Ion Analysis for the IMPROVE Program

IMPROVE Steering Committee Meeting
Durango, CO

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September 6, 2007

Topics

- RTI's role in the IMPROVE Program
- RTI's performance in NAREL's 2006 Round Robin Study (IMPROVE and STN)
- Reanalyses of archived extracts
- Questions concerning XRF sulfur/IC sulfate ratio

RTI's Analytical Support for IMPROVE 1985-Present

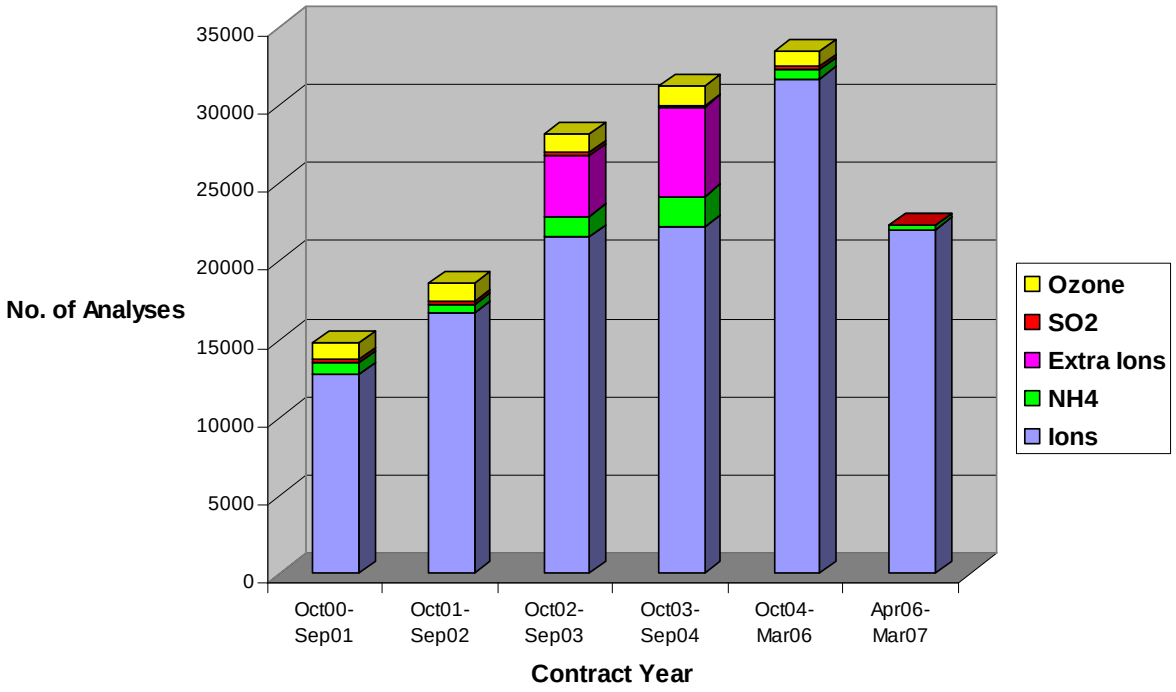
- 1985 – 1990: Ions and SO_2
- 1990 – 1995: SO_2
- 1995 – Present w/option yrs thru 2011: Ions, SO_2, and Passive Ozone (3 contracts)

Ion and Passive Ozone Analyses of IMPROVE Filters

RTI provides the following services:

1. Analysis and reporting of anion loadings (Cl^-, NO_2^-, NO_3^-, and SO_4^{2-}) on nylon filters from the IMPROVE network (~22,000 filters/yr) and of cation loadings (NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) for special studies.
2. Preparation of impregnated filters for SO_2 sampling, and analysis and reporting of sulfate mass (~250 filters/yr).
3. Loading and shipping of passive samplers for ozone, analysis of exposed collection pads, and reporting of nitrate ion loadings for calculation of average weekly ozone concentrations (~1200 samples/ozone season).

IMPROVE Analyses Performed by RTI



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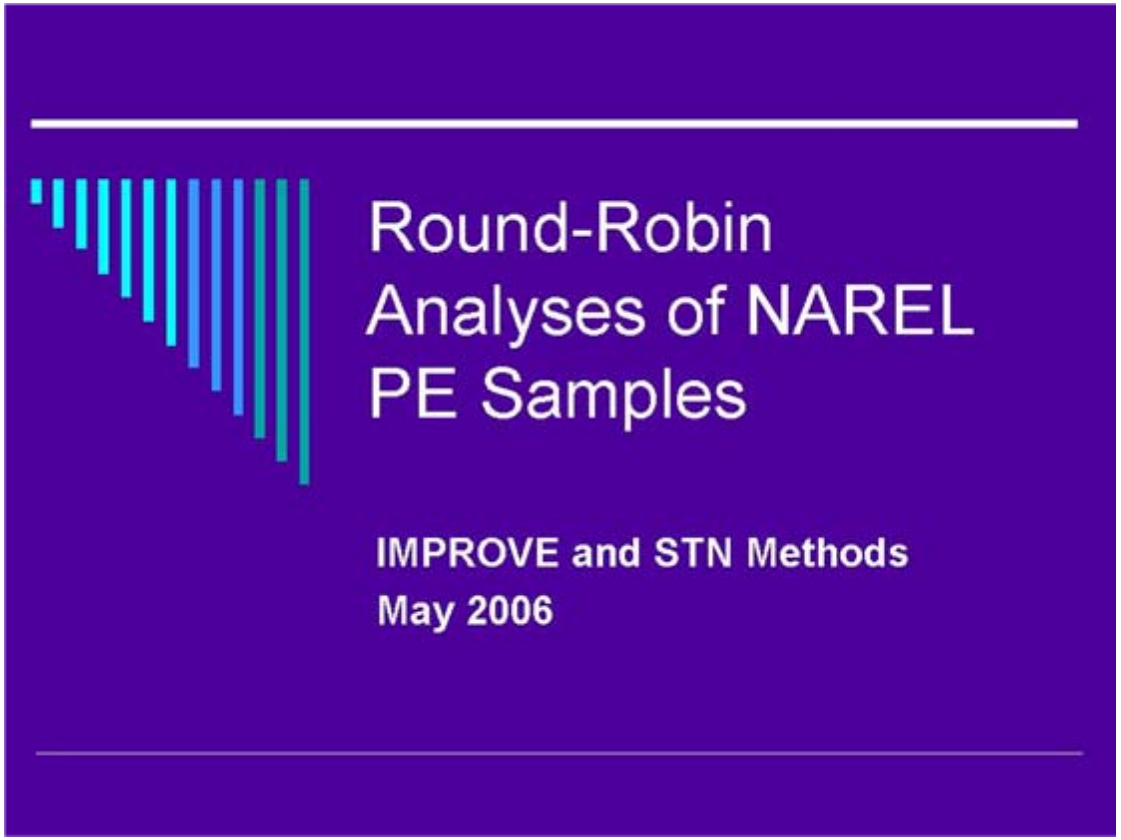
Comparison of IMPROVE and STN Filter Extraction Procedures

Variable	IMPROVE	STN (CSN)
Extractant	DI H_2O	DI H_2O or eluent *
Extract volume **	20 mL	25 mL
Sonication time	30 min	60 min
Mechanical shaking	None	Overnight in a coldroom
Additional	Let stand at RT overnight and refrigerate a 2nd day prior to analysis	May be analyzed immediately after shaking overnight

* Eluent is used for filters to be analyzed for nitrate only.

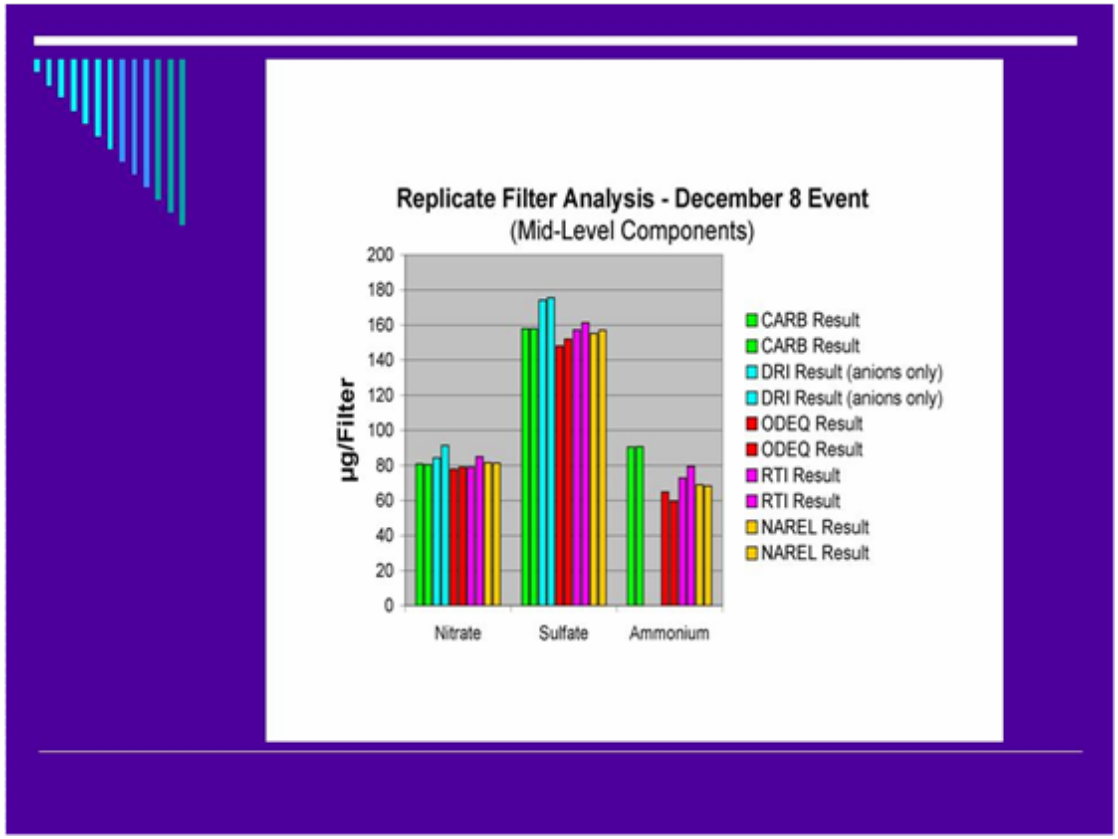
** Based upon filter size (37 mm for IMPROVE; 47 mm for STN)

Round-Robin Analyses of NAREL PE Samples



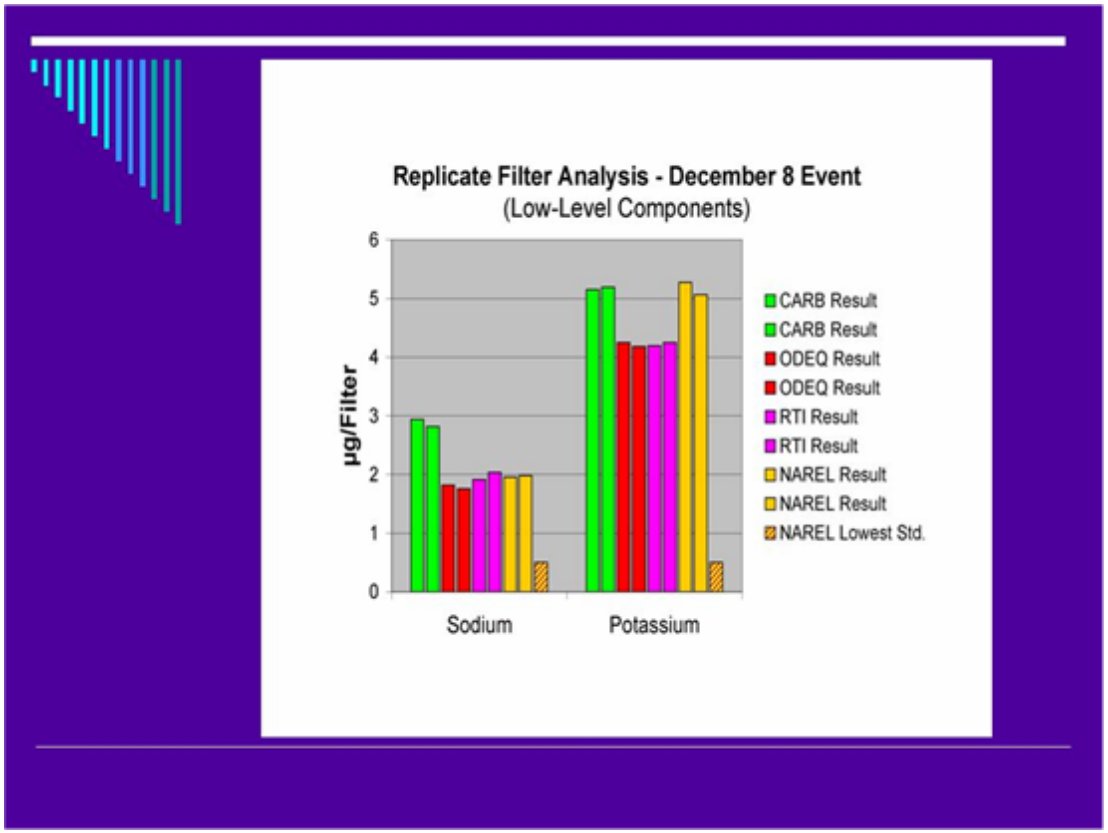
- Conducted as part of EPA NAREL's QA oversight for STN and IMPROVE PM2.5 monitoring networks
- Replicate filter samples collected using co-located Met One speciation samplers
- RTI IC lab received 6 nylon filters for IMPROVE analyses and 6 nylon filters for STN analyses

Round-Robin Analyses of NAREL PE Samples cont'd



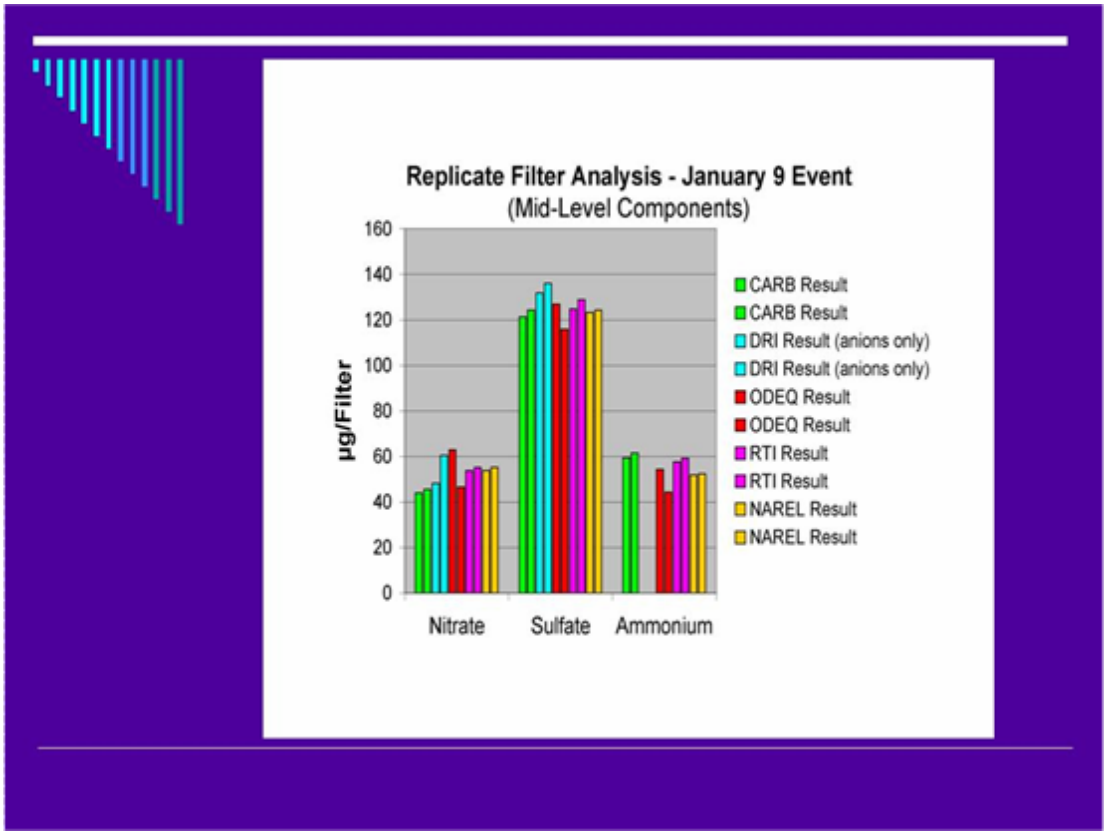
- STN procedures
- Collection times significantly >24 hr
- NO_3, SO_4, and NH_4 most abundant ions captured from Montgomery air
- Measured NO_3 loadings ~80-90 µg/filter
- Measured SO_4 loadings ~150-170 µg/filter
- Measured NH_4 loadings ~60-90 µg/filter
- All RTI values within ranges
- Reasonable precision

Round-Robin Analyses of NAREL PE Samples cont'd



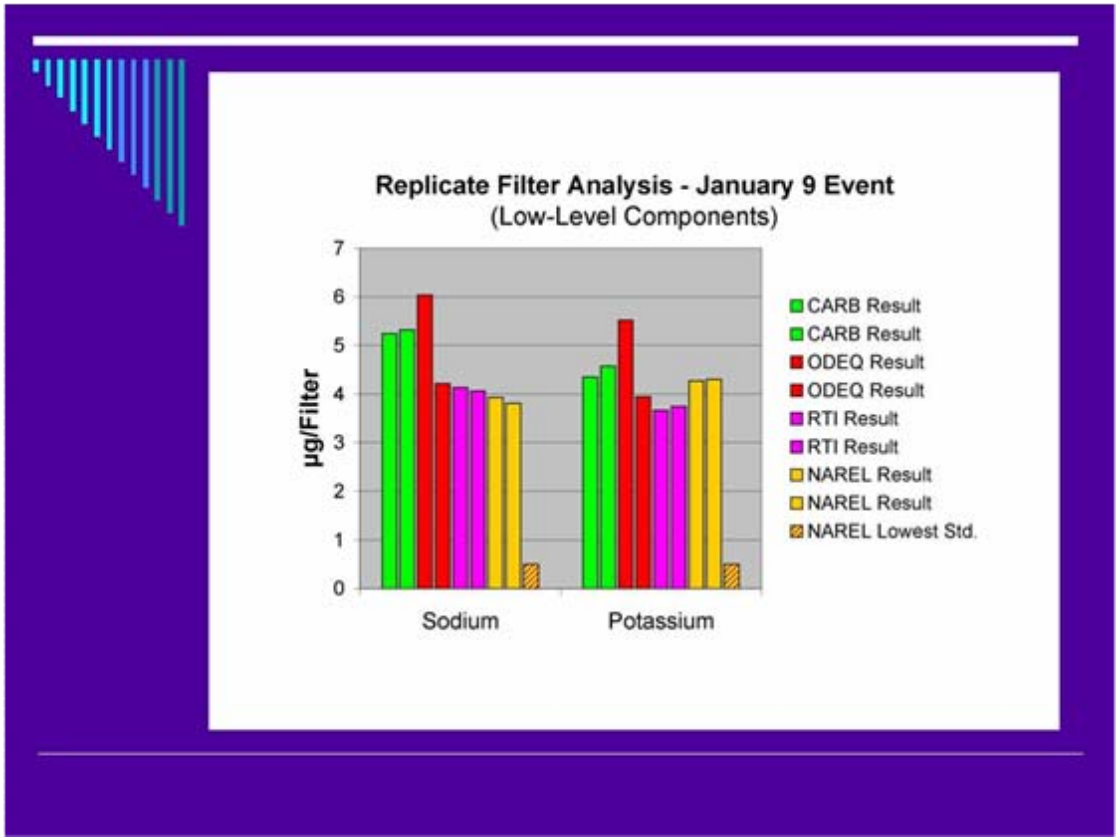
- STN procedures
- Na and K present at relatively low levels in Montgomery air
- Measured Na loadings ~2-3 ug/filter
- Measured K loadings ~4-5 ug/filter
- All RTI values within ranges
- Good precision

Round-Robin Analyses of NAREL PE Samples cont'd



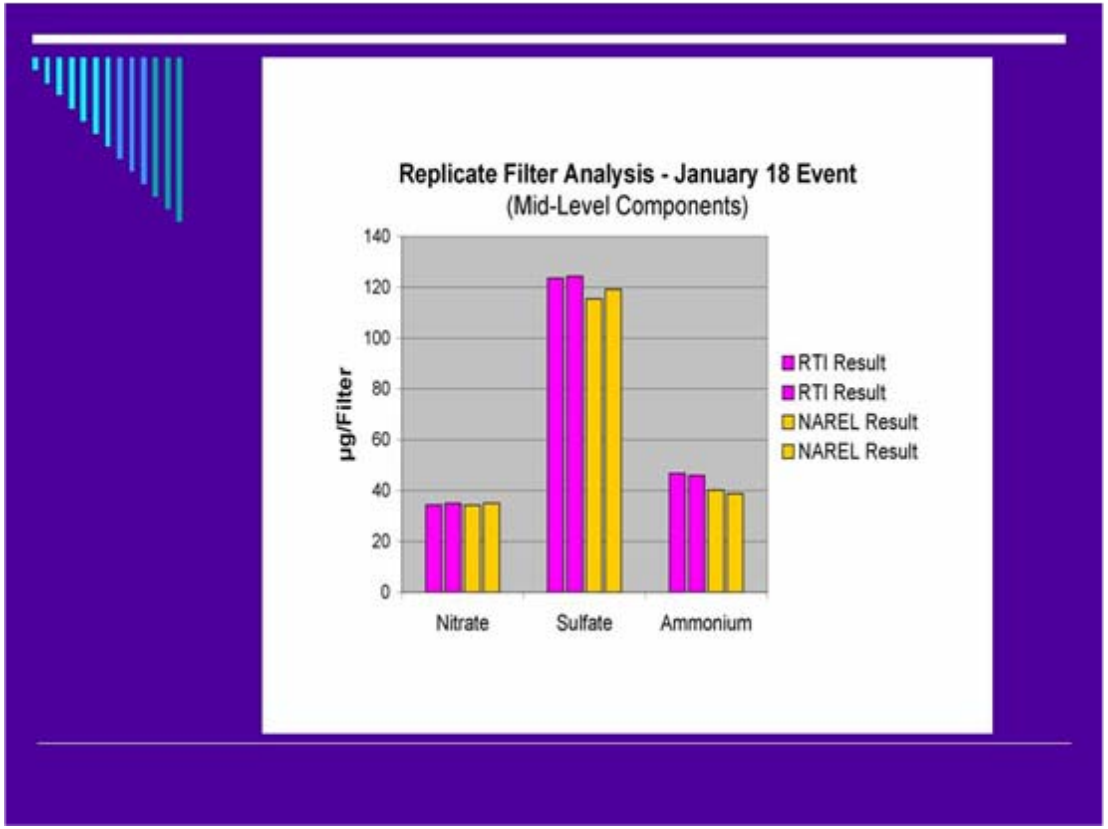
- STN procedures
- NO_3, SO_4, and NH_4 most abundant ions captured from Montgomery air
- Slightly lower loadings than for December 8
- Measured NO_3 loadings ~40-60 µg/filter
- Measured SO_4 loadings ~120-140 µg/filter
- Measured NH_4 loadings ~40-60 µg/filter
- All RTI values within ranges
- Reasonable precision

Round-Robin Analyses of NAREL PE Samples cont'd



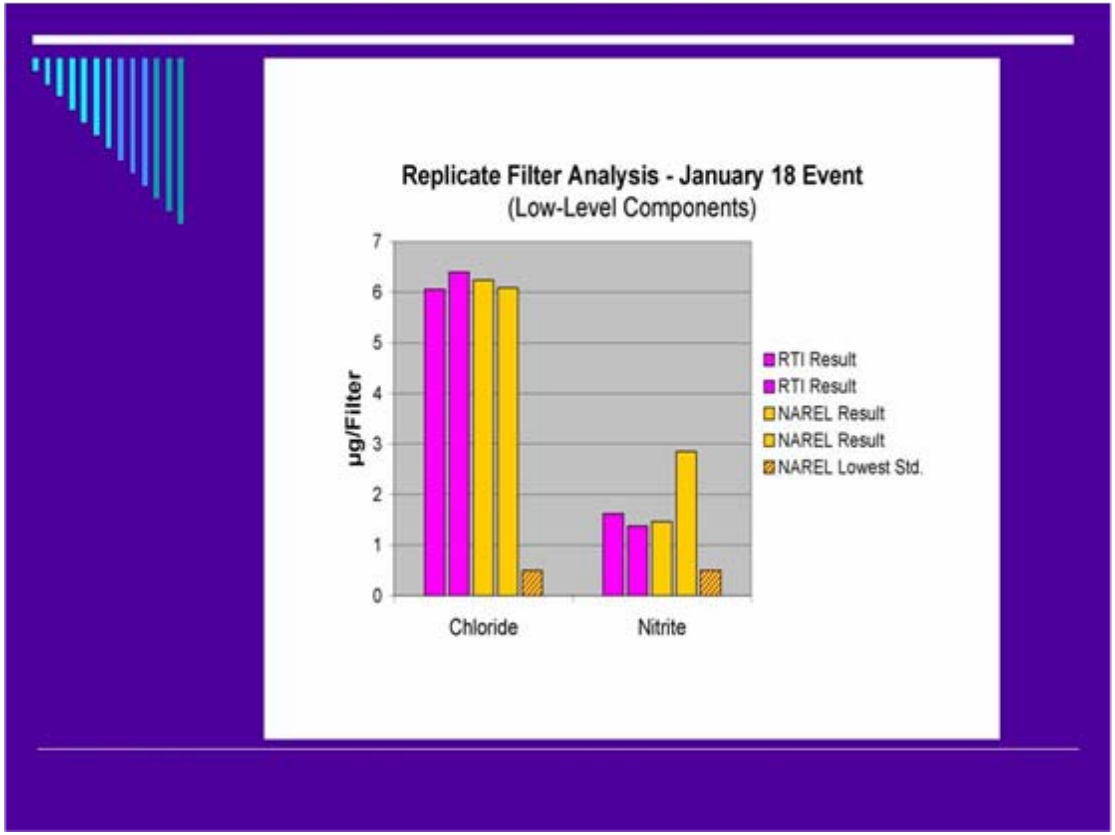
- STN procedures
- Na and K present at relatively low levels in Montgomery air
- Measured Na loadings ~4-6 µg/filter
- Measured K loadings ~4-5.5 µg/filter
- RTI Na values within range; K slightly lower
- Good precision

Round-Robin Analyses of NAREL PE Samples cont'd



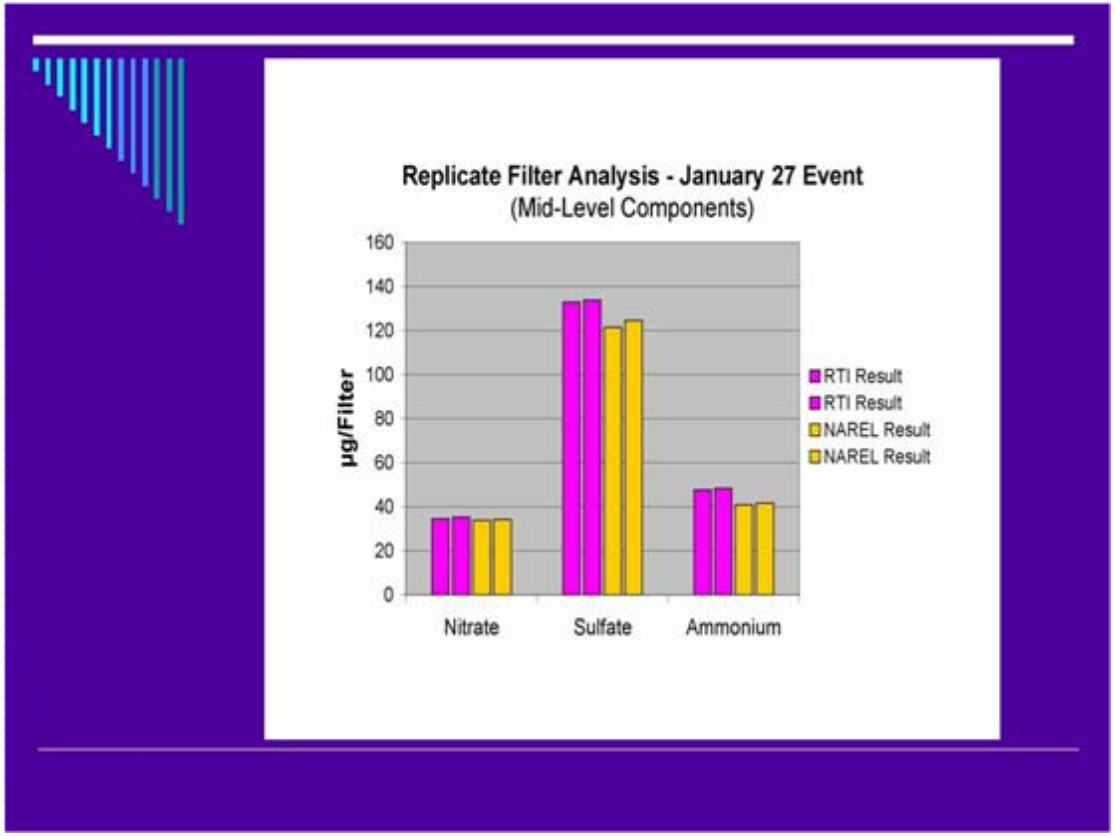
- IMPROVE procedures
- NO3, SO4, and NH4 most abundant ions captured from Montgomery air
- Measured NO3 loadings ~35 µg/filter
- Measured SO4 loadings ~115-125 µg/filter
- Measured NH4 loadings ~40-50 µg/filter
- All RTI values in reasonably good agreement with NAREL's values
- Good precision

Round-Robin Analyses of NAREL PE Samples cont'd



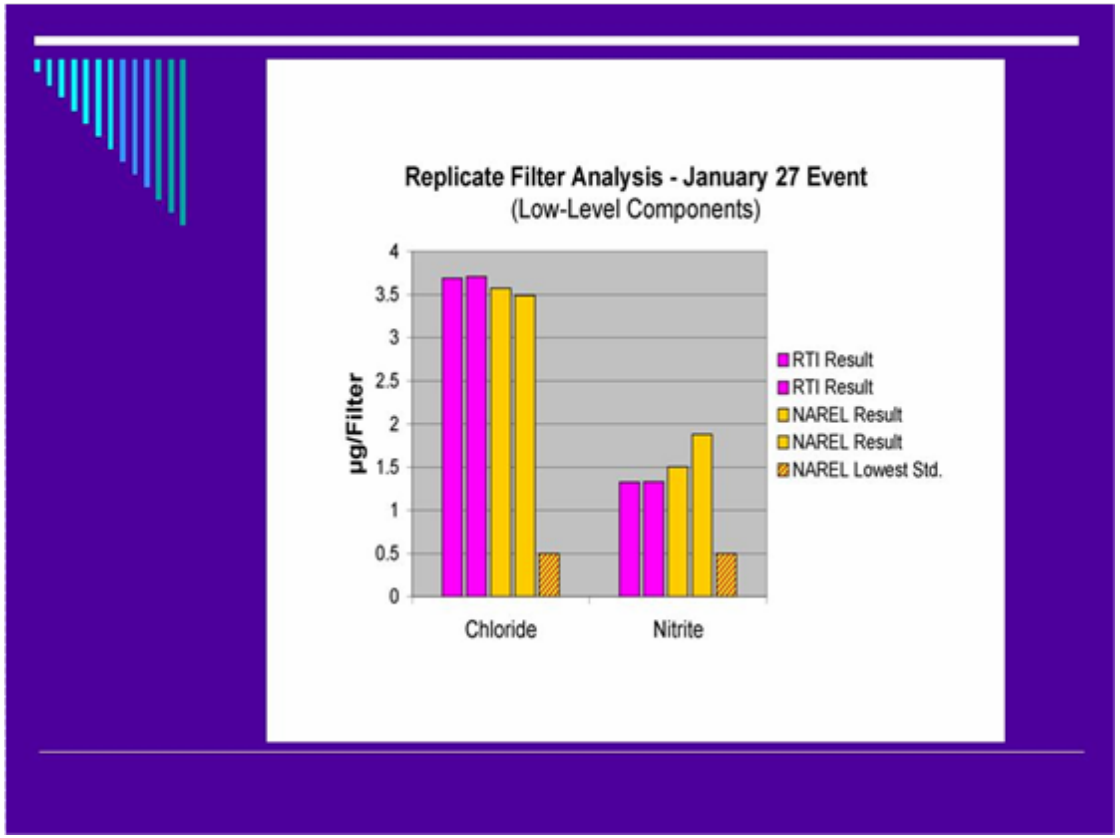
- IMPROVE procedures
- Cl and NO_2 present at relatively low levels in Montgomery air (Na and K not reported for IMPROVE)
- Measured Cl loadings ~6 µg/filter
- Measured NO_2 loadings ~1.5-3 µg/filter
- RTI values agree with NAREL's
- Worse precision for nitrite (may be due to contamination)

Round-Robin Analyses of NAREL PE Samples cont'd



- IMPROVE procedures
- NO_3, SO_4, and NH_4 most abundant ions captured from Montgomery air
- Measured NO_3 loadings ~35 µg/filter
- Measured SO_4 loadings ~120-130 µg/filter
- Measured NH_4 loadings ~40-50 µg/filter
- All RTI values in reasonably good agreement with NAREL's values
- Good precision

Round-Robin Analyses of NAREL PE Samples cont'd



- IMPROVE procedures
- Cl and NO_2 present at relatively low levels in Montgomery air (Na and K not reported for IMPROVE)
- Measured Cl loadings ~3.5 µg/filter
- Measured NO_2 loadings ~1.5-2 µg/filter
- RTI values agree with NAREL's
- Worse precision for nitrite (may be due to contamination)

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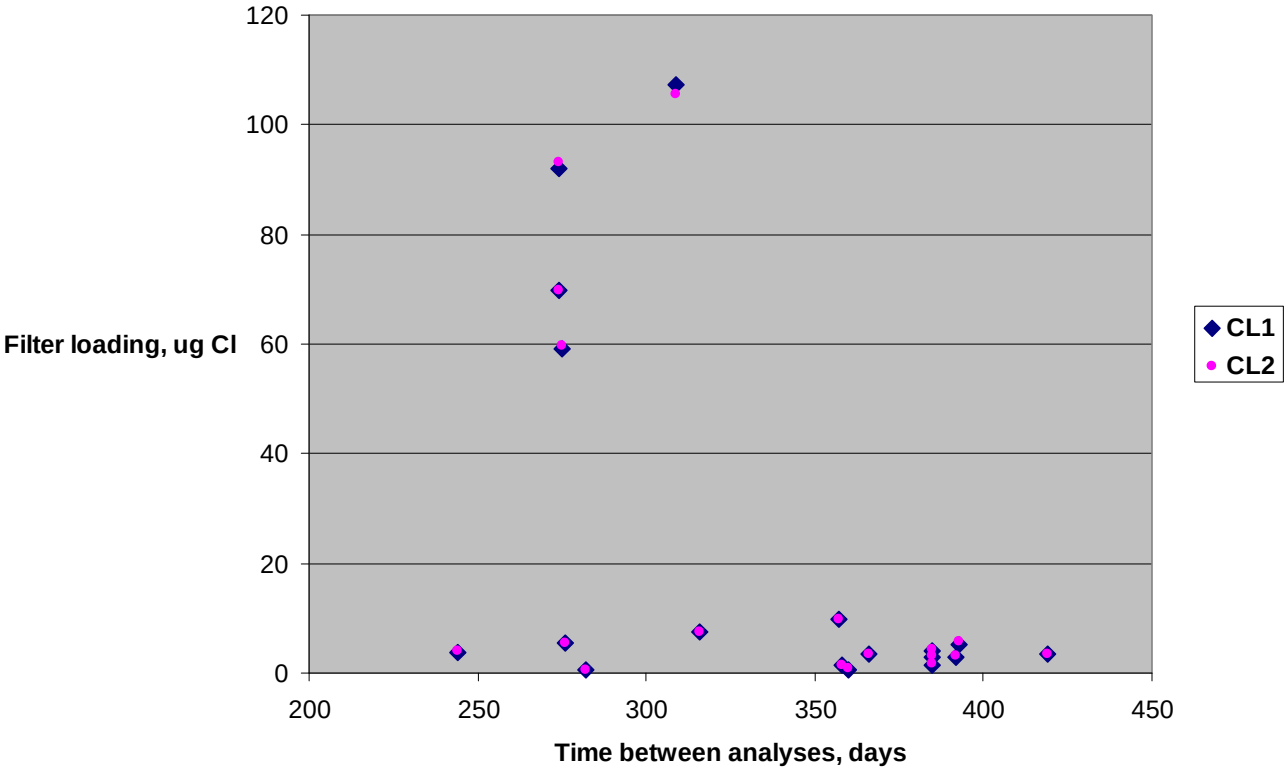
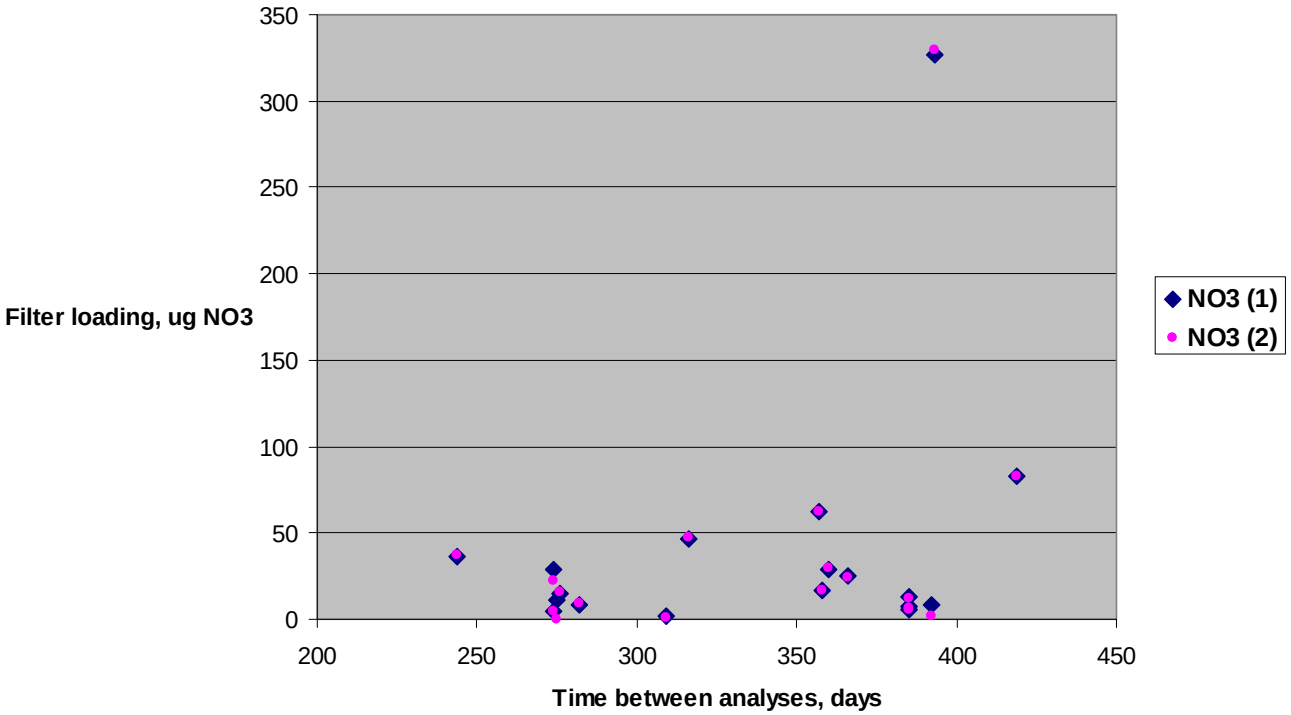
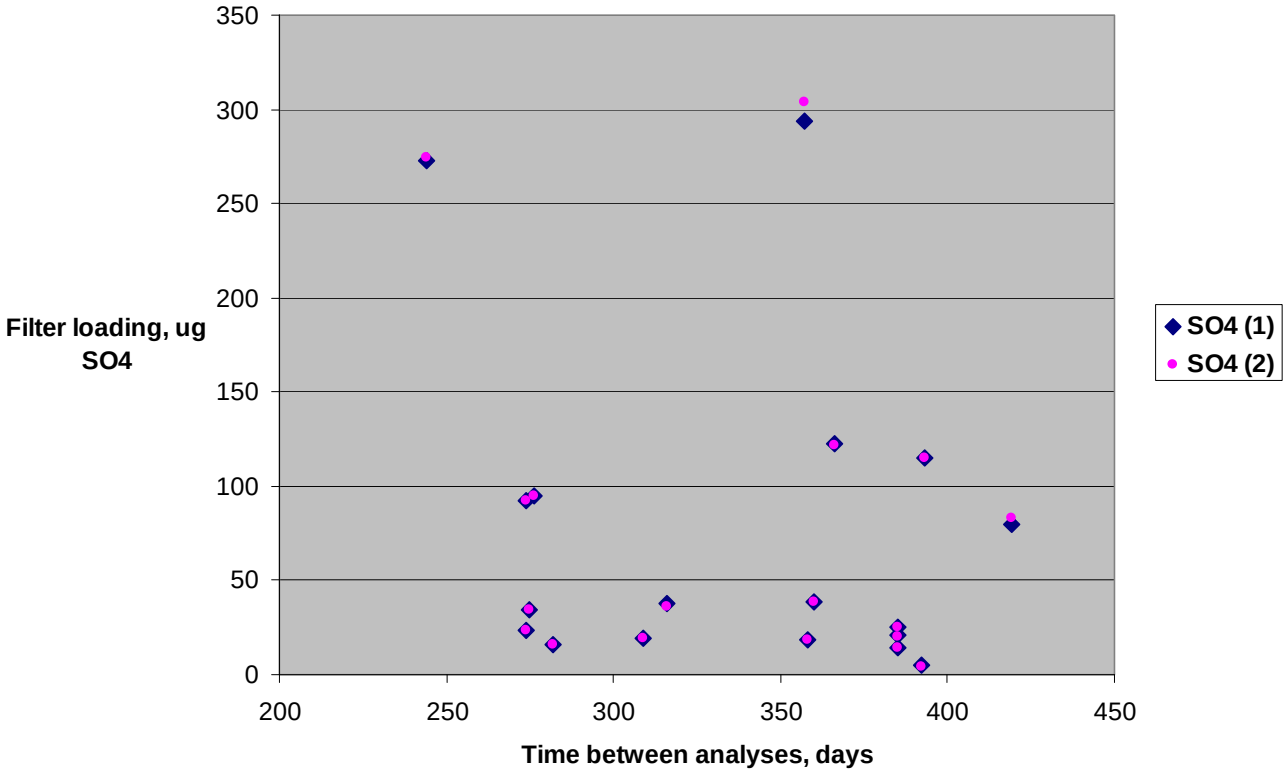
IMPROVE Chloride Reanalyses



IMPROVE Nitrate Reanalyses



IMPROVE Sulfate Reanalyses



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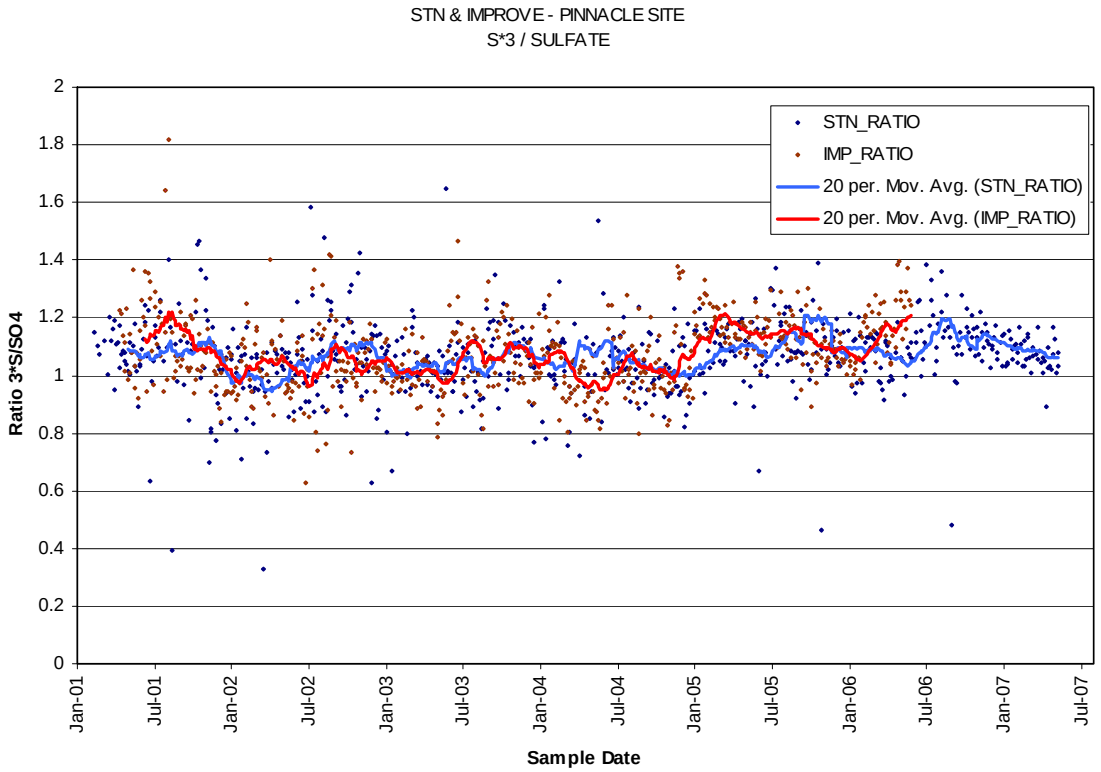
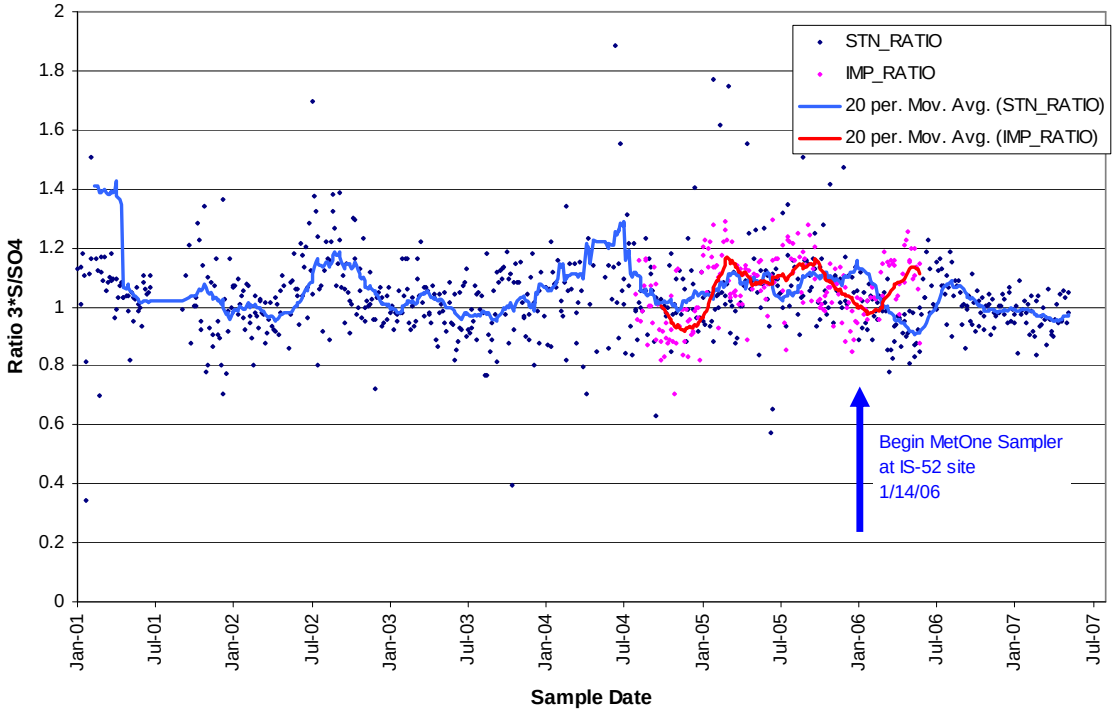
Questions Concerning the 3*S/SO_4 Ratio

- Recommendation at the 2006 Steering Committee meeting to identify IC as the preferred sulfate measurement and to temporarily withdraw XRF sulfur from the public IMPROVE data base.
- UC-Davis has found that since the change was made to the new vacuum Cu XRF system, the IMPROVE 3*S/SO_4has been running consistently higher than expected.
- A claim was made in 2007 that at one IMPROVE site 15% of sulfur is in the form of MSA and that therefore the SO_4 results by IC would be 15% lower than the sulfur measurements. The data from this site do not show this difference.
- Observation from NY State Dept of Environmental Conservation: The elemental sulfur 2005-2007 data for Pinnacle (ADPI) appears to show a small systematic higher bias compared to the IC SO_4. It is not observed in previous years at the same site. Also it is not observed in the Bronx data (STN Site IS52).

STN & IMPROVE – Pinnacle (ADPI) Site S*3/Sulfate



STN & IMPROVE – IS52 Site S*3/Sulfate



Acknowledgments

Thanks to

- UC-Davis for working closely with RTI to help ensure that the ion data reported are of the highest quality.
- NAREL for providing QA support and helpful suggestions.
- The RTI IC lab (David Hardison, Buddy Goodnight, Jennifer Garbutt, Dorie Pickett, and Christine Van Hise) for their hard work and attention to data quality.