



# Revisiting the Chemical Speciation Network's Shipping Practices

IMPROVE Steering Committee Meeting

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# Motivation for Revisiting the Chemical Speciation Network's (CSN) Current Shipping Practices

- CSN costs have increased without corresponding budget increases, and OAQPS is **looking across the program at ways to cut costs** to meet our budget.
  - **Shipping costs have doubled** (increased by \$400K/year) due to a mandatory government shipping contract change.
- We estimate that **CSN could save \$400K/year** by moving to ambient shipments (i.e., moving to lighter and slower shipments).

# Current CSN Shipping Procedures



	Speed of Shipment	Weight of Shipment
1-in-3 day sites	To sites: Overnight From sites: Overnight	4 lbs. of freezer packs (15 lbs., total)
1-in-6 day sites	To sites: 2-day From sites: Overnight	4 lbs. of freezer packs (11 lbs., total)



- Contract lab applies TT qualifier flag if shipments (from sites or between labs) arrive  $> 4^{\circ}\text{C}$  (since 2015). Affects 10-30% of data records/year.

# Background Information on Cold Shipments in CSN

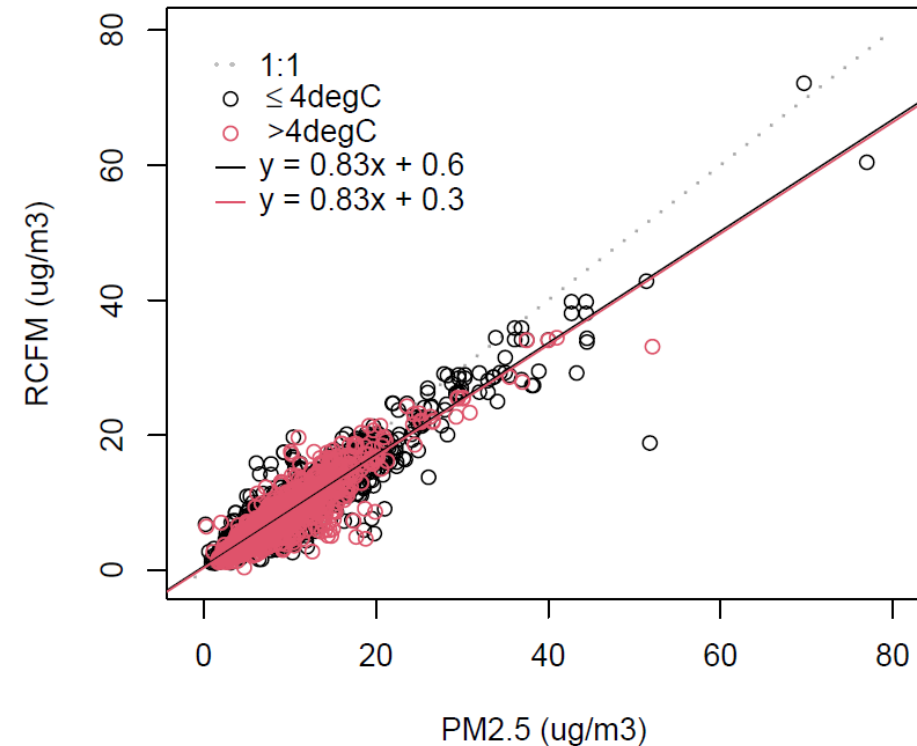
- CSN has used cold shipping since the beginning of the network in 2000.
- Why?
  - QA Guidance for PM<sub>2.5</sub> PTFE gravimetric samples is to ship samples cold to maximize time to post-weigh filters and reduce loss of volatile species.
    - However, CSN cut gravimetric analysis of CSN filters in 2014/2015.
    - CSN uses nylon filters to retain nitrate; quartz filters for carbon analysis.
  - A 2005 shipping study of collocated shipments from Atlanta, GA during summer months
    - Indicated sample precision for nitrate and OC could be adversely affected if cold shipping were eliminated.
    - Shipping was not as high of a percentage of the budget at that time, and cold shipping was retained.

# What can we learn about potential data impacts of ending cold shipping by looking at existing data?

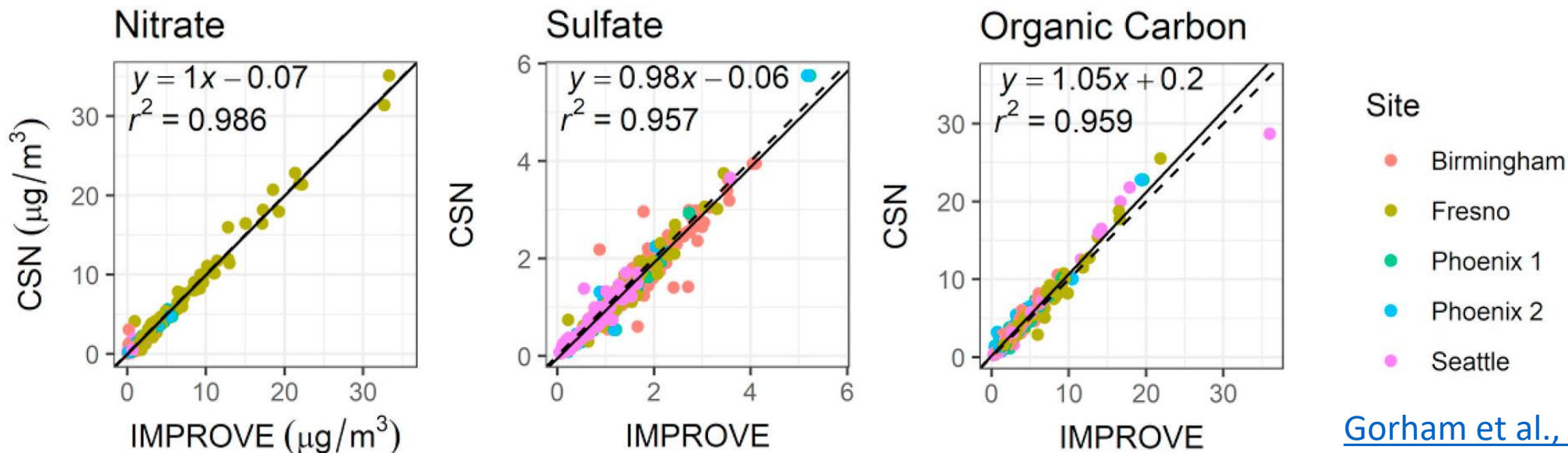
- TT qualifier and Species-Specific analysis [not shown]
  - → network-wide medians for sulfate, nitrate, EC, OC unaffected by data from filters that arrived  $> 4^{\circ}$  C.
- TT qualifier and Reconstructed Fine Mass (RCFM) analysis
- Collocated CSN – IMPROVE data

# Reconstructed Mass vs PM<sub>2.5</sub> FRM Mass using TT Qualifier

- Is there an impact on the Reconstructed Mass (RCFM) vs PM<sub>2.5</sub> mass relationship when shipments arrive > 4°C?
- Differences in slope could indicate warm (>4°C) shipments lose (or gain) mass.
- Details of analysis:
  - RCFM = 4.125\*Sulfur + 1.29\*Nitrate+Soil+1.8\*Chloride + EC + 1.4\*OC
  - Only PM<sub>2.5</sub> gravimetric method codes used (i.e., excluding PM<sub>2.5</sub> continuous methods).
  - Excluded RCFM data points with multiple qualifiers.
    - ≤4°C → no qualifiers
    - >4°C → TT qualifier
- When looking at all CSN sites no difference in slopes.



# CSN – IMPROVE Collocated Sites



[Gorham et al., 2021](#)

- IMPROVE ships at ambient; CSN ships cold
- Inter-network (CSN-IMPROVE) and intra-network (CSN-CSN) precision are similar for the species likely to be most affected by shipping conditions (i.e., nitrate and OC).

	Nitrate	Sulfate	OC
<b>CSN-IMPROVE</b> Collocated Site Precision	13%	7.8%	9.4%
<b>CSN-CSN</b> Collocated Site Precision	11%	8.5%	10%

# Summary and Conclusions

- EPA plans to stop cold shipping of CSN filters with the January 2025 sample shipments. Based on:
  - No apparent impacts on CSN data quality when recent shipments have arrived warm (i.e., when the TT flag was applied)
  - CSN no longer performs gravimetric analysis of PTFE filters
  - Practices in similar networks (IMPROVE and CASTNET)
  - CSN and IMPROVE collocated site comparisons
- 2025 CSN shipping calendar will reflect final changes.
  - For now, once sampled filters are received at the lab, we still plan to keep filters cold.
  - Plan to request operators avoid leaving sampled filters in direct sun or hot vehicles.
- We are also assessing additional CSN design changes that will be needed to meet the target budget.



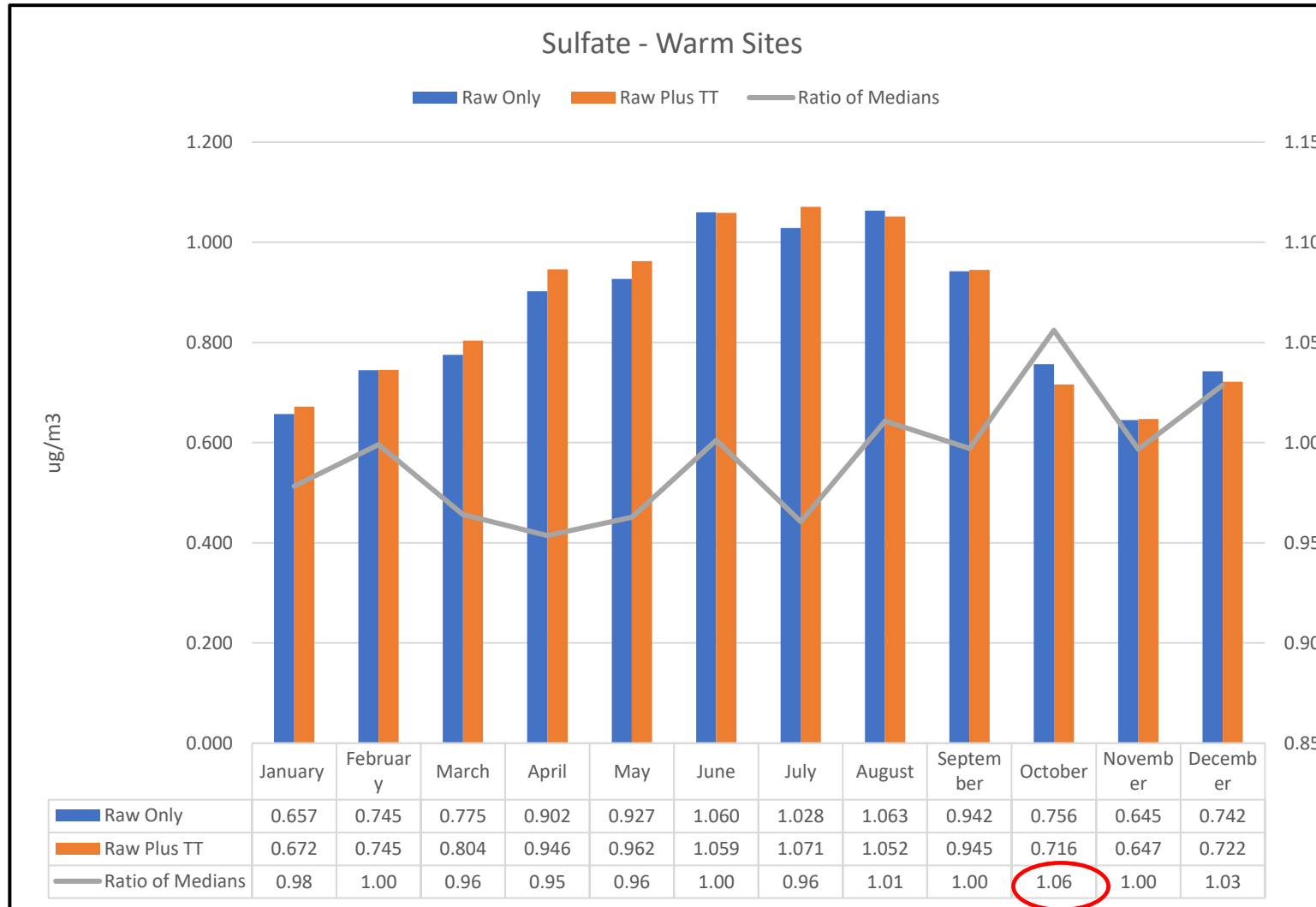


# Species-specific Analysis using TT Qualifier

- Evaluated monthly CSN data in AQS for a subset of sites at warmer locations:
  - Arizona; New Mexico; Texas; Louisiana; Alabama; Florida; Georgia; and Rubidoux CA.
- Date Range 01/1/2020 to 12/31/2023
- Parameters: EC (88380); OC (88370); Sulfate (88403); and Nitrate (88306).
- Two data sets compared:
  - Raw data: all values in date range without any flag type.
  - Raw data + TT flag: all values in date range without any flag type + data with TT flag. Multiple TT flag combinations were not included.
- Criteria used as recommended by [Expert Panel](#) and [4-City Study](#):
  - Ratio of means:  $1 \pm .15$  OC and EC;  $1 \pm .10$  nitrate; and  $1 \pm .05$  sulfate.
  - Used ratio of medians because data are not normally distributed, and means are affected by outliers.

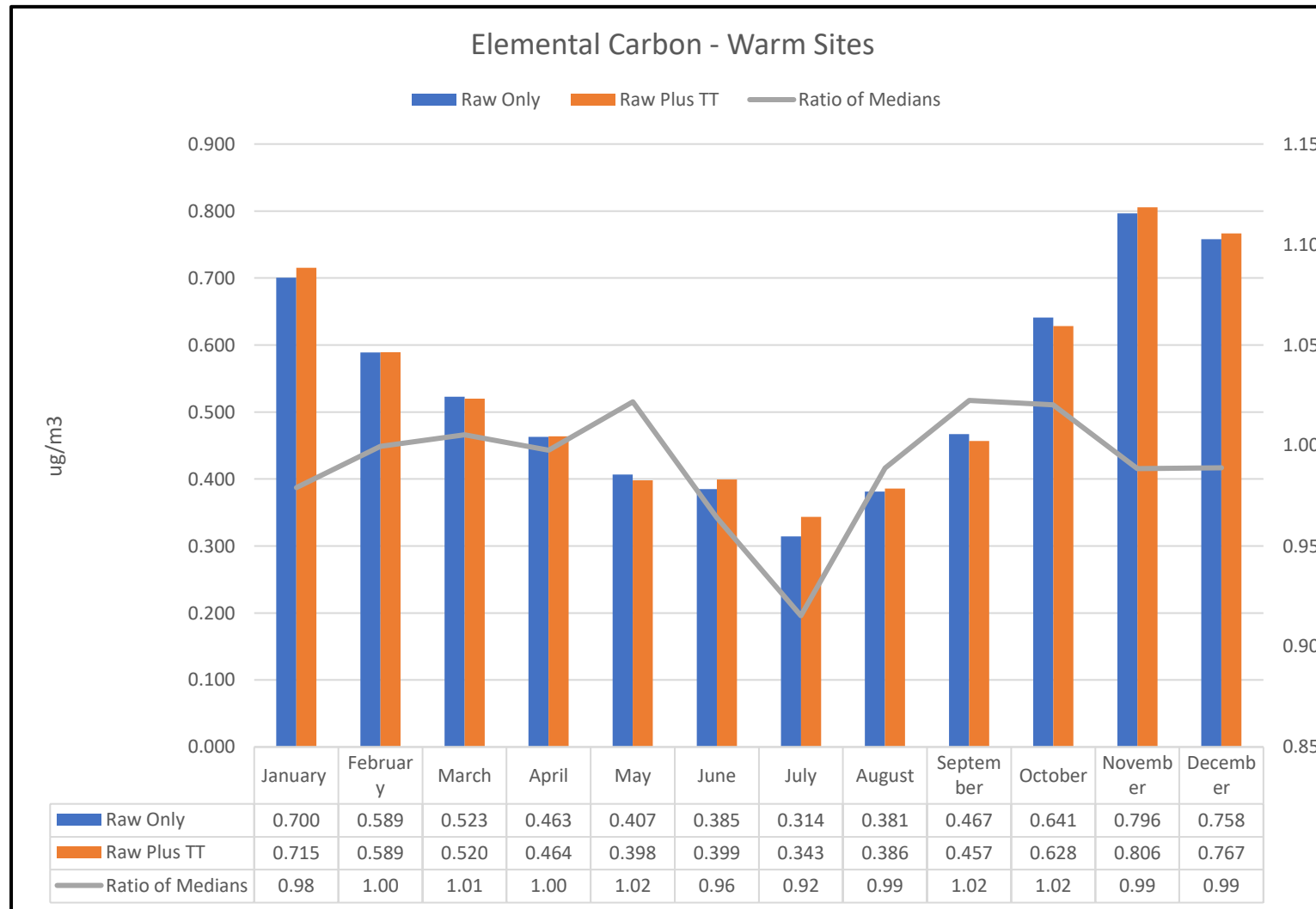
# Species-specific Analysis using TT Qualifier: Sulfate

Ratio of medians  
criteria: Sulfate  $1 \pm 0.05$



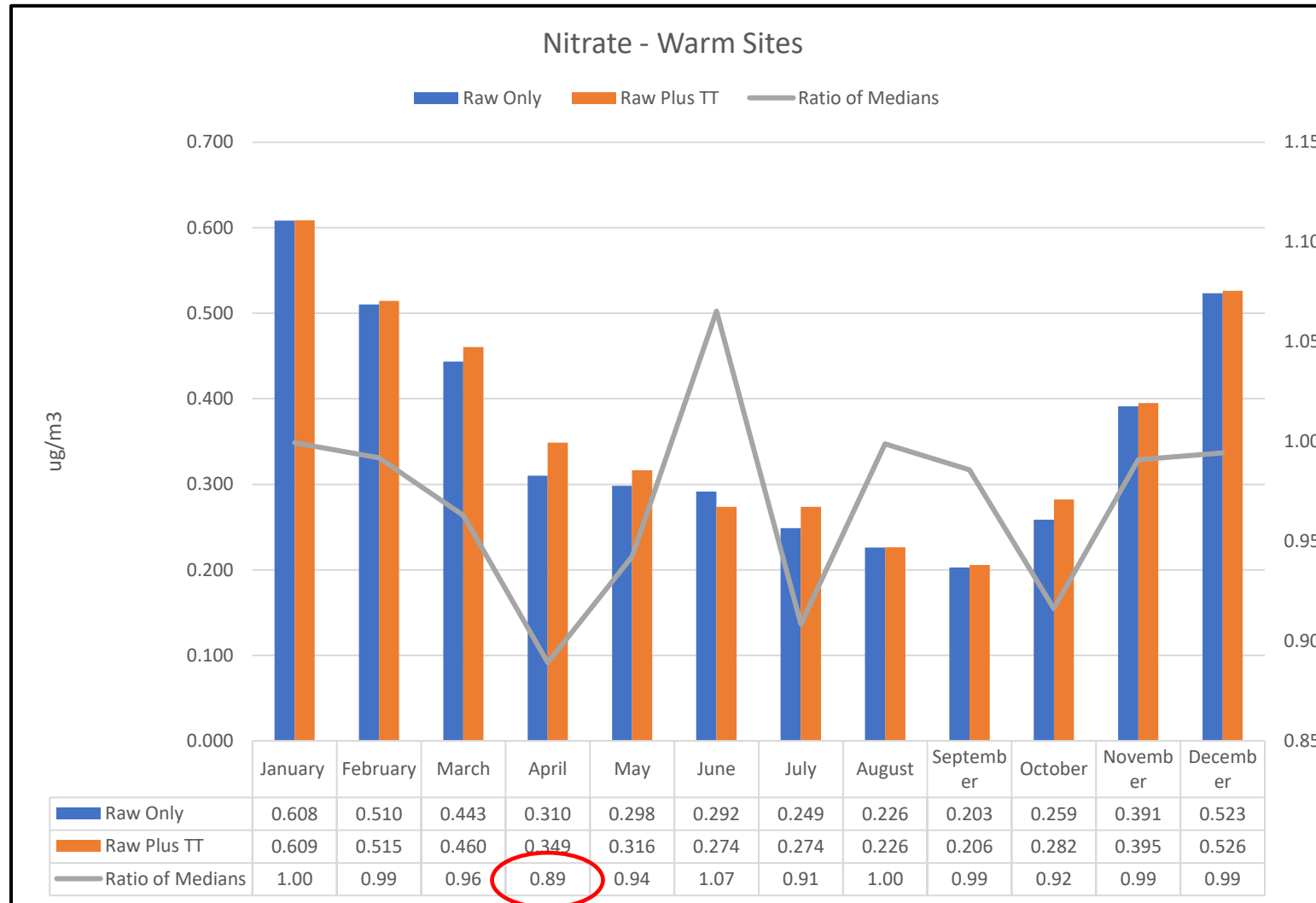
# Species-specific Analysis using TT Qualifier: EC

Ratio of medians  
criteria: EC  $1 \pm 0.15$



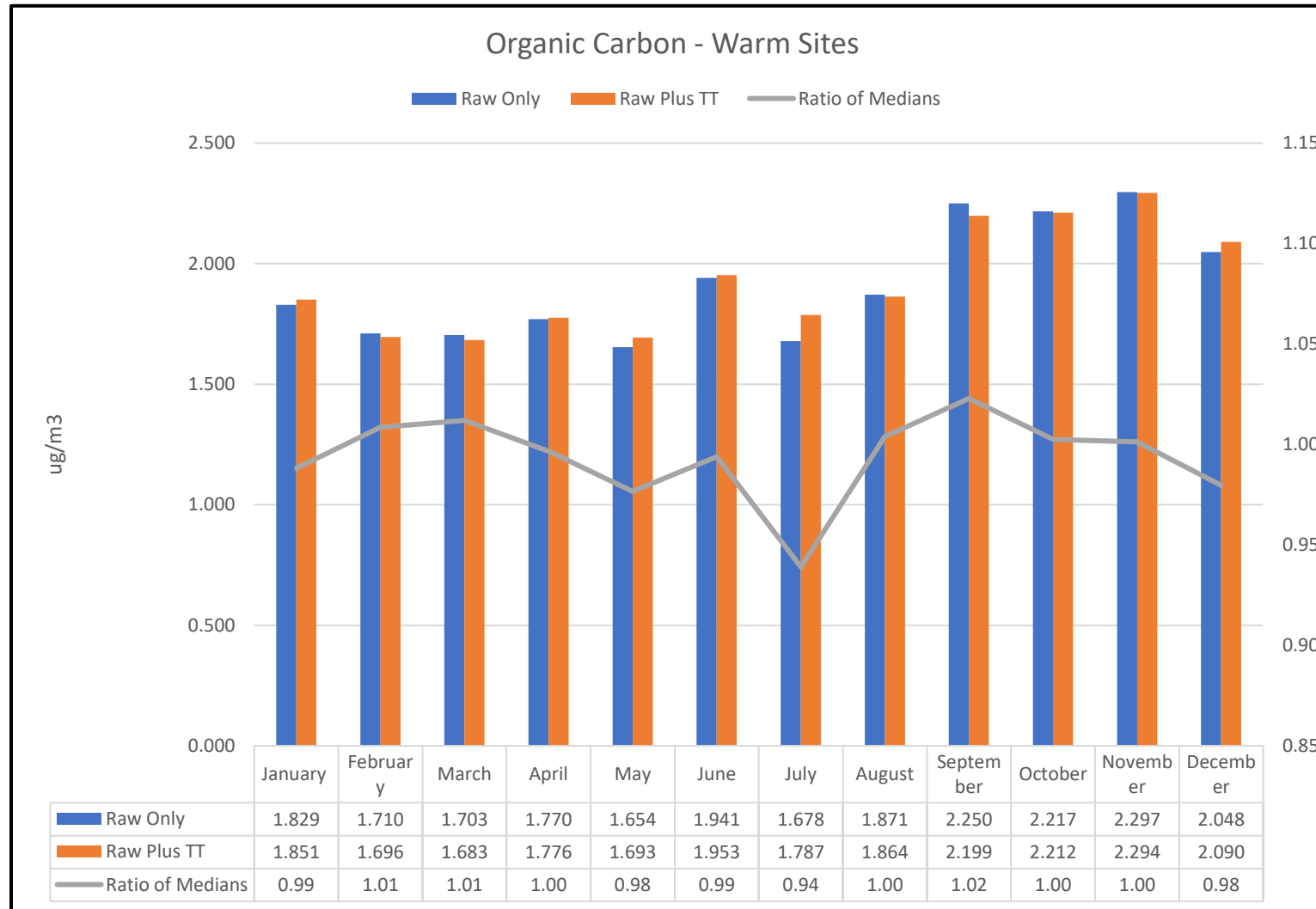
# Species-specific Analysis using TT Qualifier: Nitrate

Ratio of medians  
criteria: Nitrate  $1 \pm 0.10$



# Species-specific Analysis using TT Qualifier: OC

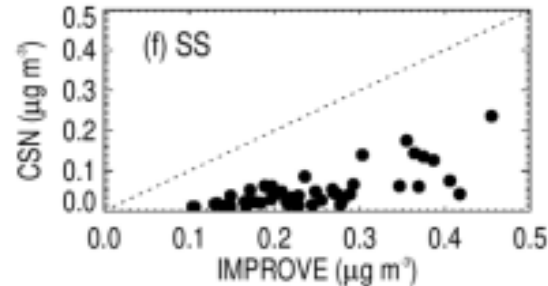
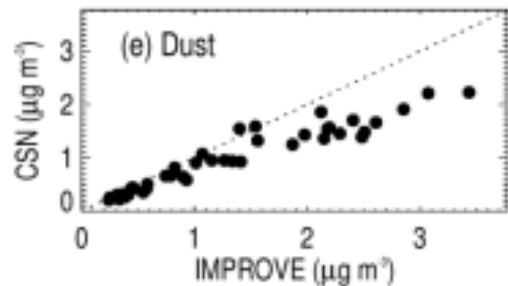
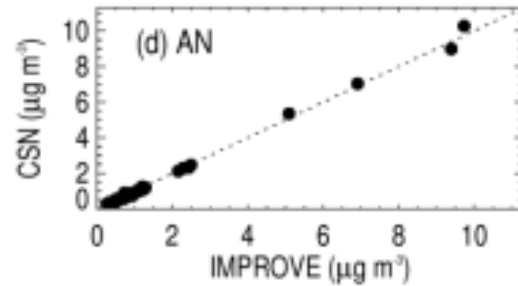
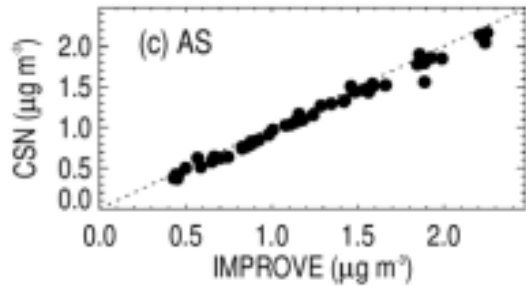
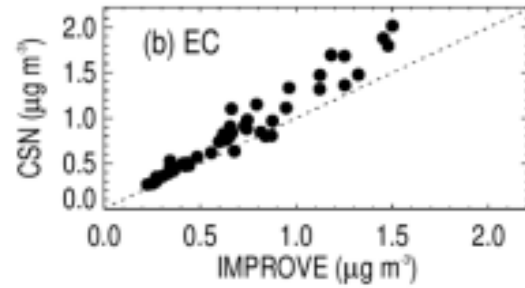
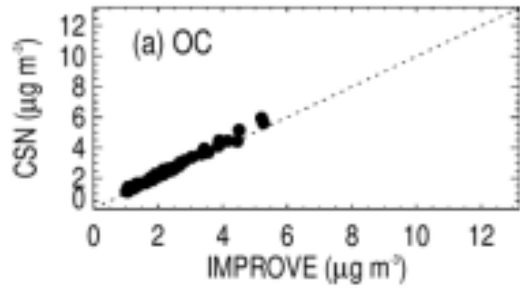
Ratio of medians  
criteria: OC  $1 \pm 0.15$



# Species-specific Analysis using TT Qualifier: Conclusions

- Organic and Elemental Carbon met the Expert Panel Criteria using ratio of medians ( $1 \pm 0.15$ ) for all months at the warm climate sites.
- Sulfate met the Expert Panel Criteria using ratio of medians ( $1 \pm 0.05$ ) for all months except October (ratio 1.06) at the warm climate sites.
- Nitrate met the Expert Panel Criteria using ratio of medians ( $1 \pm 0.10$ ) for all months except April (0.89) at the warm climate sites.
- Based on this analysis of medians, no clear adverse impact of the TT flagged data.

# CSN – IMPROVE Collocated Sites



- Six CSN – IMPROVE collocated sites: Atlanta, Birmingham, Fresno, Phoenix, Pittsburgh, and Seattle
- Monthly means, 2016 – 2019

Statistic	OC	EC	AS <sup>3</sup>	AN <sup>4</sup>	Dust	Sea salt <sup>5</sup>
Average IMPROVE (µg m <sup>-3</sup> )	2.36	0.69	1.21	1.44	1.21	0.24
Average CSN (µg m <sup>-3</sup> )	2.59	0.84	1.15	1.40	0.90	0.05
Bias <sup>1</sup> (%)	11	21	-6	-6	-20	-81
Error <sup>2</sup> (%)	11	19	6	8	21	85
r	0.99	0.97	0.99	1.00	0.96	0.71
IMP/CSN	0.91	0.82	1.06	1.03	1.34	4.75

[IMPROVE Report \(Figure 1.16 and Table 1.9\)](#)



# 2005 Shipping Study

- Conducted in South DeKalb, GA during summer when OC was high, and nitrate was low.
- Collocated samples were collected; some sample sets shipped cold, and some sample sets shipped at ambient conditions.
- Evaluation criteria were based on Expert Panel recommendations and the 4-City Study:
  - Mean ratios of  $1 \pm .10$  mass, nitrate, and ammonium;  $1 \pm .05$  sulfate; and  $1 \pm .15$  OC and EC.
  - Correlation coefficients ( $R^2$ ) of  $\geq 0.90$  for mass, nitrate, and ammonium;  $\geq 0.95$  for sulfate; and  $\geq 0.85$  for OC and EC.
  - Precision (CV) of 10% for ions and 15% for carbon

Species	N of Pairs	Regression Slope, Intercept	Criteria CV	Correlation	Criteria Correlation	Mean Concentration Ratio (cold/ambient)	Ambient CV	Cold CV
Mass (Teflon)	28	1.03, 0.66	N/A	0.98	0.90	1.07 +/- 0.14	0.05	0.06
OC (quartz)	33	1.00, -0.76	15%	0.86	0.85	0.87 +/- 0.10	0.08	0.06
EC (quartz)	31	0.91, 0.03	15%	0.99	0.85	0.94 +/- 0.12	0.09	0.09
Nitrate (Nylon)	33	1.02, 0.04	10%	0.70	0.90	1.18 +/- 0.49	0.10	0.08
Sulfate (Nylon)	33	0.98, -0.05	10%	0.99	0.95	0.98 +/- 0.05	0.02	0.03
Ammonium (Nylon)	33	0.94, -0.06	10%	0.99	0.90	0.91 +/- 0.09	0.04	0.05

# 2005 Shipping Study: Conclusions

- **No species showed consistent statistical or practical differences in average measured concentration** although other sites where volatile species like nitrate and/or OC are larger contributors to total mass may yield different results and should be investigated.
- **Important differences between cold- and ambient-shipped samples may occur during other months**, especially spring and fall when nitrate and OC are larger contributors to PM<sub>2.5</sub> mass and ambient temperatures can still be warm.
- If cold-shipping is eliminated, **sample precision may be degraded for OC and nitrate.**

# Outline

- Background on CSN's cold shipping practice
- Review current shipping procedures
- What can we learn about potential data impacts of ending cold shipping by looking at existing data?
  - TT qualifier and species-specific analysis
  - TT qualifier and Reconstructed Fine Mass (RCFM) analysis
  - Collocated CSN – IMPROVE data
- Summary and Conclusions

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