



Revisiting the Chemical Speciation Network's Shipping Practices

National Ambient Air Monitoring Conference

Melinda Beaver

New Orleans, LA

August 14, 2024

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.
- Proposing to stop cold shipments for CSN:
 - We estimate that **CSN could save \$400K/year** by moving to ambient shipments (i.e., moving to lighter and slower shipments).
 - Beginning with the January 2025 samples.

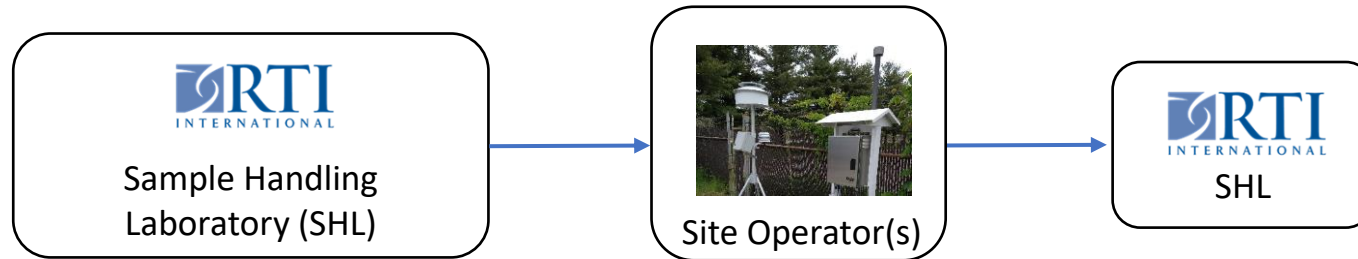
Outline

- 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

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_{2.5} 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.
 - More impacts possible during other seasons and at other sites.
- Even following cold shipment procedures, between 10 and 30% of CSN data records receive the TT qualifier each year because of shipments arriving > 4°C.
- Note, IMPROVE Network and CASTNET do NOT ship cold.

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)



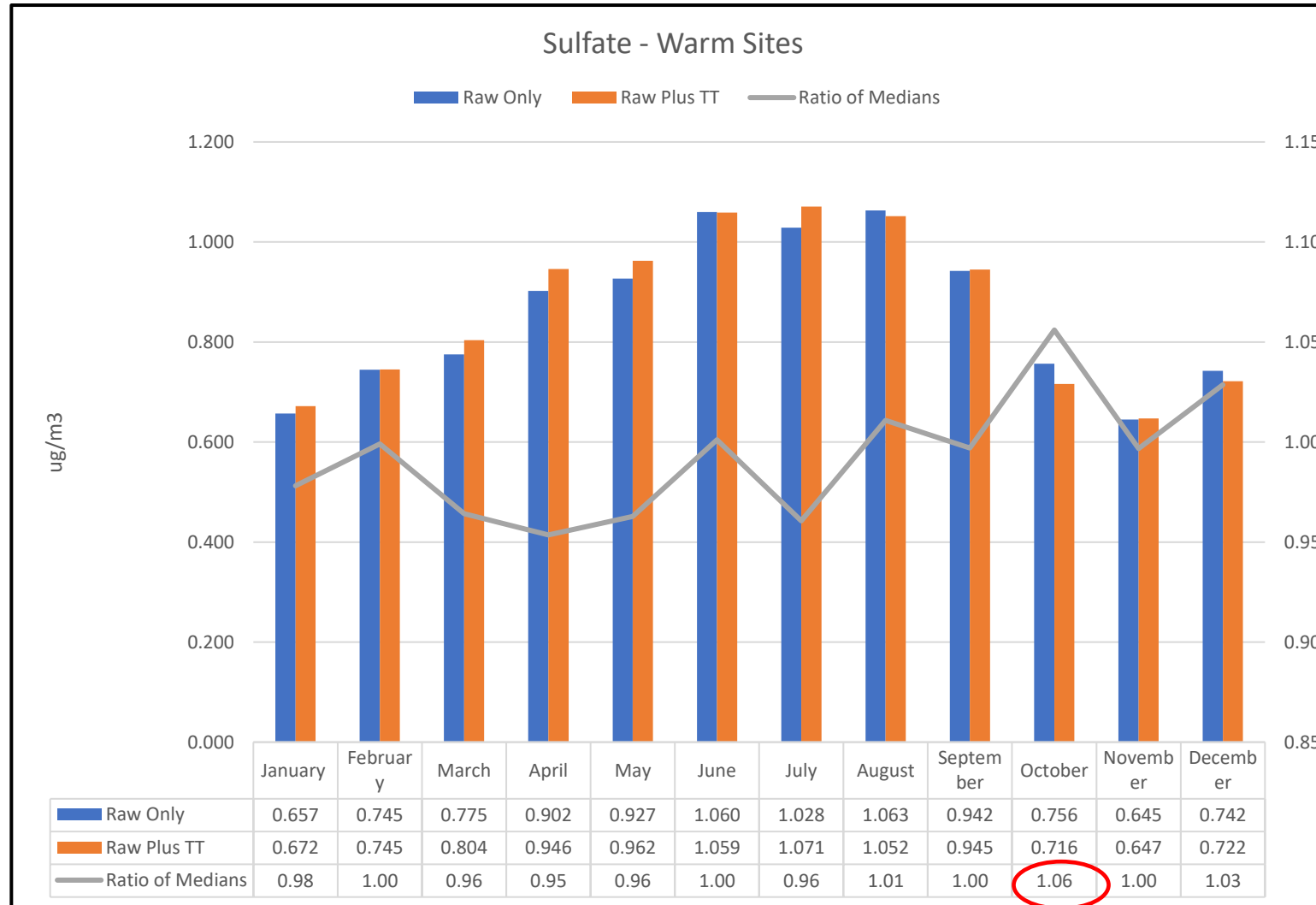
- Contract lab applies TT qualifier flag if shipments (from sites or between labs) arrive > 4°C (since 2015).

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.

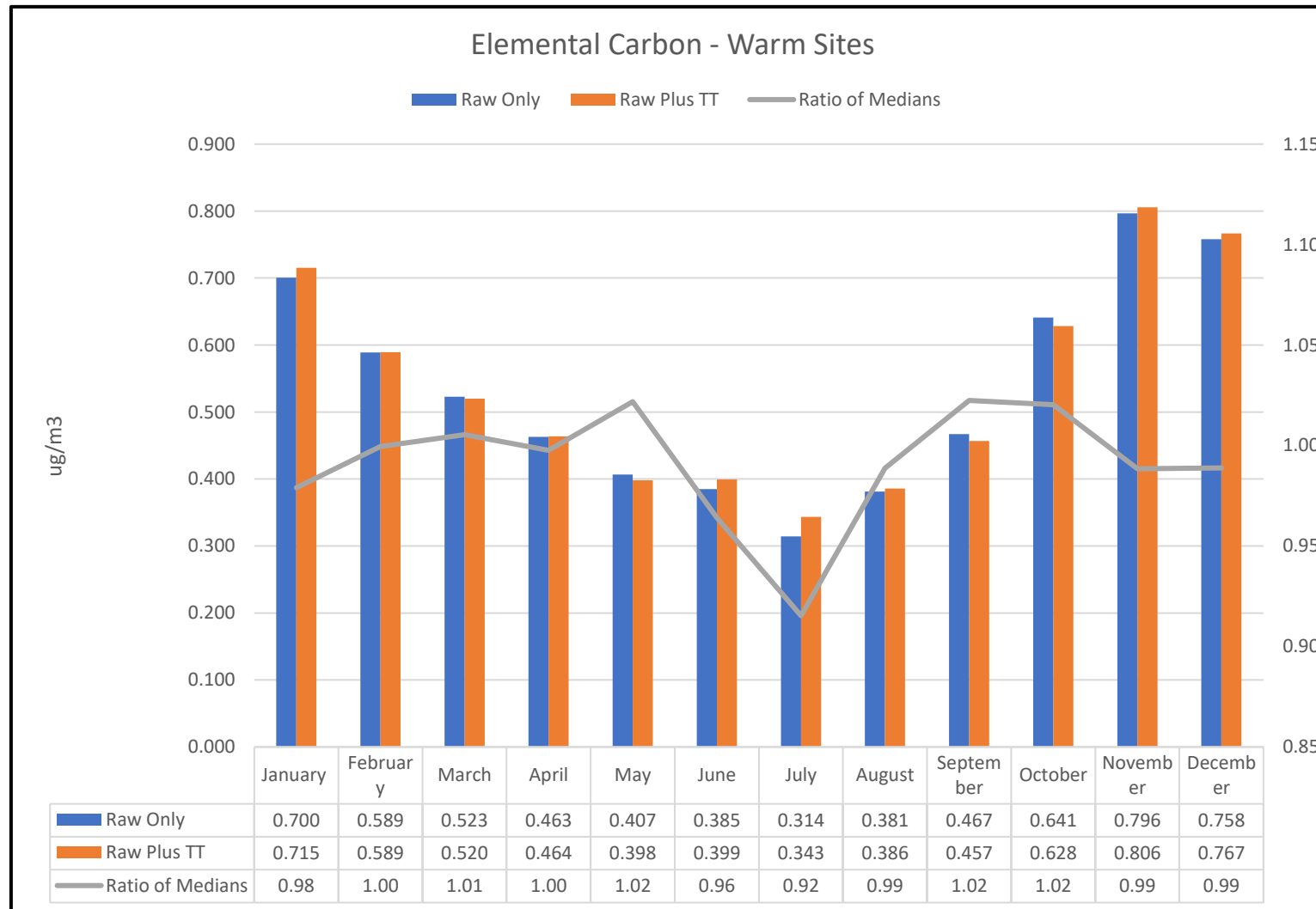
Species-specific Analysis using TT Qualifier: Sulfate

Ratio of medians
criteria: Sulfate 1 ± 0.05



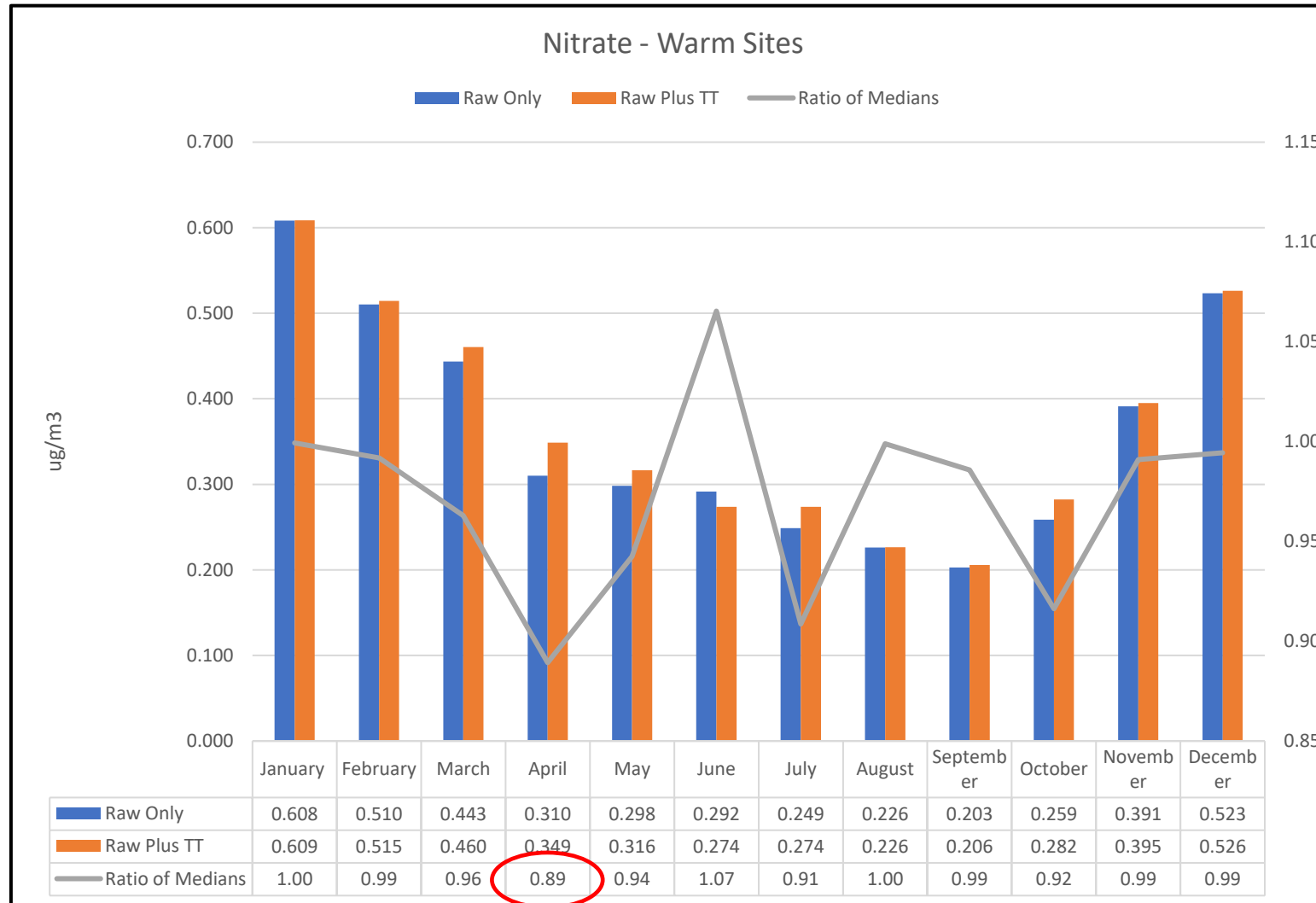
Species-specific Analysis using TT Qualifier: EC

Ratio of medians
criteria: EC 1 ± 0.15



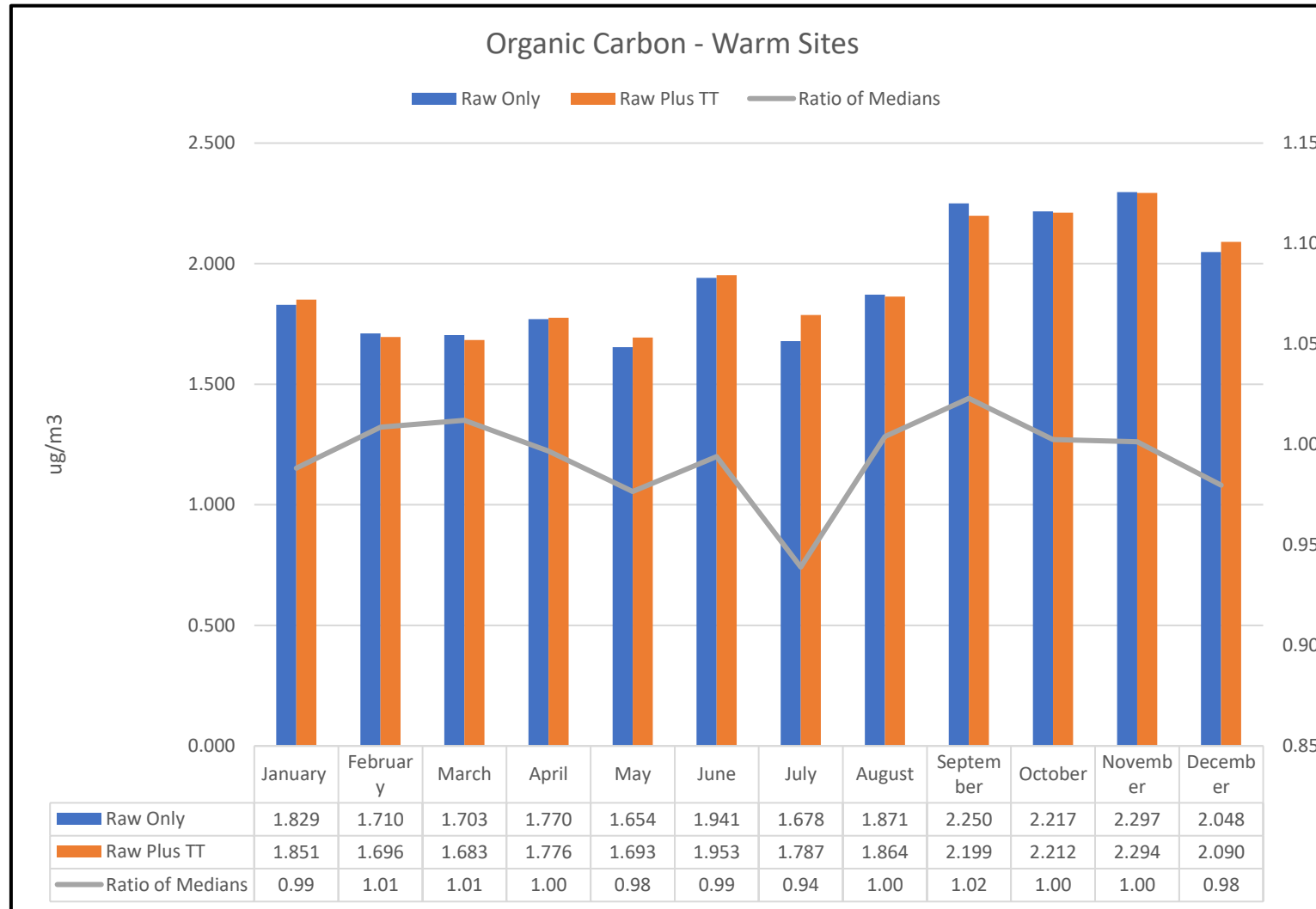
Species-specific Analysis using TT Qualifier: Nitrate

Ratio of medians
criteria: Nitrate 1 ± 0.10



Species-specific Analysis using TT Qualifier: OC

Ratio of medians
criteria: OC 1 ± 0.15

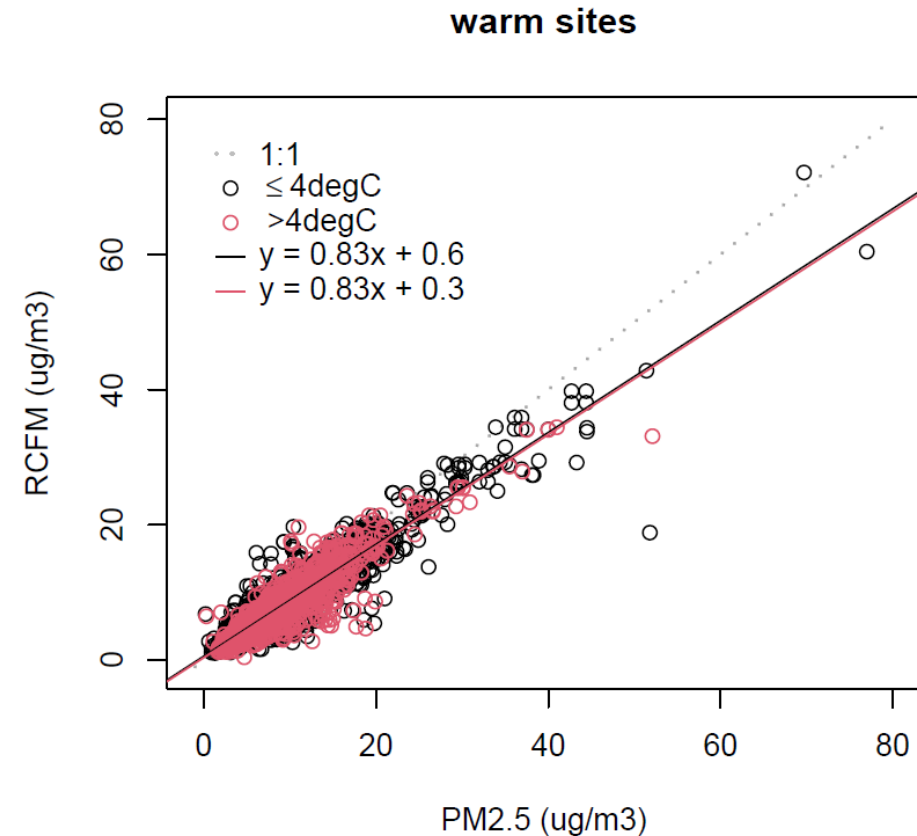


Species-specific Analysis using TT Qualifier: Conclusions

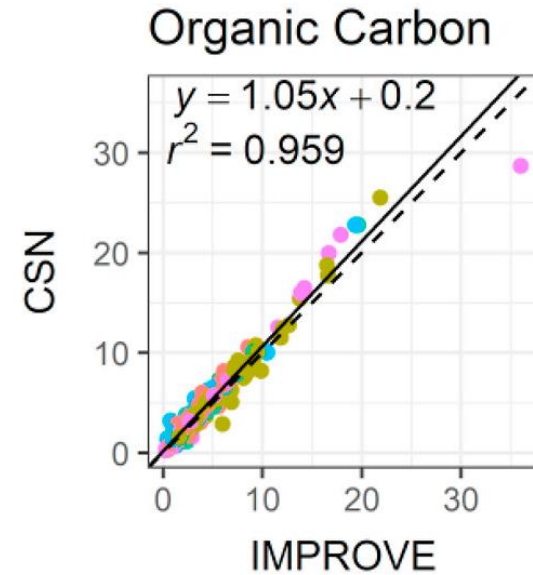
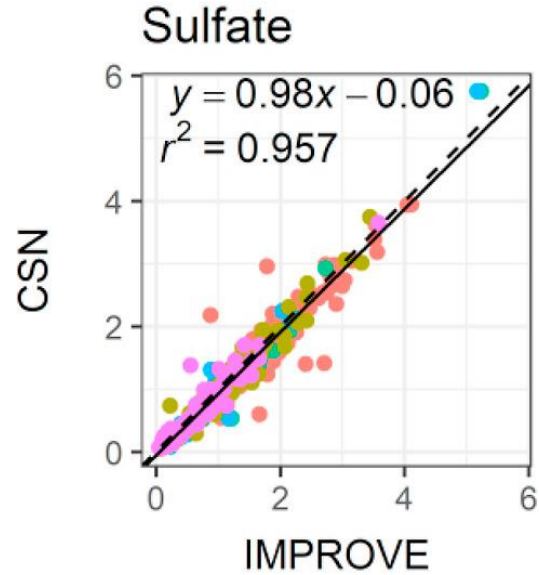
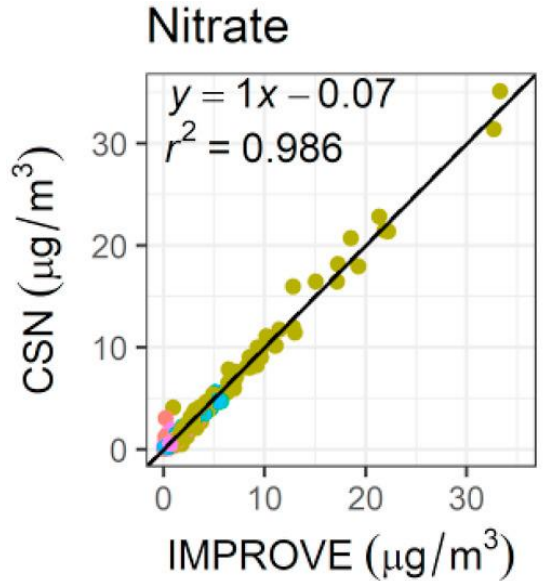
- Organic and Elemental Carbon met the Expert Panel Criteria using ratio of medians (1 ± 0.15) for all months at the warm climate sites.
- Sulfate met the Expert Panel Criteria using ratio of medians (1 ± 0.05) for all months except October (ratio 1.06) at the warm climate sites.
- Nitrate met the Expert Panel Criteria using ratio of medians (1 ± 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.

Reconstructed Mass vs PM_{2.5} FRM Mass using TT Qualifier

- Is there an impact on the Reconstructed Mass (RCFM) vs PM_{2.5} mass relationship when shipments from **warm locations** 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_{2.5} gravimetric method codes used (i.e., excluding continuous).
 - Excluded RCFM data points with multiple qualifiers.
 - ≤4°C → no qualifiers
 - >4°C → TT qualifier
 - Hawaii; Arizona; New Mexico; Texas; Louisiana; Alabama; Florida; Georgia; and Rubidoux, CA
- When looking at all CSN sites (not shown) and **warm CSN Sites**, no difference in slopes.



CSN – IMPROVE Collocated Sites



Site

- Birmingham
- Fresno
- Phoenix 1
- Phoenix 2
- Seattle

[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).

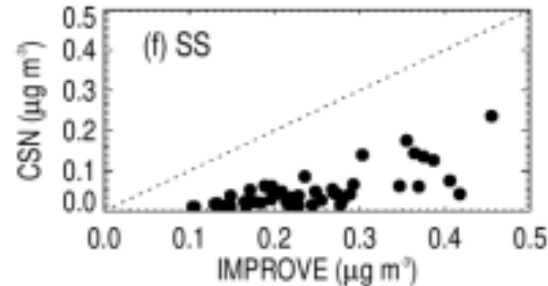
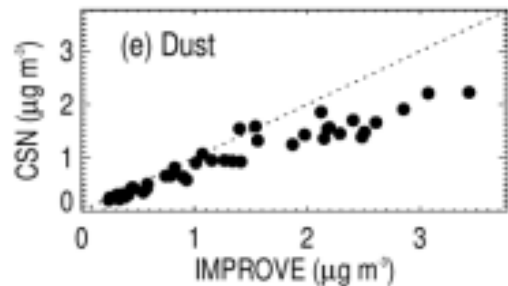
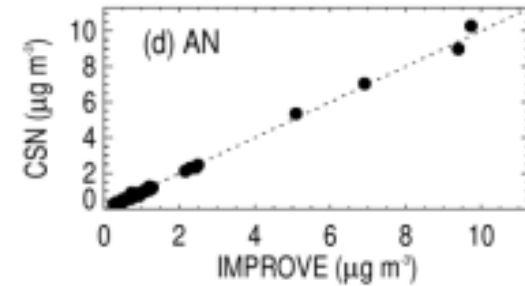
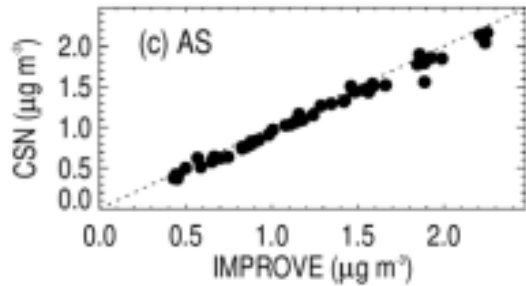
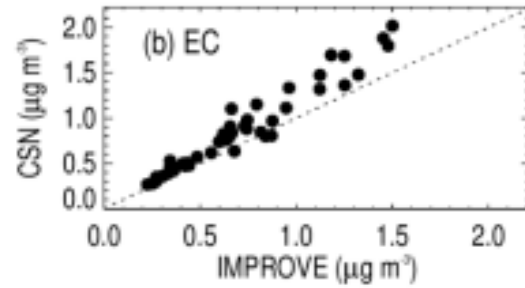
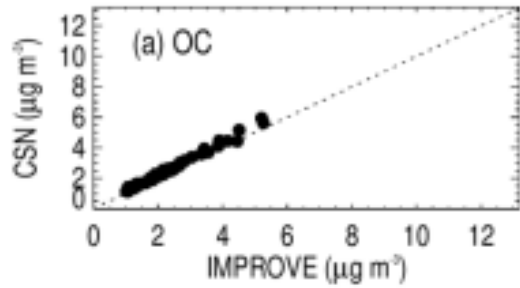
	Nitrate	Sulfate	OC
CSN-IMPROVE Collocated Site Precision	13%	7.8%	9.4%
CSN-CSN Collocated Site Precision	11%	8.5%	10%

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
 - CSN and IMPROVE collocated site precision
 - Practices in similar networks
- 2025 CSN shipping calendar will reflect any final changes.
- Interested in any feedback on or concerns with this plan.
- We are also beginning to assess additional CSN design changes that may be needed to meet the target budget.



CSN – IMPROVE Collocated Sites



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

Statistic	OC	EC	AS ³	AN ⁴	Dust	Sea salt ⁵
Average IMPROVE ($\mu\text{g m}^{-3}$)	2.36	0.69	1.21	1.44	1.21	0.24
Average CSN ($\mu\text{g m}^{-3}$)	2.59	0.84	1.15	1.40	0.90	0.05
Bias ¹ (%)	11	21	-6	-6	-20	-81
Error ² (%)	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 ≥ 0.90 for mass, nitrate, and ammonium; ≥ 0.95 for sulfate; and ≥ 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_{2.5} mass and ambient temperatures can still be warm.
- If cold-shipping is eliminated, **sample precision may be degraded for OC and nitrate.**