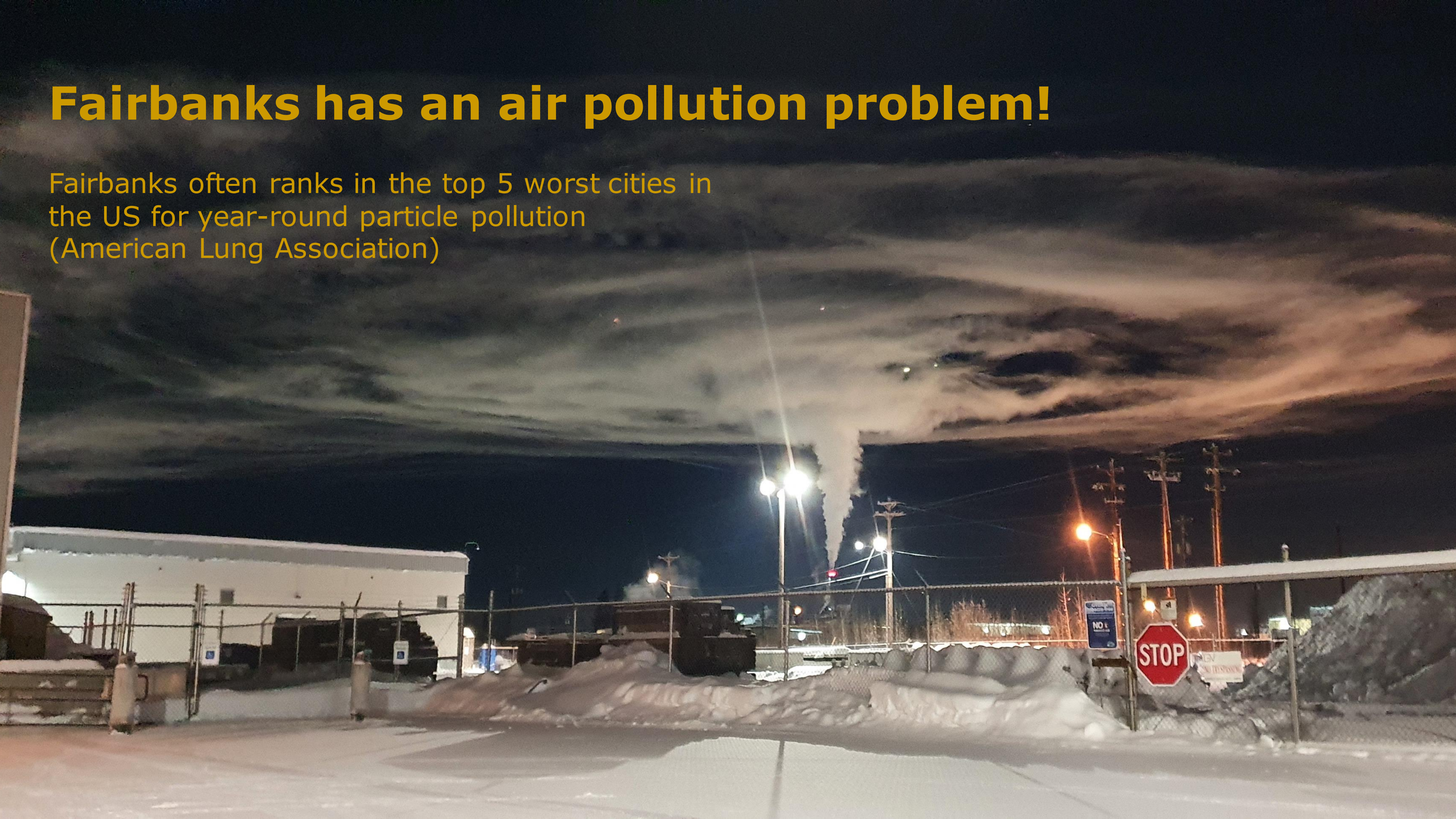
Sulfur and Oxygen Isotopes Show Primary Sulfate is the Dominant Source of Particulate Sulfate During Winter in Fairbanks, Alaska



Allison Moon, Ursula Jongebloed, Andrew Schauer, Yuk Chun Chan, Kayane Dingilian, Rodney Weber, Jingqiu Mao, Meeta Cesler-Maloney, William Simpson, Sarah Albertin, Kerri Pratt, Emily Costa, Cort Anastasio, Laura Heinlein, Michael Sunday, Alex Turner, Vanessa Martinez, Ling Tsiang, Fouad Yazbeck, Alanna Wedum, Shuting Zhai, and Becky Alexander

Fairbanks has an air pollution problem!

Fairbanks often ranks in the top 5 worst cities in the US for year-round particle pollution (American Lung Association)



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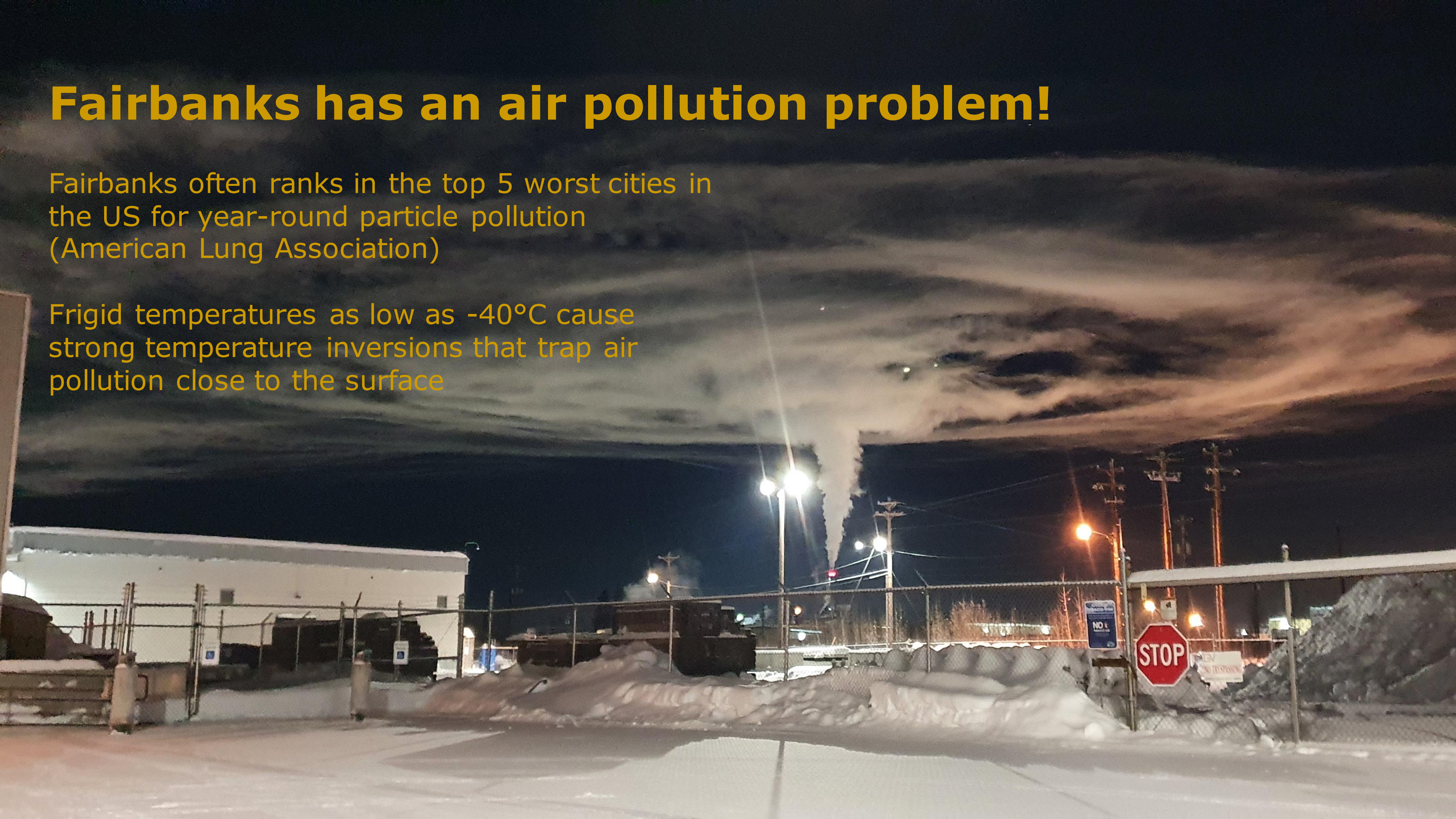
Frigid temperatures as low as -40°C cause strong temperature inversions that trap air pollution close to the surface



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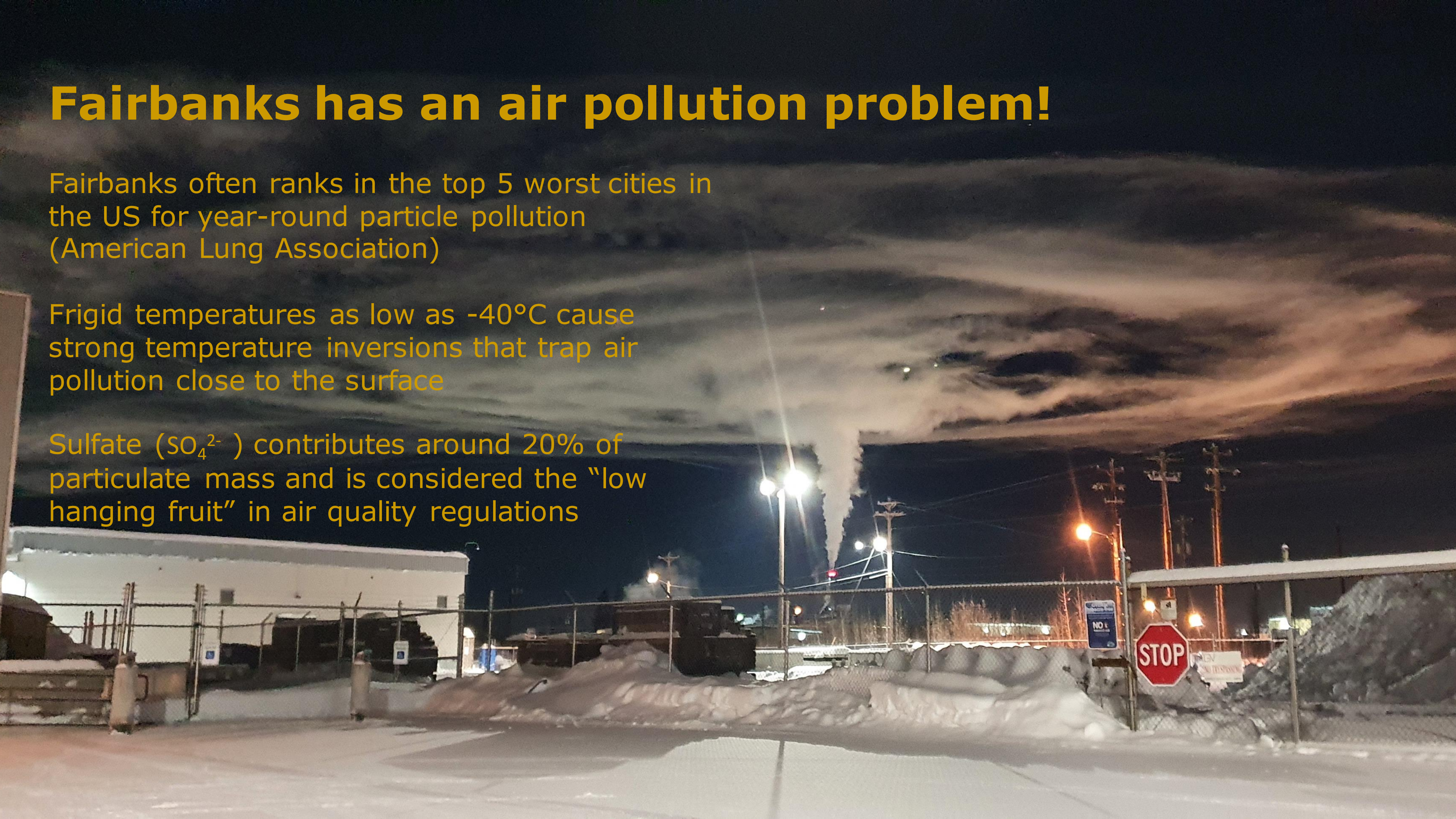
Sulfate (SO_4^{2-}) contributes around 20% of particulate mass and is considered the “low hanging fruit” in air quality regulations



The “missing sulfate problem” in Fairbanks

CMAQ underestimated sulfate by a factor of 3 during polluted episodes in Fairbanks prior to the Alaskan Layered Pollution and Chemical Analysis (ALPACA) field campaign (ADEC, 2021)

The "missing sulfate problem" in Fairbanks

So where is this sulfate coming from?

The “missing sulfate” problem in Fairbanks

Stable inversion layer:
There is a gradient of pollution below 20 meters with the highest PM concentrations on the surface

The “missing sulfate” problem in Fairbanks

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There is a gradient of pollution below 20 meters with the highest PM concentrations on the surface

Photo: LA times

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The "missing sulfate" problem in Fairbanks

Stable inversion layer:
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Ground-level emissions of fuel oil in Fairbanks

- Approximately 80% of Fairbanks residents use a central oil heating appliance for home heating and 40% of residents use fuel oil exclusively (ADEC 2019)
- On average, each household spends $2,274 on home heating annually and burns 1,230 gallons of fuel oil per year (ADEC 2019)

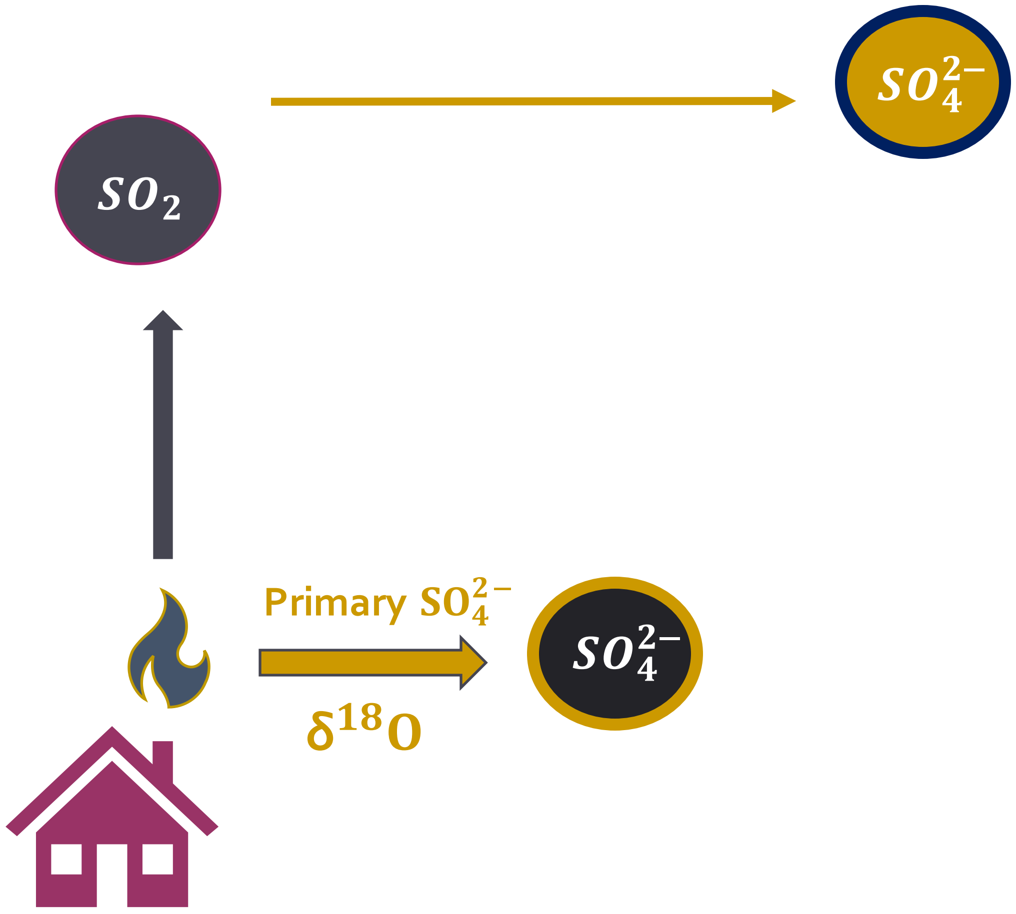
Why does fuel oil create unique air quality problems?

- The particles are really small (<100 nm or 0.1um)
- The age and burning efficiency of these boilers can vary and most boilers don't have "scrubbing" technology or oversight on emissions
- Home heating with fuel oil is difficult to parameterize in CMAQ since it relies on assumptions of emissions factors and domestic use
- We don't know if the sulfur chemistry changes in fuel oil-dominated regimes

Photo: Anchorage times

What does each type of isotope measurement tell us?

$\delta^{18}O$ How much of the sulfate is primary vs. secondary?

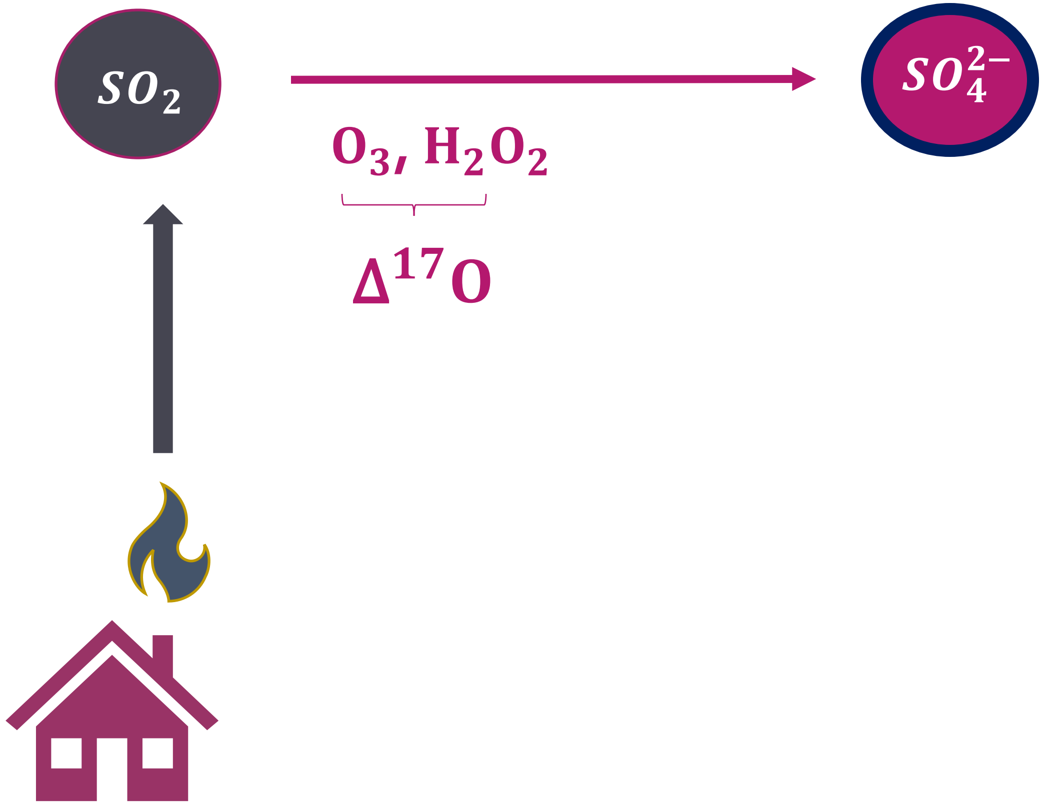


What does each type of isotope measurement tell us?

$\Delta^{17}O$

Are O_3 or H_2O_2 contributing to SO_4^{2-} formation?

$$\Delta^{17}O = \delta^{17}O - (0.52\ x\ \delta^{18}O)$$



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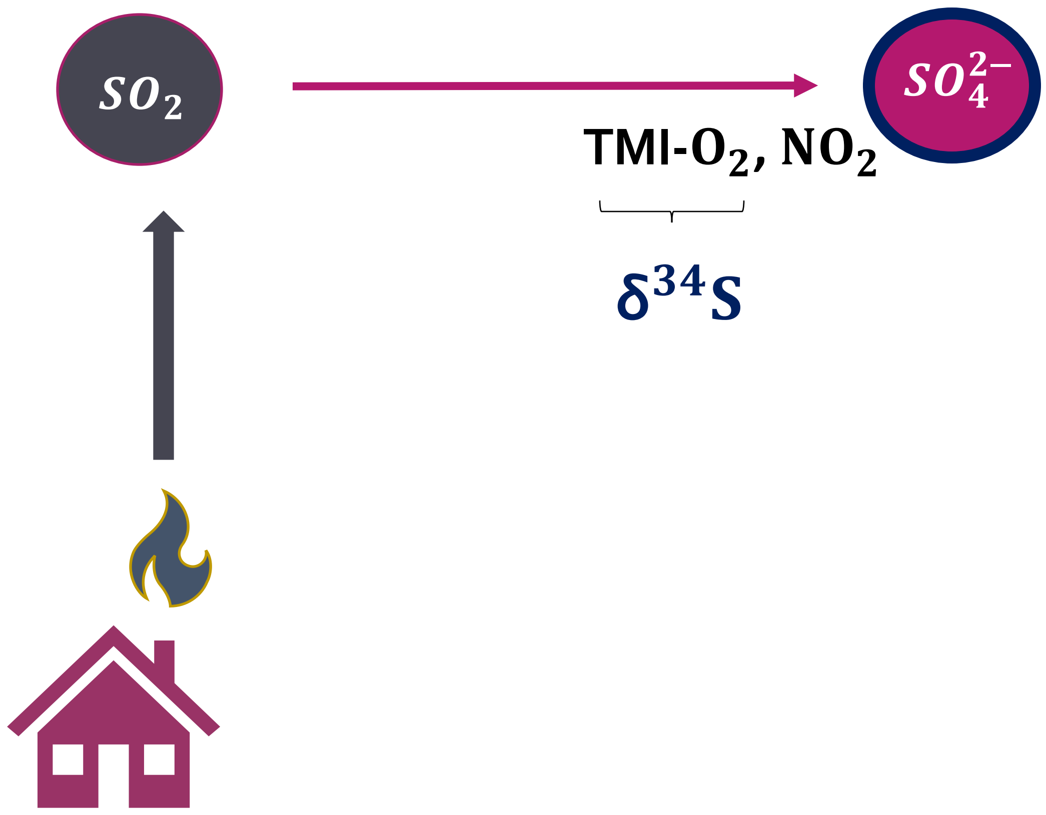

$\delta^{34}S$ Are NO2 or TMI-catalyzed oxidation dominant?

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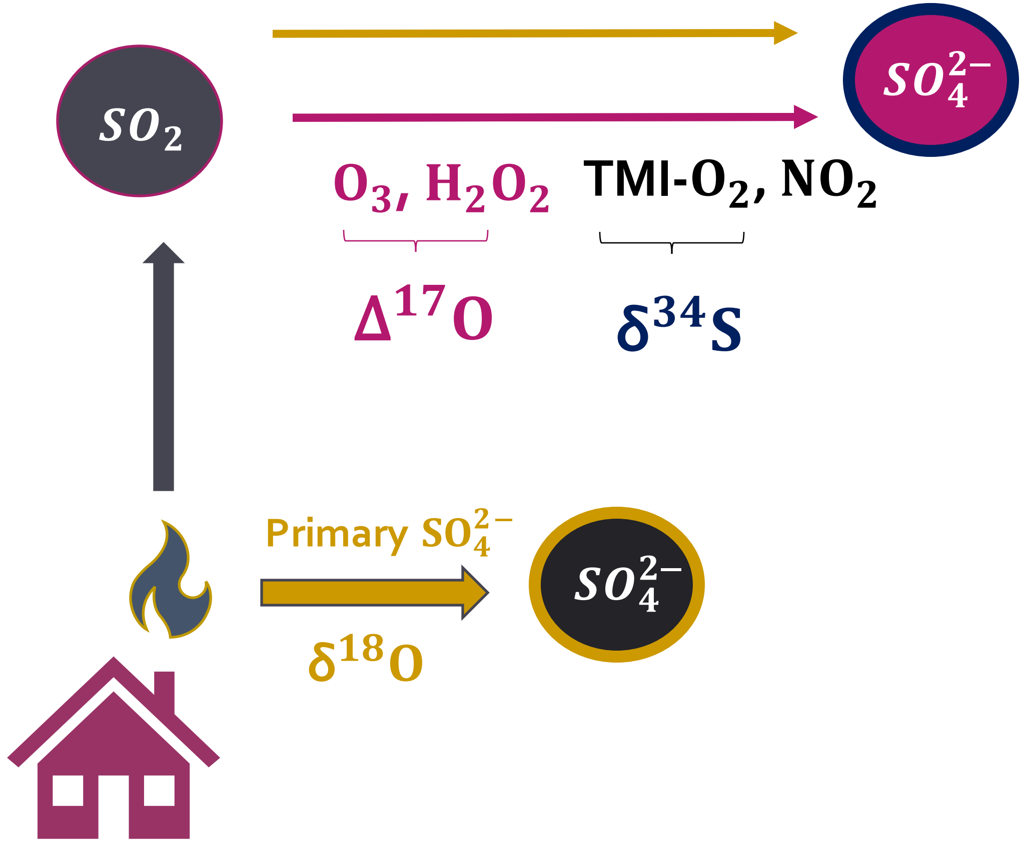
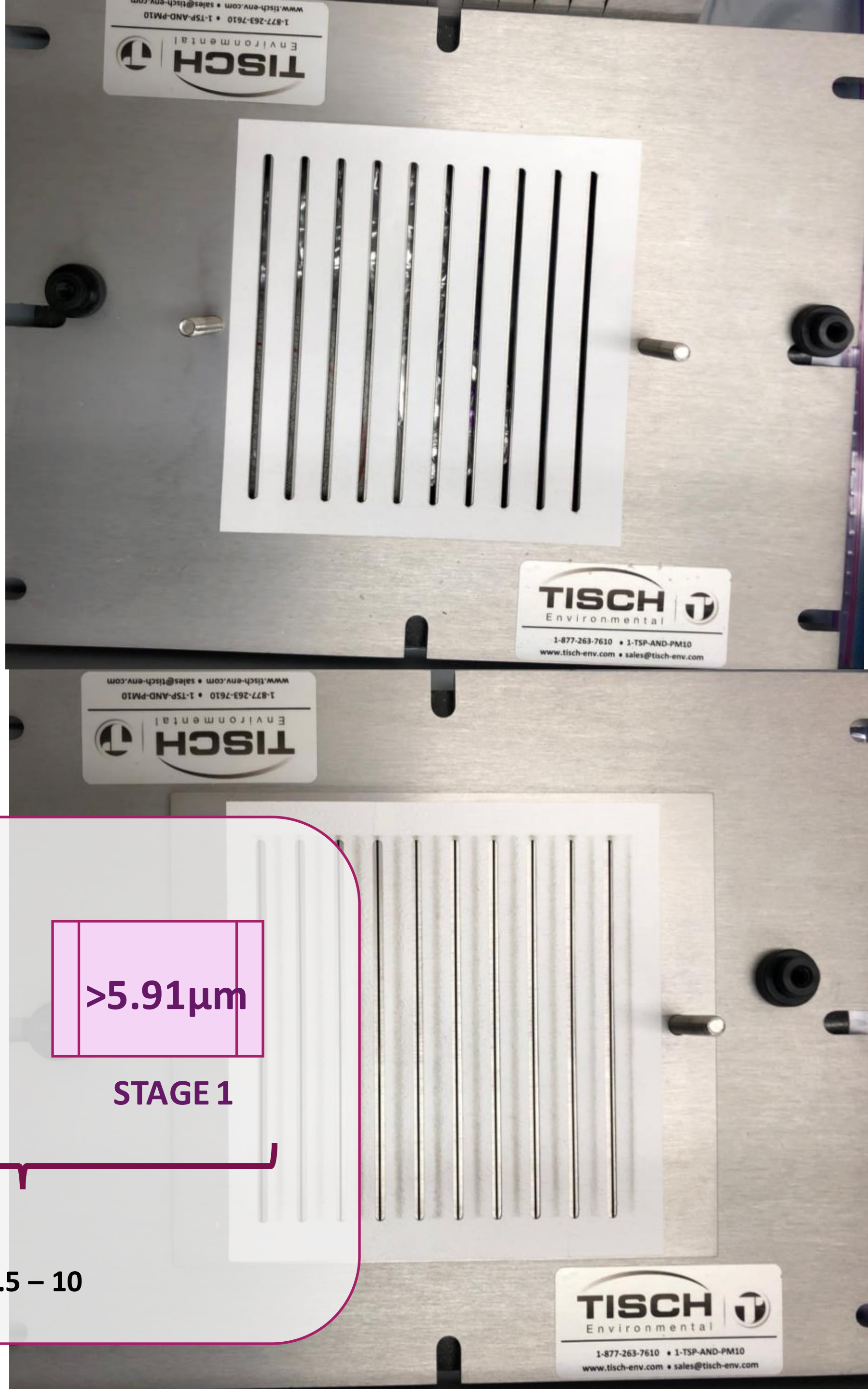
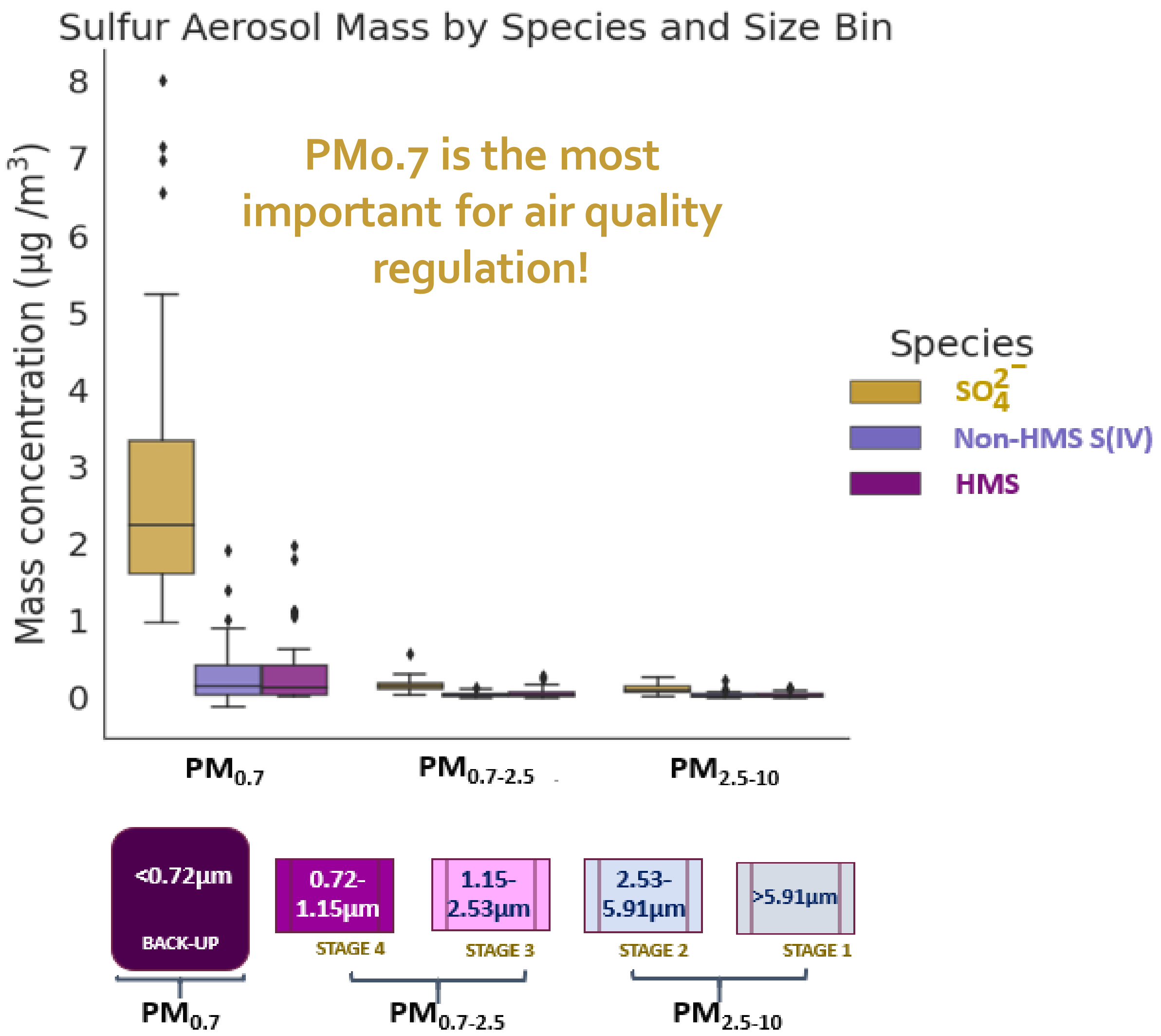




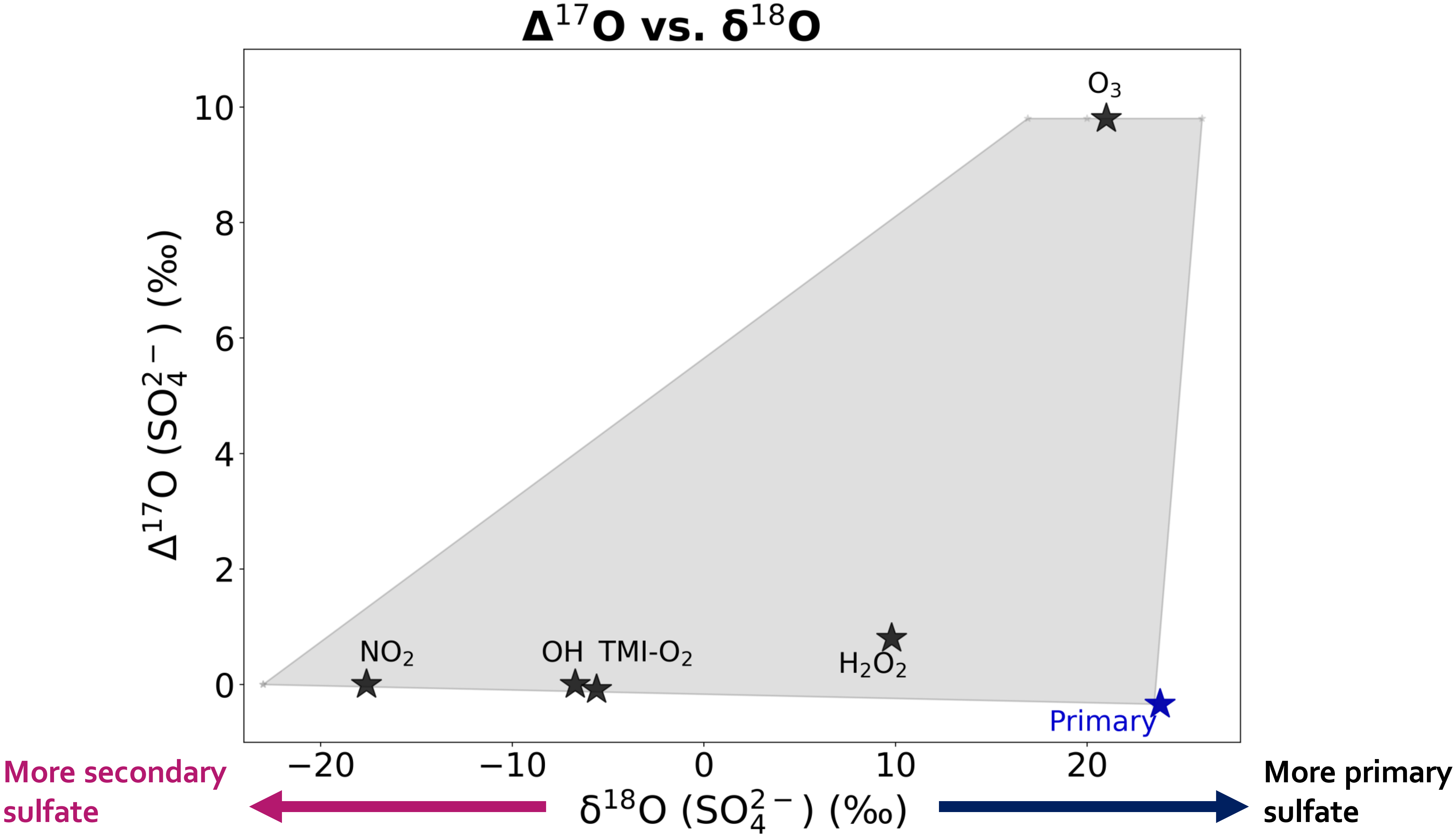
<0.72 µm BACK-UP	0.72-1.15µm STAGE 4	1.15-2.53µm STAGE 3	2.53-5.91µm STAGE 2	>5.91µm STAGE 1
$PM_{0.7}$	$PM_{0.7-2.5}$		$PM_{2.5-10}$	

Sulfate < 0.7 µm is the dominant sulfur source in Fairbanks



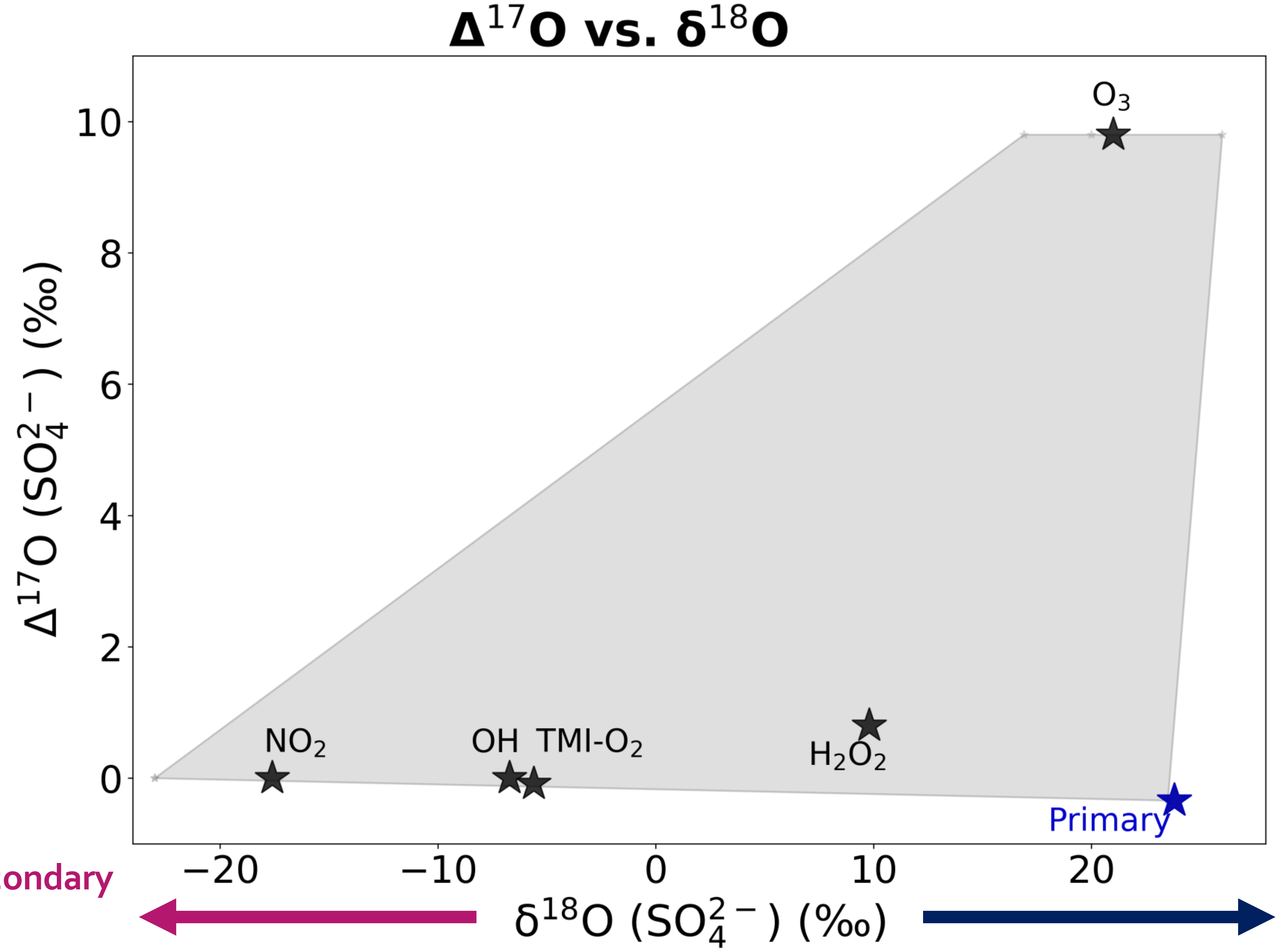
$PM_{0.7}$	$PM_{0.7-2.5}$	$PM_{2.5-10}$
90% (± 5%) of SO_4^{2-} by mass	6% (± 3%) of SO_4^{2-} by mass	4% (± 3%) of SO_4^{2-} by mass

$\delta^{18}O$ How much of the sulfate is primary vs. secondary?



$\Delta^{17}O$ Are O_3 or H_2O_2 contributing to SO_4^{2-} formation?

More secondary sulfate via ozone

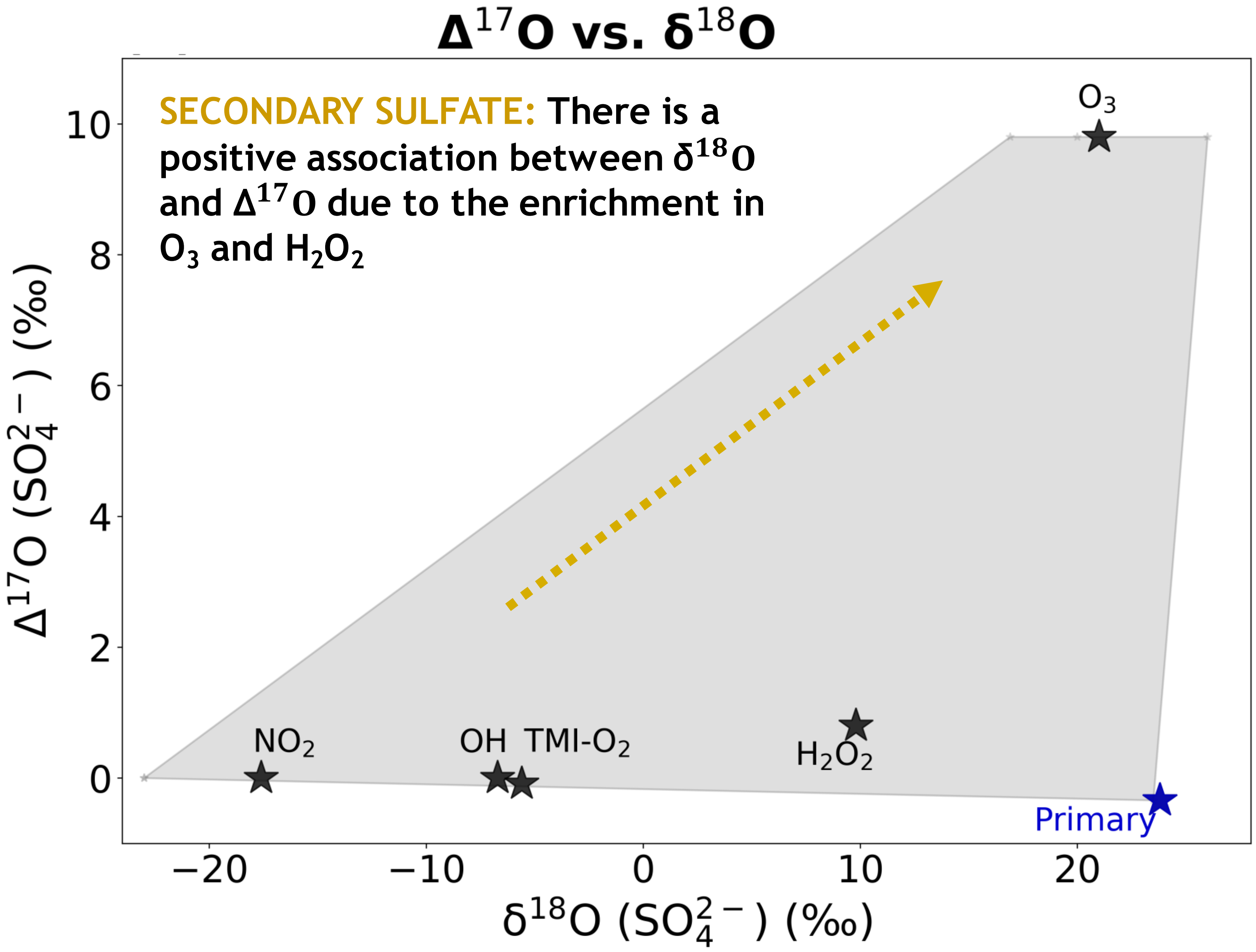


More secondary sulfate

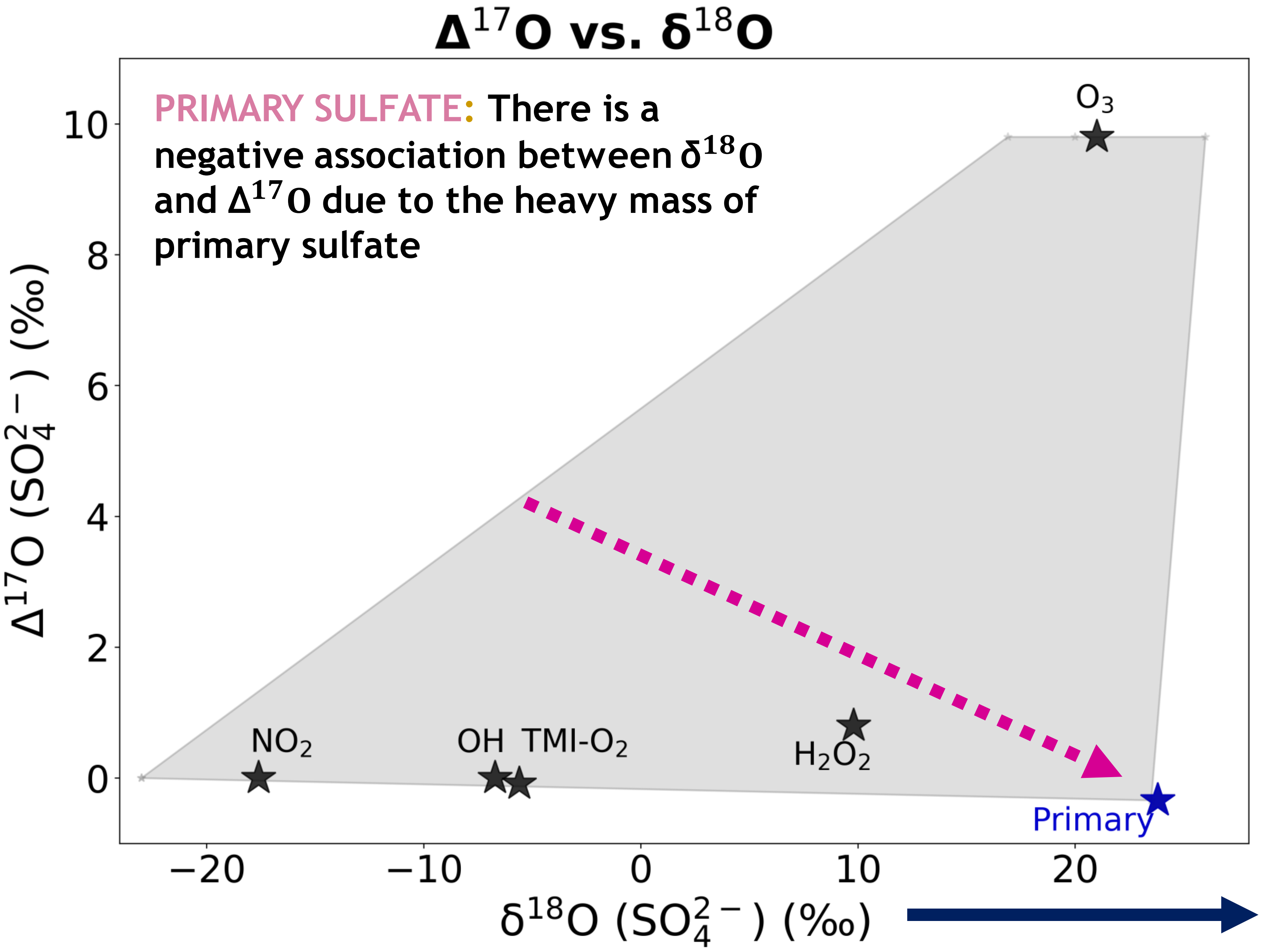
More primary sulfate

The relationship between $\Delta^{17}O$ and $\delta^{18}O$

More secondary sulfate via ozone



The relationship between $\Delta^{17}O$ and $\delta^{18}O$



More primary sulfate

The relationship between $\Delta^{17}O$ and $\delta^{18}O$

17,366 LEE AND THIEMENS: MEASUREMENTS OF $\delta^{17}O$ AND $\delta^{18}O$ IN ATMOSPHERIC SULFATE

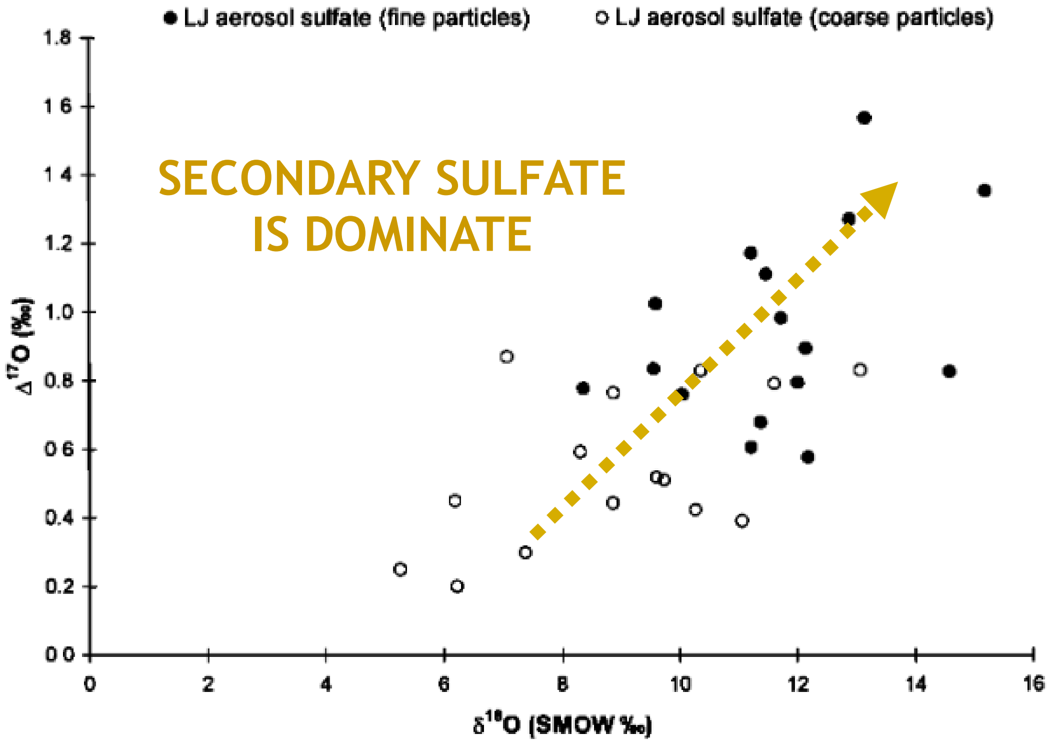
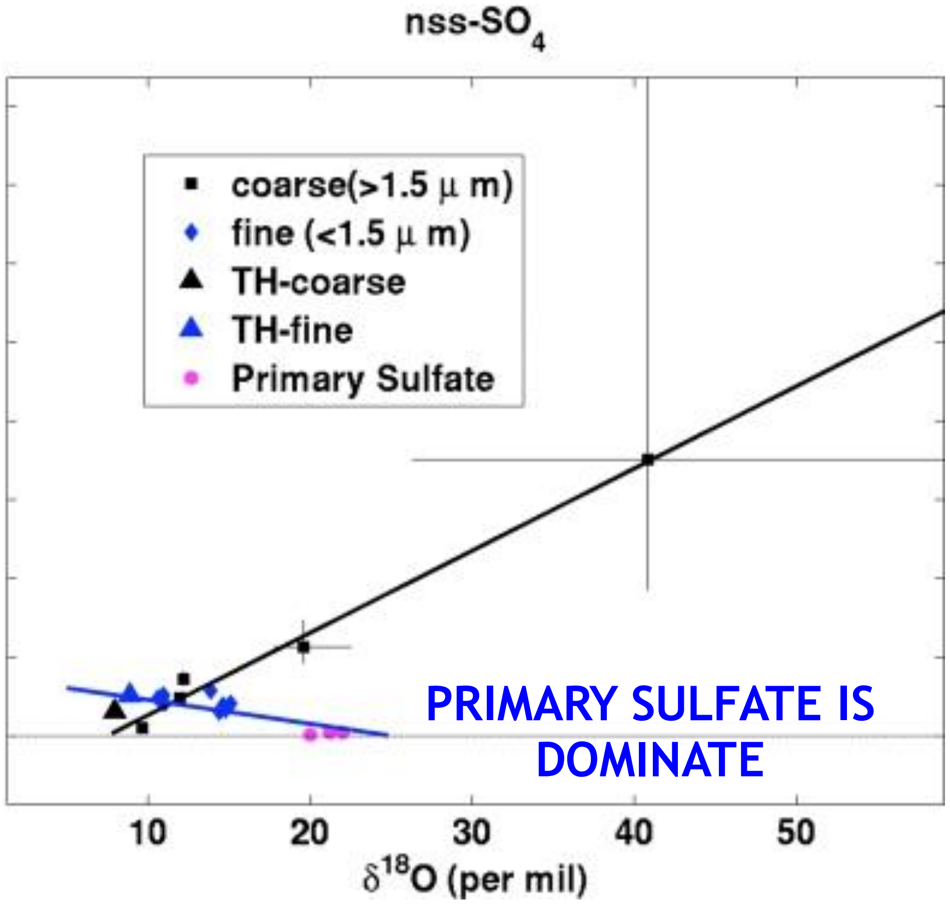


Figure 6. Correlation plot for La Jolla aerosol sulfate: $\Delta^{17}O$ versus $\delta^{18}O$. The $\delta^{18}O$ values generally increase with increasing $\Delta^{17}O$ values. The bulk data of fine sulfate particles lie above those of the coarse particles, representing greater $\delta^{18}O$ with more ^{17}O enrichment relative to mass dependent isotopic composition.

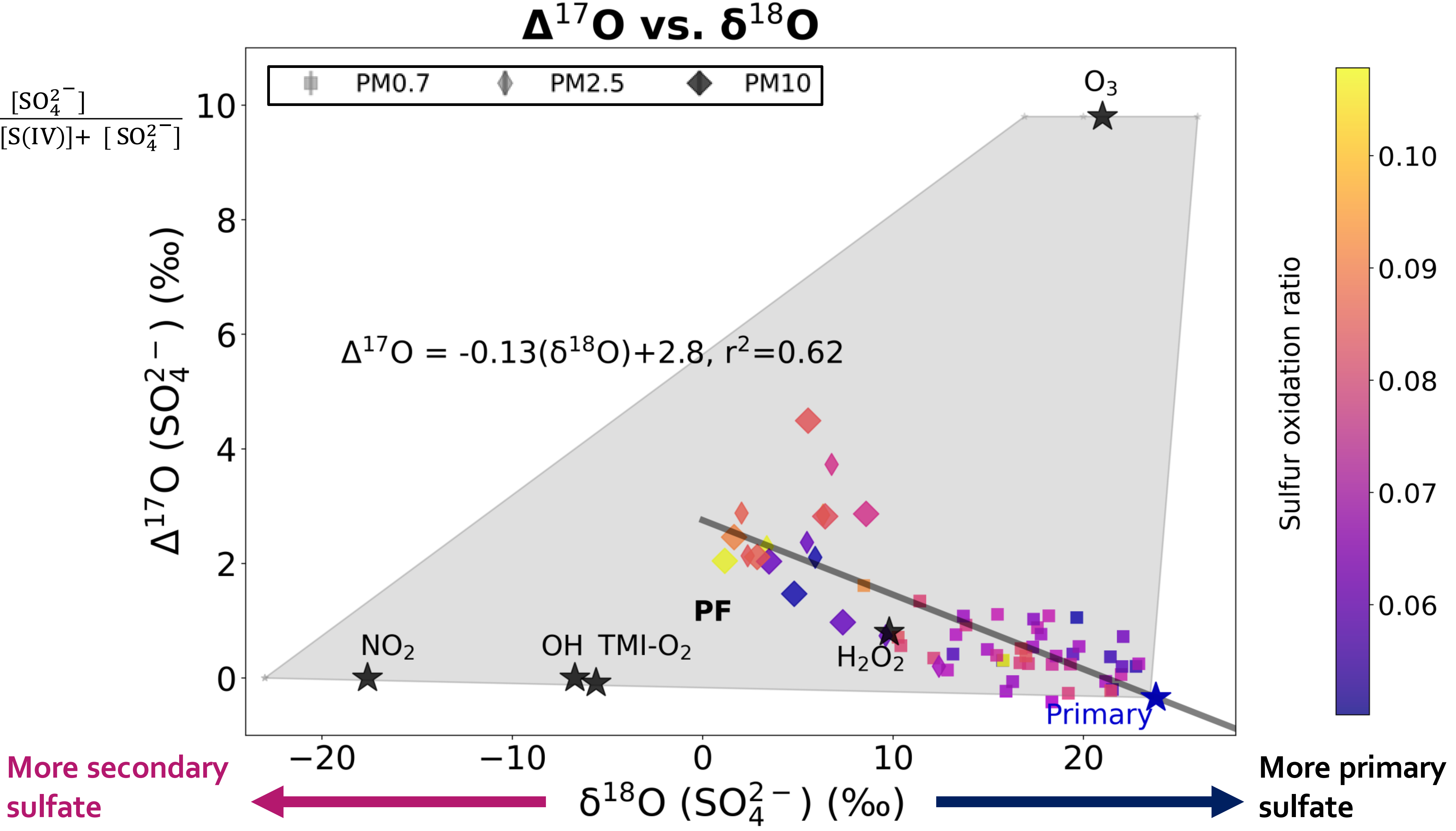


Lee and Thiemens, 2001

Domingues et al. 2008

The relationship between $\Delta^{17}O$ and $\delta^{18}O$

$$SOR = \frac{[SO_4^{2-}]}{[SO_2] + [S(IV)] + [SO_4^{2-}]}$$



$\delta^{34}S$ Is NO_2 or TMI-catalyzed oxidation dominant?

$\delta^{34}S$ emission is the source signature of SO_2

$\delta^{34}S$ Is NO2 or TMI-catalyzed oxidation dominant?

$\delta^{34}S$ emission →

O_3, H_2O_2, OH

$\delta^{34}S(SO_2) < \delta^{34}S(SO_4^{2-})$

Oxidation by O3, H2O2, and OH make the $\delta^{34}S(SO_4^{2-})$ observations heavier

$\delta^{34}S$ Is NO2 or TMI-catalyzed oxidation dominant?

← $\delta^{34}S$ emission →

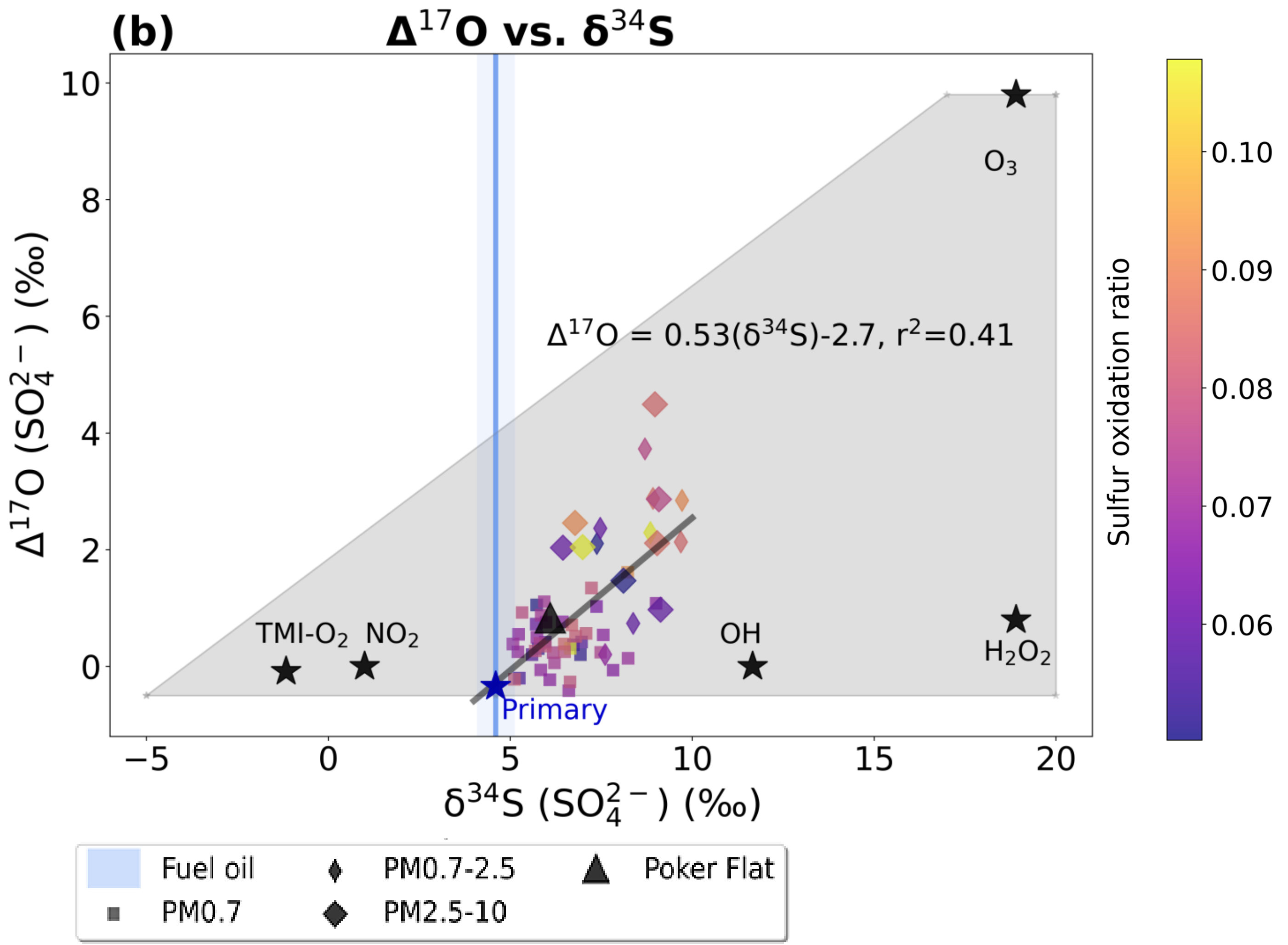
NO_2, TMI-O_2

O_3, H_2O_2, OH

$$\delta^{34}S(SO_2) > \delta^{34}S(SO_4^{2-})$$

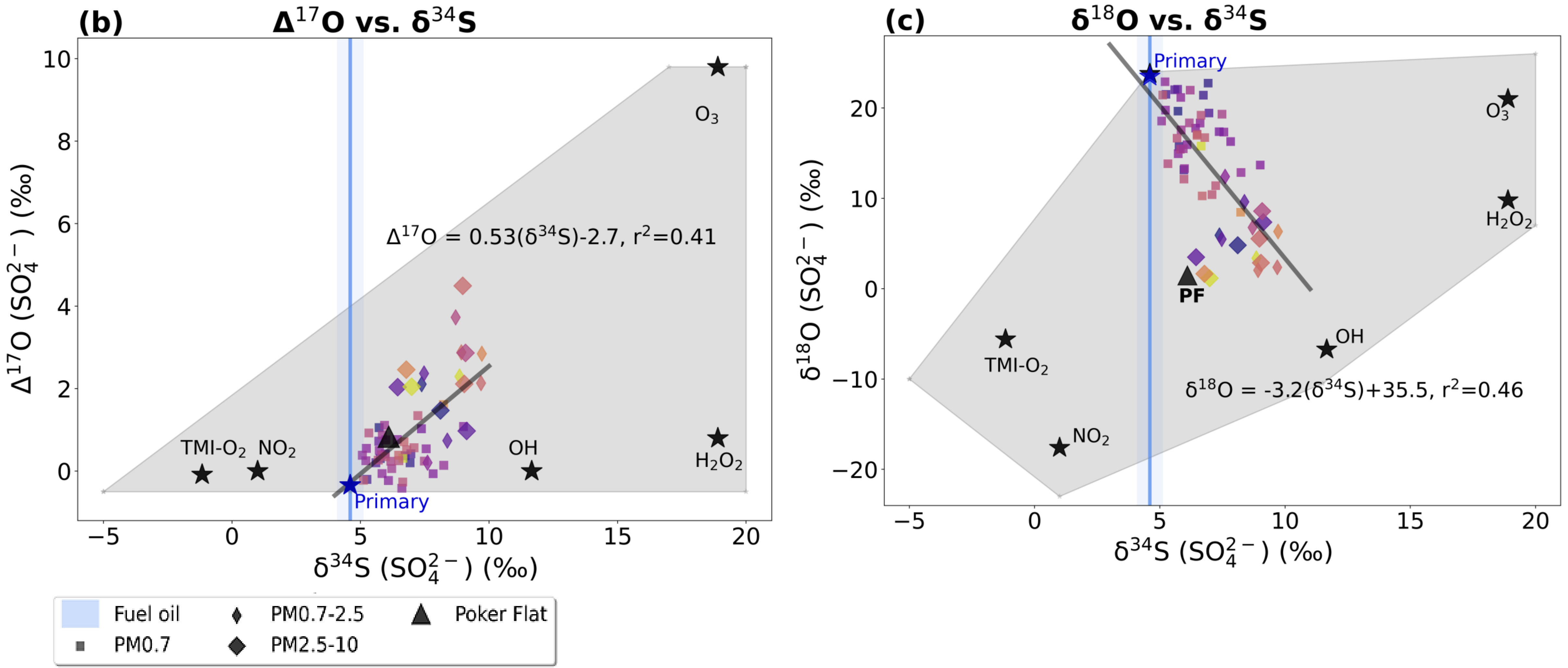
Oxidation by NO2 and TMI-O2 make the $\delta^{34}S(SO_4^{2-})$ observations lighter

$\delta^{34}S$ Is TMI-catalyzed oxidation dominant?



We see that sulfur isotopes become more enriched as the secondary sulfate fraction and aerosol size increases

$\delta^{34}S$ Is TMI-catalyzed oxidation dominant?



We see that sulfur isotopes become more enriched as the secondary sulfate fraction and aerosol size increases

Method: Bayesian Isotope Mixing Model

[1] $\delta^{18}O(SO_4^{2-})$

[2] $\Delta^{17}O(SO_4^{2-})$

[3] $\delta^{34}S(SO_4^{2-})$

→ Model input includes isotope observations, temperature, and sulfur oxidation ratio
→ The analytical error is incorporated for each measurement to help account for uncertainty in our observations

Method: Bayesian Isotope Mixing Model

[1] $\delta^{18}O(SO_4^{2-}) = f_{primary} \cdot \delta^{18}O_{primary} + f_{H2O2} \cdot \delta^{18}O_{H2O2} + f_{O3} \cdot \delta^{18}O_{O3} + f_{TMI\text{-}O2} \cdot \delta^{18}O_{TMI\text{-}O2} + f_{OH} \cdot \delta^{18}O_{OH} + f_{NO2} \cdot \delta^{18}O_{NO2}$ where $f_{primary} + f_{H2O2} + f_{O3} + f_{TMI\text{-}O2} + f_{OH} + f_{NO2} = 1$

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→ **Source signatures are calculated as a function of temperature and sulfur oxidation ratio**

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→ Model output is the fractional contribution of each sulfate formation pathway

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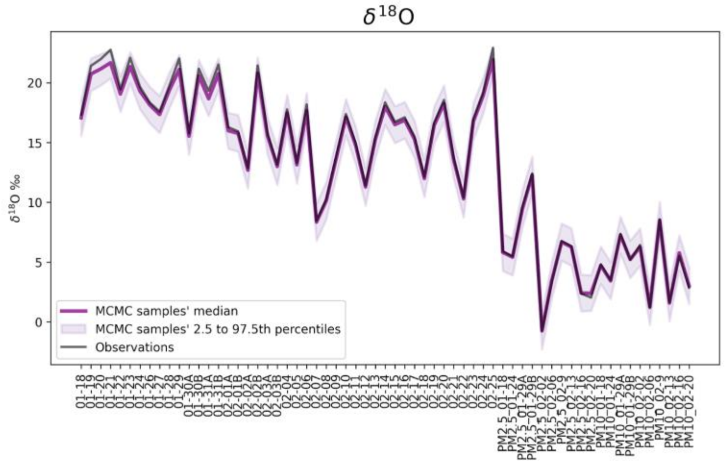

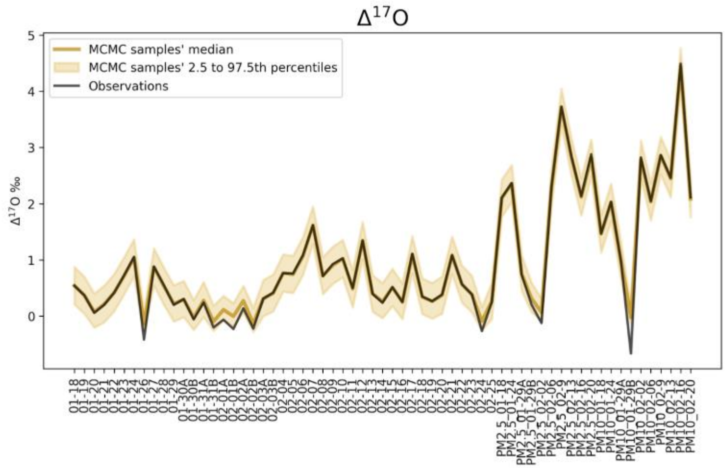

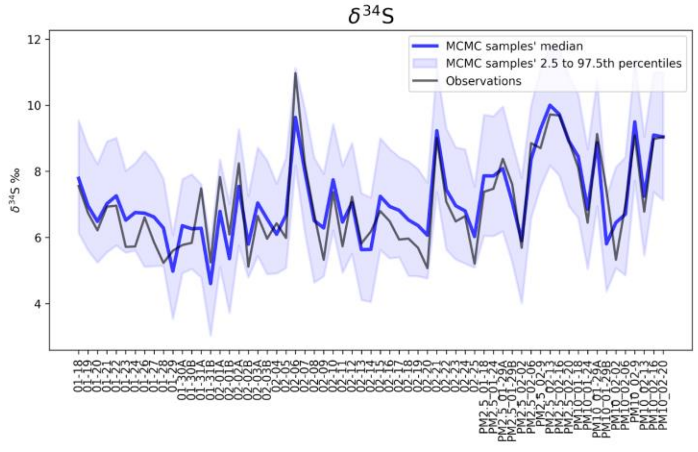

→ **The shading represents a 95% confidence interval signifies the models ability to reproduce the observations ± the analytical error**

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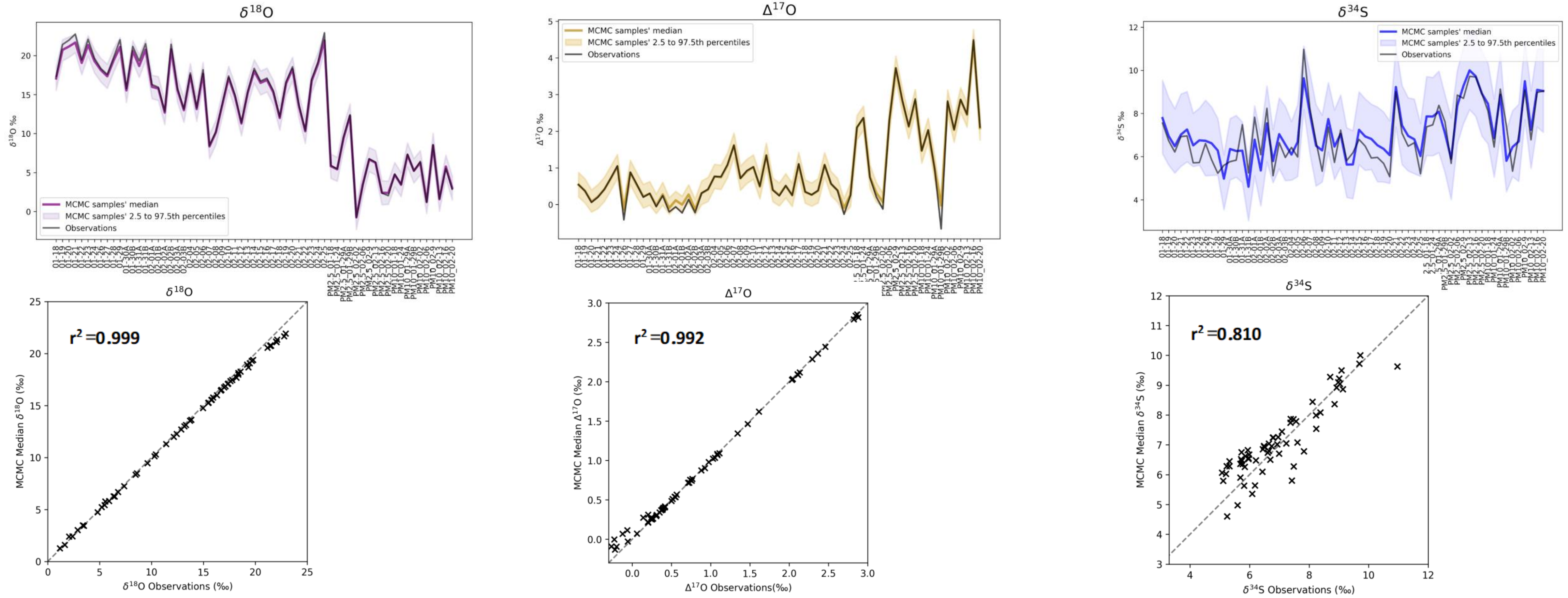
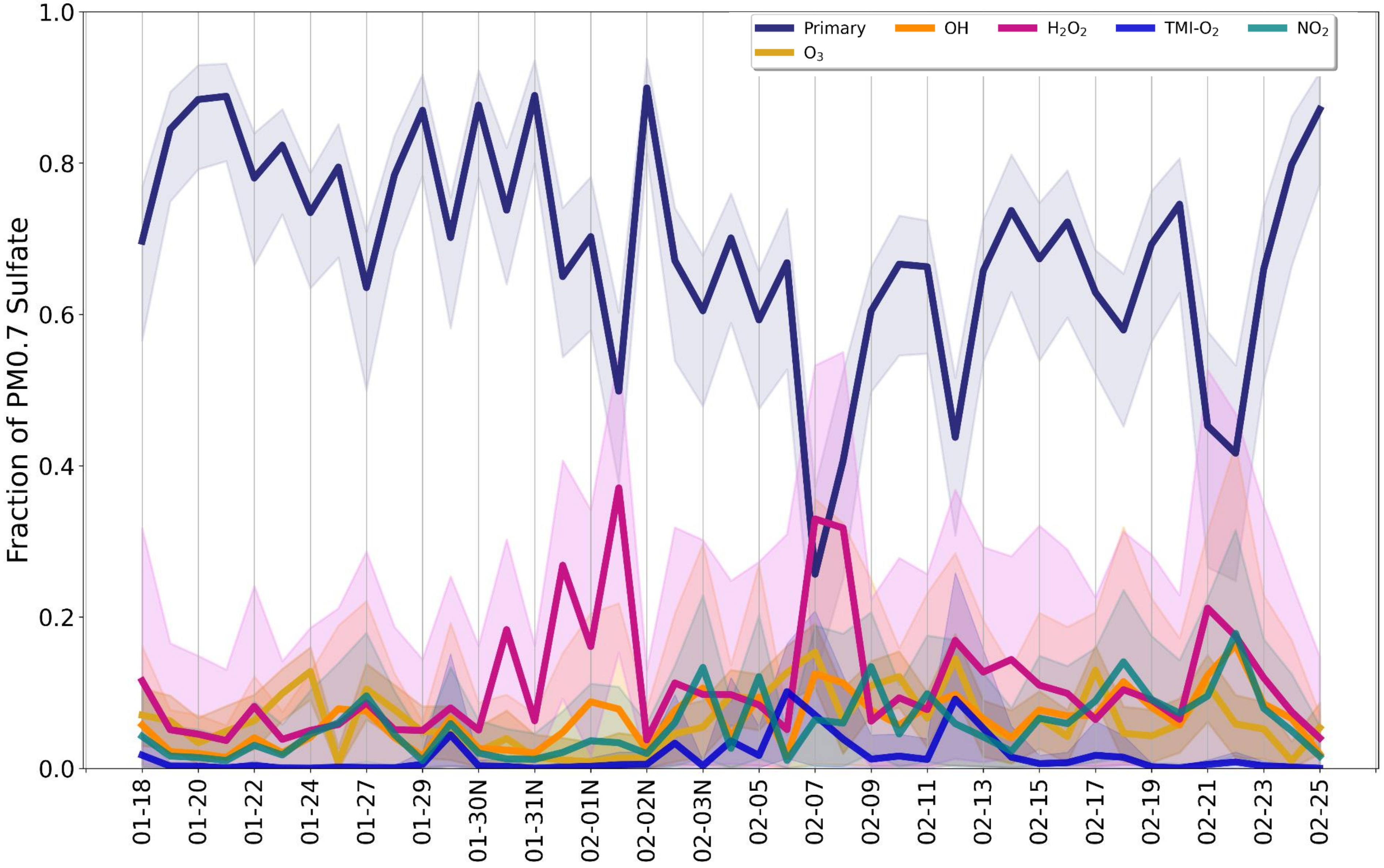


Sources and formation of PM0.7 sulfate



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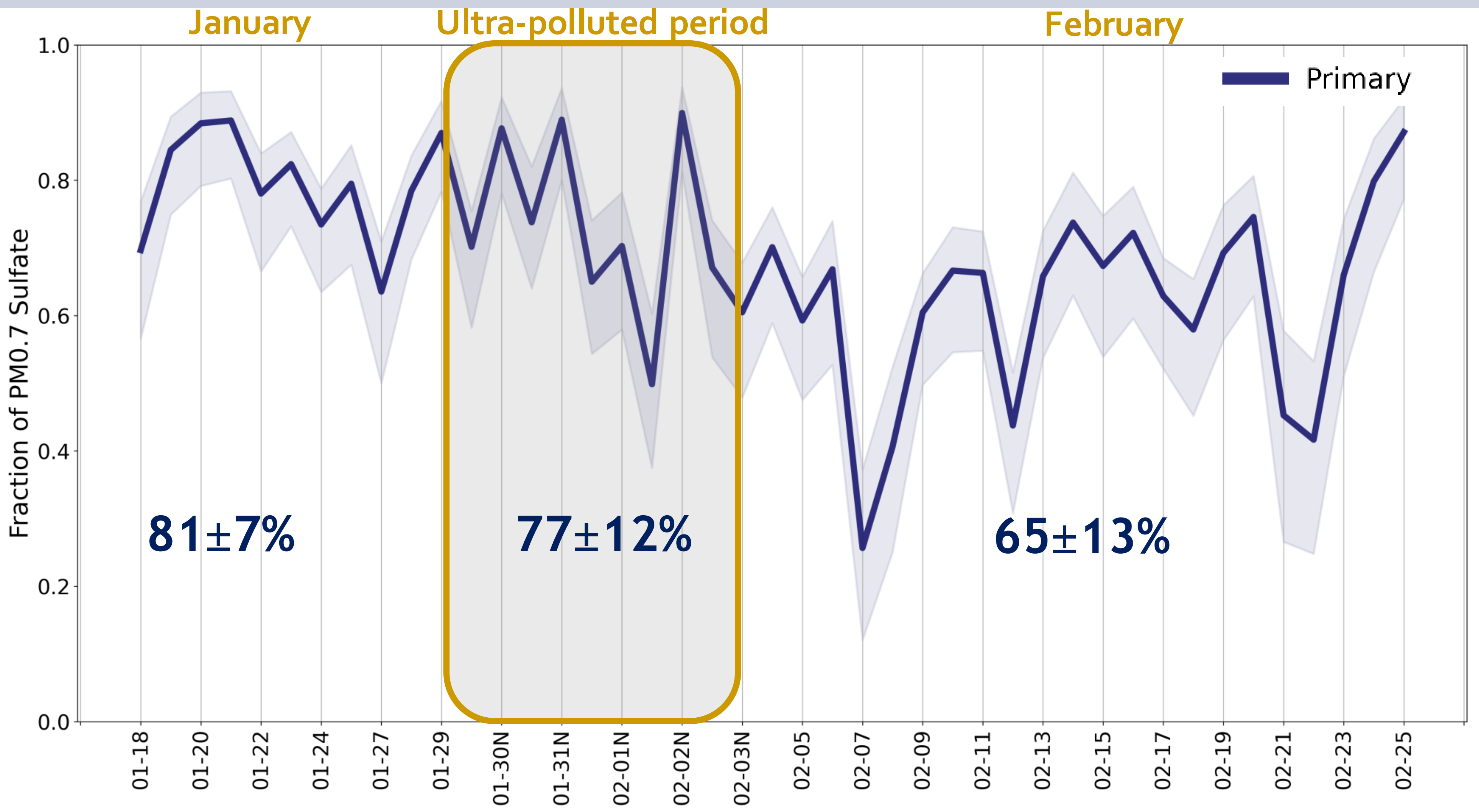
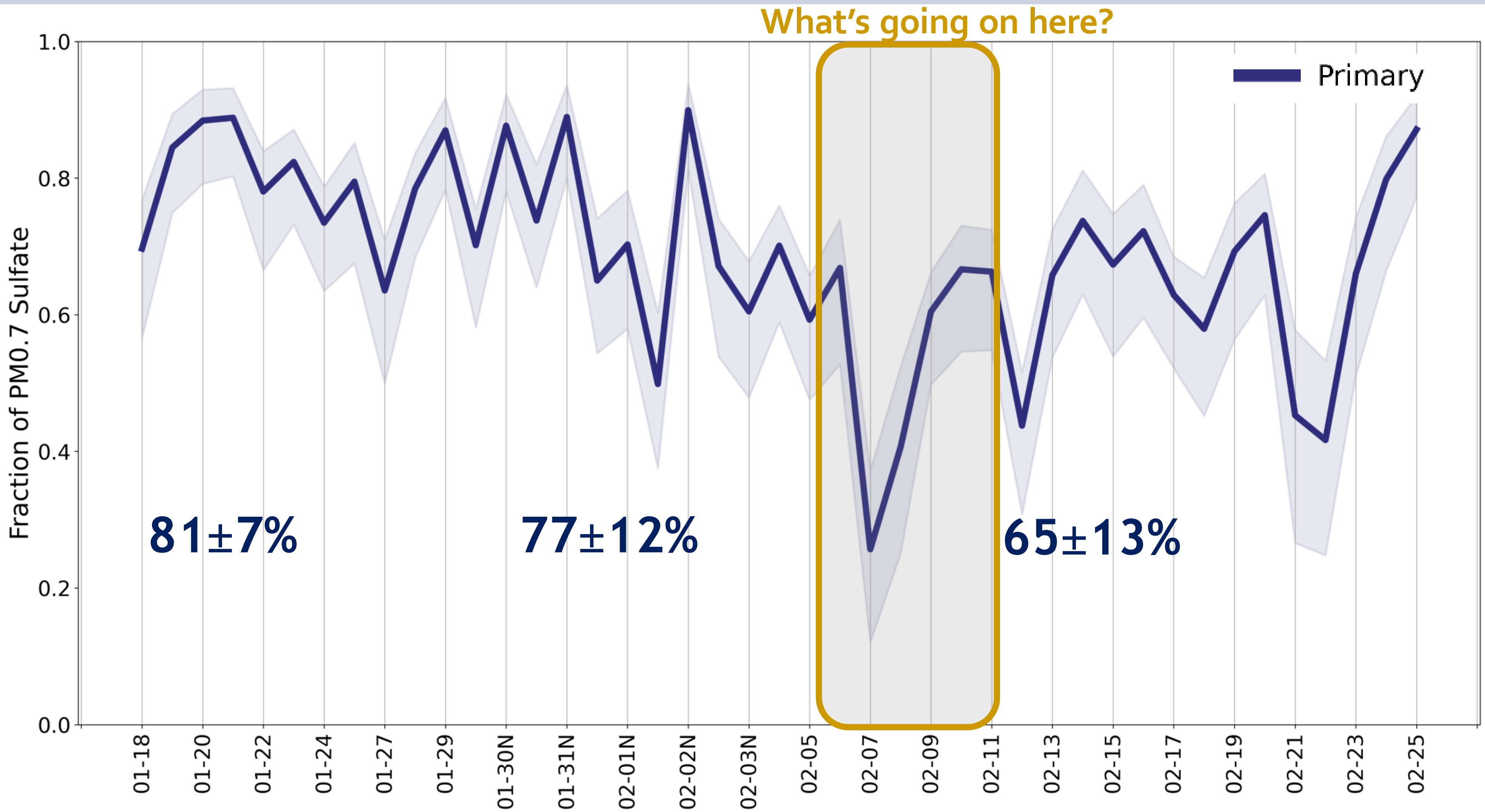


1) Primary sulfate is the dominant source of sulfate throughout the campaign, contributing 2.1 ± 1.4 μg/m³ (69 ± 15% of $PM_{0.7}$ sulfate) on average.

Sources and formation of PM0.7 sulfate



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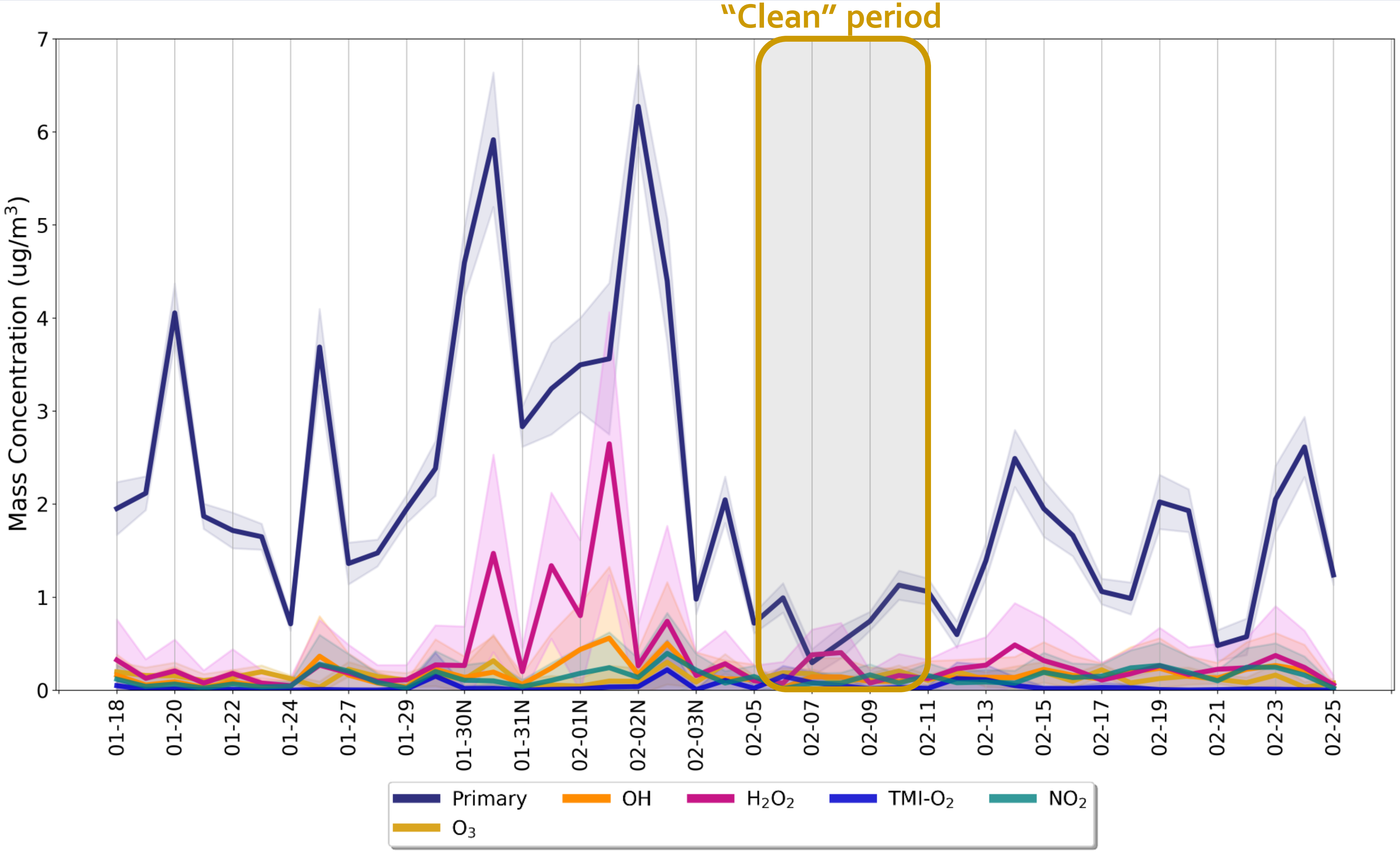

The period with the most efficient secondary sulfate formation is the cleanest of the campaign

Policy measures to reduce sulfur emissions

Table 8: Comparison of Key Emission Factors and Sulfur Content for Fairbanks Heating Fuels

Fuel	Emission Factor (lb/mmBTU)		Sulfur Content
	$PM_{2.5}$	SO_2	(ppmv)
HS No. 1 & 2	0.00340	0.215	2,053
HS No. 1	0.00365	0.102	896
HS No. 2	0.00330	0.263	2,566
Natural Gas	0.00749	0.000591	<16
Coal	0.526	0.612	2,000
Wood Burning	0.18 – 2.0*	0.023	<500
ULS	~0.003-0.004	0.00171	15

ppmv = parts per million by volume

* Covering a range of uncertified and EPA-certified cordwood and pellet devices, assuming zero (oven dry) moisture content

Source: compiled by Sierra Research, Inc

- Starting in September 1st , 2022:

fuel oil #2 (used by 66% of residents) was banned and only fuel oil #1 and ULS fuel oil could be burned

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- Starting in September 1st ,2022:
fuel oil #2 (used by 66% of residents) was banned and only fuel oil #1 and ULS fuel oil could be burned

- ULS fuel oil was not mandated because an ADEC residential fuel expenditure assessment found that this would motivate many residents to revert to wood burning. This would increase PM emissions.

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HS No. 2	0.00330	0.263	2,566
Natural Gas	0.00749	0.000591	<16
Coal	0.526	0.612	2,000
Wood Burning	0.18 – 2.0*	0.023	<500
ULS	~0.003-0.004	0.00171	15

ppmv = parts per million by volume

* Covering a range of uncertified and EPA-certified cordwood and pellet devices, assuming zero (oven dry) moisture content

Source: compiled by Sierra Research, Inc

- Starting in September 1st, 2022:

fuel oil #2 (used by 66% of residents) was banned and only fuel oil #1 and ULS fuel oil could be burned

- ULS fuel oil was not mandated because an ADEC residential fuel expenditure assessment found that this would motivate many residents to revert to wood burning. This would increase PM emissions.

- Failure to mandate ULS fuel is one of the reasons EPA rejected the ADECs air quality improvement plan in early 2023.

Policy measures to reduce sulfur emissions

Table 8: Comparison of Key Emission Factors and Sulfur Content for Fairbanks Heating Fuels

Fuel	Emission Factor (lb/mmBTU)		Sulfur Content
	$PM_{2.5}$	SO_2	(ppmv)
HS No. 1 & 2	0.00340	0.215	2,053
HS No. 1	0.00365	0.102	896
HS No. 2	0.00330	0.263	2,566
Natural Gas	0.00749	0.000591	<16
Coal	0.526	0.612	2,000
Wood Burning	0.18 – 2.0*	0.023	<500
ULS	~0.003-0.004	0.00171	15

ppmv = parts per million by volume
* Covering a range of uncertified and EPA-certified cordwood and pellet devices, assuming zero (oven dry) moisture content
Source: compiled by Sierra Research, Inc

- SO2 emissions during winter 2022-2023 were lower (by about 33%) than the historical median after banning fuel oil #2
- Sulfate concentrations were 24% lower during winter 2022-2023, but the difference is not statistically significant due to low temporal resolution of filter samples

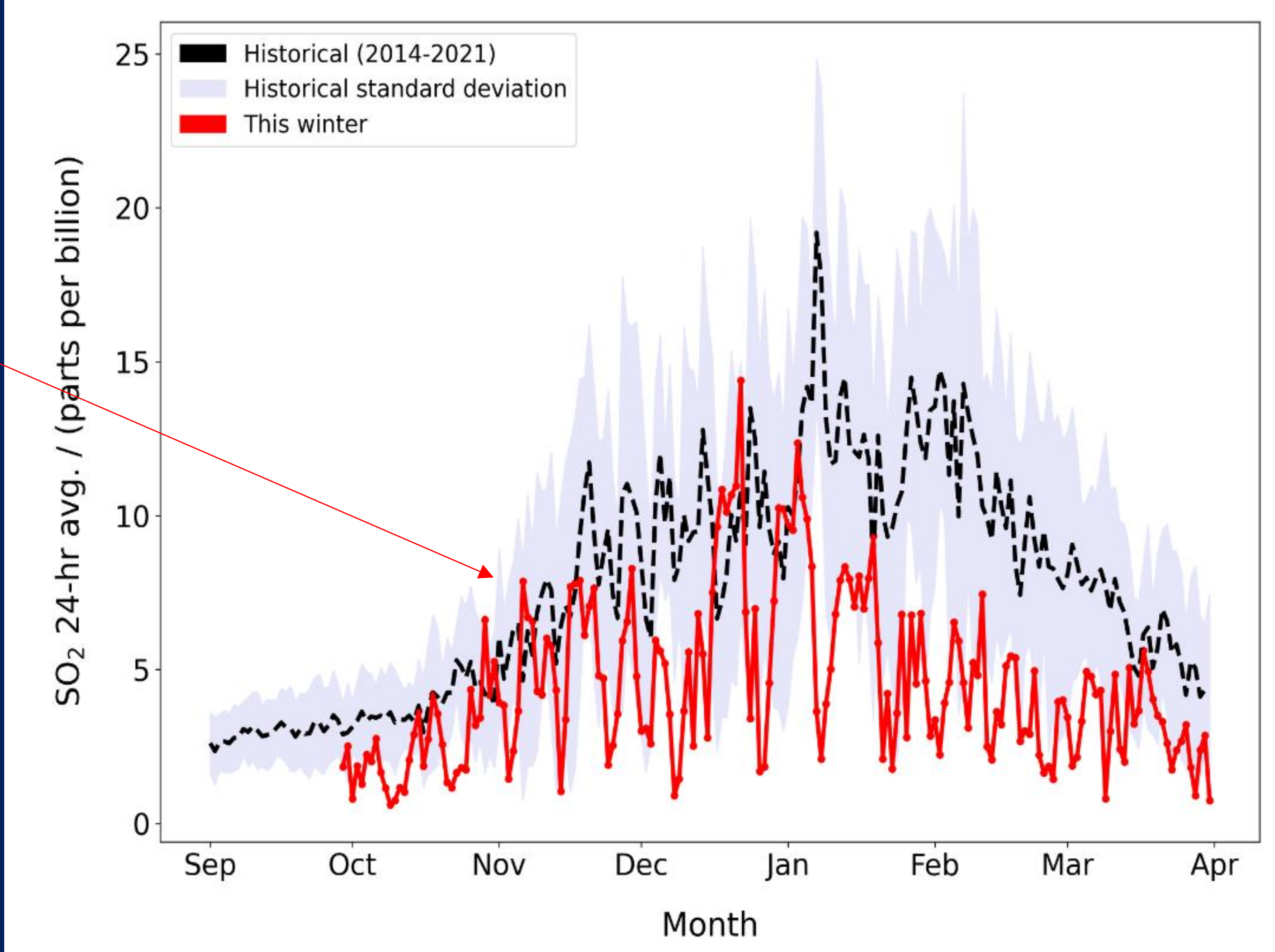


Figure from Meeta Cesler-Maloney and Bill Simpson!
Data from ADEC measurements

Conclusions

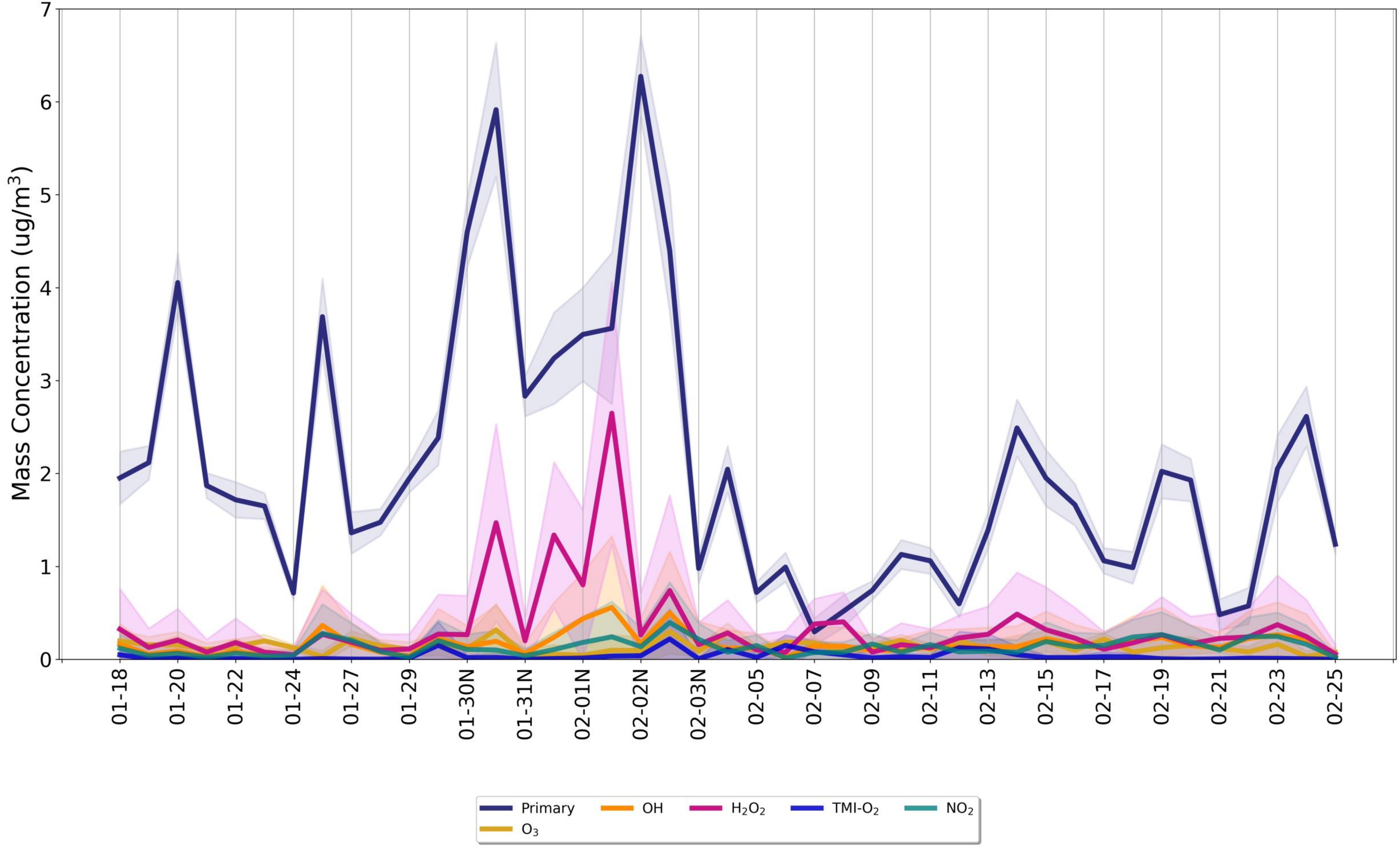
01 Primary sulfate is the dominant source of sulfate throughout the campaign

Conclusions

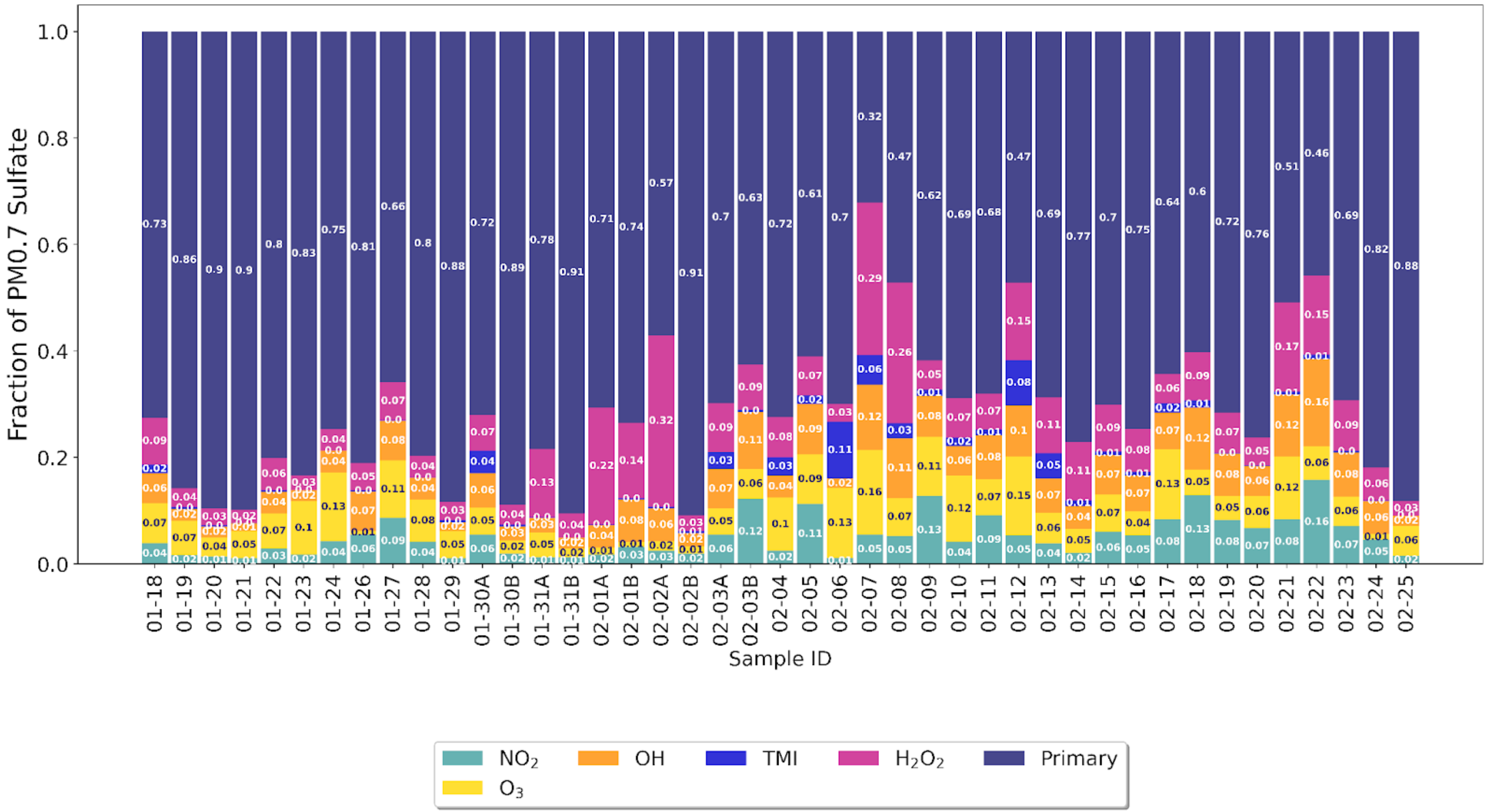
01 Primary sulfate is the dominant source of sulfate throughout the campaign

02 The ban on fuel oil #2 reduced SO2 concentrations in the Winter of 2022-2023. We hypothesize this trend likely reduced primary sulfate emissions. More work is needed to know about possible effects on secondary sulfate production due to potential changes in pH

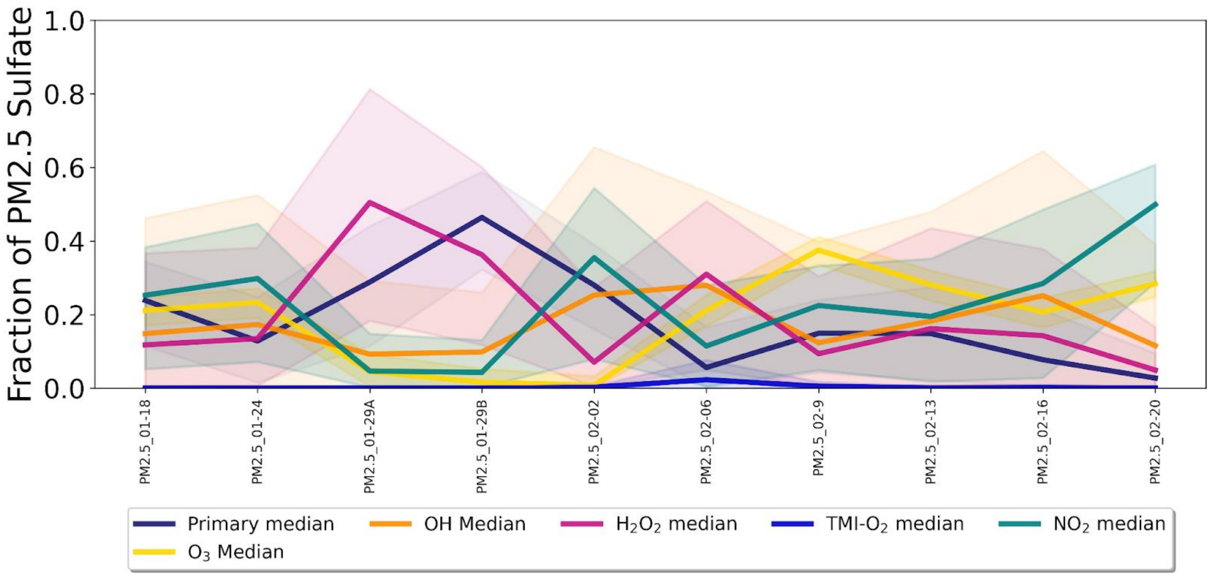
Extra slides ☺

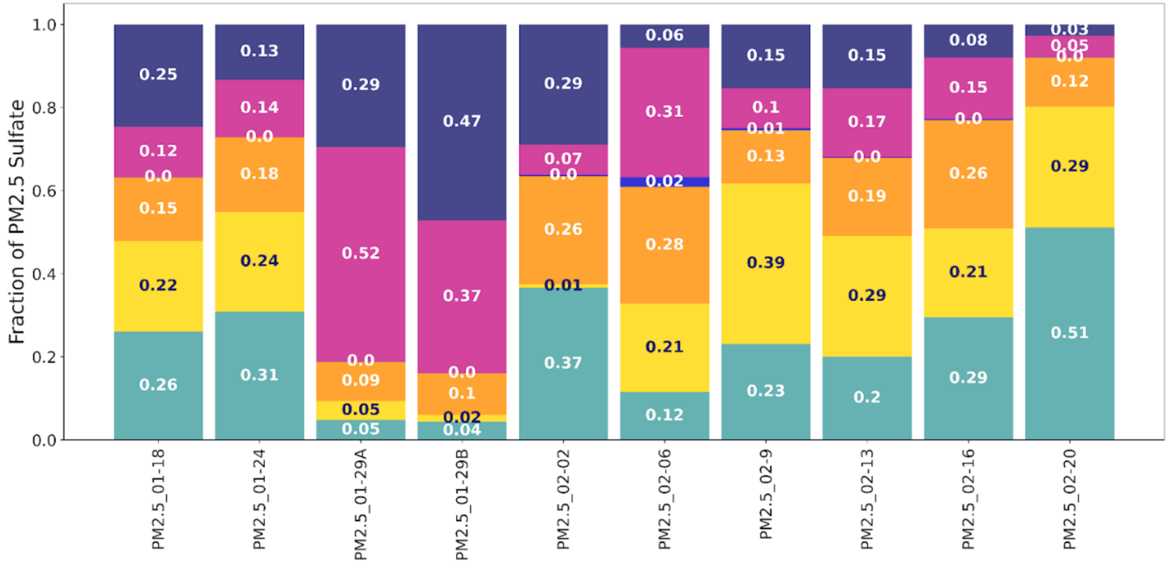

Mass Concentration (ug/m3)
0
1
2
3
4
5
6
7
01-18
01-20
01-22
01-24
01-27
01-29
01-30N
01-31N
02-01N
02-02N
02-03N
02-05
02-07
02-09
02-11
02-13
02-15
02-17
02-19
02-21
02-23
02-25
Primary
OH
H2O2
TMI-O2
NO2
O3

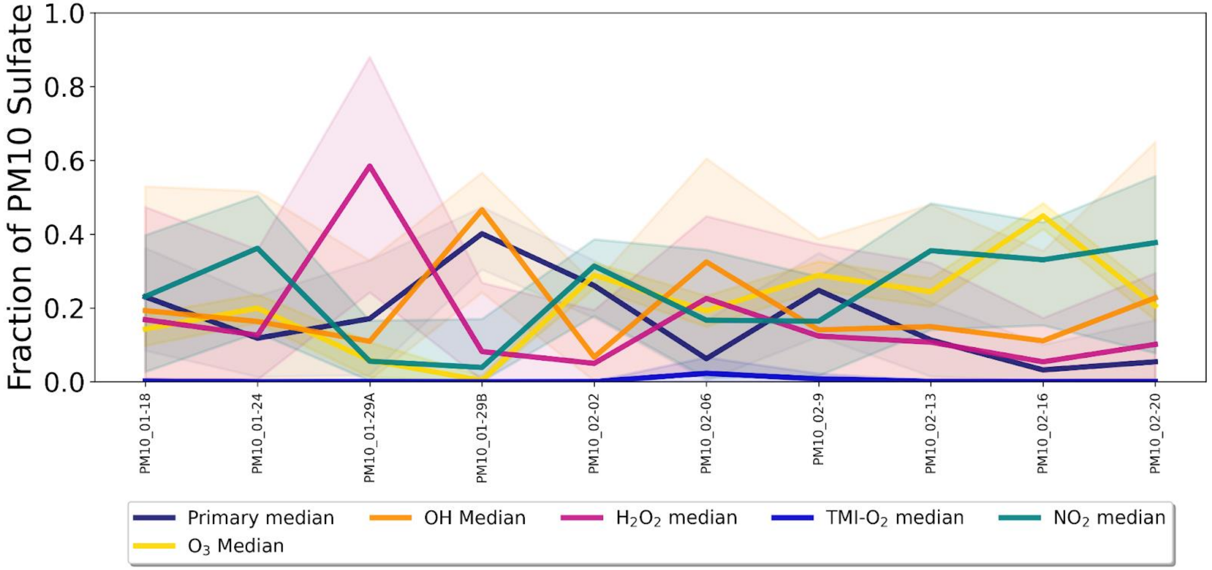
Sources and formation of PM0.7 sulfate

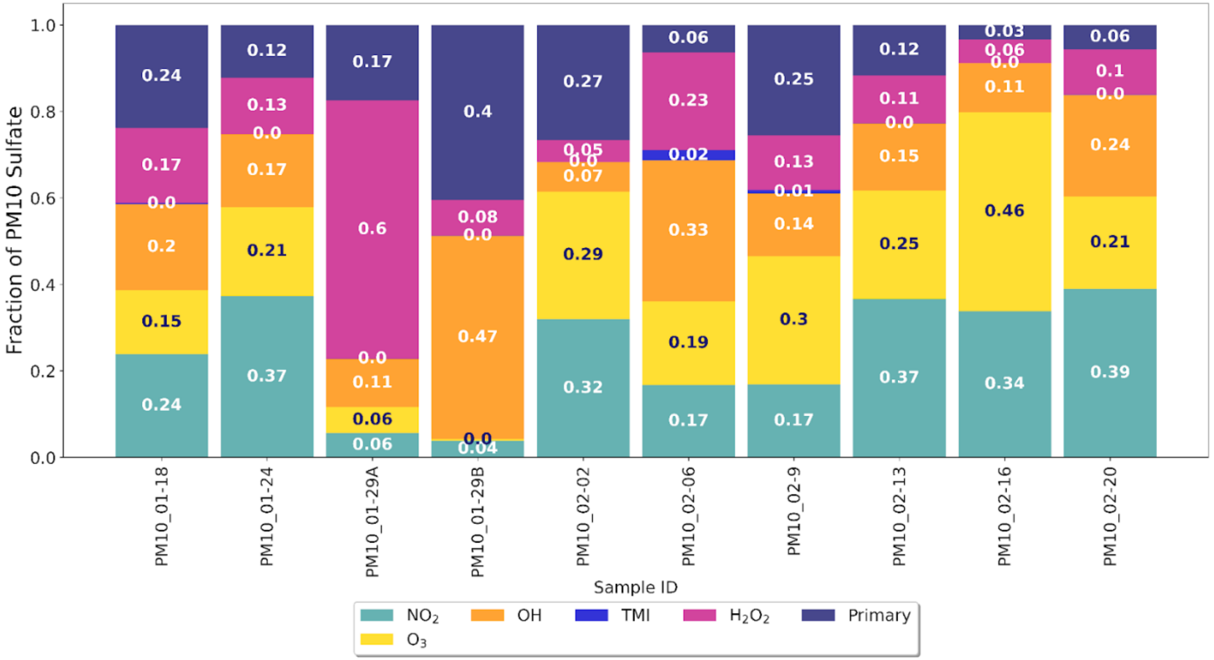


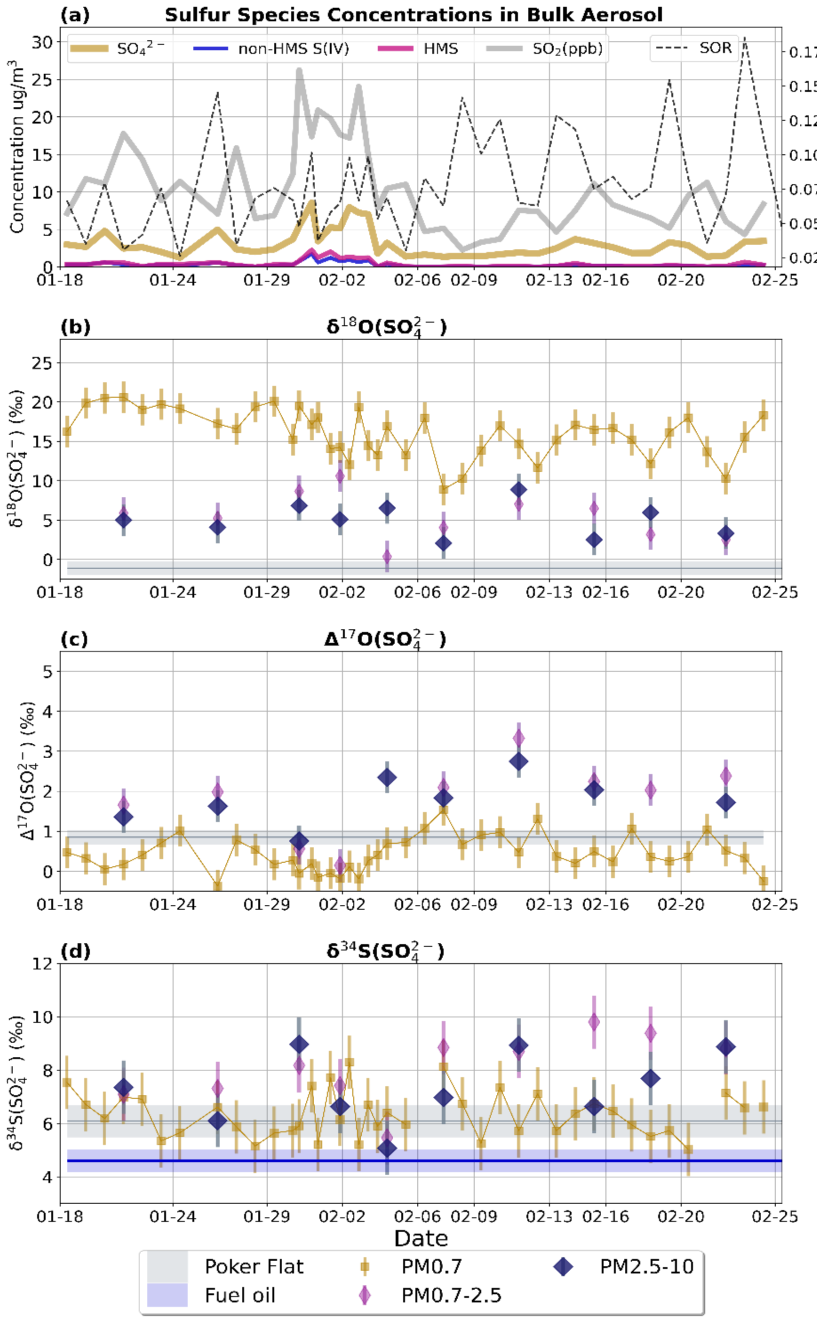
PM0.7-PM2.5 and PM2.5-PM10 size bins show much more O3 and NO2 oxidation. This is likely due to dust and road salt, which is abundant in larger size bins

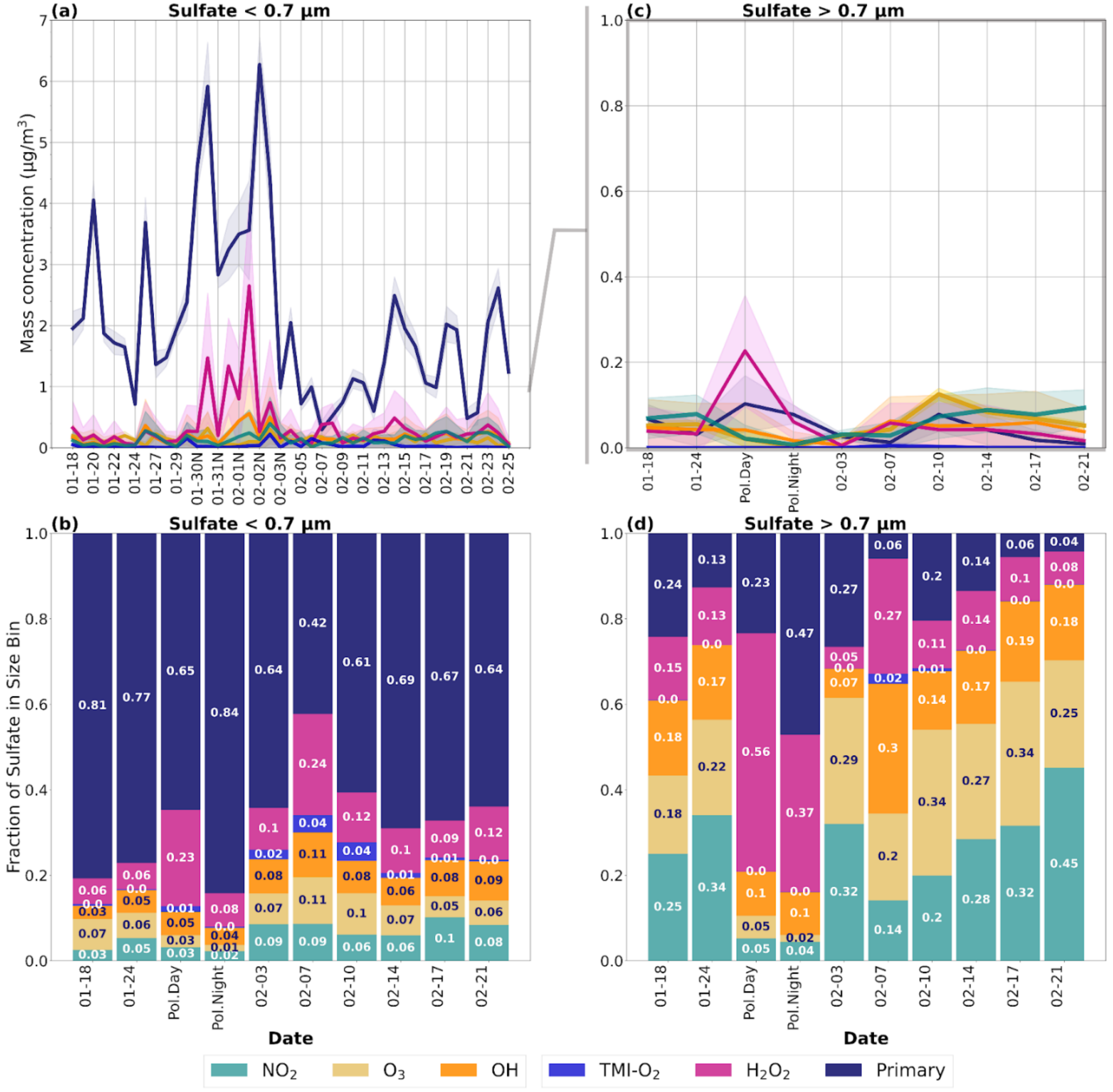


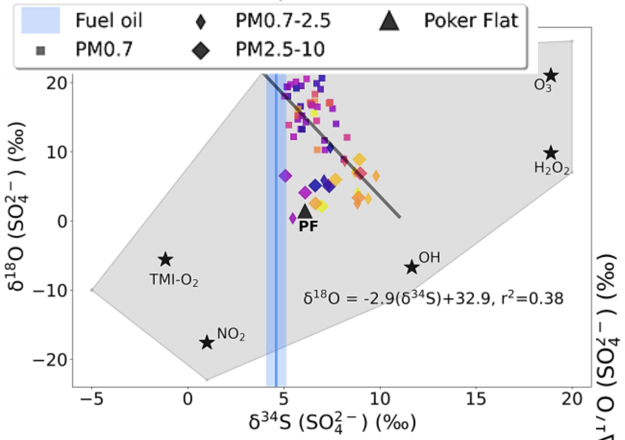







(a) Sulfur Species Concentrations in Bulk Aerosol
SO_4^{2-}
non-HMS S(IV)
HMS
SO_2(ppb)
SOR
Concentration ug/m^3
Sulfur oxidation ratio
(b) $\delta^{18}O(SO_4^{2-})$
$\delta^{18}O(SO_4^{2-})$ (‰)
(c) $\Delta^{17}O(SO_4^{2-})$
$\Delta^{17}O(SO_4^{2-})$ (‰)
(d) $\delta^{34}S(SO_4^{2-})$
$\delta^{34}S(SO_4^{2-})$ (‰)
Date
Poker Flat
Fuel oil
PM0.7
PM0.7-2.5
PM2.5-10


(a) Sulfate < 0.7 µm
Mass concentration (µg/m^3)
(c) Sulfate > 0.7 µm
(b) Sulfate < 0.7 µm
Fraction of Sulfate in Size Bin
(d) Sulfate > 0.7 µm
Date
NO_2
O_3
OH
TMI-O_2
H_2O_2
Primary



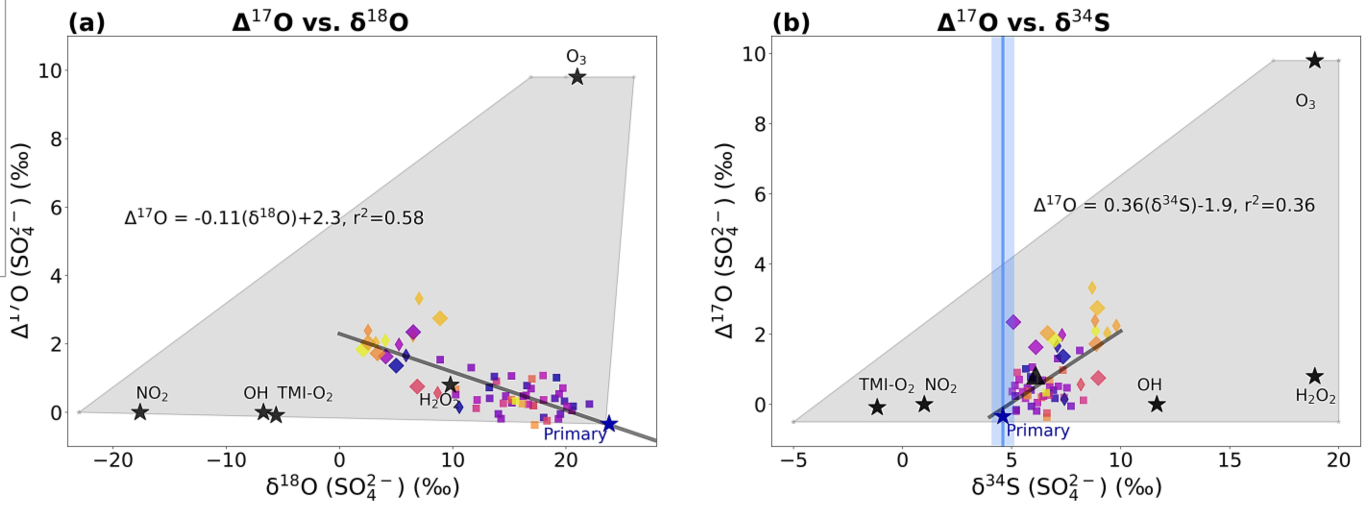
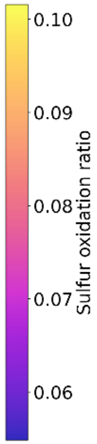
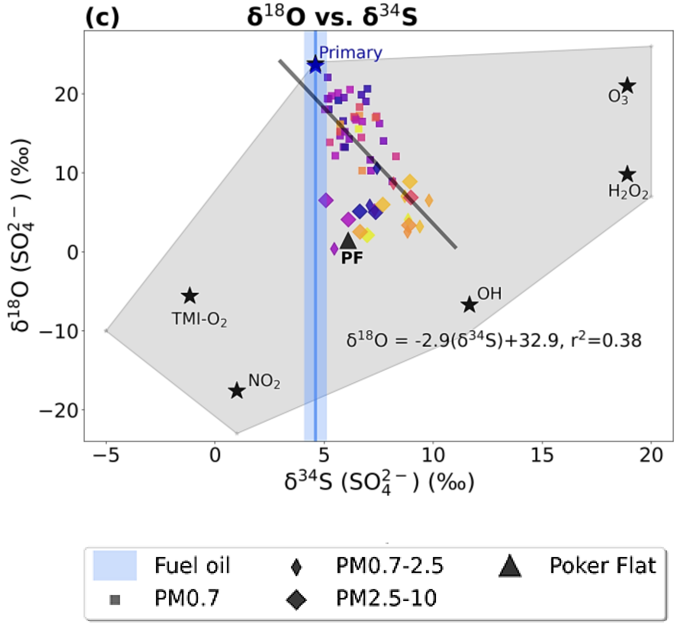


Figure 2. Regressions of (a) $\Delta^{17}O$ vs. $\delta^{18}O$, (b) $\Delta^{17}O$ vs. $\delta^{34}S$, and (c) $\delta^{18}O$ vs. $\delta^{34}S$ where the solid black line is the linear least-squares regression line. The three size bins are depicted by the shape of the marker as defined in the legend. The color bar shows the sulfur oxidation ratio (SOR) for each sample. Poker Flat measurements are depicted with black triangles. The isotopic composition of fuel oil is shown by the blue line. The gray shaded region shows the full possible range of $\delta^{18}O$, $\Delta^{17}O$, and $\delta^{34}S$ source signatures with the average source signature for each pathway plotted as a black star.





How do we measure isotopes?

Collect filter samples in Fairbanks

↓

Extract sample from filter → Convert to sodium form (Na_2SO_4) → Remove organics with H_2O_2 → Redissolve sample

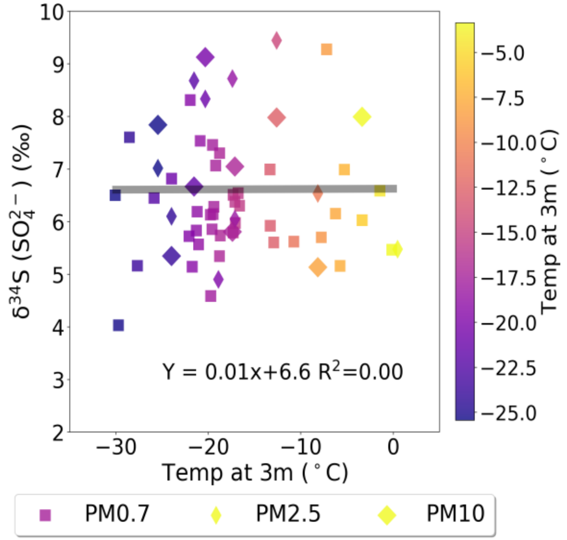
↓

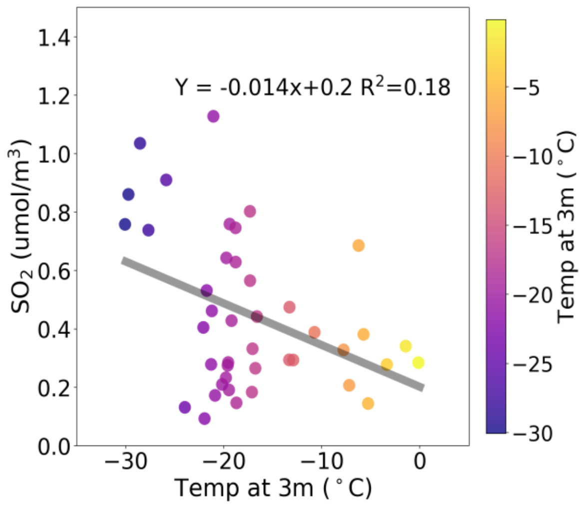
Remove organics with H_2O_2 (again) → Separate sulfate ions via ion chromatography → Covert to silver form (Ag_2SO_4) → **Measure oxygen isotopes**

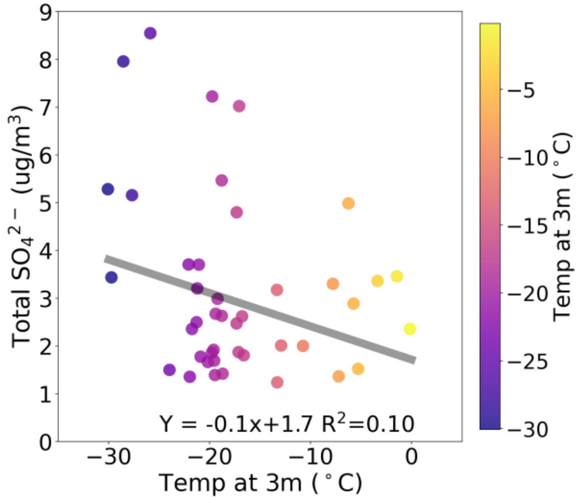
↓

Measure sulfur isotopes

PHOTO: YUK CHUN







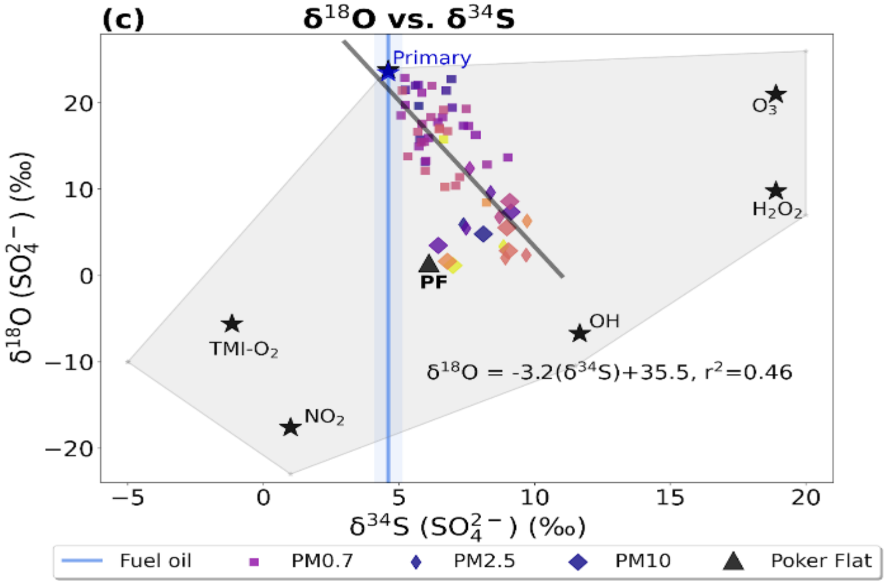
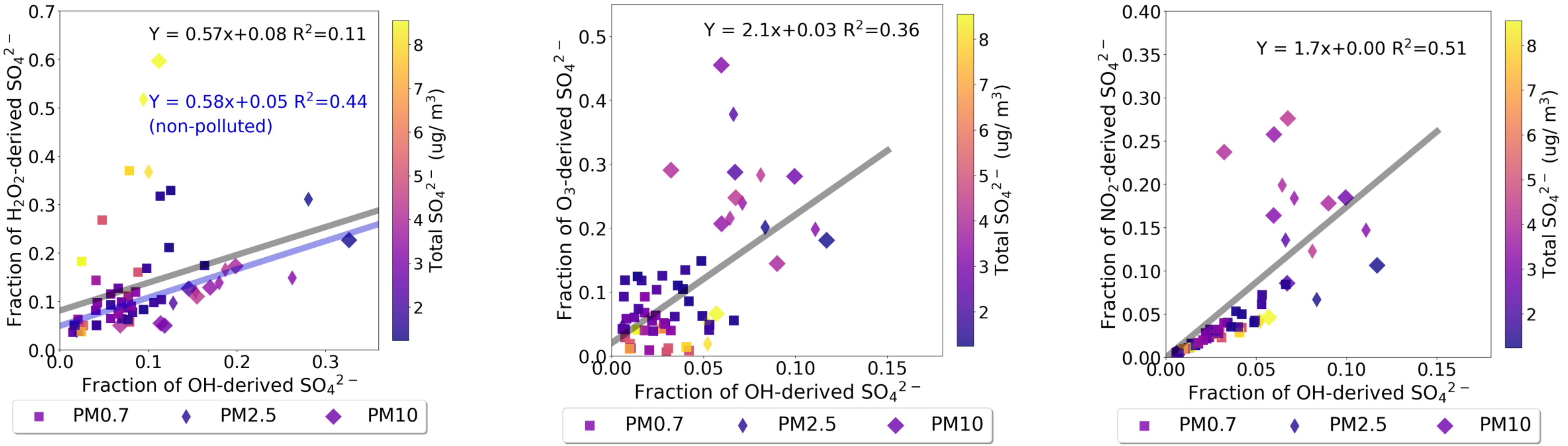
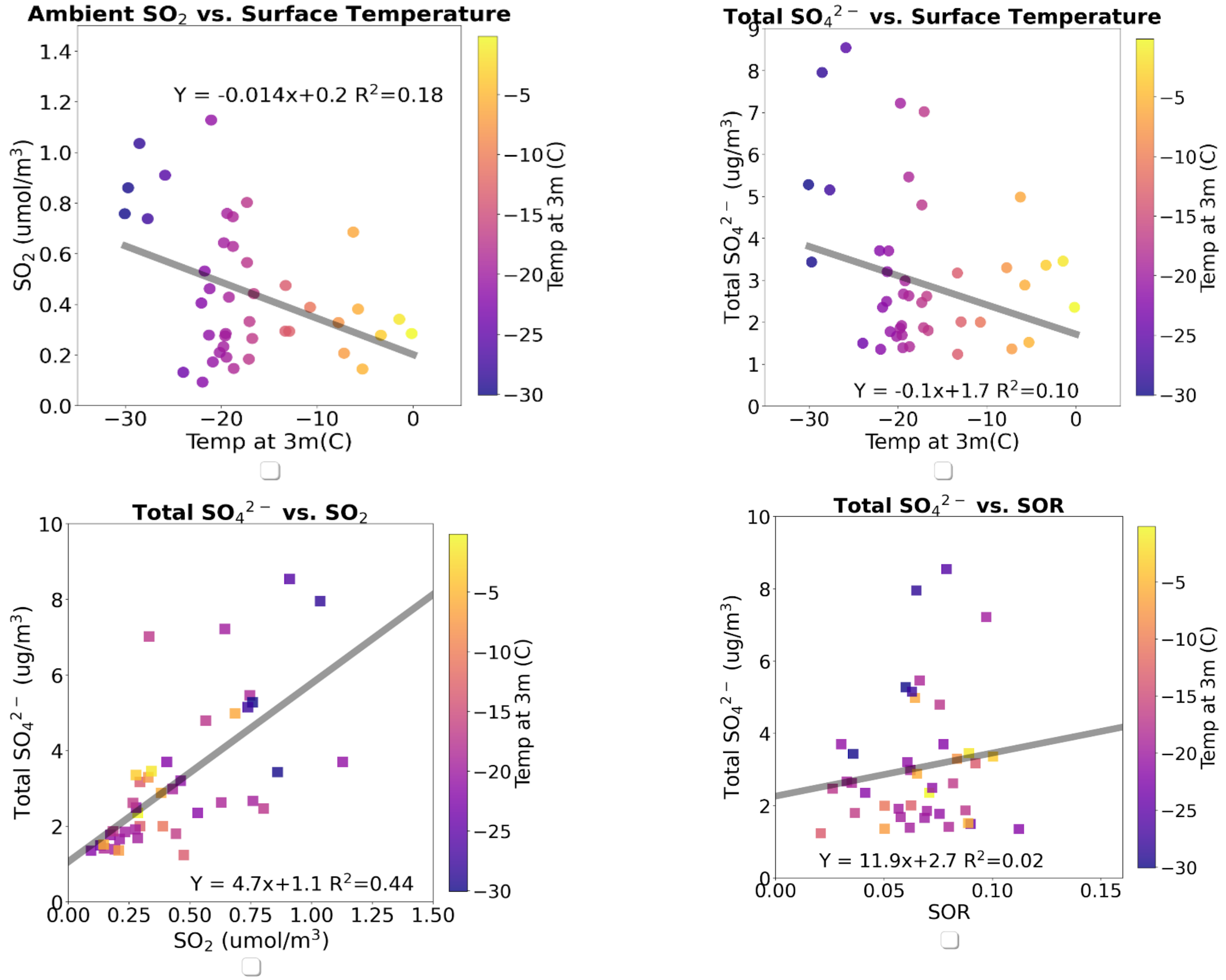


Table S4. $\delta^{34}S(S)$ measurement of Fairbanks fuel oil

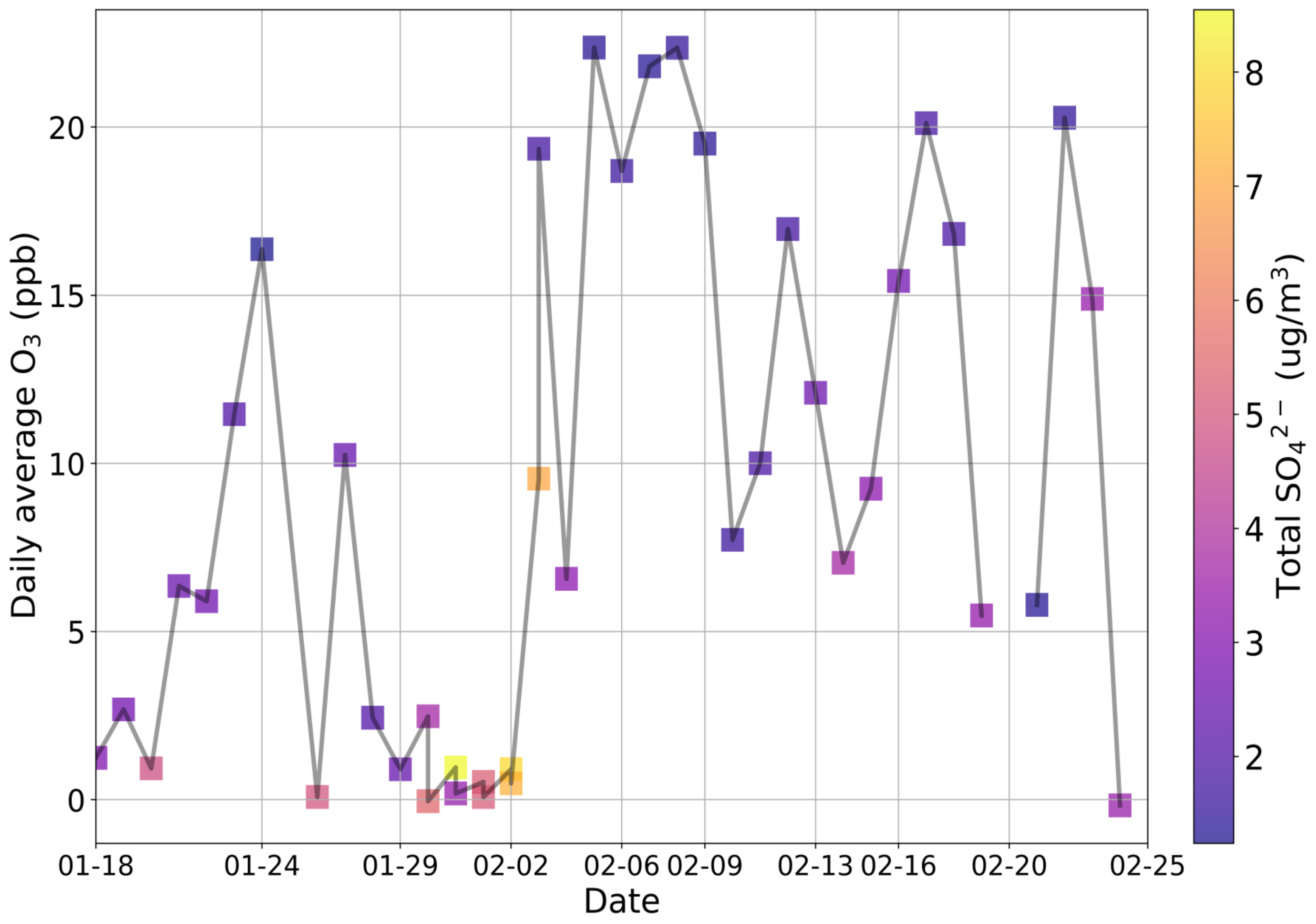
Fuel oil Type	Sulfur content (ppmv)	Quantity of fuel oil combusted	Fraction of total fuel oil used in Fairbanks (ADEC, 2019)	Estimated contribution to fuel oil-derived sulfur based on sulfur content and domestic use	Measured $\delta^{34}S(S)$	**Weighted average $\delta^{34}S(S)$**
Fuel oil #1	896	6 µL	33%	15%	3.7±0.6‰	**4.7±0.6‰**
Fuel oil #2	2,566	6 µL	67%	85%	4.9±0.1‰	

Sulfate oxidation from photochemically produced oxidants are positively associated. Additionally, sulfate from OH, NO_2, and H_2O_2 are all relatively higher in February rather than January. O_3-derived sulfate is around the same in January and February.





Ambient SO_2 vs. Surface Temperature
Y = -0.014x+0.2 R^2=0.18
SO_2 (umol/m^3)
Temp at 3m(C)
Temp at 3m (C)
Total SO_4^{2-} vs. Surface Temperature
Y = -0.1x+1.7 R^2=0.10
Total SO_4^{2-} (ug/m^3)
Temp at 3m(C)
Temp at 3m (C)
Total SO_4^{2-} vs. SO_2
Y = 4.7x+1.1 R^2=0.44
Total SO_4^{2-} (ug/m^3)
SO_2 (umol/m^3)
Temp at 3m (C)
Total SO_4^{2-} vs. SOR
Y = 11.9x+2.7 R^2=0.02
Total SO_4^{2-} (ug/m^3)
SOR
Temp at 3m (C)



Daily average O_3 (ppb)
0
5
10
15
20
01-18
01-24
01-29
02-02
02-06
02-09
02-13
02-16
02-20
02-25
Date
Total SO_4^{2-} (ug/m^3)
2
3
4
5
6
7
8