

Semicontinuous PM Composition Measurements at the St. Louis – Midwest Supersite

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St. Louis – Midwest Supersite

- Four year campaign, core monitoring site in East St. Louis, IL
 - Two years of intensive measurements (5/2001 – 5/2003)
 - Two years of measurements with a subset of the initial monitoring platform (6/2003 – 3/2005)
- Data collection and analysis to support:
 - Development and evaluation of monitoring methods
 - Exposure and health effects studies
 - Source apportionment and SIP planning



*St. Louis - Midwest Supersite
East St. Louis (IL)*

“Year 4” Measurements (ending March 2005)

- Illinois EPA
 - Hourly criteria gases (CO, NO/NO_x, O₃, SO₂)
 - Hourly PM_{2.5} mass (Met One BAM)
 - Filter PM_{2.5} mass, PM₁₀ mass, Pb
- Washington University and collaborators
 - PM_{2.5} mass (Thermo 5030 SHARP – preproduction / beta testing]
 - 20-minute sulfate (Thermo 5030SPA preproduction) - hourly
 - 10-minute nitrate (R&P 8400N) - hourly
 - 15-minute ions (Particle-into-Liquid Sampler, PILS) - hourly
 - Alternate hour OC/EC (Sunset Labs Field OC/EC analyzer)
 - 5-minute black carbon & UV-absorbing carbon (Magee Aethalometer)
 - 1-second aerosol first moment (TSI Electrical Aerosol Detector) – 5 min
 - Filter speciation and denuder gases (1-in-6 day)
 - 5-minute meteorology

Today's Presentation in Context

The plan was to present brief measurement updates on sulfate, nitrate, OC/EC, and Aethalometer BC. However...

- Monday
 - Thermo 5020SPA sulfate (George Allen)
 - Magee Scientific Aethalometer (George Allen)
 - Sunset Labs Field OC/EC Analyzer (Bob Cary)
- Tuesday
 - Carbon in NYC (Jim Schwab – next presentation)
- Wednesday
 - Thermo 5030 SHARP mass monitor (Jay Turner – 3:30 PM session)
 - Saint Louis air quality characterization (Jay Turner – 10:15 AM session)

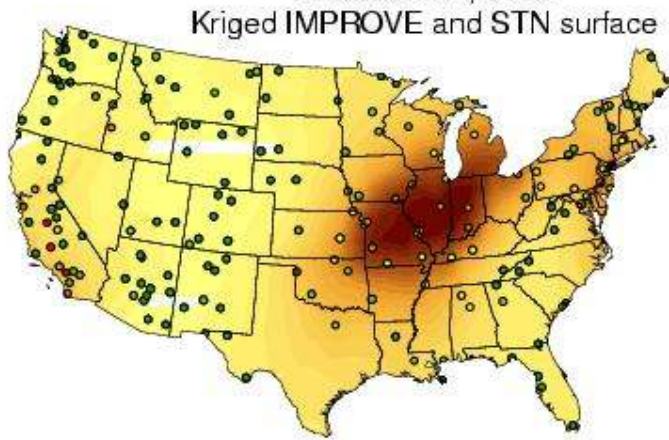
Let's talk about nitrate (C.R. Reid, M.S. Thesis, 2005)...

General Observations – Upper Midwest Perspective

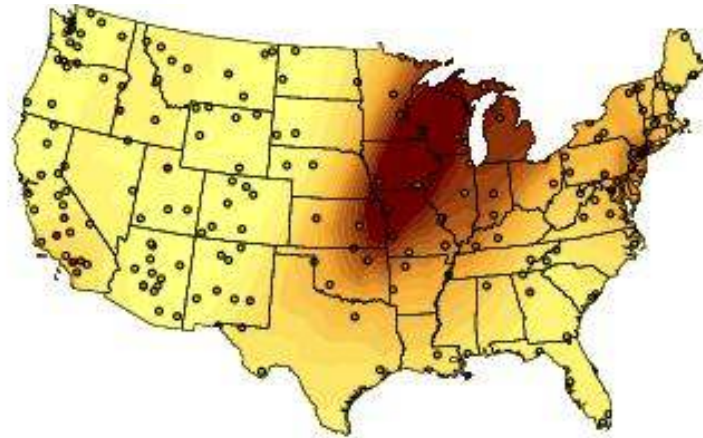
- Present as ammonium nitrate ($\text{NH}_{3,\text{g}} + \text{HNO}_{3,\text{g}} = \text{NH}_4\text{NO}_{3,\text{p}}$)
 - Dynamics governed by the ammonium / sulfate / nitrate / water system
 - Levels highest in the winter and spring, and not necessarily on the coldest days (i.e. not strictly an issue of ammonium nitrate volatility)
- Typically regional-scale nitrate events with incremental excess in the urban areas
- Current interest in ambient nitrate...
 - **Accountability:** do NO_x reductions lead to decreased levels of ambient nitrate?
 - **Nitrate Replacement:** do SO_2 reductions lead to increased levels of ambient nitrate?
- **Need high time resolution measurements for many applications, including validation of chemical transport models**

Wintertime Nitrate in the Upper Midwest

December 7, 2002



December 10

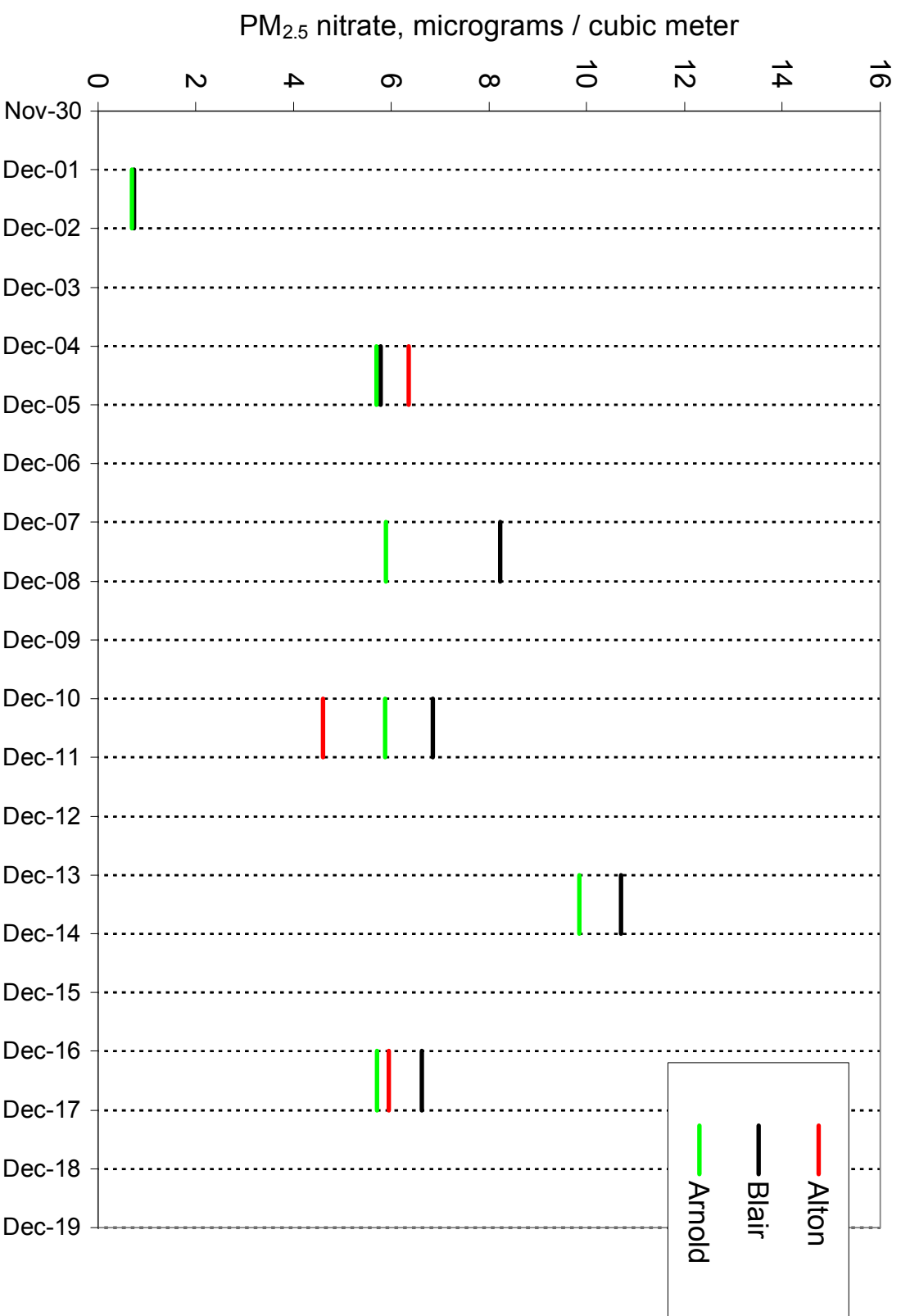


December 13



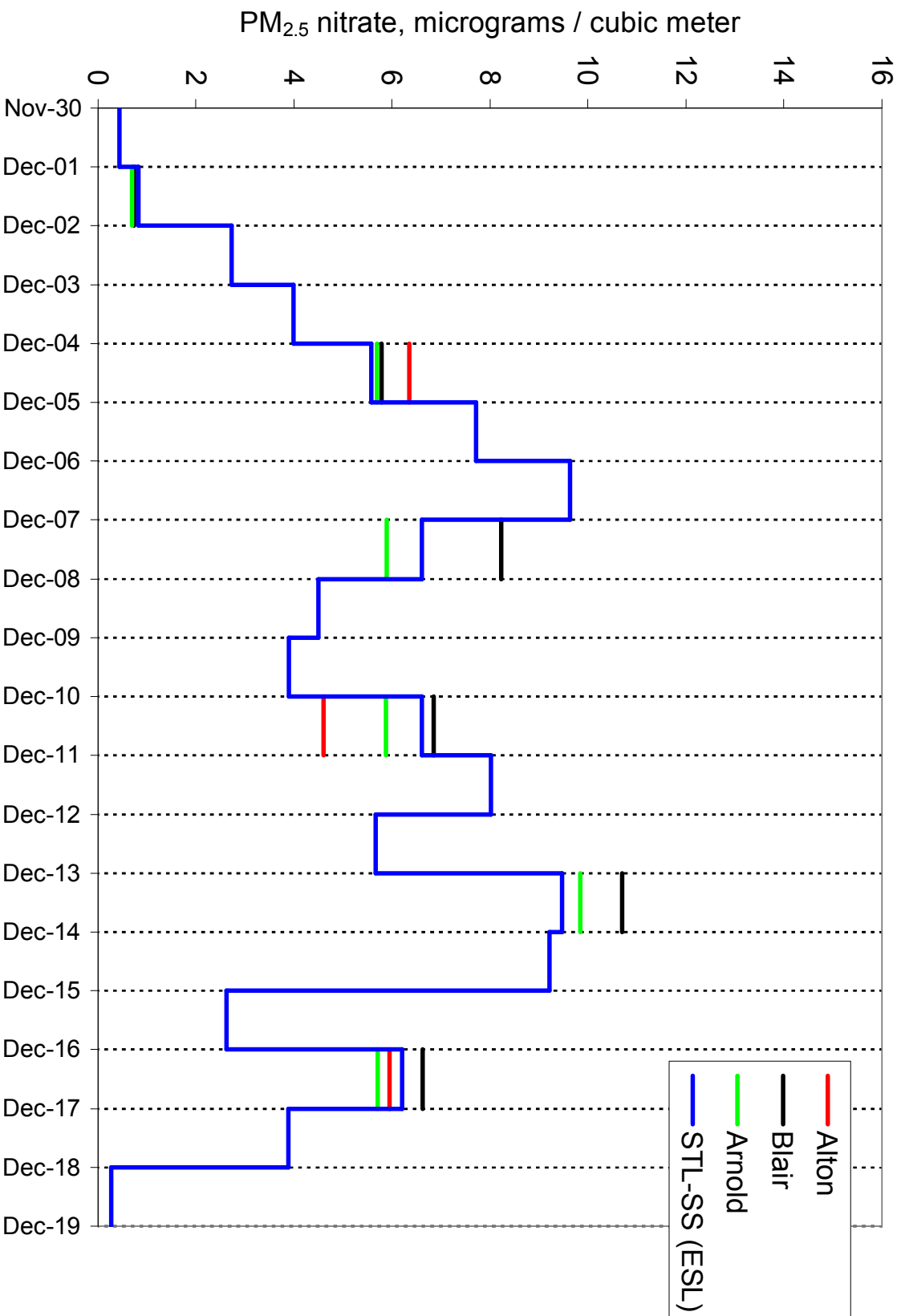
December 2002 Nitrate Episode

STL area speciation network filter 24-hour integrated filter nitrate



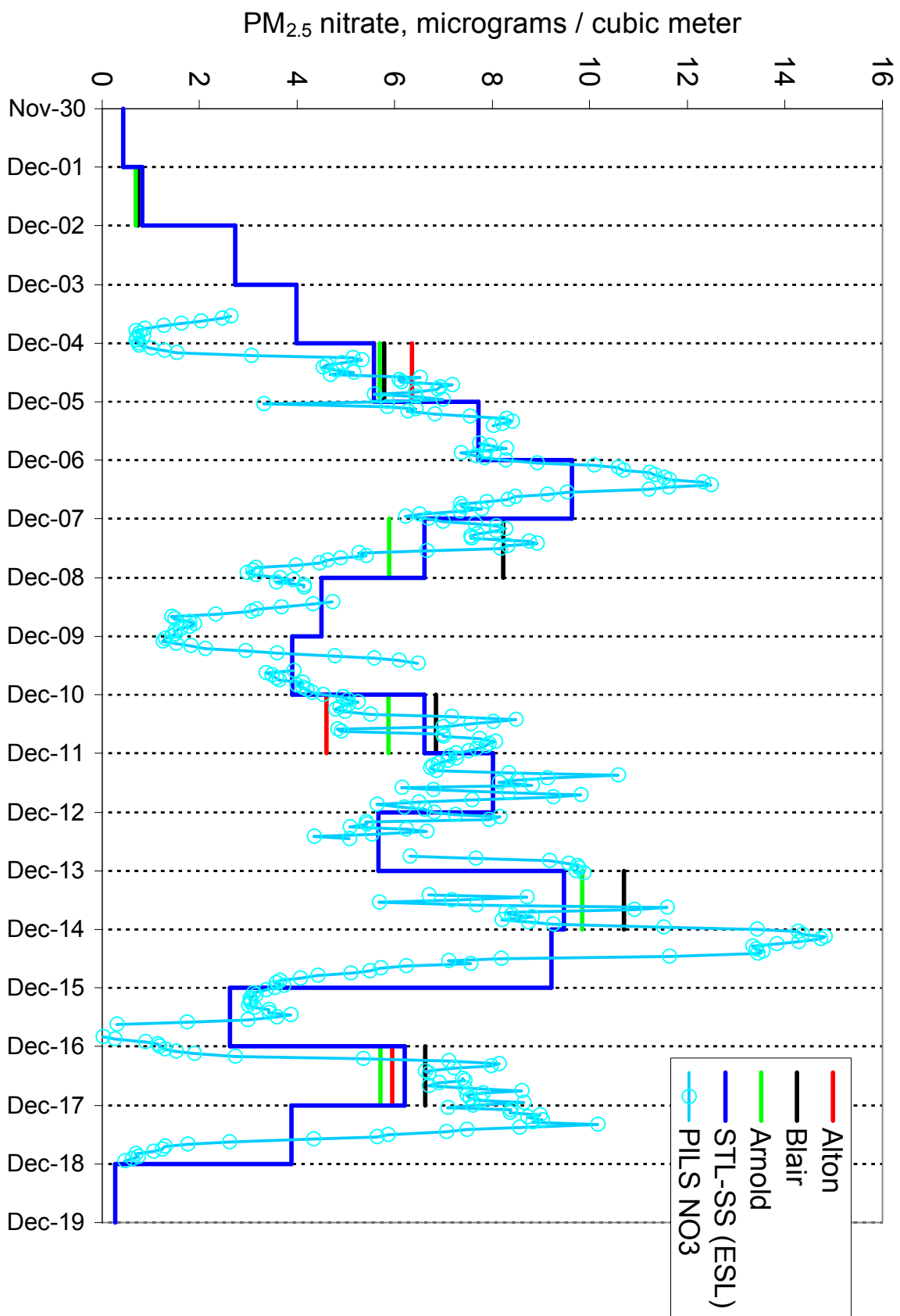
December 2002 Nitrate Episode

STL Supersite daily 24-hour filter nitrate



December 2002 Nitrate Episode

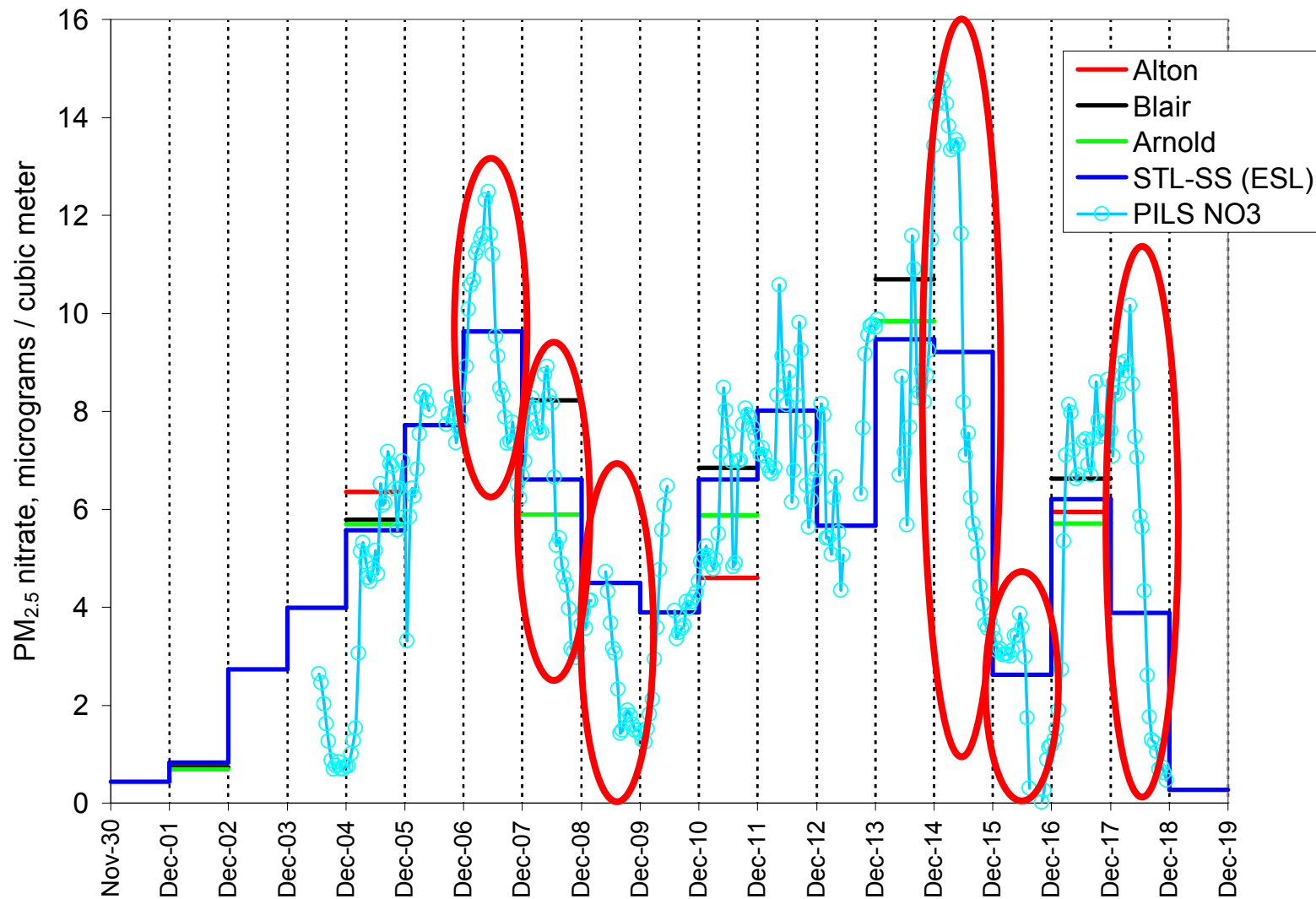
STL Supersite hourly nitrate (Particle-into-Liquid Sampler)



December 2002 Nitrate Episode

STL Supersite hourly nitrate (Particle-into-Liquid Sampler)

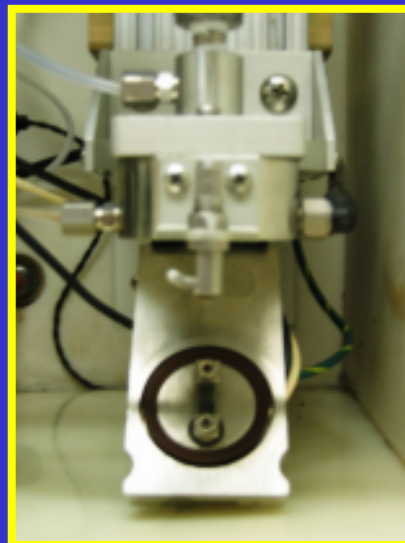
– frequent midday decreases, not captured by filter data



R&P 8400N Measurement Principle

- Commercialized version of Aerosol Dynamics, Inc. (ADI) flash volatilization instrument (Stolzenberg and Hering, 2000)
- **Inlet and Aerosol Conditioning**
- **Sample collection and flash volatilization**

objective is to convert the aerosol nitrate to gaseous NO_x (NO and NO_2)

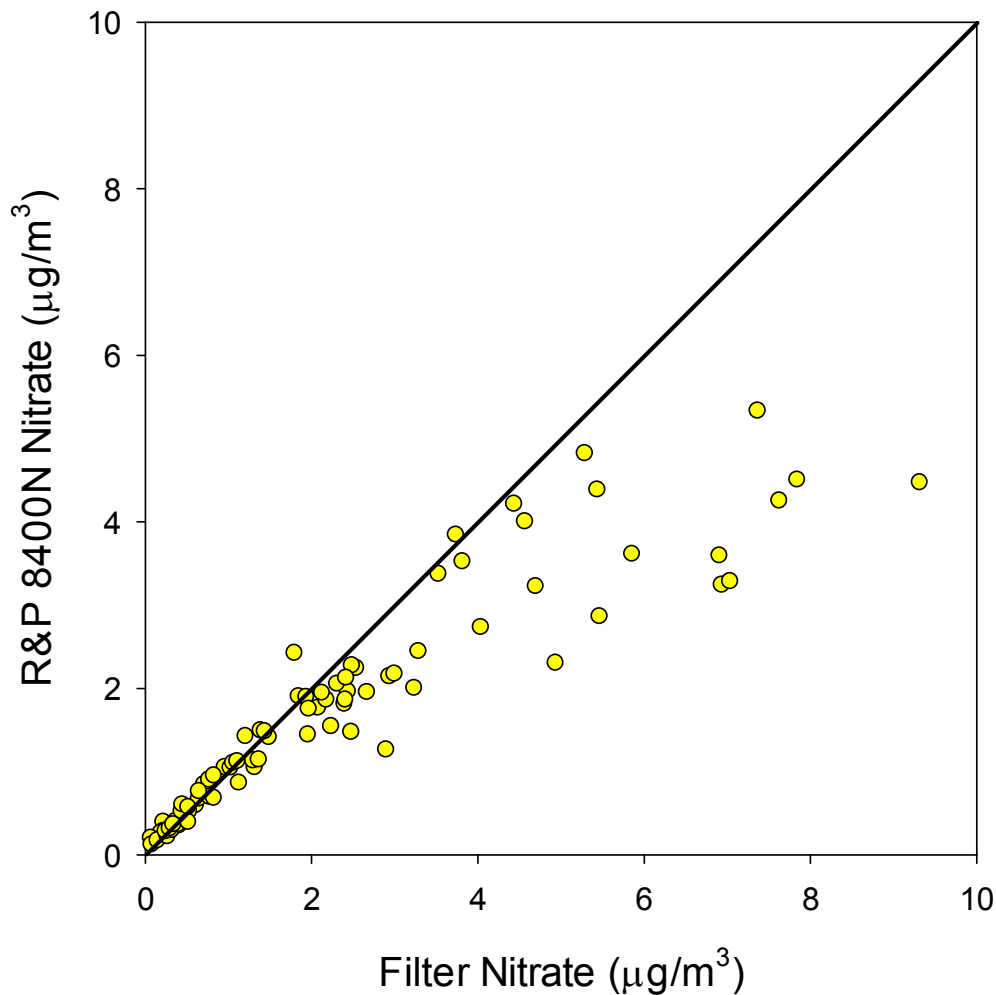


8400N Measurement Principle

- NO_x Analysis
- Data Handling and Post-processing



R&P 8400N versus 24-hour Integrated Filter NO₃ Reserve, KS (Sep-Dec 2002)



RURAL SITE...

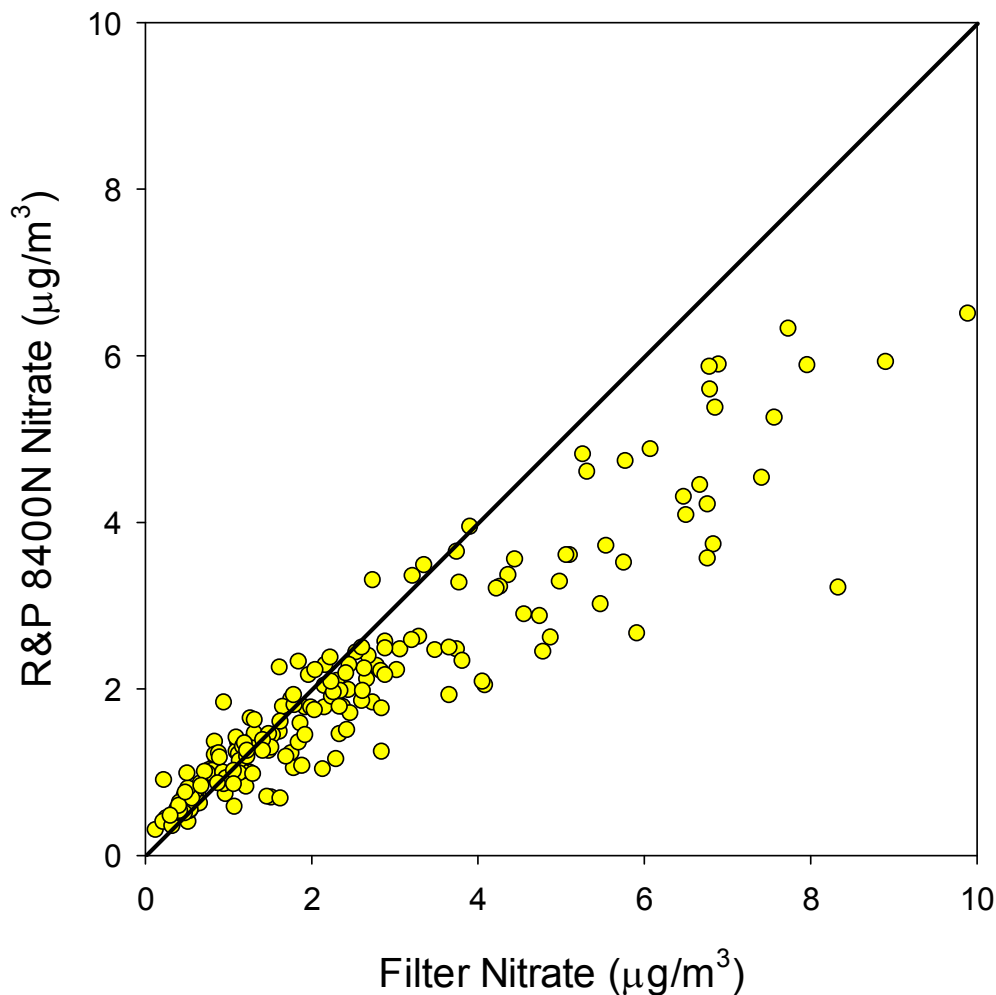
Excellent recovery with respect to filter nitrate below $\sim 2 \mu\text{g}/\text{m}^3$

Decreased recovery with respect to filter nitrate above $\sim 2 \mu\text{g}/\text{m}^3$

Actually a *range* of 8400N recoveries at a given filter nitrate concentration above $\sim 2 \mu\text{g}/\text{m}^3$

Filter nitrate by the Harvard-EPA Annular Denuder System (HEADS) – PM_{2.1} impactor, sodium carbonate denuder, citric acid denuder, and a Teflon/Nylon filter pack

R&P 8400N versus 24-hour Integrated Filter NO₃ East St. Louis, IL (Feb 2002 – June 2003)



URBAN SITE...

Same trends as observed at rural site

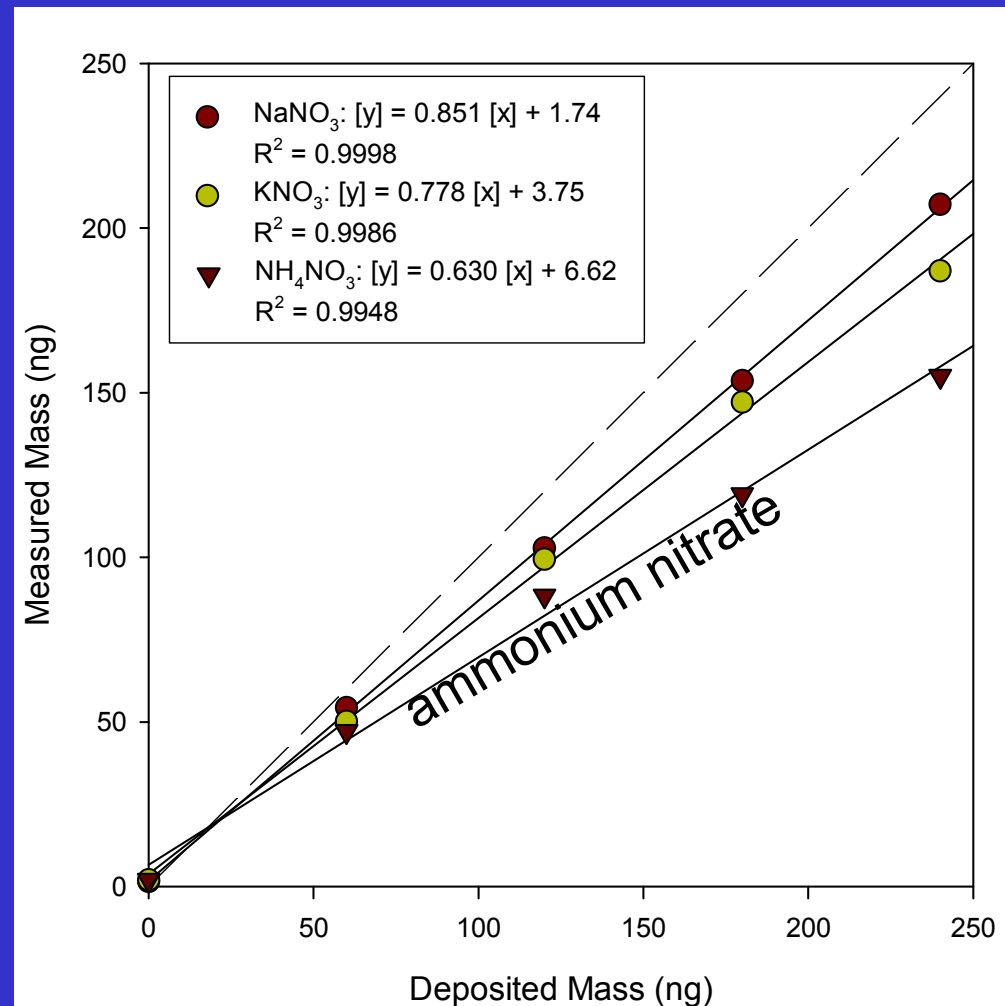
Noisier response at low nitrate concentrations, possibly due to more complex nature of the urban aerosol

Filter nitrate by the Harvard-EPA Annular Denuder System (HEADS) – PM_{2.1} impactor, sodium carbonate denuder, citric acid denuder, and a Teflon/Nylon filter pack

diagnostic/performance testing...

Where does the nitrate “conversion” take place?

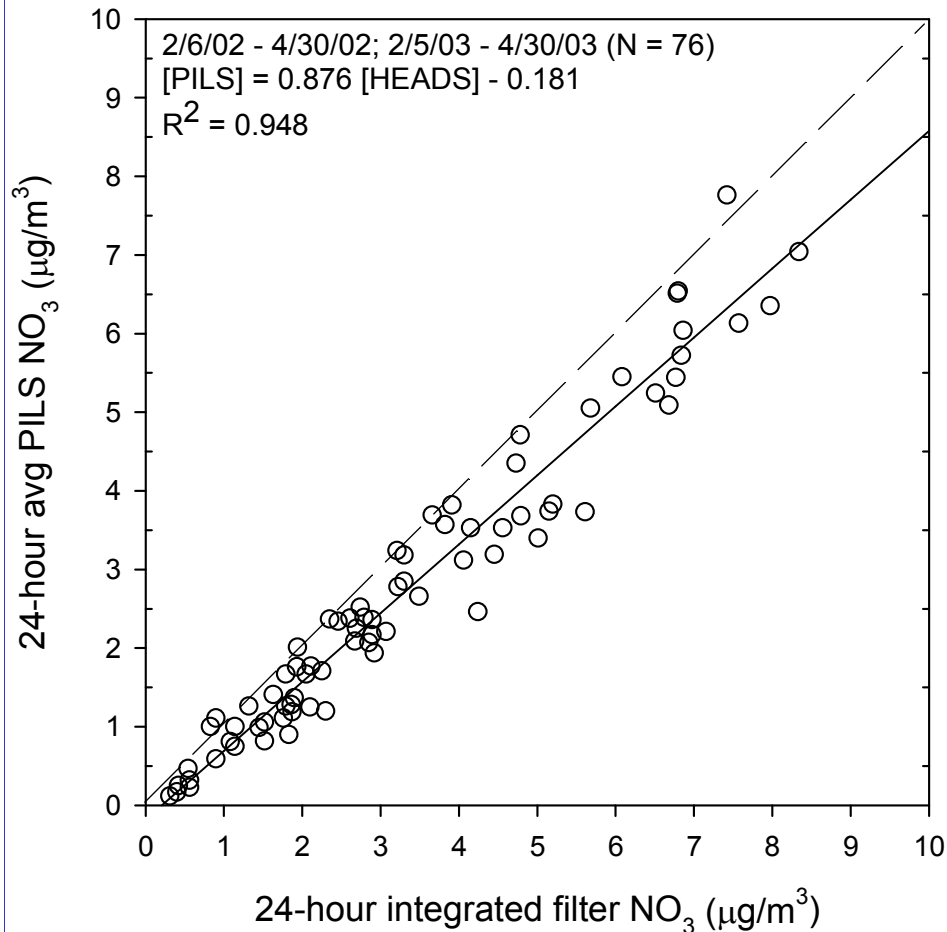
- Instrument conversion efficiency is measured by applying aqueous salt solutions directly to the flash strip
- Perform conversion efficiency tests with NH_4^+ , K^+ , Na^+ counterions
- reduced efficiency for NH_4NO_3 conversion might arise from volatilization before conversion



But what drives nitrate “conversion”?

- Nitrate conversion to NO_x (NO , NO_2) – whether on the flash strip or in the gas phase – is a reduction reaction (nitrate is an e^- acceptor)
 - Must be coupled to an oxidation reaction (there must be an e^- donor)
 - Instrument designed such that the flash strip (NiChrome) itself could serve as an e^- donor (aided by nonvolatile residue such as elemental carbon)
- Could the observed low nitrate recoveries arise from an e^- donor deficiency?
 - On the flash strip (important for all nitrate salts)
 - In the gas phase above the flash strip (important for ammonium nitrate)
- *If there is an intrinsic deficiency of e^- donors in the instrument design, is the conversion sensitive to aerosol composition? **MATRIX EFFECT***

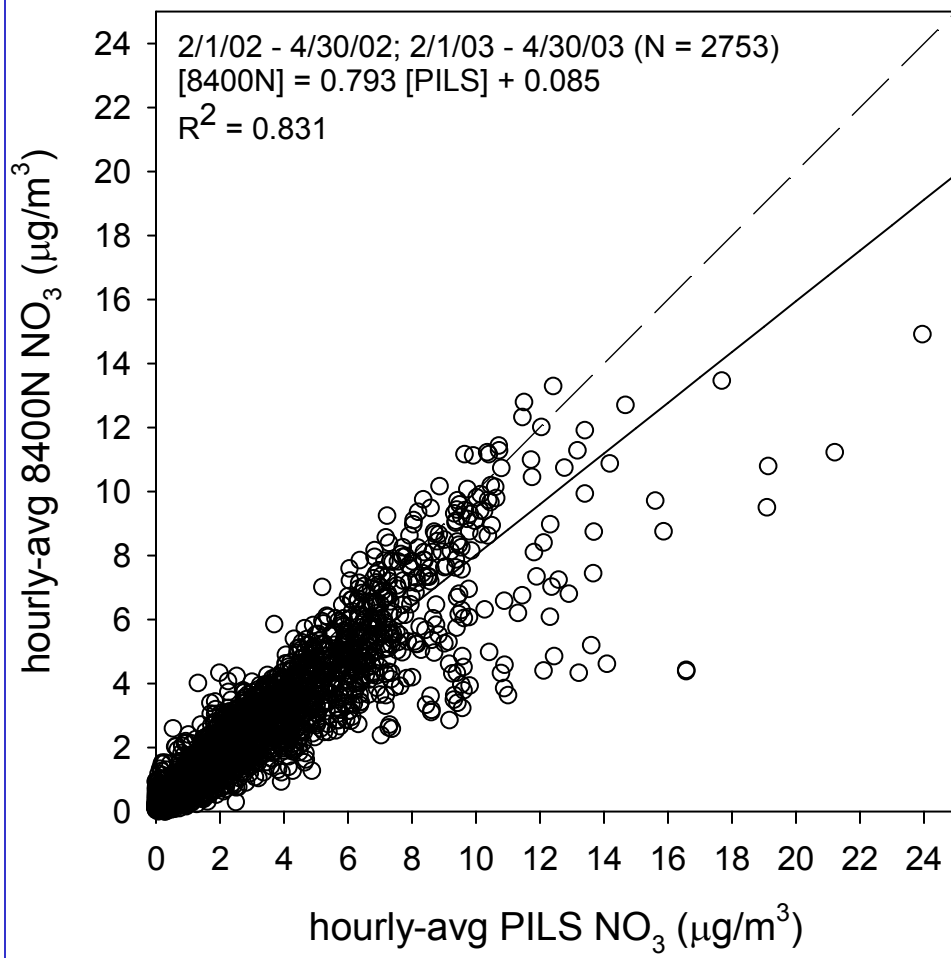
PILS-IC versus 24-hour Integrated Filter NO₃ East St. Louis, IL (Feb – Apr 2002)



While there is scatter in the data, overall the agreement is good

Filter nitrate by the Harvard-EPA Annular Denuder System (HEADS) – PM_{2.1} impactor, sodium carbonate denuder, citric acid denuder, and a Teflon/Nylon filter pack

Hourly R&P 8400N versus Hourly PILS-IC NO₃ East St. Louis, IL (Feb – Apr 2002)

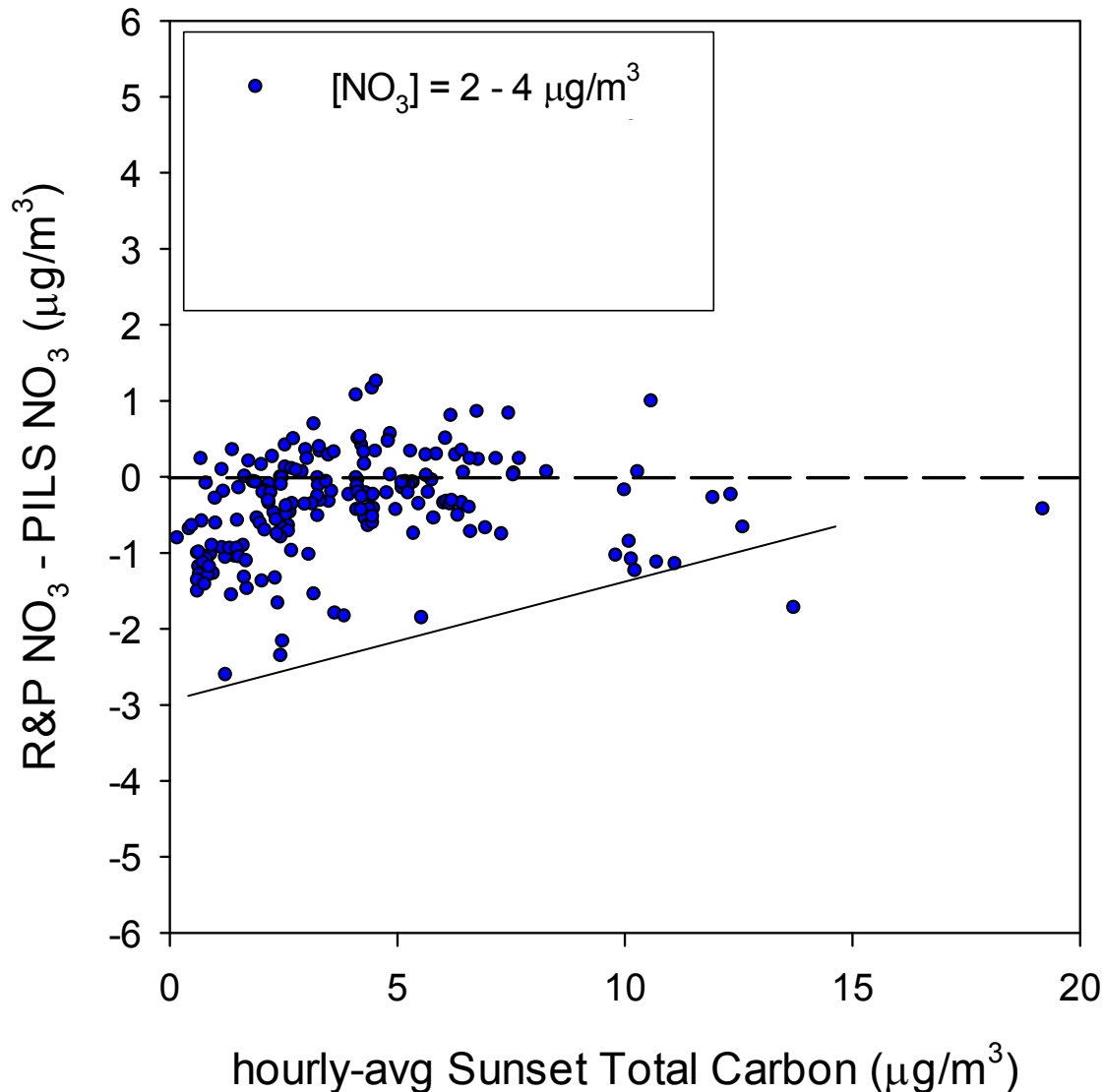


Follows same trend as 8400N
nitrate recovery with respect to
filter nitrate

More scatter in the hourly data

8400N Nitrate Recovery versus Total Carbon

Stratify by PILS-IC Nitrate (floor of $2 \mu\text{g}/\text{m}^3$)



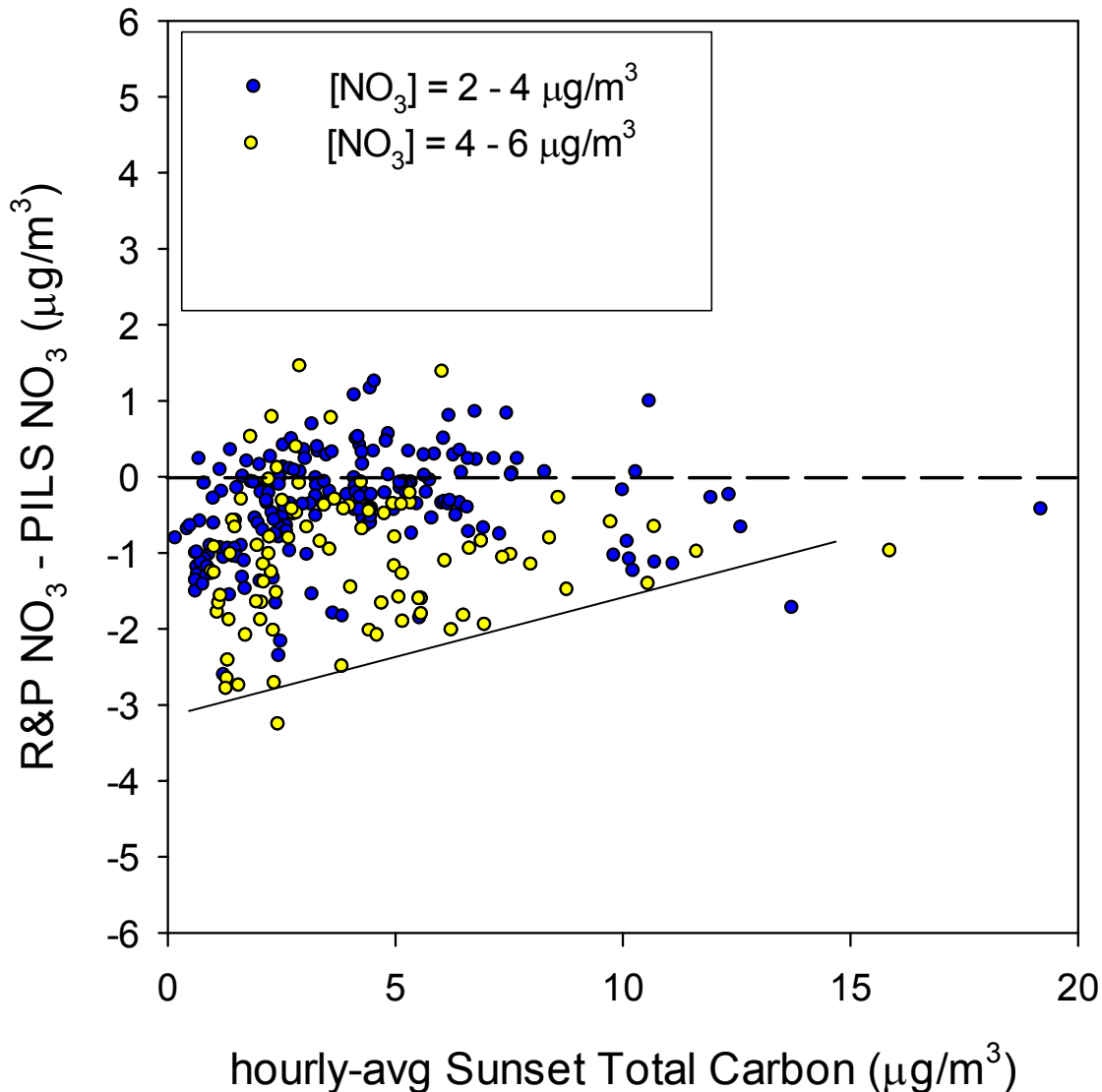
SPRING 2002

8400N < PILS nitrate for most data

The difference appears to be constrained within an envelope which narrows with increasing TC...

8400N Nitrate Recovery versus Total Carbon

Stratify by PILS-IC Nitrate (floor of $2 \mu\text{g}/\text{m}^3$)



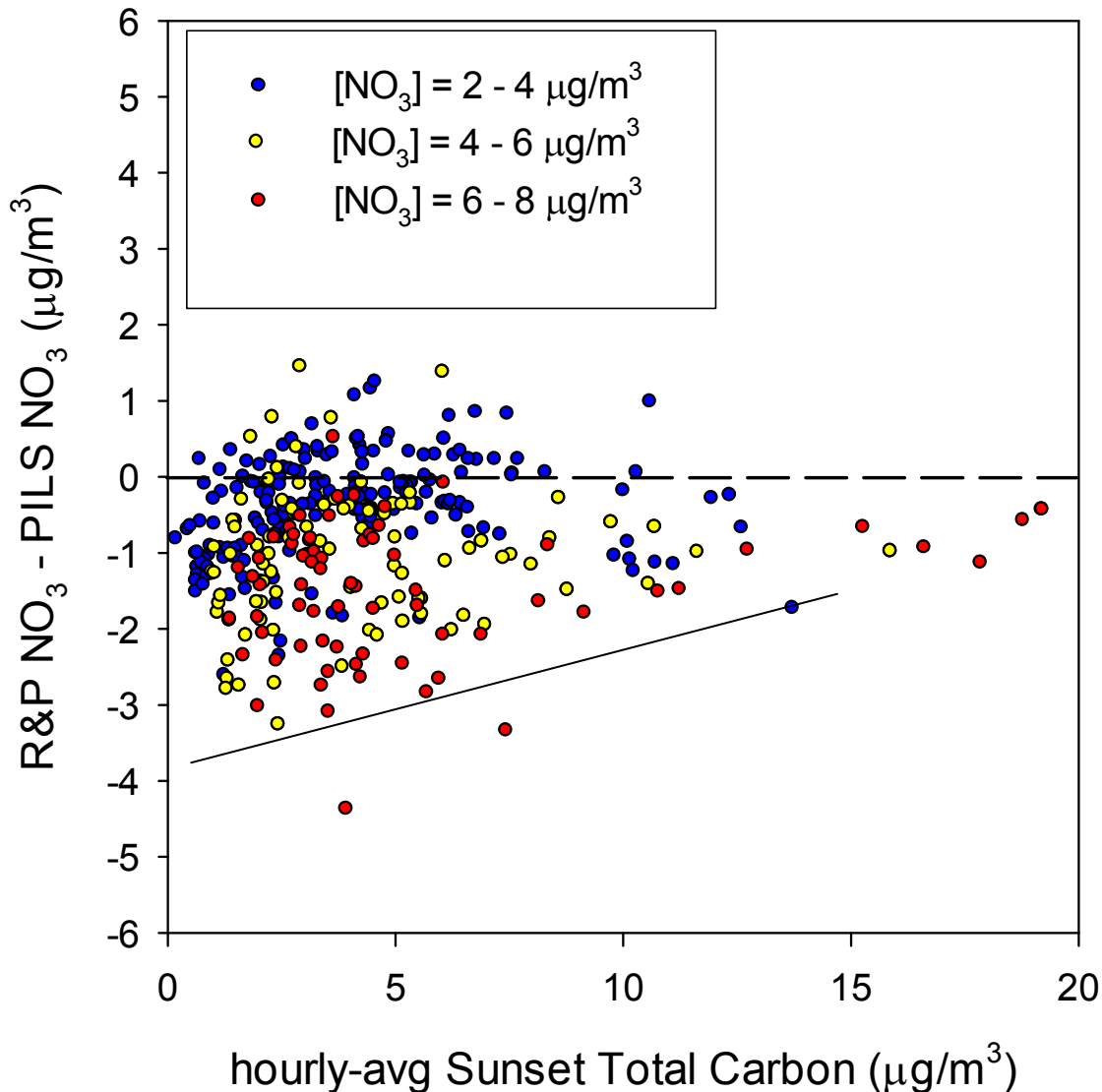
SPRING 2002

Increased range of recoveries with higher absolute nitrate concentrations

Again, the difference appears to be constrained within an envelope which narrows with increasing TC...

8400N Nitrate Recovery versus Total Carbon

Stratify by PILS-IC Nitrate (floor of 2 $\mu\text{g}/\text{m}^3$)



SPRING 2002

Increased range of recoveries with higher absolute nitrate concentrations

Good recoveries observed at high nitrate in presence of high TC (caveat – the five right-hand red points correspond to a single event)...

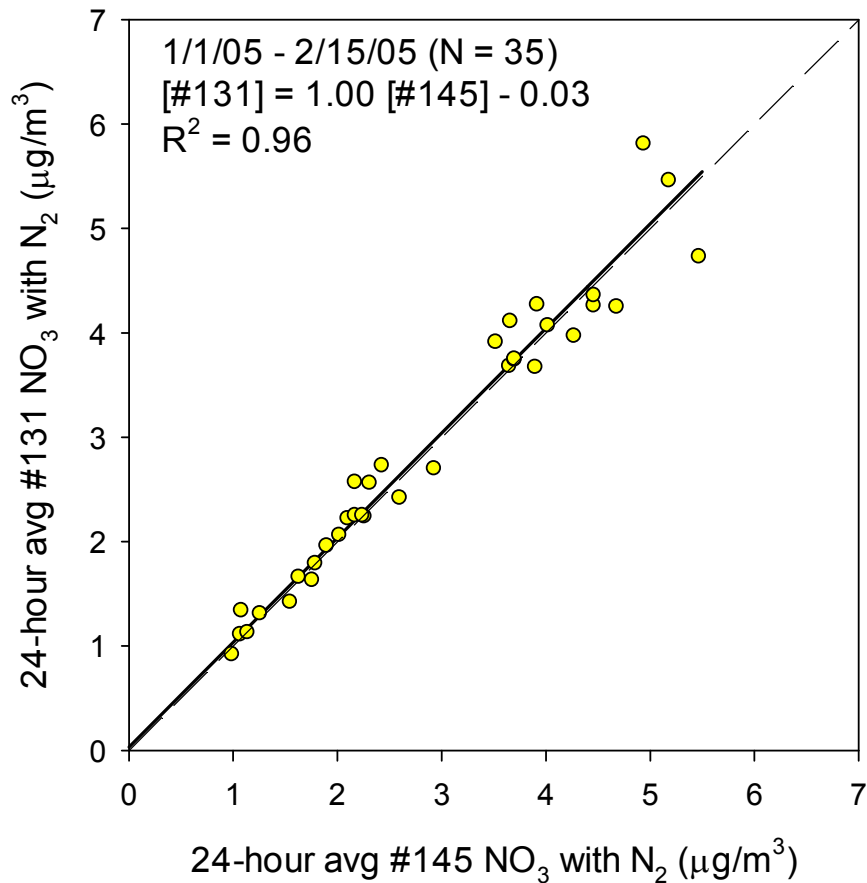
hypothesis building and special studies...

Electron Donors and the CO Doping Study

- The previous analysis suggests that in East St. Louis under certain conditions, there is a ***deficiency of electron donors to reduce the nitrate***
 - Consistent behavior also observed for Spring 2003 and 2004
 - No evidence of a matrix effect by aerosol sulfate (not shown)
- Investigate this hypothesis by ***doping the 8400N purge gas with an electron donor***
 - This only addresses nitrate which volatilized from the flash strip; likely does not influence reduction on the flash strip
 - ***10 ppm CO / balance N₂*** (hydrocarbons can donate more electrons per mole of carbon, but their redox chemistry is more complex)
 - First establish collocated precision between two 8400N units with N₂ purge gas, then switch one unit to the CO-doped purge gas

Collocated R&P 8400N Units – Spring 2005 daily nitrate with- and without CO doping

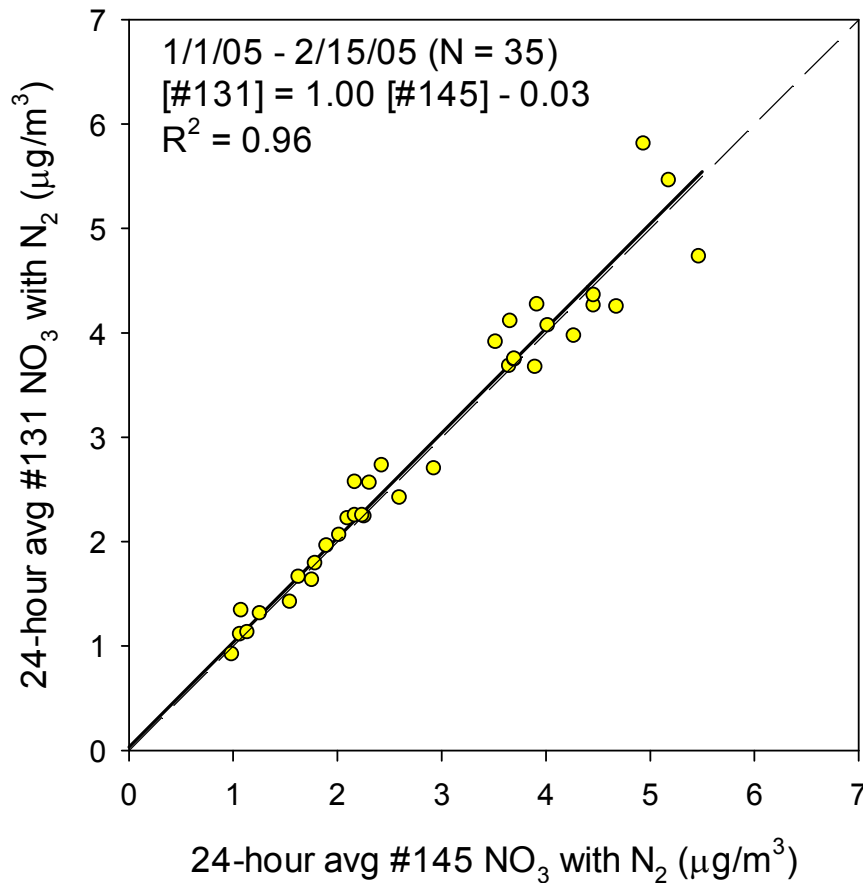
both instruments on N₂*



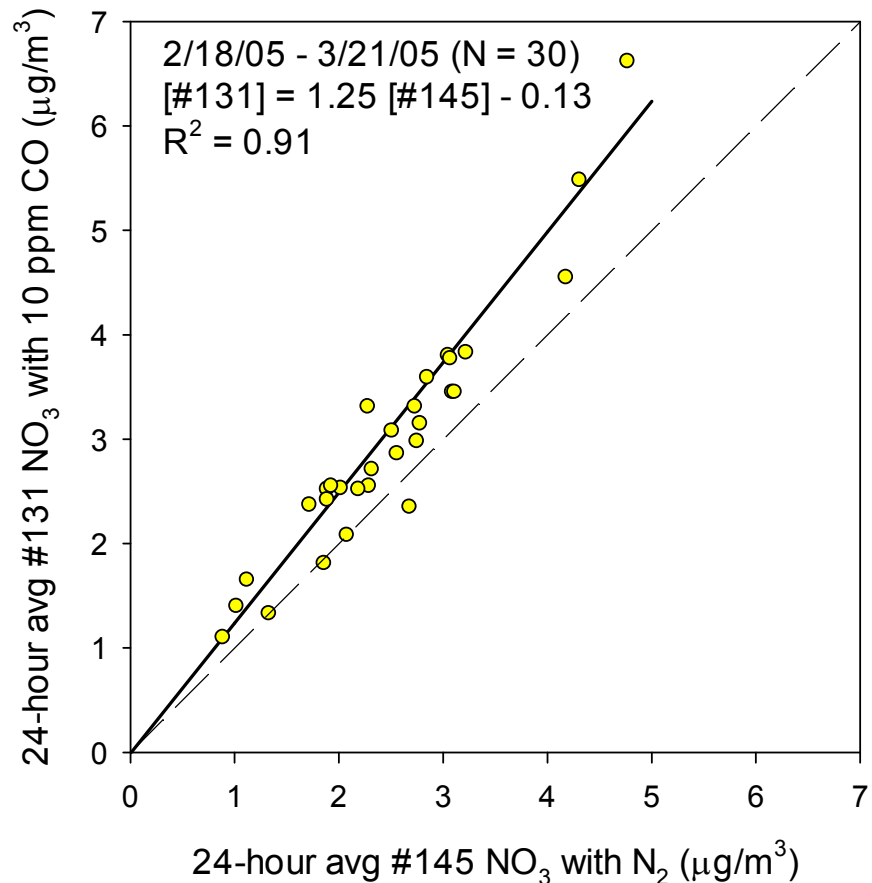
*six weeks prior to doping unit #0131 purge gas

Collocated R&P 8400N Units – Spring 2005 daily nitrate with- and without CO doping

both instruments on N₂*



one instrument on CO/N₂**



*six weeks prior to doping unit #0131 purge gas

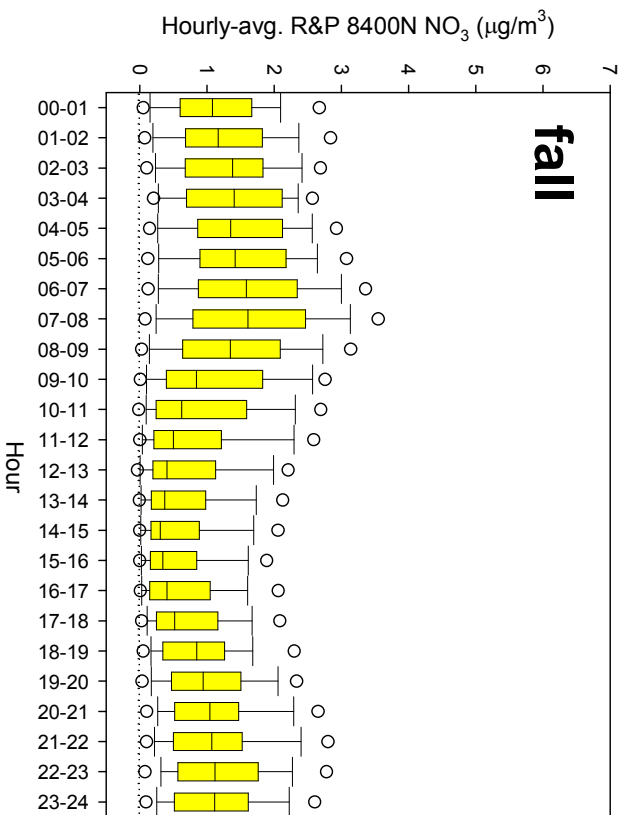
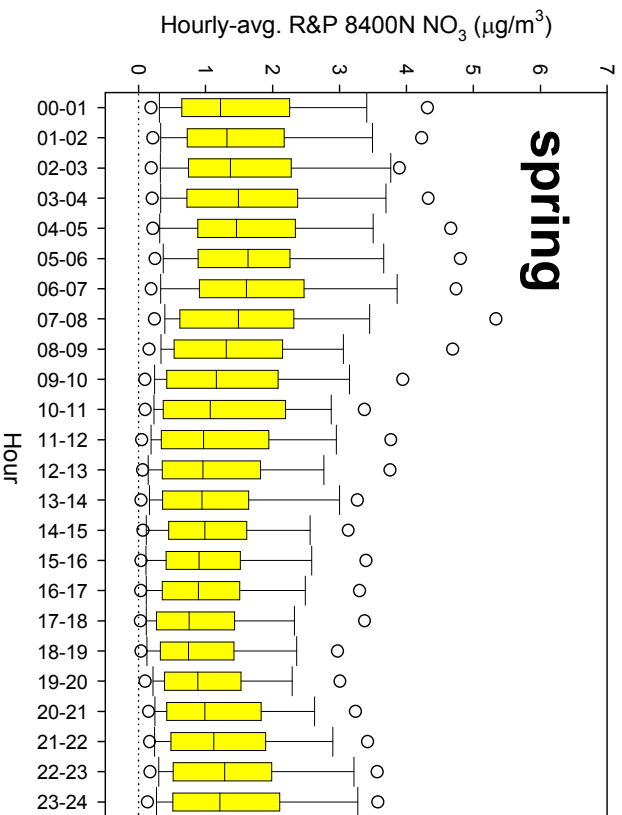
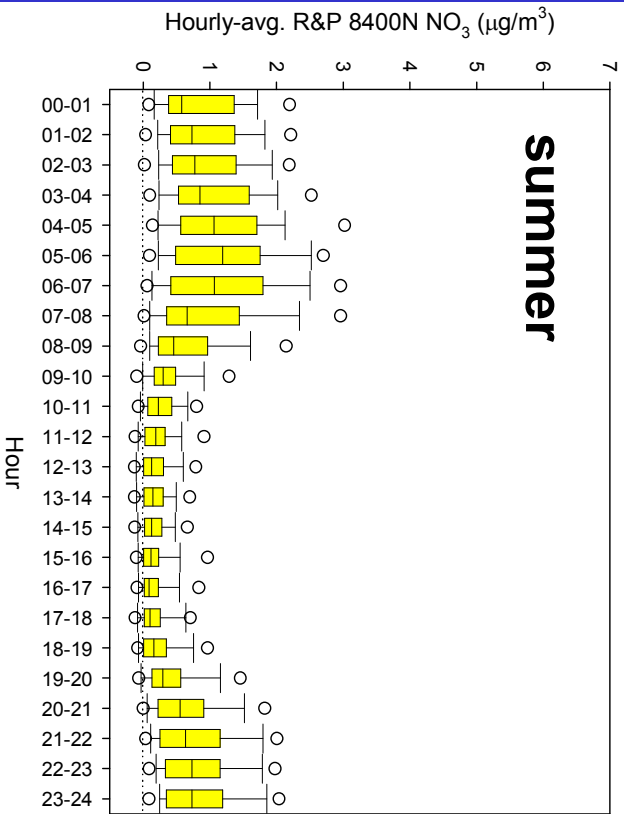
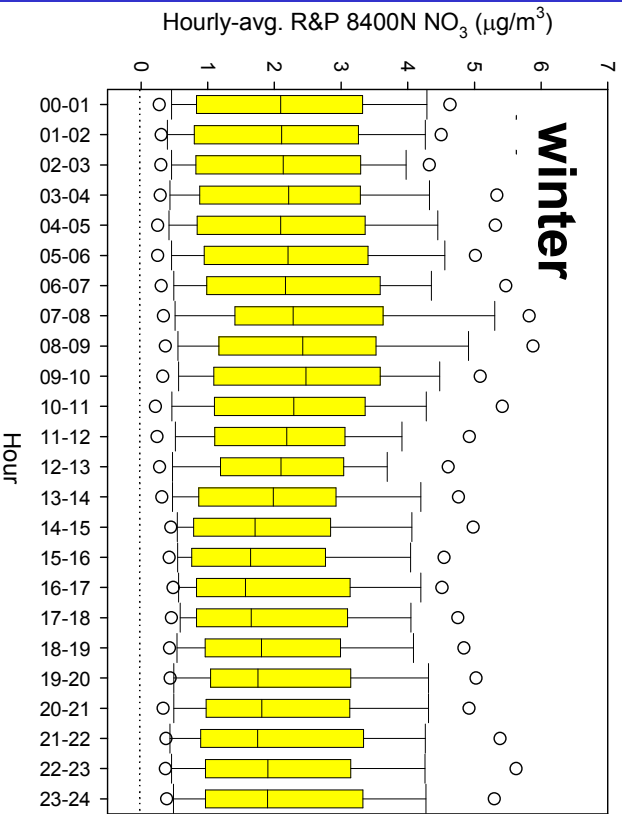
**four weeks of CO-doped purge gas for unit #0131

Nearly a 20% increase in the daily nitrate response for unit with CO-doped purge gas

Summary and Conclusions - I

- Does the 8400N nitrate unit “work”?
 - It depends on your intended use of the data!
 - Chemical transport model validation – no
 - Quantitative daily concentration estimates – maybe, with adjustments (will likely still be noisy)
 - Other analysis, including weekend/weekday differences, averaged diurnal profiles, episode periods identification – yes
 - Recommended reading:
 - Comparison of Integrated Filter and Semi-Continuous Measurements of PM_{2.5} Nitrate, Sulfate, and Carbon Aerosols in the Speciation ends Network (STN), [EPA 454/R-05-004](#), December 2005 (prepared by Sonoma Technology, Inc., for US EPA)
- Other semicontinuous monitors for nitrate
 - Water-based systems coupled to ion chromatographs
 - Other NO₃ reduction systems

Seasonal-Average Nitrate Diurnal Profiles (8400N) St. Louis, June 2004 – May 2005



Summary and Conclusions - II

- Example of diagnosing a measurement issue for a given semicontinuous instrument by running side-by-side with other instruments measuring the same species and other particulate matter components
 - (Issue identification)
 - Expanded diagnostic/performance testing
 - Data mining
 - Hypothesis development, special studies for hypothesis testing
 - Collaboration with instrument developers and vendors

Acknowledgements

- Funding...
 - USEPA Supersites Program
 - USEPA Region VII / CENRAP / Missouri DNR
 - LADCO / Midwest RPO
 - EPRI
- The nitrate story...
 - Koutrakis group at Harvard School of Public Health
 - Chow / Watson group at Desert Research Institute
 - Susanne Hering, Aerosol Dynamics, Inc.
 - Thermo (Rupprecht & Patashnick, especially Jeff Ambs)